THE EARLY DEVELOPMENT OF SPECTROSCOPY AND ASTROPHYSICS

Thesis presented for the
Degree of Doctor of Philosophy
in the field of History of Science

by

Frank Arthur John Lord James

Department of History of Science and Technology
Imperial College of Science and Technology
University of London

March 1981

The Early Development of Spectroscopy and Astrophysics

Frank Arthur John Lord James

In 1800 there was no real interest in studying either the spectrum or the constitution of the stars. By 1870 spectroscopy and astrophysics were among the most intensely pursued subjects in the physical sciences. The purpose of this thesis, therefore, is to examine how this change came about.

I shall argue that the development of the undulatory theory of light and of the first two laws of thermodynamics identified the existence of problems in spectroscopy and astrophysics, and therefore brought these sciences into being.

The success in the first half of the nineteenth century of the undulatory theory of light in accounting accurately for a large number of optical phenomena led naturally to the study of those phenomena which were not immediately reconcilable with the theory: absorption, emission, fluorescence, etc. These phenomena could be studied experimentally only by an examination of the behaviour of their spectra. Therefore, in order to reconcile these phenomena with the undulatory theory, it was necessary to devise hypotheses which described the manner in which ponderable matter interacted with the luminiferous aether.

There were two consequences of this work that were not directly related to solving the problems of the undulatory theory. It was realised that spectra could be used for the purpose of chemical analysis. And it was discovered that interpretations of the solar spectrum provided information concerning the physical constitution of the sun.

Thermodynamic arguments from about 1850 disposed of those hypotheses about the interaction of matter and light which did not consider the conservation of energy. Similarly thermodynamics also falsified traditional solar theories; the theories which replaced them provided a firmer interpretation of the solar spectrum and consequently of spectra generally. The development of thermodynamics therefore placed the study of spectra and stars on a secure theoretical basis, not previously enjoyed.

CONTENTS

		page
List of illustrations		5
Acknowledgements		7
Chapter 1	The physical interpretation of the undulatory theory of light	9
Chapter 2	Experiments on, and observations of, emission and absorption spectra to 1830	21
Chapter 3	The debate on the nature of absorption 1830-1835 and its chemical consequences	44
Chapter 4	The study of spark spectra 1835-1859	85
Chapter 5	The conservation of energy, theories of spectra and resonating molecules 1851-1854	120
Chapter 6	The conservation and dissipation of energy, and solar theories 1846-1862	148
Chapter 7	Spectro-chemical analysis 1854-1861	175
Conclusion	The early historiography of spectroscopy	207
Appendix	The mathematical proof of Kirchhoff's law of radiation	220

Contents (cont.)

	page
Notes and references	222
to Chapter 1	223
to Chapter 2	230
to Chapter 3	238
to Chapter 4	247
to Chapter 5	256
to Chapter 6	268
to Chapter 7	279
to the Conclusion	291
Bibliography 1 Manuscripts	293
Bibliography 2 Printed sources	295

Erratum. For Waterson read Waterston

LIST OF ILLUSTRATIONS

Chapter 2

Fig. 1	Fraunhofer's apparatus to obtain homogeneous light of different colours	facing p25
Fig. 2	Fraunhofer's illustration of his samples of homogeneous light	p25
Fig. 3	Fraunhofer's solar spectrum	facing p27
Fig. 4	Herschel's spectrum of light transmitted through blue glass	p32
Fig. 5	Herschel's diffraction spectrum	p41
Fig. 6	Young's diffraction spectrum	p42

Chapter 3

Fig. 1	Herschel's sound interference pipes	p57
Fig. 2	Wrede's reflecting surfaces	p64
Fig. 3	Wrede's spectral map	facing p66
Fig. 4	Wrede's spectrum of iodine	p67
Fig. 5	W. A. Miller's spectra of light transmitted through various gases and vapours	facing p80
Fig. 6	W. A. Miller's spectra of coloured flames	p81

Chapter 4

Fig. 1	Wheatstone's apparatus to measure the velocity of electricity	facing p87
Fig. 2	Wheatstone's spark spectra of various metals	p89
Fig. 3	Masson's spark spectra of various metals	facing p102
Fig. 4	Ångstr¨m's atmospheric spectra	facing p108
Fig. 5	Ångström's spark spectra of various substances	facing p109

List of illustrations (cont.)

Chapter 5

Figs. 1 & 2	Stokes's experiment to confirm his idea of the causal agent of fluorescence	p126
Fig. 3	Kelvin's experiment to confirm the identical refrangibility of the R and D lines	p143

Chapter 7

Fig. 1	Kirchhoff's aragonite apparatus	facing p182
Fig. 2	Kirchhoff's spectroscopic apparatus with which he first observed reversal	p187
Fig. 3	Kirchhoff's second (terrestrial) experiment to display reversal	p188
Fig. 4	Kirchhoff's system of plates used to prove his radiation law	p193
Fig. 5	Bunsen and Kirchhoff's spectral maps	facing p199
Fig. 6	Crookes s map of the thallium spectrum	p204

Footnotes to Chapter 2

Fig. 1	Wollaston's solar spectrum	p231

ACKNOWLEDGEMENTS

I wish to thank my supervisor Dr. Marie Boas Hall for every encouragement and criticism during the writing of this thesis. I also thank Professor A. Rupert Hall for his help. I thank Mrs. Magda Whitrow for employing me as an assistant editor on volumes four and five of the "ISIS Cumulative Bibliography" during the first two years of my research. I thank the University of London for providing me with a research scholarship for the following two years and for a travelling scholarship to Germany.

I wish to thank Professors G J. Whitrow (Imperial College), D. Cardwell (UMIST), A. J. Meadows (University of Leicester), Drs. N. Smith (Imperial College), G. Cantor (University of Leeds), C. Smith (University of Kent), M. Sutton (Newcastle Polytechnic), K. Dawson (Imperial College), B. Bowers (Science Museum, London), D. B. Wilson (Iowa State University), D. Roos (North-Western University), J. Burchfield (Northern Illinois University), J. Paradis (MIT), Messrs J. T. LLoyd (University of Glasgow), and N. Lingard (Manchester Polytechnic) for discussions and assistance on various topics within this thesis. I also thank Mrs Felicity Secretan and Mrs Gunnel Ingham for help with and translations from German and Swedish respectively. I also wish to thank members of the now defunct Department of History of Science and Technology, Imperial College, for their help. I also thank Mrs. Frances De Marion de Glatigny for preparing the line drawings and Miss Heather Stanley for typing the manuscript.

I gratefully acknowledge the help and assistance provided by the archivists and staffs of the following institutions. In England: Cambridge University Library, Royal Society Library, Imperial College, King's College London, University College London, Royal Society of Chemistry, Science Museum London, Public Record Office Kew, Principal Registry of the Family Division of the High Court, Royal Greenwich Observatory Hurstmonceux,

The National Trust at Lacock Abbey, and Williams (Hounslow) Ltd. In Scotland: Glasgow University Library, Department of Natural Philosophy Glasgow University, St. Andrews University Library, Edinburgh University Library, The National Library of Scotland and the Scottish Record Office. In Germany: Heidelberg University and the Deutsches Museum Munich.

I thank the librarians and staffs of the following libraries for use of their facilities. At Imperial College: The Lyon Playfair Library (especially Miss G. McGurk and Miss J. Lewis of inter-library loans for finding the locations of so much obscure material); the libraries of the Chemistry, Mathematics, Physics, and Chemical Engineering departments and the Haldane Library. The libraries of the following institutions: The Science Museum, Victoria and Albert Museum, The Natural History Museum, The University of London, The Royal Society, The Royal Astronomical Society, Cambridge University and the British Museum.

And, finally, I thank my parents for all forms of support and I dedicate this thesis to them.

Chapter One

THE PHYSICAL INTERPRETATION OF THE UNDULATORY THEORY OF LIGHT

> That the undulatory theory [of light] is defective as a physical representation of the phaenomena of light, has been admitted by the more candid of its supporters (1)

With this statement written in 1833 David Brewster (2) summed up his fundamental objection to the undulatory theory of light and thereby touched off a sharp reaction from those people who did believe in the physical validity of the theory. Thus G. B. Airy (3), then Plumian Professor of Astronomy at Cambridge, had some very strong words to say both in public (4) and in private about the whole of Brewster's attitude towards the undulatory theory:

> Apropos of optics - I have just been looking at some numbers of Brewster's journal which I had not seen before: also at his new book. My estimation of Brewster has sensibly dropped. What an insolent fellow he is, on the strength of experiments which are very valuable but which he does not know how to interpret (for nothing can be more awkward than his theories) to set about abusing the rest of the world in that way. There are many persons at Cambridge who understand the subject much better than he does, though they have made few experiments. There is also a hopeful protegé of Brewster's, Mr. R. Potter, who has made some good measures (apparently) and excells in this as if he had settled the whole theory of optics. Really these gentlemen of the northern school ought to be taught better (5).

The reason why Brewster, who, as Airy had indicated, was highly esteemed as an experimentalist, produced such an effect on people like Airy who supported the undulatory theory was that he had deliberately touched on one of the weakest points of the undulatory theory - its lack of physical validity.

In order to understand the implications of Brewster's views and the hostile reaction which his theoretical work generated, it is necessary to examine the views on the physical validity of the undulatory theory of light held by the founders of the theory (6): Leonhard Euler (7), Thomas Young (8), and

Augustin Fresnel (9). The problems which surrounded the physical validity of the undulatory theory centred on two different but interconnected questions. Firstly what was the physical structure of the luminiferous aether (10), the existence of which had to be immediately inferred once it was assumed that light was undulatory and, secondly, what was the relationship of ponderable matter to the luminiferous aether? Neither of these questions was specifically asked in this form until fairly late in the development of the undulatory theory. But the very fact that these scientists believed that light was undulatory meant that they had to deal incidentally with these problems.

According to this theory the whole of the material universe was bathed in a fluid luminiferous aether which transmitted light waves longitudinally as did any other fluid; light was caused by the self-vibrating molecules of self-luminous matter (e.g. flames, the sun, etc) transmitting their motion to the aetherial molecules. As Euler wrote after his discussion on the nature of sound:

> The propagation of light, in the ether, is produced in a manner similar to that of sound, in the air; and, just as the vibration occasioned in the particles of air constitutes sound, in like manner, the vibration of particles of ether constitutes light, or luminous rays; so that light is nothing else but an agitation, or concussion, of the particles of ether, which is everywhere to be found, on account of its extreme subtility, in virtue of which it penetrates all bodies (11).

In other words if a molecule of ponderable matter immersed in the aether vibrated quickly enough, the aether would be disturbed and this disturbance would be transmitted through the aether to be perceived as light. Therefore the fundamental postulate of the undulatory theory demanded that the luminiferous aether be closely connected with ponderable matter; and the behaviour of the aether in transmitting light could be used to infer the behaviour of ponderable matter. For example the very fact of the propagation of light indicated that the ponderable molecules in self-luminous matter were vibrating at a considerable rate.

According to the undulatory theory of light the colour of a particular ray was determined by its wave-length. The theory could therefore account for the colour of light emitted by self-luminous bodies since it could be easily imagined that their molecules could only vibrate at certain frequencies. However, it did not immediately account for the colour of bodies which were not self-luminous. Euler must have realised this for he devised a theory of resonance to account for the colour of bodies which he set out, again using the analogy of light and sound, in his "Nova Theoria Lucis et Colorum" of 1746 (12):

> Just as a stretched cord therefore is agitated by a sound which is equal to that which it gives forth, so those least particles placed on the surface of an opaque body can be vibrated by rays of the same or similar kind and are able to produce pulses speeding in all directions. And so the rays of light since they include pulses of every kind in proportion to the frequency, impell the particles of all opaque bodies into motion; for even though there is not the same frequency of pulses in the rays, yet still be it two or three times greater or less, it will produce a vibration though perhaps a weaker one (13).

Now if the particles on the surface of the body were not able to vibrate at a particular frequency then the body could not emit light of that wave-length. Therefore the colour of the body would be the combination of colours that the body did re-emit.

Euler's theory of resonance which explained the colour of bodies illustrates the idea, not consciously expressed by him, that the study of optical phenomena could be used to examine the nature of matter. By this I mean that those optical phenomena which were affected by the nature of ponderable matter, such as the colour of bodies, could be used to elucidate properties of matter which could not otherwise be deduced. In this case Euler inferred that the surfaces of bodies were composed of particles which became self-luminous on exposure to light of certain wave-lengths. This result was a consequence of the assumption that light was undulatory; Euler had no reason to construct an elaborate theory of the aether since all he had to assume was that it existed so that light could be transmitted. In other words he could use the known properties of

waves to explain optical phenomena without considering how the particular physical processes of the transmission of light waves and their interaction with ponderable matter could occur.

This same attitude towards the aether can be discerned in Young's work on the wave theory of light and the principle of interference. It would appear that Young had been predisposed towards the undulatory theory some time before he made his first public commitment to it in his 1800 paper "Outlines of Experiments and Inquiries Respecting Light and Sound" (14). In this paper Young dealt mainly with acoustical phenomena, but in section ten "Of the Analogy between Light and Sound" (15) he said that he was certain that an aether existed because the phenomenon of the electrical discharge required an aether to transmit the electricity (16). He then speculated on the possibility of there existing an aether which would also transmit light waves (17), and the optical phenomena which could be explained by assuming light to be undulatory.

In his second Bakerian lecture (18) Young was much clearer about the nature of light which he thought could be defined in four hypotheses:

1 A luminiferous Ether pervades the Universe, rare and elastic in a high degree
2 Undulations are excited in the Ether whenever a Body becomes luminous
3 The Sensation of different Colours depends on the different frequency of Vibrations, excited by Light in the Retina
4 All material Bodies have an Attraction for the etherial Medium, by means of which it is accumulated within their Substance, and for a small Distance around them, in a State of greater Density but not of greater Elasticity (19).

This latter hypothesis which connects ponderable matter and the aether was necessary in order to explain phenomena such as refraction, reflection etc. Each species of ponderable molecule would be surrounded by an atmosphere of aether of a different degree of density in order to account for different refractive indices etc. Young had therefore effectively stated that there existed unique relationships between matter and aether, though he did not go into further details, nor did he suggest any mechanism which might cause such relationships.

Within the context of these four hypotheses and his underlying assumption that there was a "strong resemblance between the nature of sound and that of light" (20) Young ennunciated his principle of interference:

> Wherever two portions of the same light arrive at the eye by different routes, either exactly or very nearly in the same direction, the light becomes most intense when the difference of the routes is any multiple of a certain length, and least intense in the intermediate state of the interfering portions; and this length is different for light of different colours (21).

It has been argued (22) that this principle which, Young said, he had discovered in the May of 1801 (23) was derived from his consideration of the principle of coalescence of musical sounds which he had discussed in his first paper (24). However he discovered the principle, Young argued that it could only be sensibly interpreted in terms of the undulatory theory of light. With the principle of interference alone - ignoring any questions concerning the nature of light - Young was able to advance explanations for optical phenomena such as the colour of fibres (25), thin (26), thick (27) and mixed plates (28) and he also attempted to explain diffraction (29). If these and other phenomena could be explained in terms of the principle of interference then, according to Young, they could be explained in terms of the undulatory theory. But because Young had suggested explanations of a number of optical phenomena in terms of the principle of interference as opposed to explaining them directly in terms of the undulatory theory, there had been no need for him to investigate either the structure of the aether or its relationship with ponderable matter, except for what he had stated in his fourth hypothesis. Young, like Euler before him, had assumed that light was undulatory; he, like Euler also but for different reasons, could infer that the luminiferous aether existed without investigating its physical validity too closely.

Fresnel began his optical work with a similar attitude in his paper on diffraction (30), written for a prize of the Académie de Sciences (31). Fresnel asserted that he had confirmed experimentally the observation of Berthollet and Malus that diffraction phenomena were independent of the nature of the

body which diffracted the light (32). The only thing on which diffraction did depend was the size of the diffractor and the size of the aperture through which the light passed. Therefore the problem of diffraction should be solved by considering only the behaviour of waves passing by an obstacle without reference to the nature of the obstacle. Fresnel showed that the velocity (u) of a particle of aether, at time t, and distance x from its centre of vibration was given by

$$u = a \sin 2\pi\left(t - \frac{x}{\lambda}\right)$$

where a is the intensity of the wave of length λ (33). Using this equation Fresnel was able to describe mathematically diffraction phenomena with a considerable degree of accuracy. One of the judges of the prize, Poisson (34), an opponent of the undulatory theory, calculated, using Fresnel's equations, that a bright spot of light would occur in the centre of the diffraction pattern of a small round diffractor. This he thought was a phenomenon which could not occur and thus falsified the theory; however, Arago (35) experimentally verified Poisson's prediction (36). From the outset therefore Fresnel's work displayed both a remarkably accurate explanative power, and a considerable predictive ability. These two aspects of the theory led Fresnel and his successors to assume that the luminiferous aether must exist as a physical entity. But apart from this Fresnel had made no other assumptions about the aether; consequently there was no need for Fresnel to postulate anything about the interaction of light and matter other than that self-luminous matter imparted vibrations to the aether.

When Fresnel began extending the undulatory theory to optical phenomena other than diffraction, and in particular to polarisation and double refraction, he discovered that it was necessary both to construct an aether and to posit a structure of matter for media which possessed these optical properties. Fresnel had been led to investigate these phenomena after he and Arago (36) had observed that

> two rays of light polarised at right angles do not produce any effect upon each other under the same circumstances in which two rays of ordinary light produce destructive interference (37).

In the paper in which they reported this observation neither Fresnel nor Arago offered any explanation for it according to the undulatory theory. The implication of this observation was as Fresnel wrote later

> that the luminous vibrations, instead of pushing the aetherial molecules parallel to the rays, caused them to oscillate in perpendicular directions, and that these directions were at right angles to each other for two beams polarised at a right angle (38).

In other words light waves were transmitted transversely to their direction of propagation, whereas it had been previously assumed that light waves were propagated longitudinally (39). This posed considerable conceptual difficulties for Fresnel since no fluid was known to transmit this type of wave and from his account he took some time to accept the implication of his and Arago's work. However, he thought

> the facts which already furnish so many probabilities in favour of the wave system, and so many objections against that of emission, compel us to recognise this character in the luminous vibrations (40).

Fresnel considered that a theory which had already explained and predicted many phenomena must be true, even if the consequences led to peculiar inferences. After demonstrating mathematically that polarised light "cannot have any vibration normal to the waves" (41) Fresnel had to "suppose that neither does this mode of vibration exist in ordinary light" (42) since otherwise there would be nothing to prevent the light behaving longitudinally once it left the polarising medium.

Now in order to explain why some media polarised and doubly refracted light Fresnel postulated that it was "relative to the nature of the...constitution of the media possessing the property of double refraction" (43) which in this case meant that the

> molecules of doubly-refracting media do not exhibit the same mutual dependence in all directions; so that their relative displacements will give rise to different elasticities according to their directions (44).

With these hypotheses - of the structure of matter and of aether - Fresnel was able to explain the phenomena of double refraction and polarisation with as much accuracy as he had accorded previously to diffraction phenomena.

This power of explanation alone seems to have been sufficient to convince Fresnel of the physical reality of an aether which transmitted light transversely. However, not surprisingly, he felt compelled to give an account of the "possibility of the propagation of transversal vibrations in an elastic fluid" (45). He considered that such a wave propagation could be imagined if

> we may suppose that the resistance of the aether to compression is much greater than the force opposed by it to the small displacements of these layers along their own planes (46).

In other words the particles could only move in the plane of the wave, since according to this hypothesis any normal movement to the plane of the wave was insignificant compared to the force which existed between planes of aether to overcome it. Therefore Fresnel concluded:

> I think I have sufficiently proved that there is no mechanical absurdity in the definition of luminous vibrations which the properties of polarized rays have compelled me to adopt, and which has led me to the discovery of the true laws of double refraction. If the equations of motion of fluids imagined by geometers are not reconcilable with this hypothesis, it is because they are founded on a mathematical abstraction... It would...be but little philosophical to reject an hypothesis to which the phaenomena of optics so naturally lead, for no other reason than because it does not agree with these equations (47).

Fresnel was really only concerned with the waves propagated through the aether rather than with the aether itself. He thought that even though the equations of fluid mechanics did not at that moment allow for the transmission of transverse waves through a fluid, this was no reason to reject the possibility that such a fluid could exist. It would appear that it had not occurred to Fresnel that an aether which would transmit transverse waves would have to be solid; he preferred to think that mathematical equations of such a fluid had yet to be constructed. Nevertheless because he had explained certain phenomena, hitherto difficult to explain, according to his hypothesis of transverse light waves, then such a fluid must exist as a physical reality. Fresnel's hesitation in accepting the implication of his and Arago's experimental work on the

interference of polarised light indicates that Fresnel spent considerable time in coming to this conclusion; it is therefore reasonable to suppose that he was not simply offering a rationale for accepting transverse waves, but had come to believe in their physical reality, and the consequent reality of the luminiferous aether required to carry them.

With this new work on light and the physical implications contained therein Fresnel had turned the undulatory theory from one that was not greatly concerned with the nature of matter to one intimately concerned with it. This he fully realised in the essay on light which he wrote for the French translation of Thomas Thomson's "System of Chemistry" (48)

> If any thing can contribute very essentially to the advance of this great discovery [of the principles of atomic mechanics], and to assist us in penetrating the secrets of the internal constitution of bodies, it must be by the minute and indefatigable study of the phenomena of light (49).

This was new. Up to that time it had been purely incidental what the relationship between matter and light was, although it was realised that some relationship must exist. But Fresnel in his work on constructing a structure of matter for doubly refracting and polarising media had made this relationship explicit and further he considered that it could be extended by studying other optical phenomena, though he did not follow the consequences through.

Despite Fresnel's confidence in the physical reality of his theory, and his optimism regarding its possible consequences, his work was viewed with extreme caution. Young in an addition to his translation of Arago's "Notice sur la Polarisation de la Lumière"(50), written in January 1823, commented that

> This hypothesis of Mr. Fresnel [of transverse waves] is at least very ingenious, and may lead to some satisfactory computations: but it is attended by one circumstance which is perfectly appalling in its consequences... [This is] that the luminiferous ether pervading all space, and penetrating almost all substances, is not only highly elastic, but absolutely solid!!! (51)

Then, after a passage defining the nature of a solid body, Young continued

> It must, however, be admitted that this passage by no means contains a demonstration of the total incapability of fluids to transmit any impressions by lateral adhesion, and the hypothesis remains completely open for discussion, notwithstanding the apparent difficulties attending it (52).

Young did not deny the existence of the aether suggested by Fresnel; he merely pointed out that the physical assumptions involved were decidedly difficult to comprehend. He did moreover suggest, as Fresnel had done, that it might be possible for a fluid to possess the property of transmitting transverse waves, although the mathematical equations which would describe such a fluid had yet to be devised. Both Fresnel and Young it would appear were willing to imagine the existence of a fluid which transmitted transverse waves rather than to deny the existence of transverse waves or to admit that the aether was solid.

The undulatory theory as devised by its founders possessed a marvellous explanative power for numerous optical phenomena which had hitherto been ill explained. Also, as it turned out, Fresnel's theory had a considerable power of prediction exemplified by W. R. Hamilton's discovery of conical refraction (53). This explanative and predictive power was the basis for the claim by the supporters of the theory that light was a transversely propagated undulation in the luminiferous aether. In other words since the theory could explain optical phenomena by simply making this assumption there was no pressing need to worry about how exactly the aether worked. So when it came to stating that the theory provided a physical representation of optical phenomena, there was some degree of reservation on the part of its founders. In the case of Fresnel not very much, in the case of Young considerably more. While Brewster's motivation in objecting to the physical validity of the undulatory theory was based on his philosophical ideas of what constituted a "true" hypothesis (54), he did have a valid point when he claimed that the undulatory theory was not a physical representation of phenomena.

Brewster disliked the way in which scientists had assumed the physical validity of the theory without having demonstrated that it was in fact physically valid. To Brewster the undulatory theory must have seemed like some sort of vast calculating

device with the ability to predict new facts. But he considered:

> The power of a theory,...to explain and predict facts, is by no means a test of its truth; and in support of this observation we have only to appeal to the Newtonian Theory of Fits, and to Biot's beautiful and profound Theory of the Oscillation of Luminous Molecules (55).

Brewster did not suggest that either Newton's or Biot's theories were true, indeed he tended to regard himself as a "rienist" (56) so far as optical theories were concerned, that is someone who attempted to avoid theory altogether in his work. Brewster simply meant that these two theories existed as alternative hypotheses by which optical phenomena could be explained. This agreed with John Herschel's (57) view of the undulatory theory of light in the early 1830s.

> It is by no means impossible that the Newtonian theory of light, if cultivated with equal diligence with the Huyghenian, might lead to an equally plausible explanation of phenomena now regarded as beyond its reach. (58).

In other words Herschel, though he was more favourably inclined towards the undulatory theory of light than Brewster, and was later to become an ardent undulationist, long treated the validity of the theory with caution. For example when he discussed polarisation in his so-called "Essay on Light" (59) he commented after stating the laws of interference of polarised light

> We use in their ennunciation, and indeed throughout the sequel of this part of the doctrine of Light, the language of the undulatory system, as really the most natural, and adapting itself with the least violence and obscurity to the facts (60).

Again Herschel implied that the undulatory theory was at present the best available theory which fitted the facts, but not necessarily true.

Brewster was quite correct when he suggested that the undulatory theory was defective as a physical representation of optical phenomena. At that time the possibility of the physical validity of the aether had not been examined in any depth by the founders of the theory. Euler, Young and Fresnel had all been mainly concerned with examining and explaining optical phenomena, for which it was only necessary to study

the behaviour of waves rather than to consider the medium in which they were transmitted. The fact that, by assuming that light was transversely propagated, Fresnel had been able to explain both polarisation and double refraction was sufficient reason for him to assume that the aether required to transmit such waves existed. Because the undulatory theory was so successful in explaining phenomena scientists appeared to have felt very little need to examine the physical structure of the aether - they were more concerned with elucidating the theory rather than dealing with its physical implications. With an aether whose physical structure was unclear, it was difficult to reconcile optical phenomena to the undulatory theory where matter and light interacted; it was here that Brewster concentrated his attack on the theory, for if the theory was physically invalid then the interaction of the aether with ponderable matter ought not to be explicable by the theory. By bringing the attention of scientists to this problem Brewster, as we shall see, forced scientists to pay considerable attention to the problems surrounding the interaction of matter and light.

Chapter Two

EXPERIMENTS ON, AND OBSERVATIONS OF, EMISSION AND ABSORPTION SPECTRA TO 1830

The first thirty years of the nineteenth century was a period in which optical phenomena were increasingly studied, both experimentally and theoretically, and with an attention to detail previously unknown. One of the results of this increased activity was the realisation by various scientists that light of a single colour - homogeneous light - needed to be employed in performing some optical investigations such as, for example, the examination of interference and diffraction phenomena (1). There were essentially two reasons for using homogeneous light in optical experiments: firstly since such light was not subject to chromatic aberration when passed through lenses and consequently would not present a confused pattern of colour to the observer, the use of homogeneous light ensured that accurate measurements of optical phenomena could be made; secondly if the light used in any set of experiments was of a single, determined refrangibility then the results obtained on different occasions could be readily compared where this was required.

These reasons for using homogeneous light were expressed in different ways by the scientists who sought to discover a usable source of such light. For example Joseph von Fraunhofer (2) required such light to compare the refractive indices of different kinds of glass; David Brewster needed it to make better microscopic observations and John Herschel wanted to employ such light to examine the effect which crystals exercised on different colours.

The only way in which these scientists could ascertain whether or not a ray of light was truly homogeneous was by examining its prismatic spectrum. If the spectrum of a ray of light showed only one colour then it was homogeneous; otherwise it was not. It seems probable therefore that the search for a source of homogeneous light provided the motivation for these scientists to conduct their initial investigations of spectral phenomena.

There were essentially only three methods available by which early nineteenth century scientists thought that they could produce homogeneous light: firstly by passing ordinary light through coloured pieces of glass; secondly by passing ordinary light through a prism and isolating one particular ray; and finally by using the light emitted by flames containing different chemical substances. All these methods had disadvantages: pieces of coloured glass did not transmit light of a single refrangibility, but light of many different colours; in the spectrum produced by the prism it was difficult to orientate oneself with any certainty; and the light produced by flames was not totally homogeneous. Fraunhofer, Brewster and Herschel all had to discover and overcome these inherent difficulties in the available methods for the production of homogeneous light, in order to produce a source of light which they could use in their experimental work.

Fraunhofer, according to the title of his first paper published in 1817, began his optical investigations with an intention to perfect the achromatic telescope (3) by eliminating chromatic aberration from the object lens. In order to do this the object lens had to be composed of at least two lenses each made of a different type of glass with complementary refractive indices. To construct such an achromatic lens it was essential to know not only the refractive indices of the pieces of glass which made up the lens as accurately as possible, but also the ratio of dispersion for particular sections of the spectrum between the two pieces of glass. This latter could be calculated quite easily using the refractive indices of the two pieces of glass at each end of the section of the spectrum under examination.

Such calculations would, as Fraunhofer realised, be wasted, if the glass used in the lenses was not as homogeneous as possible. Fraunhofer had learnt the art of making homogeneous glass in 1809 from Pierre Guinand (4) while working for the optical instrument making firm founded by Joseph von Utzschneider (5) in Munich in 1802; Utzschneider had employed Guinand to teach Fraunhofer who two years later was to become director of glassmaking. Thus by 1811 Fraunhofer was in a position to begin detailed studies of the optical properties of the homogeneous glass he produced.

In every experiment Fraunhofer made to determine the index of refraction of a different piece of optical glass he had to use homogeneous light of the same refrangibility, since otherwise he would not be able to validly compare his results, nor use them to calculate ratios of dispersion. He stated that in order to obtain these ratios for different pieces of optical glass "It would be of great importance to determine for every species of glass the dispersion of each separately coloured ray" (6); this meant that he had to obtain homogeneous light of known refrangibility for every colour. Fraunhofer first attempted to produce homogeneous light by using pieces of coloured glass or coloured liquids as light filters, but vainly, for he discovered that

> In every case, the white light which passed through [the filter] was still decomposed into all its colours, with this difference only, that in the spectrum, the colour peculiar to the glass or the fluid was more brilliant than the rest (7).

It was therefore impossible to use simple glass or liquid filters to obtain homogeneous light.

Fraunhofer next examined the light originating from flames produced by burning sulphur or alcohol, but he discovered that they too did not produce homogeneous light. However, in the course of this work he observed that flames

> such as that of a lamp, particularly that of a candle, and, in general, the light produced by the flame of a fire, exhibit between the red and yellow of the spectrum a clear and well marked line, which occupies the same place in all the spectra... It appears to be formed by rays which are not decomposed by the prism, and which consequently are homogeneous (8).

Fraunhofer had observed what he was later to call the R line, caused, though he did not realise it, by the presence of sodium in the flame. It is clear that Fraunhofer, for reasons which he did not state, had decided that the refrangibility of the yellow line was invariable; the R line was therefore ideally suited to his purpose of examining the optical properties of glass.

Although Fraunhofer had discovered a species of light which possessed an invariable refrangibility and could be easily identified this was not enough, for "it was, however, absolutely necessary for me to have homogeneous light of each colour" (9). To this end he constructed an apparatus (fig. 1) whereby light from six flames (BC), fixed on a table, was passed through six slits

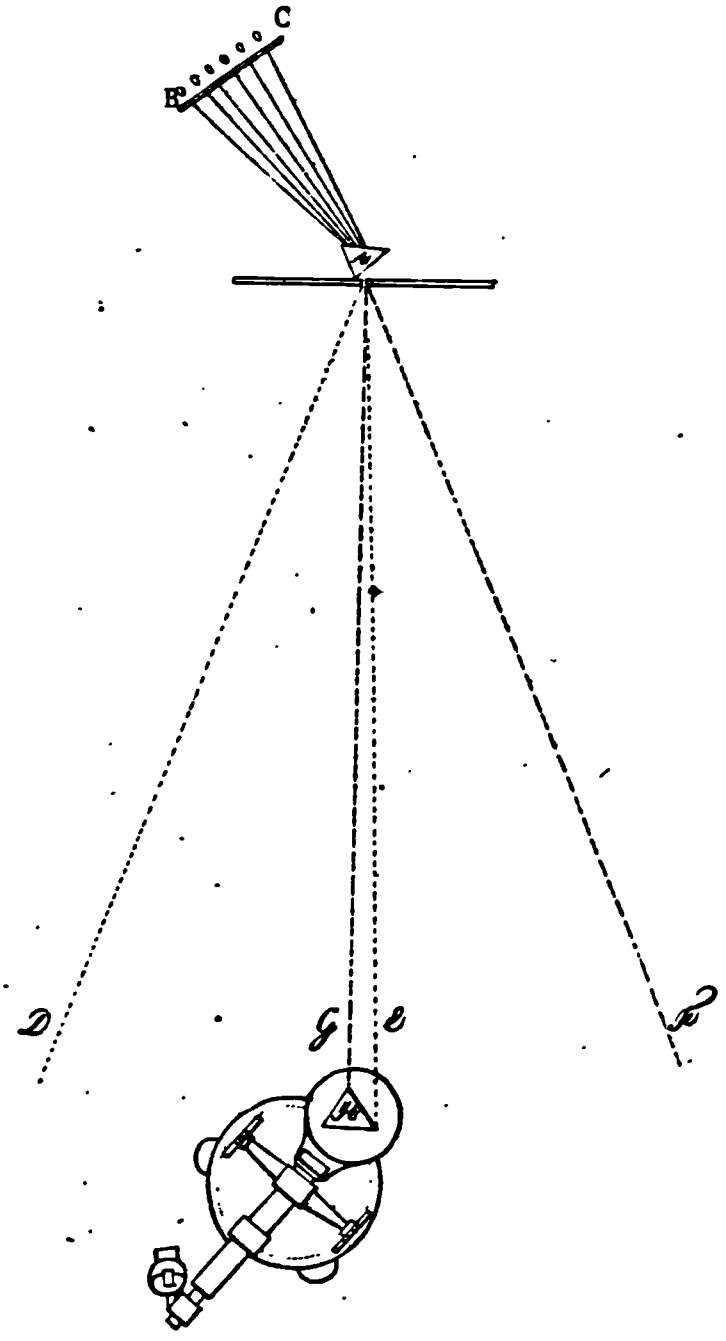


fig.1

Fraunhofer's apparatus to obtain homogeneous light of different colours.

onto a prism and slit (A). 692 feet (10) from this latter slit Fraunhofer placed a prism (H), the refractive index of which was to be determined, in front of the telescope of a modified theodolite. The image in the telescope was a set of six coloured spots of light (fig. 2),

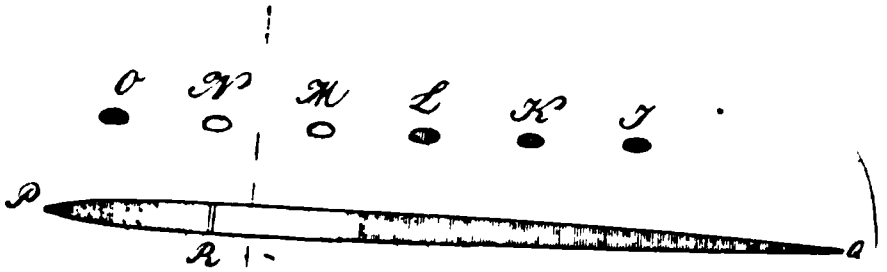
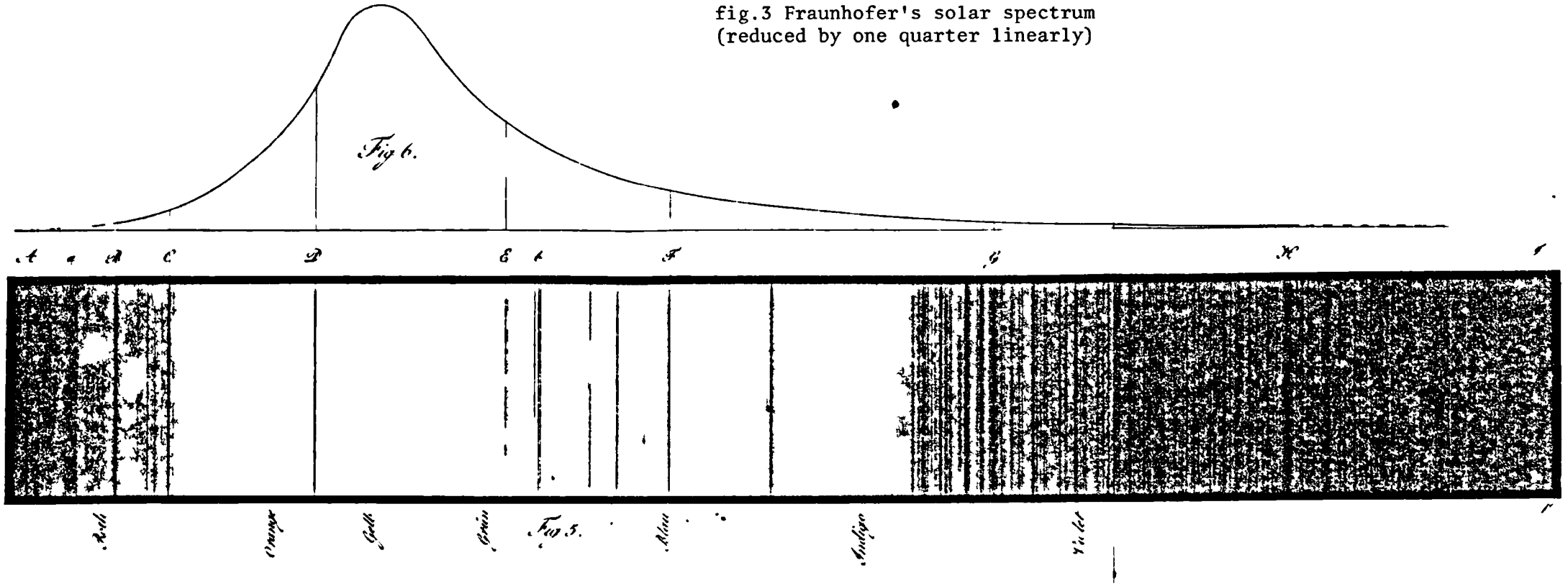


fig.2

the red light originating from the flame at C, while the yellow light originated from the flame at B; the other four colours were generated by the remaining flames. To ensure that the same spots of light were always observed by the telescope, Fraunhofer adjusted the position of the flames until the yellow spot of light (N) was in the same position as the R line which was produced by another flame. Since the six flames were fixed relative to each other, the same six spots of light would always be observed in the telescope whenever the position of the flames were properly adjusted. With this apparatus Fraunhofer was able to determine the refractive indices of various pieces of optical glass for each of the six colours to what he considered to be six significant figures. Consequently he was able to calculate the ratio of dispersion between two consecutive spots of colour to three significant figures (11). This apparatus had a major disadvantage in that the brightness of the light from the six flames was considerably reduced in intensity after passing through two prisms and 692 feet of air. It appears therefore that Fraunhofer could only use the apparatus at night (12) which meant that observations of the fainter spots of light (red, violet and blue) proved difficult to make (13). Consequently he decided that in order to obtain greater accuracy in his measurements he would need to use a light source which would produce brighter red, violet and

fig.3 Fraunhofer's solar spectrum
(reduced by one quarter linearly)



Zu Fraunhofers Abh. Denkschr. 1814 13

blue spots of light than that given by his original six flames.

The only possible source of light available to Fraunhofer which was bright enough for his purpose was the sun, which he next employed. He passed the light of the sun through a slit and thence onto a prism which he examined with the telescope of a theodolite. He originally sought to locate the bright yellow line in the solar spectrum but

> discovered, instead of this line, an infinite number of vertical lines of different thicknesses. These lines are darker than the rest of the spectrum, and some of them appear entirely black (14).

On further investigation he observed

> The proportion...of these lines to one another appeared to be the same for all refracting substances; so that one line is found only in the blue, another only in the red, and hence it is easy to recognise those which we are observing (15).

Fraunhofer counted 574 of these dark lines in the solar spectrum and he labelled the more prominent among them with the letters A (in the red), a, B, C, D, E, b, G, H, I (in the violet) (fig. 3). He did not say why he had used both upper and lower case letters, but it appears from an examination of his map of the solar spectrum that a and b are groups of three or four lines rather than the prominent single lines which he denoted by the use of upper case letters.

Fraunhofer realised that the refrangibility of the yellow R line and the dark D line was exactly the same, and he confirmed this identity experimentally by passing light from a flame through the slit which he had used for solar light when he observed that the R line occurred in "exactly the same place" as the D line (16). He did not observe that the D line was in fact composed of two lines very close together until some years later (17) when he also noted, presumably as a consequence of this observation, that the R line was also double (18).

Fraunhofer's discovery of these "fixed" lines in the solar spectrum meant that he no longer had to employ his earlier apparatus to ensure that he obtained the same homogeneous light for his experiments, since this could now be done simply by identifying the reqired lines in the solar spectrum. Using these lines Fraunhofer was able to determine the refractive indices of various media to seven significant figures, and consequently the ratios of

dispersion to four significant figures. Fraunhofer had therefore achieved his original purpose, namely discovering a means of producing homogeneous light which could be used repeatedly in optical experiments. He was able with these techniques to build refracting telescopes such as the 9½ inch at Dorpat used by F. G. W. Struve and the 6½ inch heliometer at Königsberg used by Bessel to detect stellar parallax (19).

Fraunhofer, in addition to demonstrating the utility of these lines, was also, to a certain extent, concerned with their nature. In particular he wanted to be sure that they were not caused by some peculiarity of his optical apparatus; for, if this were the case, it would render his work invalid. As he stated

> Various experiments and changes to which I have submitted these lines, convince me that they have their origin in the nature of the light of the sun, and that they cannot be attributed to illusion, to aberration, or to any other secondary cause (20).

Although he did not describe what these "experiments and changes" were he presumably relied on the fact that, since these lines persistently recurred with their invariant refrangibilities in all possible circumstances, they could not be caused by such chance phenomena. Fraunhofer did describe his investigation of the possibility that the lines might be caused by the diffraction of the solar light as it passed through the slit: to show that this was not the case he replaced the slit with a small round hole which when viewed through the telescope appeared as a thin strip of light; he then placed a plano-convex lens in front of the theodolite telescope objective, which turned the strip into a broad band, in which the lines were still present. From this Fraunhofer concluded that the lines could not be caused by the diffraction of light by the slit (21).

In his paper on diffraction gratings (22), Fraunhofer stated that the principles of diffraction and interference could "furnish an explanation of the cause of the origin of the lines and bands which are seen in the prismatic spectrum" (23). He added that he would leave the elucidation of this to another paper, but he never wrote this paper, and the cursory manner in which he treated the problem of the cause of the lines in the solar spectrum implies that he thought that it was not really essential to his work. To him it was sufficient to show that these lines did

actually exist in the solar light and that their property of invariant refrangibility could be utilised in the making of optical experiments. Apart from his vague statement as to cause, Fraunhofer maintained this pragmatic attitude towards the lines in his paper on diffraction gratings. There he was concerned with the phenomena produced by the gratings, and he employed the lines simply to make accurate measurements of the phenomena.

The plano-convex lens which Fraunhofer had used in his apparatus to show that the lines were not caused by diffraction enabled him to analyse prismatically faint sources of light. In particular he was able to examine the spectra of some planets and some stars. Thus when he examined the spectrum of Venus, he was able to identify the lines D, E, b and F which convinced him "that the light of Venus is, in this respect, of the same nature as that of the sun" (24). On the other hand his examination of the spectrum of Sirius and other (unnamed) stars revealed that they possessed lines which did not occur in the solar spectrum (25) and were indeed different from each other. Fraunhofer simply reported these observations, and did not draw any conclusions from them about either the nature of the lines, or the nature of Venus or of the stars which produced them. When a few years later he extended these observations he discovered that, as with Venus, the spectra of the Moon and Mars were the same as that of the sun (26), and that the spectrum of Pollux resembled Venus, i.e. the sun, and definitely showed the D line. Castor showed a spectrum which resembled Sirius, while Capella showed the D and b lines as did Betelgeuse, while he observed only the D line in the spectrum of Procyon (27). But as with his earlier observations of planetary and stellar spectra, Fraunhofer drew no conclusions from these new observations. Indeed Fraunhofer gave no reason for making these observations, nor did he record why he had examined the spectrum of electric light produced by a friction machine, which he found to possess several bright lines in different positions from the lines which occurred in flame spectra (28).

I would suggest that for Fraunhofer these results were interesting, but not particularly relevant to his main work, and that he added them at the end of his papers to show that the lines he had discovered could be detected in a wide variety of light

sources. As he commented at the end of his first paper, he had been mainly concerned with the practical utility of the lines but he thought that they might

> furnish interesting results in physical optics; and it is therefore greatly to be wished that skilful natural philosophers would condescend to give them some attention (29).

It would therefore have been quite natural for Fraunhofer to give as much experimental information as possible about the lines, even though it was not relevant to his main optical work of isolating a source of homogeneous light.

Attempts to isolate homogeneous light were not over, since it took some time for knowledge of Fraunhofer's work to be disseminated in Europe; in particular it appears that it was not until mid-1822 that it became generally known in Britain. Thus both Brewster and Herschel appear to have been in ignorance of Fraunhofer's work when they began their own attempts to obtain homogeneous light in the early 1820s (30). Indeed Brewster and Herschel were ignorant even of each other's work until Brewster read a paper in April 1822 to the Royal Society of Edinburgh in which he described the experiments he had performed on the absorption of light passing through various media, and on the emission of light by various flames all designed to isolate homogeneous light (31). Herschel responded immediately by writing a paper to the Royal Society of Edinburgh describing experiments he had himself performed which were similar to those reported by Brewster (32).

Brewster wanted to overcome the problem of chromatic aberration in microscopes, which had not yet been successfully overcome by the use of achromatic lenses (33). He therefore tried to avoid the problem by using homogeneous light which would not be subject to chromatic aberration when passed through the lenses of ordinary microscopes.

Brewster's original method of obtaining homogeneous light was to pass ordinary light through various coloured media, which he fully expected would produce such light. But when he analysed the light so produced prismatically, he discovered that these media transmitted light of various colours and intensities. This observation Brewster thought "remarkable", implying that he had, at

that time, no knowledge of Fraunhofer's work (34). From his observation of the above experiments he was, he said, led to investigate "the manner in which coloured media absorb the different portions of the prismatic spectrum" (35). The substances through which he passed light were mostly pieces of coloured glass, but he also used materials like copper sulphate in the form of a thin lamina (36). The results showed him that a wide variety of absorptive actions could occur. Although these experiments were to lead him during the 1820s to develop theories of the colour of natural bodies and of the tri-coloured constitution of the spectrum (37), they did not assist him in his attempt to obtain a source of homogeneous light.

Brewster's next idea was to investigate Thomas Melvill's (38) observation, reported in 1752, that yellow homogeneous light could be produced by placing salt in a flame (39). Melvill's method of obtaining the homogeneous light had the defect that the light so produced lasted for only a short time, and hence it was not suitable for the purpose of prolonged microscopic illumination. According to Brewster's account, after much experimentation he discovered that substances whose combustion was imperfect (i.e. paper, linen, cotton etc) gave, when mixed with water, a bright homogeneous yellow light which he found could provide illumination for any desired period of time (40).

When he employed this light to illuminate objects for microscopic examination Brewster found it very successful, reporting that

> The images of the most minute vegetable structures were precise and distinct, and the vision in every respect more perfect than it could have been, had all the lenses of the microscope been made completely achromatic by the most skilful artist (41).

Brewster had therefore achieved his original object of isolating a source of homogeneous light which could be used to eliminate the problem of chromatic aberration from observations made with the microscope. He continued to develop techniques to take full advantage of this yellow light (42), but he was now no longer concerned with developing new methods of obtaining homogeneous light or with trying to isolate homogeneous light of different colours, since that obtained satisfied his requirements.

This was not the case with Herschel, who in 1819 had performed a series of experiments on the colours developed by crystals when homogeneous light of various colours was passed through them (43). For this he had needed to discover as many varieties of homogeneous light as possible, so that he could examine the phenomena produced by the crystals on light over the full range of the spectrum. Thus when Herschel sent his paper on homogeneous light to the Royal Society of Edinburgh in response to a report of Brewster's paper (44), he had already been working for some time on the problem of obtaining a sustained source of homogeneous light.

Herschel had originally approached the problem of obtaining homogeneous light in the same way as Brewster, that is by examining light which had been passed through coloured media (45). In this way he had determined the absorptive characteristics of a large number of substances - mainly coloured glass. His diagrams of absorptive action of each medium were graphs of the intensity of light of particular substances produced at each point of the spectrum (fig. 4).

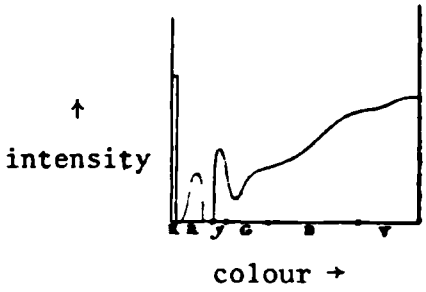


fig.4
intensity of light transmitted through blue glass

One of the results of this graphical method was Herschel's observation that although "a solution of oxalate of nickle [$NiC_4H_4O_4$] (free from cobalt) in ammonia, may at first sight be mistaken for ammonia-carbonate of copper" (46), because both substances were a similar shade of blue, there was a difference between the absorption spectra of each substance. (Although he did not draw such a conclusion, an optical test could have been provided to distinguish between the two substances). But the main result of these graphs was that Herschel discovered, as

Brewster and Fraunhofer had done, that homogeneous light could not be obtained by passing ordinary light through coloured media.

Like Fraunhofer and Brewster, Herschel went on to experiment with flame spectra. But unlike them, he examined and described the spectra produced by many different flames, including those produced by burning salts of sulphur, strontium, calcium, barium, and copper, as well as boric acid in the flame of the spirit lamp (47). He described how different types of homogeneous light could be produced by using these flames together with combinations of coloured glass filters in order to achieve his original object, but he did not describe how he had put this light to use.

Thus Fraunhofer, Brewster and Herschel had all succeeded in obtaining a sustained source of homogeneous light for use in their various optical experiments. Neither Brewster nor Herschel needed to make measurements with anything like the accuracy which Fraunhofer had required. There was therefore no necessity for them to devise such a complicated experimental apparatus for isolating homogeneous light as that which Fraunhofer had utilised. For the same reason there was no need for Brewster or Herschel to examine the solar spectrum. All three scientists wanted to devise techniques for obtaining homogeneous light which would satisfy their own particular experimental requirements. Their differing needs caused them each to pursue different courses of experiment. In the case of Fraunhofer the need for accurate measurements led to his examination of the solar spectrum. Brewster, on the other hand, wanted homogeneous light specifically in order to perform microscopical observations and he ceased any new work on flame spectra once he had achieved this. Herschel who, like Fraunhofer, required homogeneous light of a number of colours, was led to investigate the spectra produced by different flames. Common to all their work on absorption and flame spectra was the desire to devise methods for the production and use of homogeneous light rather than the consideration of the origin of this light. The possibility of using such light to determine the physical or chemical composition of the substances which produced the light did not occur to them, even though it was obvious from their work that the differences in the light produced by absorption through different coloured pieces of glass, or by different

flames, must be produced by differences in the matter within the glass or flame.

However, the use of light for chemical analysis did occur to Henry Fox Talbot (48), who in 1826 published a paper on a general system of chemical analysis using flame spectra (49). While Brewster and Herschel had shown that a particular flame always produced the same spectrum, Talbot, on the other hand, wanted to be in a position such that:

> a glance at the prismatic spectrum of a flame may show it to contain substances, which it would otherwise require a laborious chemical analysis to detect (50).

The difficulty was to establish which substances produced which spectra. Talbot was not a particularly good chemist, as he fully recognised, writing on one occasion "I am not much of a chemist, but sometimes amuse myself with experiments"(51). The isolation of the substances which caused a particular line in a flame spectrum was therefore to prove a difficult task for Talbot, since he could not easily use the required analytical chemical techniques. On the other hand Talbot's motivation in doing this work was to provide an easy method of qualitative chemical analysis which would avoid the need to use quantitative techniques when they were not really required.

Talbot's examination of the flame spectrum of various salts of sodium showed that an apparently homogeneous yellow line occurred in each spectrum (52). He claimed that whenever this line was present in the spectrum, sodium was present in the flame. But he had also observed that the yellow line "frequently appear[ed] where no soda can be supposed to be present" (53). Substances in which the yellow rays occurred where according to Talbot they should not if sodium was the cause included "wood, ivory, paper, &c" (54). Talbot had not realised that sodium was present in all these substances nor that only a very little sodium was required to produce the yellow light. This failure meant that he had to consider those cases where the yellow light did occur in the spectrum and where sodium should not, in his opinion, exist. For example he had noted that

> Salt sprinkled on the platina [held in a flame], gives yellow light while it decrepitates, and the effect may be renewed at pleasure by wetting it (55).

Talbot did not realise that the sodium of the salt had been reactivated to emit yellow light when he wetted the platina; instead he supposed that the renewal of the yellow light was produced by the water. Talbot consequently suggested that the yellow light caused by the salts of sodium might be due to the water of crystallisation in those salts. This he said would explain why wood, ivory and paper etc showed the yellow light since "the only principle which these various bodies have in common with the salts of soda, is water" (56). In other words Talbot was looking for a common substance which caused the yellow light; unfortunately he failed to realise the wide spread distribution of sodium and so chose water as the common substance instead.

Two problems arose from postulating that water was the cause of the yellow light. Firstly Talbot had observed that the salts of potassium did not show the yellow light which they should have done were it caused by water of crystallisation; secondly sulphur, which did not have any obvious connection with water, did, as Herschel had observed, produce the yellow light. In this latter case Talbot tentatively suggested that this production of the yellow light might be connected with the fact that the specific gravity of water was almost half that of sulphur which, to him, suggested that there might be further connections between these apparently dissimilar materials other than his newly discovered optical similarity (57).

In spite of Talbot's evident confusion about where the cause of the yellow light lay, he seems to have eventually concluded, for reasons which are not at all clear, that it was caused by sodium. His examination of various salts of potassium (nitrate, chlorate, sulphate and carbonate) had shown him that each produced red light of a definite invariable refrangibility (58). From these two observations - of homogeneous light produced by sodium and by potassium - Talbot concluded·

> That whenever the prism shows a homogeneous ray of any colour to exist in a flame, this ray indicates the formation or the presence of a definite chemical compound (59).

That is, if a spectrum of a flame was observed to possess a

homogeneous ray of light, then in that flame, according to Talbot, there existed a chemical compound which could be identified. The existence of a homogeneous ray indicated which metal was present (i.e. sodium, potassium, strontium, etc (60)) but not its particular salt. It was from this work that Talbot derived his conclusion that prismatic spectra could be used to show the presence of certain substances in a particular compound, though at this time he did not think it could identify the compound entirely.

Talbot, like Fraunhofer, Brewster and Herschel failed to express any opinion as to the cause of the discontinuities in spectra; he was merely concerned with demonstrating their existence, describing them, and, where possible, suggesting their use for chemical analysis. This attitude is reflected in his views on the solar spectrum and the spectrum of the flame of cyanogen (C_2N_2) which for reasons that are not clear, he chose to investigate. While he recorded Fraunhofer's observation that the solar spectrum was crossed by innumerable dark lines, he added that no other spectra like this, apart from those of the stars and planets, had been discovered (61). The following year (1827) Talbot and Faraday, presumably at the former's instigation, jointly examined the spectrum of the flame of cyanogen. They discovered that its spectrum was

> crossed by innumerable dark lines like the solar spectrum, & there are two broad dark belts in the violet as in the solar light (62).

This observation did not aid Talbot in interpreting the meaning, chemical or otherwise of either the solar or the cyanogen spectrum; Talbot simply did not have any views on the cause of these discontinuities in spectra.

Talbot had tried to establish his particular physical use of line spectra by purely experimental means. He does not appear to have considered the physical nature of the lines and therefore he could not form any notion of why spectral lines were caused or whether or not a particular line was caused by a single chemical element. When he came to conduct his experiments in an attempt to devise an easy method of qualitative chemical analysis, Talbot was easily confused by the ubiquity of the yellow light

because he had no idea either from chemical or optical considerations why such light should exist. Talbot did believe that his experiments alone were sufficient to justify his conclusions regarding the physical uses to which line spectra could be put. However this work could not be formalised into a usable system of chemical analysis until better analytical chemical techniques were employed to determine which lines belonged to which chemical element, and until a theory of spectral lines had been devised which would ensure that problems of the ubiquity of line spectra would not occur.

Talbot's paper represents a significant change in attitude towards line spectra. Up to that time Fraunhofer, Brewster and Herschel had used the fact that the lines possessed invariable refrangibilities as a reliable means of producing homogeneous light. Talbot on the other hand had realised that the lines must have some physical meaning and consequently investigated their use for chemical analysis. In other words Talbot investigated the lines as an end in itself while his predecessors used the lines as a means to an end. None of them tried to develop a theory of line spectra, and, indeed, they must have thought that there was little reason for them to do so. All that they needed to show was that the lines (bright or dark) were inherent in certain varieties of light, and that they could be utilised effectively.

Herschel in his synthesis of optical knowledge, the so-called "Essay on Light" completed in 1827, did not deal with the use to which the lines could be put, but rather concentrated on questions concerning their nature. He did not offer any explanation for the existence of the lines in terms of either the undulatory or particulate theories of light, but he did attempt to show where the cause of the lines in various spectra lay. This he could do to a certain extent without reference to any theory of light.

In particular Herschel considered the nature of the dark lines in the solar spectrum in the context of his theory of the sun (63). He based his theory of the physical constitution of the sun on his explanation of the sun spots, supposing that the sun possessed a hot luminous central body surrounded by an even

hotter atmosphere. Sun spots, he thought, were gaps in the solar atmosphere exposing the central body of the sun which, because it was cooler, would appear black in comparison with the rest of the solar atmosphere (64). Using this theory of the sun Herschel had no difficulty in suggesting a cause for the Fraunhofer lines:

> It is no impossible supposition, that the deficient rays [dark lines] in the light of the sun and stars may be absorbed in passing through their own atmospheres, or, to approach still nearer to the origin of the light, we may conceive a ray stifled in the very act of emanation from a luminous molecule by an intense absorbent power residing in the molecule itself; or, in a word, the same indisposition in the molecules of an absorbent body to permit the propagation of any particular coloured ray through or near them, may constitute an obstacle in limine to the production of a ray from them (65).

Because Herschel had postulated both a luminous central body and atmosphere for the sun it was necessary for him to suggest that the solar atmosphere not only absorbed light from the central body of the sun but also did not emit light of certain refrangibilities. This inability of molecules to emit light of certain refrangibilities Herschel thought might also be the cause of the absorption of light from the central body of the sun. He no doubt thought that it would be highly unlikely for molecules which could not emit light of certain wave-lengths to be able to transmit light of these same refrangibilities. But beyond this Herschel was not prepared to commit himself; he did not have an effective explanation of the absorption lines. He had argued that the Fraunhofer lines were caused by absorption and non-emission of light by the molecules in the solar atmosphere; but he had not suggested how this could take place. In effect he had located where the cause of the Fraunhofer lines lay, but not what it was.

One of the results of this work was that Herschel was able to establish a close connection between the absorption and emission of light. He had argued that there existed molecules which even at high temperatures could not emit light of certain refrangibilities. A flame spectrum instead of being viewed as a set of bright emission lines could be perceived as a set of dark spaces which were caused by the inability of the molecules in the flame to emit light of those refrangibilities. If it could be

explained why the absorption of specific rays of light should occur then it would be possible to explain why the emission of specific rays should also occur. The difficulty was that despite his identification of a close relationship between emission and absorption Herschel could go no further unless he explained these phenomena according to either the undulatory or particulate theories of light, and this, it appears, he was reluctant to do in his "Essay".

Similarly Herschel was also reticent in discussing the work on flame spectra which had been so recently performed both by himself and by Talbot (66). He did not specifically describe the use of flame spectra produced by various substances but instead recorded the individual colours imparted to flames by the salts of sodium, potassium, calcium, strontium, magnesium, lithium, barium, copper and iron (67). He concluded from this work that

> The colours...communicated by the different bases to flame, afford in many cases a ready and neat way of detecting extremely minute quantities of them; but this rather belongs to Chemistry than to our present subject (68).

Herschel using the flame test for the presence of chemical substances was able to achieve exactly the same result as Talbot had using the more complicated method of spectrum analysis; that is by using light they were both able to identify the metal of a salt. In the cases of strontium and calcium, however, since both substances imparted red to the flame, Herschel had to describe their prismatic spectra in detail in order to distinguish between them. It would appear therefore that Herschel was well aware of the value of using flame spectra to differentiate chemical substances from each other, since otherwise he would not have reported the differences which existed between the flame spectra of calcium and strontium.

One of the reasons which may have caused Herschel to describe the flame test rather than Talbot's spectral analysis was because he considered that there was an explanation for the colour of flames produced by different substances. He held that these differences were due to "the molecules of the colouring matter reduced to vapour, and held in a state of violent ignition" (69). This, though Herschel did not say so explicitly, is independent of any

hypothesis respecting the nature of light, since the molecules could be either emitting light particles or producing vibrations in the aether. Herschel was prepared to describe the use of optical phenomena, in this case the colour of flames, for which he could provide an explanation, but since he did not have an explanation for the discontinuities in flame spectra, he was prepared only to describe their use in circumstances where the flame test was inadequate. For these two reasons - the simplicity of the flame test for chemical substances when compared with flame spectra, and the fact that Herschel did not have any explanation for the existence of discontinuities in the flame spectrum - he refrained from giving a full account of Talbot's work on flame spectra. This position contrasts strongly with Herschel's handling of the subject of the polarisation of light in his "Essay". After he had outlined Fresnel's explanation of polarisation according to the undulatory theory, Herschel proceded to agree with Fresnel that polarisation laid open "the constitution of natural bodies, and the minuter mechanism of the universe" (70).

Thus where Herschel had an explanation of optical phenomena according to the undulatory theory, as in the case of polarisation, he was quite prepared to outline its physical consequences, while in the case of line spectra for which no explanation according to the undulatory theory had been devised, Herschel was not prepared to commit himself to any view concerning their physical meaning. A lack of a physical explanation for the existence of line spectra had not been a hindrance to Talbot in positing a connection between emission spectra and the chemical constitution of particular substances, but to Herschel it appears to have been a considerable obstacle, for he did not mention either that the obstacle existed or Talbot's explicit suggestion that flame spectra could be used for chemical analysis. Presumably this was because it would have required an explanation for the existence of line spectra which Herschel did not have.

Besides the problem of the cause of the spectral lines there was another question concerning their nature: namely whether or not they followed any pattern of distribution. This problem was originally discussed by Herschel in reference to the dark solar

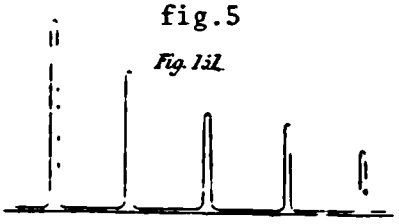
lines produced by diffraction gratings. In his "Essay", when discussing Fraunhofer's work on diffraction gratings, Herschel noted that

> On either side of this [the centre of the diffration grating image] was a space perfectly dark, after which succeeded a series of prismatic spectra, which he [Fraunhofer] calls spectra of the second class, not consisting of tints melting into each other, according to the law of the coloured rings, or any similar succession of hues depending on a regular degradation of light, but of perfectly homogeneous colours; so much so, as to exhibit the same dark lines crossing them as exist in the purest and best defined prismatic spectrum (71).

Turning to the theoretical problems of diffraction gratings he thought that

> The most interesting and remarkable point about them [diffraction grating spectra] is the perfect homogeneity of colour in the spectra, indicating a saltus, or breach of continuity, in the law of intensity of each particular coloured ray in the diffracted beam. For it is obvious, that taking any one refrangibility (that corresponding to the fixed line C, for example ,) the expression of its intensity in functions of its distance from the axis must be (analytically speaking) of such a nature as to vanish completely for every value of that distance, excepting for a certain series in arithmetical progression, or, as it is called, a discontinuous function; so that the curve representing such value, having the distance from the axis [of the diffraction grating] for its abscissa, must be a series of points arranged above the axis at equal intervals; or, at least, a curve of the figure represented in fig. 151 [5] (72).

fig.5



He commented that the function could be derived from Fresnel's equation of diffraction but added that it "involves too many complicated considerations to enter into in this place" (73).

He argued that since Fresnel's equation for the intensity of diffracted light possessed singularities at regular intervals, the function which would describe the position of the spectral lines must also possess singularities at regular intervals. In other words because spectral lines could be produced by diffraction phenomena they were therefore capable of a mathematical description. To account for the observation that line spectra did not appear to be equally spaced, Herschel supposed that there existed a set of lines with different but related intensities which would consequently account for the wide variety of lines in the solar spectrum.

After reading Herschel's "Essay", Young took up the problem of the nature of the function which would describe the spectral lines produced by diffraction gratings (74). He agreed with Herschel that the distribution of the lines produced by the grating could be described in an analytical formula, but he was not sure in what way such a function could be devised. However, it did occur to him, as he put it, that

> the very simple formula $\cos x + \cos 2x + \cos 3x + \ldots + \cos nx$ will give the discontinuous spectra exactly thus
>
> 
>
> the sum being $\frac{\sin nx}{x}$ very nearly. It requires no demonstration and I am rather proud of it (75).

This he may well have derived from the work of Fourier of which he was certainly aware (76). The curves which are generated by this formula are dependent on n, and possess singularities whenever x is a multiple of 2π, as Young pointed out (77). Although he did not go into details, it may easily be imagined that if the spaces between the x's were suitably determined then an approximation to the distribution of line spectra, though not to their intensity, might be achieved.

Thus both Herschel and Young were prepared to theorise about the distribution of the dark solar lines provided that these were caused by diffraction gratings which, for them, ensured that a regular distribution of the lines, amenable to mathematical description, must exist. They both suggested how empirical formulae

could be devised which would describe the distribution of line spectra; but these formulae were not based on any theory concerning the nature of the lines.

Out of the search for a source of homogeneous light, Fraunhofer, Brewster and Herschel had thus discovered a new class of optical phenomena - line spectra. By 1830 the existence of the lines was well known; their place of origin had been located; but there was no theory which explained why they should exist. This meant that those scientists who were interested in the theory of the lines were cautious in their conclusions except when they were on safe theoretical ground. This then was the situation when Brewster renewed his interest in line spectra.

Chapter Three

THE DEBATE ON THE NATURE OF ABSORPTION 1830-1835 AND ITS CHEMICAL CONSEQUENCES

The success of the undulatory theory of light in the early nineteenth century in accounting accurately for a large number of previously inexplicable optical phenomena in a relatively simple and elegant manner highlighted those phenomena which were not yet explicable according to the theory. In 1830 phenomena for which explanations still had to be provided included the absorption, dispersion and diffusion of light; within a very few years each of these phenomena were to be used by some opponent of the undulatory theory as a negation of that theory. It was therefore ensured that a good deal of attention would be directed towards understanding each of these phenomena in terms of the undulatory theory.

Fresnel in 1822, in his elementary account of the undulatory theory of light, had fully realised that absorption was a phenomenon which had not been explained according to the theory. As he remarked.

> Without doubt there are still many obscurities [in the theory] to be enlightened, especially such as relate to the absorption of light, for instance,... in the passage of light through bodies imperfectly transparent (1).

Although during the 1820s scientists such as Brewster, Herschel and Talbot had discovered considerably more experimental and observational information than Fresnel had known in 1822, yet by the end of the decade none of these observations had been explained in terms of the undulatory theory. All that had been effectively established by 1830 was that absorption must be caused by the ponderable matter which constituted absorptive media. The question which then arose was how could ponderable matter prevent the transmission of light of certain refrangibilities? In other words, why should the Fraunhofer lines exist

in the solar spectrum and why should pieces of coloured glass selectively absorb light of particular refrangibilities but not others?

It was David Brewster, one of the originators of the experimental study of absorption, and a person whose views on the undulatory theory were ambiguous to say the least, who drew the attention of the scientific world to the fact that absorption had not been explained according to this theory. Brewster, as mentioned in the previous chapter, had in the 1820s been mainly concerned with questions relating to the mixing of colours (2), which had been raised as a result of his original work on absorption. In the early 1830s he returned to the study of absorption convinced that his investigation would provide

> a general principle of chemical analysis, in which simple and compound bodies might be characterised by their action on definite parts of the spectrum (3).

There is no indication as to how Brewster arrived at this conclusion, as there is nothing in his writings in the 1820s which remotely suggests that he held such an idea. Nevertheless he now initiated the series of experiments required to turn this idea into a practical method of qualitative chemical analysis. He began by examining the absorption spectra produced by various compound bodies (not named) which he found produced absorptive actions at different points in their spectra (4). He then investigated the hypothesis that these actions were the result of the combined absorptive properties of the chemical elements which formed the compound bodies. In particular he examined the absorptive action which a thin lamina of sulphur and a thin layer of the vapour of iodine (presumably held within some sort of glass container) exerted respectively on a beam of white light (5). Both of these observations confirmed him in his idea that the absorptive action which compound bodies exerted on light was caused by the absorptive properties of the individual chemical elements. For reasons which are not clear Brewster next examined the absorptive action of "Nitrous Acid Gas" NO_2) (6)

> a gaseous substance which produces more than a thousand dark lines in the spectrum of ordinary flames (7).

This phenomenon, which he probably discovered in the February or March of 1832 (8), Brewster thought bore "strongly on the rival

theories of light" (9) and he ceased, temporarily, his work on spectro-chemical analysis in order to pursue the physical consequences of this observation.

This process he began in his "Report on the recent Progress of Optics" delivered to the second meeting of the British Association held at Oxford in June 1832. At the end of a fairly comprehensive analysis of which optical phenomena had or had not been explained according to the undulatory theory of light Brewster commented that

> one of the finest fields of optical inquiry, and one almost untrodden, is that of the absorption of definite rays of the spectrum by the specific action of material atoms of those bodies through which light is transmitted (10).

Brewster had concluded from his experimental work that the cause of absorption lay with the chemical elements; this led him to assume that absorption must be caused by the simple chemical atoms which comprised the absorptive media, acting individually rather than as a group in a larger molecule. This restriction which Brewster was led to impose on any theory of absorption because of the results of his experimental work meant that he had considerably more difficulty in explaining absorption according to the undulatory theory than he would have had if he had assumed that it was caused by the molecules of a medium which could be imagined to possess complicated structures which would prevent the transmission of a number of wave-lengths.

Until his discovery of the absorptive property of nitrous acid gas Brewster's views on the undulatory theory of light had been equivocal. He had used the numerical results of Fresnel's version of the theory in his experimental work (11), without either accepting the undulatory theory as being a physically valid representation of optical phenomena, or explicitly rejecting it. Brewster, like many of his British contemporaries, had so far been carefully ambiguous in his attitude towards the theory. Thus in his "Treatise on Optics" (12) of 1831 he wrote that

> the theory of undulations has made great progress in modern times, and derives such powerful support from an extensive class of phenomena, that it has been received by many of our most distinguished philosophers (13).

Brewster thus did not state whether or not he thought the theory was true, but restricted himself to saying that the theory had been accepted by a considerable number of scientists. Even at this comparatively late stage in the development of the undulatory theory he had apparently not made up his mind as to whether the undulatory theory was a true representation of optical phenomena. But he was in a diminishing minority of scientists who failed to accept the undulatory theory completely. Those scientists like Herschel or Talbot who had been as ambiguous as Brewster about the theory in the 1820s, had by the early 1830s become committed adherents of the theory.

Brewster's main methodological objection to the undulatory theory was that in his opinion its physical validity was unproven. Its proponents on the other hand claimed that because the theory explained so many optical phenomena it must be true. Brewster, in line with his Scottish philosophical training considered that this was a necessary condition for a theory to be true but not a sufficient one (14). In his view none of the founders and subsequent supporters of the undulatory theory had attempted to show that the theory was a physically valid representation of optical phenomena, and this, for him, would alone render it sufficient as an explanation of the behaviour of light. The physical validity of the undulatory theory was a problem which had been avoided by the founders of the theory such as Young and Fresnel since it meant justifying the existence of an elastic solid aether pervading the universe. Consequently problems relating to the interaction of ponderable matter and light, such as absorption or dispersion, had not been examined theoretically according to the undulatory theory (15).

By the time Brewster wrote his British Association "Report" he had not made up his mind about the theoretical significance of the absorption spectrum of nitrous acid gas. In his "Report" he fully described the absorption spectrum of nitrous acid gas, but he did not state the name of the gas which possessed this peculiar property. He did however suggest how the phenomenon might be accounted for according to both the particulate and undulatory theories of light.

According to the former theory, Brewster supposed that when a light beam was passed through the gas

> a thousand different portions of that beam are stopped in their passage, in consequence of a specific action entered upon them by the material atoms of the gas... Such a specific affinity between definite atoms and definite rays, though we do not understand its nature, is yet perfectly conceivable (16).

Brewster is quite clear here that it is the individual atoms of oxygen and nitrogen which possess an affinity with definite particles of light. This was in line with Brewster's experimental observation that since there subsisted an unique relationship between the chemical elements and light of particular refrangibilities, the light should interact with the chemical atoms of the medium, rather than with the molecules of the medium. Despite offering this explanation of absorption according to the particulate theory of light, Brewster did not commit himself to saying that he thought that it was the correct explanation of absorption.

According to the undulatory theory Brewster postulated that the thousand wave-lengths which were absorbed by the nitrous acid gas would have been stopped by the gas

> while all waves or rays of intermediate velocities and refrangibilities are freely transmitted through the same medium: that is, a wave of red light, the 250 millionths of an inch broad, and another wave of the same light the 252 millionths of an inch broad, are capable of transmitting vibrations freely through the gas, while another red ray the 251 millionths of an inch produces vibrations which are entirely stopped by the medium. There is no fact analogous to this in the phaenomena of sound... [This] leaves the mind impressed with the conviction that the production of such a system of defective rays by the action of a gaseous medium presents a formidable difficulty to the undulatory theory (17)

Brewster here only described what would happen to light waves which were absorbed by a medium; since he could not conceive how any medium could behave in this way this was to him a difficulty in the undulatory theory; but here he did not say that this phenomenon was inexplicable according to the theory. Brewster's inability to conceive how absorption could be explained according to the undulatory theory is not particularly surprising; the pioneers and subsequent proponents of the theory had carefully avoided problems which dealt with the physical aspect of the theory. In this "Report" Brewster, I would suggest, was simply speculating

about what he appears to have considered a puzzling problem; he had as yet come to no firm conclusions concerning its theoretical significance.

Brewster had raised two points about absorption phenomena in his "Report". Firstly, and most obviously, he noted that no explanation had been devised to account for absorption according to the undulatory theory. Secondly, although in his "Report" he only hinted at this, if absorption could not be reconciled with the undulatory theory then the theory itself would be falsified. Both these points and especially the latter he was to make much more explicitly, but Brewster needed more time "maturing his ideas" as Talbot phrased it (18) before he was ready to elucidate fully the theoretical consequences of his observation.

Brewster's refusal to name the gas which had the properties which he so fully described in his "Report" is puzzling, the more so since he informed Talbot of the name of the gas; Herschel by some means unclear was also in the secret (19), and it seems probable that John Frederic Daniell (20) and William Hallowes Miller (21) also knew of it (22). It seems possible that Brewster did not want others to publish speculations on the subject based on experiment before he had fully worked out his own ideas. His telling only in private those people who would be interested naturally prevented them from doing anything prior to his own publication. This in fact restrained Talbot from publishing his discovery of a similar type of action produced by iodine vapour (23), so that he was eventually anticipated in claiming this discovery by the publication of an inferior observation of it by Daniell and W. H. Miller (24).

Brewster's first public announcement of the name of the gaseous substance was in a paper to the Royal Society of Edinburgh in April 1833 (25). Here Brewster restricted himself to providing a detailed account of his experimental findings on absorption phenomena, with no reference to any theoretical implications. He described the absorptive behaviour of nitrous acid gas, adding to the description which he had provided at the British Association the fact that the intensity of the absorption lines increased as the temperature of the gas rose (26).

Brewster's observations of the large number of dark lines in this absorption spectrum appears to have led him, quite naturally, to examine the dark lines present in the solar spectrum (27). In the course of this work on the Fraunhofer lines Brewster observed that as the sun descended towards the earth's horizon, the lines grew thicker and some new lines appeared in the spectrum (28). He argued that these phenomena were caused by the increased absorptive action exerted by the greater thickness of terrestrial atmosphere through which light from the sun had to pass when it was nearer the earth's horizon, than when it was higher in the sky. He contended that it followed that some of the lines were caused by the absorption of solar light by the terrestrial atmosphere (29). But apart from the new lines in the spectrum, it was difficult to decide which lines were caused by the earth's atmosphere and which were caused by the solar atmosphere (by which Brewster probably meant the zodiacal light (30)) absorbing light of certain refrangibilities from below (31). It was conceivable that the sun caused some lines which were simply intensified by the terrestrial atmosphere. Brewster certainly thought that some of the lines were caused by the sun since he argued that the spectra produced by each of the fixed stars would be the same if the lines were caused by the terrestrial atmosphere alone. But this had been observed by Fraunhofer not to be the case (32).

The difficulty was to determine which lines originated in the solar atmosphere, and which in the terrestrial atmosphere, and which were a combination of both processes. This Brewster was unable to do. He thought that the terrestrial atmospheric lines might be detected

> in the spectrum of a Lime Ball light condensed by a polyzonal lens, and acted upon by thirty miles of atmosphere (33).

But this experimental arrangement was difficult to execute and Brewster appears not to have even attempted to try it for a quarter of a century (34). Nevertheless, he thought that the

> general description of the solar and terrestrial atmospheric lines,...indicates the remarkable fact, that the same absorptive elements which exist in nitrous acid gas exist also in the atmospheres of the sun and of the earth (35).

In other words Brewster thought that the study of the absorptive behaviour of terrestrial materials would provide an analysis of the chemical nature of the solar and stellar atmospheres.

There were two threads running through Brewster's work on absorption: firstly the desire to know how the chemical elements, whether on the earth or in the sun, affected the behaviour of light and secondly to examine the theoretical implications of this behaviour. Brewster it would appear attempted to keep these two aspects of his work on absorption as separate as possible, since he never discussed both aspects in the same paper after his "Report" (36).

Thus in the May 1833 Philosophical Magazine he continued his theoretical examination of absorption, without mentioning the chemical aspect of his work. In this paper, for the first time, he explicitly attacked the physical validity of the undulatory theory (37). He pointed out the strong analogy which must exist between light and sound if the former were supposed undulatory:

> Generally speaking,...,light differs from sound, according to this theory, only in the undulations being performed in media of very different elasticities (38).

He then listed substances in which only one ray of light was absorbed such as "that very remarkable salt the oxalate of chromium and potash" [$K_2C_2O_4.Cr_2(C_2O_4)_3$] (39); or substances which absorbed two thousand individual rays such as nitrous acid gas. He pointed out that in the liquid state, where he supposed that according to the undulatory theory the aether would be denser, nitrous acid allowed all the light to pass through unabsorbed whereas in the gaseous state where the aether would, he supposed, be less dense, some light was absorbed. This observation he found "strange" (40). He concluded

> Among the various phaenomena of sound no such analogous fact exists, and we can scarcely conceive an elastic medium so singularly constituted as to exhibit such extraordinary effects. We might readily understand how a medium could transmit sounds of a high pitch, and refuse to transmit sounds of a low pitch; but it is incomprehensible how any medium could transmit two sounds of nearly adjacent pitches, and yet obstruct a sound of an intermediate pitch.
>
> Such are the grounds upon which I stated to Mr. Potter that the absorption of light militated strongly against the undulatory theory (41).

This was Brewster's first public disavowal of the undulatory theory; in the past he had pointed out where the theory had failed, but equally he had also pointed out where it had succeeded. But in this polemic against the undulatory theory he concentrated entirely on phenomena which the theory did not explain. Brewster never had accepted, and now never would accept, the physical validity of the undulatory theory. Since he did not think that the theory was physically valid, optical phenomena which were connected with the interaction of ponderable matter and light could not in his view be explicable according to the theory. It is true that Fresnel had devised a theory which explained polarisation and double refraction, phenomena which he had shown were intimately connected with the nature of ponderable matter. But the explanation of these phenomena did not deal generally with the interaction of matter and light, for it was from these phenomena that Fresnel had devised his own version of the undulatory theory in which the light waves vibrated transversely. Brewster thought that any other optical phenomenon, including both absorption and dispersion, connected with the nature of ponderable matter ought not to be explicable if the undulatory theory was physically invalid. Therefore he asserted that if it could be shown that there existed such an optical phenomenon, then the physical validity of the theory would be falsified. He considered that he had shown that absorption phenomena were inexplicable according to the undulatory theory and had thereby falsified the theory.

As may be easily imagined, opposition to Brewster's objections to the undulatory theory was not long in forthcoming. Brewster had criticised the theory on two levels: the theoretical and the experimental although he had used his experimental work as evidence for his theoretical contention that the undulatory theory could not be a true physical representation of the behaviour of light. Attacks on Brewster's views could therefore be directed at him on either or both these levels. G. B. Airy and William Whewell (1794-1866), who had just resigned from the chair of mineralogy at Cambridge, were the first to take issue with Brewster over his philosophical attitude.

In a letter which he wrote to the Philosophical Magazine in June 1833 (42) Airy sought to demolish Brewster's theoretical arguments against the undulatory theory. He pointed out how successful the undulatory theory had been in explaining optical phenomena, while the particulate theory had notably failed in many areas. He further pointed out that although Fresnel had not originally explained all optical phenomena according to his theory he had eventually been able to extend it to explain double refraction and polarisation, phenomena which it had not originally encompassed, and that the theory had predicted the existence of phenomena previously unknown. Airy concluded that although he acknowledged

> as fully as any opposer of the theory can desire, that no explanation of absorption has been given upon the undulatory system (43).

he considered that it would be eventually explained and that an explanation of it was unnecessary for the acceptance of the theory. Essentially Airy asserted that because of the success of the theory, it could not be the case that absorption was incompatible with the theory, though he offered no explanation for it himself. Consequently he did not attempt to argue against the specific experimental objection which Brewster had raised as evidence for his theoretical contentions.

This situation could scarcely be described as satisfactory, as Whewell pointed out at the June 1833 meeting of the British Association at Cambridge. In the course of an address to the Association (44), he reviewed the debate about the nature of absorption which had been conducted in the year since the last meeting of the Association (45), agreeing with Airy that the undulatory theory had explained a multitude of phenomena which the particulate theory had come nowhere near accounting for. But he did not agree with Airy's view that an explanation of absorption was unnecessary, for

> if the undulatory theory be true [Whewell wrote], there must be solutions to all the apparent difficulties and contradictions which may occur in particular cases (46)

and in the case of absorption this meant that

> the whole doctrine of the absorption of light is at present out of the pale of its calculations; and if the theory is ever extended to these phae-

> nomena, it must be by supplementary suppositions concerning the ether and its undulations, of which we have at present not the slightest conception (47).

Like Airy, Whewell had only attacked Brewster's philosophical views, and, like Airy also, he had only made a statement of faith that absorption was compatible with the undulatory theory. But he disagreed with Airy and thereby implicitly agreed with Brewster that absorption must be explained or else the theory would be falsified. Both Airy and Whewell had admitted that no satisfactory theory of absorption had been offered to explain it according to the undulatory theory; and neither had shown that absorption was compatible with the theory.

Neither Airy nor Whewell had attempted to defend the physical validity of the theory on grounds other than its successful predictive and explanative power which, to them, implied that the theory must be a true representation of optical phenomena. Both contended that since the undulatory theory was a valid representation of optical phenomena, they were under no compulsion to answer Brewster's specific objection to it. To Brewster it was impossible to prove that the theory was physically valid, and possible to negate it by a single optical phenomenon which could not be reconciled with the theory. To Airy and Whewell it was impossible to show that a particular phenomenon could be irreconcilable with the theory; supplementary hypotheses would, Whewell supposed, be eventually employed to explain every optical phenomenon.

This attitude, while it might well be philosophically sound from the point of view of the supporters of the undulatory theory, was scarcely satisfactory from a scientific point of view. It was to the problem of Brewster's specific assertion that absorption was incompatible with the undulatory theory that Talbot and Herschel, the other two surviving originators of the study of line spectra, addressed themselves.

Talbot was still very much concerned with his idea of using line spectra as a means of chemical analysis. In the case of absorption this idea now took the form of discussing the possible chemical utility of the Fraunhofer lines in the solar spectrum. In a letter to Herschel Talbot argued against Brewster's view on the chemical analysis of the solar atmosphere, saying that there was "not much likelihood" (48) of

using the lines to discover its chemical constitution since

> it [the solar atmosphere] has probably a very slight absorptive power & only produces so much effect owing to the immense thickness of it which the light traverses. Thus, it may be oxygen or some other gas [is in the solar atmosphere] which produces no perceptible effect in the small thickness which we can experiment with (49).

Those gases such as nitrous acid gas, or iodine, of which only a thin layer was required to absorb light of specific refrangibilities could not, Talbot argued, be present in the very thick solar atmosphere since the lines would be much more intense than was observed to be the case. In this Talbot was specifically arguing against Brewster's contention that media which showed absorption lines on earth must, in all probability, be present in the sun. Talbot accepted the theoretical idea that there was a possibility of using the Fraunhofer lines as a means of determining the chemical composition of the solar atmosphere, but he thought that it was impracticable as yet to establish this experimentally. But this argument does show that Talbot was still concerned with the chemical use to which line spectra could be put.

Although in 1826 Talbot had not devised any explanation for the existence of the spectral lines he now attempted to do so in the case of absorption. To explain the production of the dark lines in the absorption spectra of iodine vapour and consequently to explain absorption generally Talbot suggested

> that the vibrations of the vapour of Iodine have a degree of rapidity which is comparable to those of the luminous aether which constitutes light, and that the Iodine being caused to vibrate by the light passing thro' it, its vibrations are successively in complete accordance & in complete discordance with those of the light (50).

Talbot argued that the light passing through the vapour of iodine caused the iodine atoms to vibrate; some of the molecules then vibrated in such a way that they absorbed particular rays of light, while others vibrated so that the remainder of the light was transmitted through the iodine and subsequently emitted. In effect he said the iodine atoms possessed particular periods of vibration which did not permit them to transmit light of those periods.

To provide a mechanism which would enable the atoms of iodine to behave in this way Talbot postulated that

> As each particle of the Iodine is probably surrounded with an atmosphere of heat, which is perhaps a fluid of the same nature as light, if not the same, I conceive that there is nothing incredible in supposing that the vibrations of the heat may interfere with those of the light, which hypothesis I would prefer to that of supposing the particles of the gas themselves to act (51).

Talbot appears here to have adopted Dalton's atomic theory in order to place his idea of using light for the purpose of chemical analysis on a secure theoretical basis. From Talbot's point of view this was an hypothesis which would, if it could be justified, provide a firm theoretical basis for his assertion that line spectra were uniquely characteristic of chemical elements. Dalton had supposed that each chemical element had its own unique type of atom surrounded with an atmosphere of heat (52). Talbot had supposed in his 1826 paper that each chemical element produced a characteristic spectrum, but he had not provided any theoretical justification for this idea. In this work on iodine Talbot supposed that the individual chemical atoms possessed their own peculiar rates of vibration which would mean that iodine produced its own characteristic spectrum. By extension therefore, since the atoms of each element were different, it would be reasonable for Talbot to suppose that they would each have uniquely characteristic rates of vibration which would determine their interaction with light. This therefore provided a theoretical justification of his earlier spectral work.

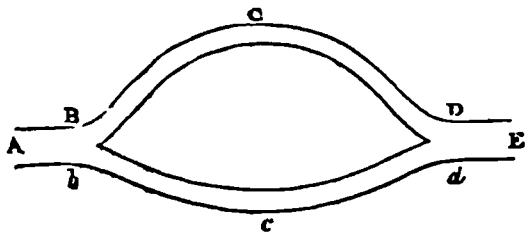
By attempting to explain the absorption of light Talbot appears to have attempted to devise a theoretical basis for the existence of line spectra which would justify the validity of his work on the chemical use of spectra. If he could rigorously show that line spectra were unique to the chemical elements, then it would justify his theory of absorption and contradict Brewster's claim that absorption could not be explained according to the undulatory theory of light.

But Talbot had not done this and he showed no interest in doing so; he was concerned only to develop his idea of the

chemical use of line spectra which he now realised required a suitable theory of the interaction of light and matter. The arguments advanced by Herschel were very different, for he was solely interested in dealing with Brewster's objections to the undulatory theory, and he must have realised that Talbot had not done this, though he had devised a theory of absorption. The difference between Herschel's work and Talbot's was that the latter was interested in establishing a theory of absorption for his spectro-chemical analysis while the former was interested in showing that absorption was not incompatible with the undulatory theory and thereby demolishing Brewster's assertion that it falsified the theory.

This Herschel did at the same British Association meeting at which Whewell presented his review of the problem (53).

fig.1



In what Herschel made clear was a thought experiment (54), but which Robert Kane (55) later performed experimentally (56) Herschel described the system of pipes outlined in fig. 1. Here the bottom pipe was shorter than the top pipe by half the wave-length of a note which was to be absorbed. Herschel argued that if this note was sounded at A then its vibrations would divide at Bb to meet again half an undulation out of phase at Db and thus they would cancel each other out so that no note would be heard at E. On the other hand if a "concert of music" was played into A, every note would be heard at E except that which the pipes absorbed. He concluded that

> If several such chambers were disposed in succession, communicating by compound pipes, rendered impervious... to so many different notes, all these would be

> wanting in the scale on its arrival in the last chamber; thus imitating a spectrum in which several rays have been absorbed in their passage through a coloured medium (57).

This analogy applied only to those absorbing media, such as pieces of coloured glass, which were not self-luminous, i.e. those which did not vibrate. Herschel had therefore effectively distinguished between those substances which absorbed light but were not self-vibrating, e.g. coloured pieces of glass, and those which were self-vibrating and therefore self-luminous, e.g. flames. (This distinction Herschel had not made in his "Essay on Light" because there he had not attempted to explain absorption according to the undulatory theory of light). He had now answered Brewster's criticisms that the absorption of light by coloured glass was incompatible with the undulatory theory by showing that analogies to it did exist in acoustical phenomena.

Herschel was left with the task of explaining the existence of the Fraunhofer lines and "(pari ratione) of the deficient or less bright spaces in the spectra of various flames" (58). To do this he returned to his supposition linking absorption and emission which he had offered in his "Essay on Light" some six years earlier (59). In order to elucidate this in terms of the undulatory theory of light he described the behaviour of tuning forks not only as an illustration of his ideas regarding the cause of the Fraunhofer lines but also as a further rebutal of Brewster's claim that there was nothing analogous to the absorption of light in acoustical phenomena.

In order to do this Herschel made what he called disked tuning forks. To one tuning fork he attached a disk of card to each arm; and to another he attached a disk to one arm and a piece of wax to the other arm in order to balance the weight. The first tuning fork made no sound at all, while the second emitted a loud sound - far louder than could be normally heard from a tuning fork without a sounding board (60). He concluded that

> We have a case in which a vibrating system in full activity is rendered, by a peculiarity of structure, incapable of sending forth its undulations with effect into the surrounding medium; while the very same mass

> of matter, vibrating with the same intensity, but more favourably disposed as to the arrangement of its parts, labours under no such disability (61).

He had thus shown that it was possible to conceive of a system which vibrated but would not send forth a particular undulation; and, of course, it was impossible for such a system to permit other undulations of the same wave-length to pass through it. Indeed if the tuning fork which emits the sound is brought close to the absorption tuning fork its vibrations are rapidly damped. But, as Herschel pointed out, if the absorption tuning fork was not of the same pitch as other tuning forks, then the sound of these would be transmitted through the air without interference. This phenomenon brought him by analogy to an observation which he had reported in his so-called "Essay on Sound" (62): if a vibrating tuning fork was placed over a pipe of the same pitch as the fork, then the pipe "will speak by resonance" (63).

These and other phenomena which he reported in his paper were, he said, referable to the principle of forced vibrations which he had mathematically demonstrated in his "Essay on Sound" (64). This principle stated that any system already vibrating, or with the potential to vibrate, will adopt, after a time, the period of any incident vibrations (or will cancel them out). In the case of the tuning fork which absorbed sound of a particular wave-length this principle implied that the fork was vibrating, because sound of that wave-length was impinging upon it, in such a manner as to absorb that sound. Consequently he had shown that Brewster's claim that there were no phenomena in acoustics analogous to absorption in optics was false, although he never mentioned Brewster explicitly, and only once obliquely (65).

Herschel wanted to go still further in showing that absorption phenomena were compatible with the undulatory theory of light. From the principle of forced vibrations he considered that absorptive media must consist

> of innumerable distinct vibrating parcels of molecules, each of which parcels, with the portion of the luminiferous aether included within it, (with which it is connected, perhaps, by some ties of a more intimate nature than mere juxtaposition,) constitute a distinct compound vibrating system, in which parts differently elastic are intimately united and made to influence each other's motions (66).

According to Herschel then, if a ray of light of a particular wave-length passing through a medium impinged on a molecule of that medium which could not vibrate at that wave-length, then the molecule would destroy, or at least severely restrict, the passage of the ray. Rays of other wave-lengths impinging on that molecule would, according to the principle of forced vibrations, make it adopt their own period of vibration. However since

> we know nothing of the actual forms and intimate nature of the gross molecules of material bodies, it is open to us to assume the existence, in one and the same medium, of any variety of them which may suit the explanation of phaenomena (67).

Here he tacitly admitted that he could go so far and no further in reconciling absorption with the undulatory theory of light. He had shown that the undulatory theory had the same ability as the particulate theory to explain absorption: that is, he showed that it depended on the nature of matter in the absorbing medium.

This point Herschel reiterated when he discussed the distribution of the lines in the spectrum:

> If we represent the total intensity of light, in any point of a partially absorbed spectrum, by the ordinate of a curve whose abscissa indicates the place of the ray in order of refrangibility, it will be evident, from the enormous number of maxima and minima it admits, and from the sudden starts and frequent annihilations of its value through considerable amplitudes of its abscissa, that its equation, if reducible at all to analytical expression, must be of a singular and complex nature, and must at all events involve a great number of arbitrary constants dependent on the relation of the medium to light, as well as transcendents of a high and intricate order (68).

This represents a complete departure by Herschel from the position which he and Young had held in the late 1820s, when they had both argued that since line spectra were produced by diffraction gratings their distribution must be amenable to a comparatively simple mathematical description. From this they had both suggested how to obtain purely numerical formulae which would describe the distribution of the lines, formulae which however were not dependent on any physical theory concerning the

origin of the lines. Since Herschel's analogical arguments suggested to him the existence of a very complicated structure of matter within absorption media, he must have thought that the distribution of the lines could not be described by the simple analytical expressions which he and Young had earlier proposed. Herschel realised that in order to demolish Brewster's arguments he must have a physical description for spectra even if this meant that there was no possibility of obtaining a mathematical description for the distribution of line spectra. This was as far as he could go; he had shown by making this sacrifice that Brewster's argument that absorption phenomena were incompatible with the undulatory theory was invalid.

Whewell was not happy with Herschel's proposition that the material structure of an absorbing medium must necessarily be complex. This he made clear in his comments on Herschel's paper at the following meeting of the British Association held at Edinburgh in September 1834 (69). He remarked that to Herschel's views on the nature of absorption

> might be objected
> (1) the great number of the dark lines in many kinds of light, which would appear to make a very complex structure of media necessary,
> (2) the difficulty of conceiving that, on such an hypothesis, the absorptive properties of media should be the same in all directions (70).

But he raised these problems in order to demolish them and thus simplify Herschel's theory of absorption. With regard to the first he argued that if a medium absorbed one (fundamental) vibration then the medium would also destroy all the harmonics of that wave-length. In addition since the aether was a vibrating solid, the undulations might well be divided by the nodal surfaces of the aether in the medium in ways which would produce differences in the absorption pattern produced by the harmonics. As he said

> In this way the rates of vibration for which the vibration is extinguished may become as numerous as any observations can require (71).

He did not suggest here how the particles of matter and aether were distributed, but he did deal with this when he came to discuss the second problem he had raised, as follows:

> Let a medium consist of certain particles regularly distributed, the intervening space being filled by a medium capable of vibration. Let it be supposed, also, that each vibration, on reaching a medium so disposed, proceeds in part directly, and in part by the indirect routes which go round some of the particles and rejoin the direct course. We have thus combinations of ramifying and reuniting paths, which, though very complex in each direction, are the same in different directions, in consequence of the regular distribution of the particles (72).

In this way Whewell "diluted" (73) those objections to Herschel's theory which he had himself raised, since it could now be conceived how the different varieties of absorption could be reconciled with the undulatory theory without having to postulate a complex structure of matter in the absorbing medium, which all the participants in the debate, with the exception of Herschel, deemed undesirable.

Herschel had assumed that if a proposition could be demonstrated in acoustics then it must necessarily have an exact analogy in optical phenomena. A strong supporter of the undulatory theory, Whewell no doubt accepted this, but he had shown how the analogy could be applied in this particular case and had simultaneously also simplified the structure of matter required for an absorptive medium. Besides Talbot, only Whewell was interested in finding an explanation for absorption; both Airy and Herschel were content to show, in their different ways, that Brewster was "wrong". But in either case as Whewell put it

> The object is to show that there is no incongruity between the undulatory theory and the phaenomena of absorption (74).

This Airy and Herschel had done, but they had not really dealt with the problems of why the lines existed in particular positions, or why they possessed different intensities and so on; Whewell and Talbot had implicitly touched on these problems but they had not provided any solutions.

The same year (1834) in which Whewell modified Herschel's work, Baron Fabian Jakob von Wrede (75) offered a mathematical description, based on the undulatory theory and on a physical hypothesis of the structure of matter, of the distribution and

intensity of a wide variety of spectral lines (76). Wrede had closely followed the public debate conducted in Britain between Brewster, Herschel, Whewell and Airy on the nature of absorption. Like Herschel, Wrede regarded Brewster's objections to the undulatory theory as valid, but felt that they could be overcome by an extension of the theory. He criticised Airy for saying that it did not really affect the issue whether absorption was explicable or not, because if absorption could not be reconciled with the undulatory theory then the theory must be physically invalid (77). Wrede also rejected the structure of absorbing media which Herschel had postulated using the analogy of light with sound as being far too complicated (78).

Wrede had conducted experiments on absorption which showed him that the spectra of light transmitted through iodine and bromine vapours both possessed lines which occurred with increasing frequency towards the blue end of the spectrum (79). From this observation Wrede deduced, by means which are not clear, that these phenomena must be due to interference (80). Wrede therefore had to devise a structure of matter in absorbing media in which interference of light could take place; to this end he postulated that absorbing media were

> composed of particles which are kept by certain forces at a determinate distance from one another, [and] we may also imagine that these particles are capable of offering a resistance to the traversing wave of light, and consequently of partially reflecting it.
>
> The light thus reflected, which proceeds in a direction contrary to the one it originally had, must now be in like manner reflected in the original direction, in order to experience again a partial reflection in the contrary one, and so on ad infinitum. Thus arises an endless series of systems of waves of light, each one of which possesses a feebler intensity than the one which had immediately preceded it, and which has been, in comparison with this, diminished by one portion equal to the double distance between the reflecting surfaces (81).

Wrede proposed that the ponderable matter in the absorbing medium partially reflected light of particular wave-lengths which would then interfere and partially annihilate light of those wave-lengths following them; in effect he suggested that interference caused the diminution of light in certain parts of the spectrum. Using this hypothesis Wrede was able to show

that an analytical function could be devised which would describe the absorption characteristics of a number of media. He continued by adding that he would "endeavour to prove" (82) that absorption

> may be...reduced to one, or at least to a very limited number of causes, and that it may be all comprehended in one very simple analytical expression, which contains very few constants, and those dependent on the nature of the absorbing medium (83).

He showed mathematically that only a system of two surfaces partially reflecting light in an absorbing medium need be considered in order to establish where the maxima and minima of the spectra would occur since the function which would represent the intensity for n reflecting surfaces would have its stationary points at the same values as for two systems (84). Therefore an analysis of the behaviour of the function for a system of two partially reflecting surfaces should be sufficient to generate the maxima and minima of a spectrum.

Wrede derived this function by considering two surfaces which produce reflections at a distance b from each other, and which partially reflect a proportion r (< 1) of any light (of intensity a) incident upon them. A series of rays of ever diminishing intensity would be reflected between the two surfaces AB and CD (fig. 2).

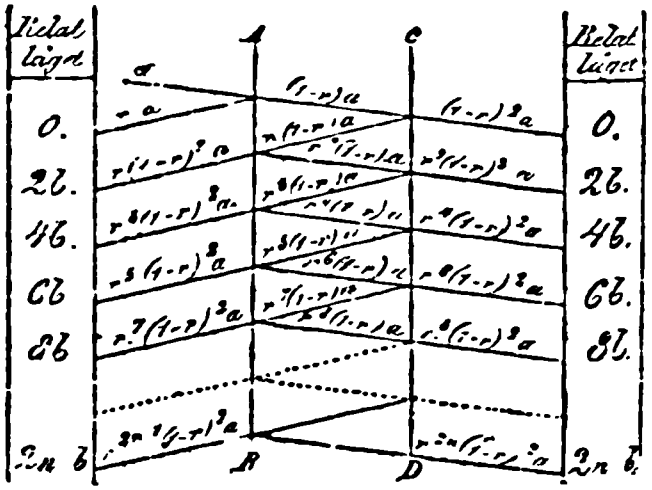
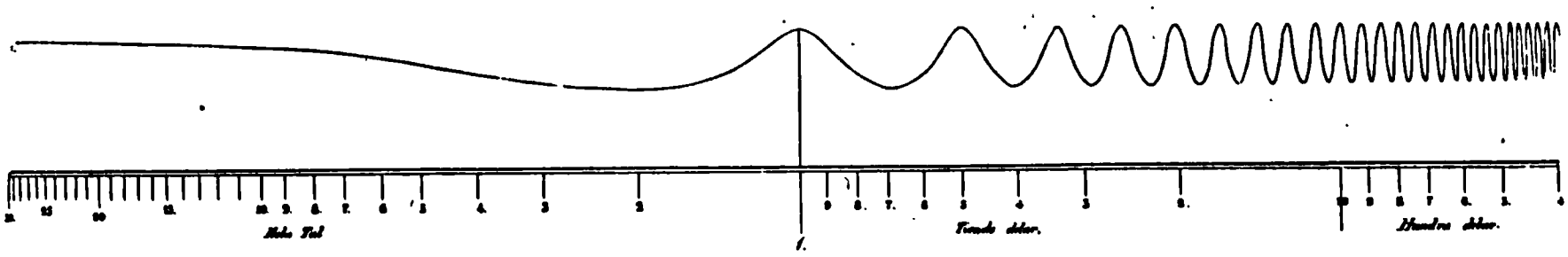


fig.2

fig.3

Wrede's spectral map



Using Fresnel's formula for diffraction (85) Wrede found that the formula of the intensity of light of wave-length λ after passing through the medium was

$$A = \frac{(1 - r)^2 \ a}{\sqrt{1 - 2r^2 \ \cos 2\pi \ \frac{2b}{\lambda} + r^4}}$$

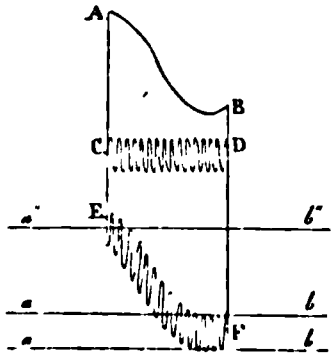
From this it is apparent that the intensity of light for particular wave-lengths is dependent on $\frac{2b}{\lambda}$. Wrede showed that this formula had the same points of maxima and minima as when only a single wave-length was considered. Thus instead of considering each individual wave-length, as Herschel had thought necessary, Wrede found that the whole spectrum could be described by one continuous function with its maxima and minima representing emission and absorption respectively.

To provide a graph of this function, Wrede plotted it against $\log_{10}$ of $\frac{\lambda}{2b}$ in order to make the difference between the undulations of the function independent of the linear spacing of $\frac{\lambda}{2b}$ (86) (fig. 3). Now the ratio of the wave-lengths of the extreme ends of the visible spectrum is 1.58; therefore by measuring any length of $\log_{10}1.58 = 0.1987$ ($\simeq .2$) along the abscissa of the graph Wrede was able to describe properties of absorption of particular substances. For example, if a distance of .2 was measured at the extreme left of the graph, hardly any absorption would occur and that which did would be spread evenly. If however the middle of the spectrum was placed at .3 on the graph then all the light would be absorbed. As we proceed further along the spectrum it is obvious that the position of many more points of absorption will be described. When $2b = .004$ inches, as Wrede commented "we obtain about the same number of absorptions as by iodic gas [iodine vapour]" (87), the substance with which he had commenced his investigation. By assuming a structure of matter Wrede thus derived a mathematical representation of the absorptive action of iodine vapour which conformed to the undulatory theory.

Brewster had observed in the spectrum of nitrous acid gas that the absorption lines grew thicker, and new ones appeared as the temperature of the gas increased (88); this phenomenon had

also been noted in the behaviour of iodine vapour. Wrede showed that he could describe this phenomenon by synthesising two or more equations of intensity into a single equation to produce maxima and minima at various intensities along the spectrum (89). In the case of iodine vapour he showed that only two equations of intensity need be synthesised in order to provide a description of its behaviour; the two values of 2b which were required to produce these equations of intensity were the wave-length of red light and 150 times greater than the wave-length of red light (fig. 4).

fig.4



To describe the behaviour of the absorption of light by iodine as the temperature increased Wrede imagined a line termed "limit of perception" (90), which when placed at any particular point on the ordinate of the diagram would, he found, accurately describe for a particular temperature, the number and intensity of the absorption lines present in the iodine absorption spectrum. In a similar manner Wrede provided descriptions of the absorption spectra of bromine vapour and the oxalate of chromium and potash (91). He further showed that this formula accurately described the ratio of lines to be found in one part of the spectrum compared to another part (92); consequently

he had accurately described the absorptive properties of various substances which he could not have known would have been describable when he made his original hypothesis.

Though Wrede had devised an hypothesis as a result of observing relatively simple spectra he was quite well aware that other spectra were more complicated. To overcome this problem he thought that it was

> quite natural to assume that the e ementary constituent parts of a compound body may each of itself cause different retardations; and if we consider nitric acid gas as a compound of n tric acid and nitrogen, instead of considering it as a binary compound of azote and oxygen, we then easily conceive how very possible it is that a great number of retarding causes may be contained therein, each of which arises in the same manner as in the single gases (93).

Therefore to describe the absorption spectra of nitrous acid gas or euchlorine (chlorine heptoxide, $C1_2O_7$) (94) Wrede supposed that several equations of intensity had to be synthesised. However he did not go into as much detail with these gases as the other substances he worked with.

When Wrede turned his attention to the spectra of coloured flames he agreed with his predecessors that flame spectra "may be explained in the same manner as the phaenomena of absorption" (95). However, he had to make the extra hypothesis "that certain flames can only produce light of a certain length of wave" (96). He suggested that the flames were enveloped by luminous atmospheres which absorbed light from the interior of the flame. Using this hypothesis Wrede was able to describe the flame spectra of such compounds as copper chloride (97). Finally he turned his attention to "the most complex of all the phaenomena of absorption" (98), the solar spectrum. He supposed with Herschel that the Fraunhofer lines were caused by the absorption of light in the solar atmosphere (99). He considered that there must be a large number of reflecting surfaces in such a thick medium; the amount of light therefore reflected by each surface must be very small or no light would be able to pass through the medium at all. After calculating the intensity of light which passed through such a medium he discovered that its

maximum and minimum values occurred in exactly the same places as in the case of two reflecting surfaces. He calculated the ratio between the maximum and minimum values of the function A, in order to show that according to his theory it was possible to describe the solar spectrum with all its lines of different intensities, although as with flame spectra he did not go into the same amount of detail as he did with gas absorption spectra.

Wrede had thus fulfilled the purpose with which he had set out: to show that the wide variety of absorption phenomena could be described by a set of mathematical rules. As regards the physical hypothesis of the structure of matter in an absorbing medium on which Wrede had based his work, he considered that while it might well be incorrect (100), he had, he thought, "shown... that the phaenomena of absorption may be reduced to a simple mathematical principle" (101). He attempted to maintain both the physical and mathematical validity of his work while at the same time trying to disassociate the mathematical analysis from his physical hypothesis. In other words he maintained that if his physical hypothesis should prove incorrect then the formulae which he had devised at least gave insight into the internal constitution of matter. As he said,

> We must not be thought too bold when we suggest that by observations on the absorption of light we may find a new way opened to us of viewing the constitution of matter which may perhaps lead to results that could be attained in no other way (102).

Since the formulae described accurately both the position and intensity of absorption lines, they must, he thought, have some physical meaning, which he had not necessarily discovered with his physical hypothesis. His paper should not be viewed as an explanation of absorption but rather as a mathematical description which conformed pretty well to observations of those absorption phenomena already known, and which above all showed that absorption was compatible with the undulatory theory.

Wrede's work attracted little attention even though it was quickly translated into German (103) and English. In the main this lack of interest was because scientists appeared to have lost interest in the problem of absorption - this was not helped by the fact that one of the main protagonists in the debate,

Herschel, was at the Cape of Good Hope, mapping the southern skies. But more importantly Brewster did not reply directly to any of the avalanche of criticism which had descended on him. Without his continued participation in the debate it naturally fell rather flat since almost everybody else believed that light was indeed undulatory. As an explanation of Brewster's attitude I can only suggest that he had realised that he was not going to convince anyone who already believed in the undulatory theory of his views and so gave up further debate along the lines he had pursued, although he continued to believe that the undulatory theory was physically invalid Had he continued the argument then it would have meant that he would have to concentrate on explaining absorption according to the particulate theory of light. This, it appears, he was unwilling to do, not because he could not have devised such a theory, which at one point he had tentatively done, but because he did not like theorising at all, prefering to remain within the optical facts which he considered could be directly deduced from experimental observations. For all these reasons the debate drew to a close, but its consequences, especially in chemistry, were considerable,

From the initiation of the debate by Brewster, through Talbot's unpublished contribution to Whewell's simplification of Herschel's work, there was an undercurrent of chemical considerations, which tended to modify, or at least to impose boundary conditions on the structure of matter required in order to explain the absorption of light. But the participants in the debate had not in their writings made this chemical influence explicit since their main purpose had been to discuss the nature of absorption. It was however explicit to those participants in the debate who afterwards worked on spectrochemical analysis. Brewster and Talbot were both completely satisfied, for different reasons, that line spectra were uniquely characteristic of the chemical elements, and were thus caused by the atoms of those elements. Herschel on the other hand thought that his theory of spectra implied that the matter which produced line spectra had a much more complicated structure:

> There is no necessity to suppose the luminiferous molecules of gross bodies should be identical with their ultimate chemical atoms. I should rather incline to consider them as minute groups, each composed of innumerable such atoms (104).

For Herschel, therefore, it was the physical structure of the molecule, rather than the atoms of which it was constituted, that was the cause of the spectra. This naturally introduced considerable difficulties in the use of spectra for chemical analysis as he had at one stage tentatively tried to do; it was conceivable, though Herschel did not say so, that two different combinations of chemical atoms might produce identical spectra. This would invalidate any possibility of using spectra for rigorous chemical analysis.

It was the publication of Wrede's paper in English which appears to have induced Talbot to repeat in print his ideas on the use of line spectra for the purpose of chemical analysis. Wrede was the first person to publish the observation that the absorption lines of iodine and of bromine vapour occurred with increasing frequency towards the blue end of the spectrum. Daniell and W. H. Miller had reported that the lines were equally spaced (105), but Talbot had observed that this was not the case (106), although he did not publish this observation until after the publication of Wrede's paper; then he cited Wrede's "actual measurement" (107) of the phenomena as evidence. Talbot considered that these phenomena were "a consequence of some simple general law" (108) but he did not specify what law this was. He added that while he agreed with Wrede that absorption was caused by the particles of an absorbing medium, he disagreed with him in supposing that the molecules remained motionless in order to reflect light and cause interference. Talbot preferred to suppose, as he had done two years earlier (109), that some rays of light vibrated "in accordance, and others in discordance, with the vibrations of the iodine gas" (110) and would consequently either transmit or absorb light. Between Wrede and Talbot we can discern two approaches to the problem of absorption. On the one hand Wrede's mathematical description of the position and intensity of the absorption lines based on a by no means firm physical hypothesis. On the other Talbot's determination to maintain a view based on an a priori hypothesis of the structure of matter which would, he hoped, lead to the establishment of a system of chemical analysis using light. This meant that Talbot had to reject Wrede's work since there was nothing in it which

would guarantee the uniqueness of line spectra to the chemical elements, which was what Talbot required for his work.

The following year (1836) Talbot restated his view that given sufficient experimentation it would be possible to use spectra for chemical analysis:

> The definite rays emitted by certain substances, as, for example, the yellow rays of the salts of soda, possess a fixed and invariable character, which is analogous in some measure to the fixed proportion in which all bodies combine, according to the atomic theory (111).

This meant, for Talbot, that each type of atom must have unique periods of vibration which naturally determined the type of light a particular substance emitted. It therefore seems apparent that the atoms of each chemical element, being unique to each element, would produce unique spectra; but Talbot did not publish the theory, about which he had told Herschel concerning the mechanism by which this would be effected (112).

Talbot had emphasised the point that spectral analysis could be used effectively for chemical analysis by showing that the spectra of lithium and strontium, otherwise substances difficult to distinguish, were totally different:

> I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty, if not more, than any other known method (113).

He also described the flame spectra of chromium, cyanogen, salts of copper, boric acid, etc. (114).

The explanation of absorption which Talbot postulated and the way in which he used it illustrates the general opinion then current that there must be a strong connection between the emission and absorption of light. This went beyond Herschel's assertion that the dark bands in flame spectra were caused by the same mechanism which caused ponderable matter to absorb light. Theoretical explanations of absorption which naturally dealt with the interaction of matter and light provided information not only about absorption but also about emission. Talbot was able to take advantage of this in his work on flame spectra to confirm theoretically that line spectra were indeed uniquely characteristic of the chemical elements.

Since there was thought to be a close mechanical connection between emission and absorption, albeit the precise nature was not clear, it followed that there ought to exist, in some cases at least, emission and absorption lines of identical refrangibilities. Although up to this time (mid 1830s) nobody had attempted to discover the emisssion spectrum of an absorptive medium and vice versa, there was one example where this identity might well exist - the R/D line. Fraunhofer in his first paper on spectra had established that the yellow R line had the same refrangibility as the dark D line of the solar spectrum (115); but he had done this when he thought that the line was single. It would therefore be an interesting confirmatory experiment to check that Fraunhofer's observation was correct and that it applied to both the lines which formed R/D. This was the task which W. H. Miller undertook in 1837 (116); he told G. G. Stokes about it, and Stokes in turn informed William Thomson, later Lord Kelvin, of the conversation, writing in 1854 that

> [W. H.] Miller told me [Stokes] that an experiment of his which he performed many years ago for testing the coincidence of the dark double line D of the solar spectrum with the bright line in the light of a spirit lamp. The sun's light was introduced by a slit, and refracted by 3 good prisms, and then viewed through a telescope with a pretty high mag. power. The two lines forming the line D were "like that" (as he said holding two of his fingers about 3 inches apart) and he counted six fixed lines between them. The whole apparatus was left untouched till dusk, and then a spirit lamp was placed behind the slit. This gave two bright lines coinciding, as near as measurement could give, with the two dark lines D (117).

This coincidence Miller thought was due to some physical connection between the two sets of lines (118), but what precisely he thought this was is not clear. This experiment would have been valuable had the lines not coincided. In this case doubts would have to have been raised about the validity of the theories of spectra which assigned the same mechanism for emission as for absorption. The actual result simply confirmed what was already known from the theories of spectra about emission and absorption, and, I would suggest that this was the reason why Miller did not publish it.

Although Brewster did not directly answer his critics, he still took a strong interest in the other aspect of his spectral work - spectro-chemical analysis. Brewster, like Talbot, had a mechanism for the explanation of line spectra; although in the debate Brewster had not committed himself to the particulate theory of light, his suggestion that each atom of a chemical element would have a specific affinity with light of particular refrangibilities would ensure the existence of a characteristic relationship between matter and light. All that he had to do therefore, once he knew which lines belonged to which element was to look for evidence for the existence of this relationship and he would learn immediately which elements were present in a particular flame. This appears to have given Brewster the necessary theoretical basis for carrying out his subsequent experimental work on the chemical uses of line spectra. I would suggest that Brewster thought that if he could develop a general system of spectro-chemical analysis he would then be able to argue that he had made a discovery based on his own ideas regarding the interaction of matter and light, which could not have been made using the undulatory theory; this would be further evidence for the physical invalidity of the theory. But at the 1842 meeting of the British Association in Manchester, where he announced that he had "obtained 200 or 300" (119) flame spectra, he could make no such assertion. He said that he had not any leisure to "group" his observations but he did describe the flame spectra produced by strontium and sodium. By "grouping" Brewster presumably meant isolating which lines belonged to which chemical element, by comparing the spectra of different salts of the same metal, but he did not make it clear that this was the case. He had not established a general system of spectro-chemical analysis, and therefore any theoretical arguments concerning the nature of spectra could not be discussed, because he had not been able to provide the necessary evidence.

Brewster's lack of success in dealing with the problem of spectro-chemical analysis made it impossible for him to discuss the meaning of the identical refrangibilities of emission lines and some Fraunhofer lines. Brewster compared the solar spectrum with the lines produced by potassium nitrate (KNO_3), which Talbot

had shown to possess a homogeneous red line (120). This line, Brewster found, corresponded with Fraunhofer's A line; he also found, to his surprise, that another red line produced by potassium nitrate had the same refrangibility as Fraunhofer's B line. Further he observed that both the potassium nitrate lines were double and when he looked at the solar spectrum he found that both A and B were double (121). But apart from reporting this work he drew no explicit conclusions about what these results meant in terms of the chemical constitution of the solar atmosphere. This I would suggest can be attributed to Brewster's lack of certainty about whether these particular lines were caused by the solar atmosphere or by the terrestrial atmosphere. All that Brewster and indeed Miller could do was to say that there existed certain coincidences between some emission lines and some of the Fraunhofer lines and leave it at that.

Brewster did not return to the subject of line spectra until the early 1850s when in the fourth and much revised edition of his "Treatise on Optics" (122), he listed the flame colours produced by 46 different substances (123), making it clear that he had been studying "184 substances...though my main object was to discover fixed lines in their spectra" (124). Brewster had presumably not developed an experimentally rigorous method of spectrochemical analysis, and so since he could not discuss spectra, he chose to discuss flame colours instead, which he appears to have thought safer ground.

His attitude towards the solar spectrum and its relation with emission spectra did not change. He expanded his experimental detail slightly by sayin that the spectrum of the flame of potassium nitrate, in addition to possessing the equivalents of A and B which he had already noted, also produced the same emission lines as Fraunhofer's group a (125). But again he made no comment about what this implied for either the nature of the Fraunhofer lines or the constitution of the sun.

Of those people who had participated in the debate on the nature of absorption only Brewster and Talbot continued and extended their investigation of the possibility of using light for the purpose of chemical analysis. Both worked within theories of the interaction of matter and light - albeit they were different

theories - which permitted them to assume the uniqueness of spectra to particular chemical elements. Herschel on the other hand had uncovered with his theory of absorption a complex structure of matter which would not necessarily ensure unique relationships between matter and light, and he therefore did not attempt any further spectro-chemical experiments, despite the fact that Whewell had in 1834 greatly simplified the required structure of matter which Herschel had supposed. Indeed Whewell had suggested that

> When the laws of...absorption... are known, the undulatory theorist will have before him the task of pointing out what <u>is</u> the constitution of transparent media (126).

But Herschel had not taken up this suggestion. An understanding of absorption phenomena led to a more general understanding of the interaction of matter and light. The various theories which were devised to account for the interaction led, if they were simple, to research into the chemical use of light; if on the other hand they were complex, no research was pursued, since the theory suggested that such an effort would be wasted. But the idea of using light for chemical analysis had been conceived, as a theoretical principle, although the experimental application was to prove difficult to effect.

By the early 1840s others besides Brewster and Talbot had become interested in working on spectro-chemical analysis, especially the chemists at King's College, London: J. F. Daniell and his successor W. A. Miller (127). Daniell had already performed some work on line spectra in conjunction with W. H. Miller; besides iodine they had also worked on the spectra of bromine, chlorine, euchlorine and indigo. In Daniell's "Introduction to the Study of Chemical Philosophy" (128) he described the absorption spectra of nitrous acid gas, bromine and iodine (129), commenting that

> The arrangement of the lines [of bromine] is quite different from that of the lines presented by an atmosphere of nitrous acid,...although the two vapours cannot be distinguished from each other by colour (130).

Daniell was not interested in the cause of the lines: he was concerned simply with their chemical utility. He felt under no

compulsion to argue that a set of lines was unique to a particular element or compound. This had, after all, been argued for in the debate on absorption by both Brewster and Talbot and established experimentally, for bromine and nitrous acid gas at least, by Daniell and W. H. Miller.

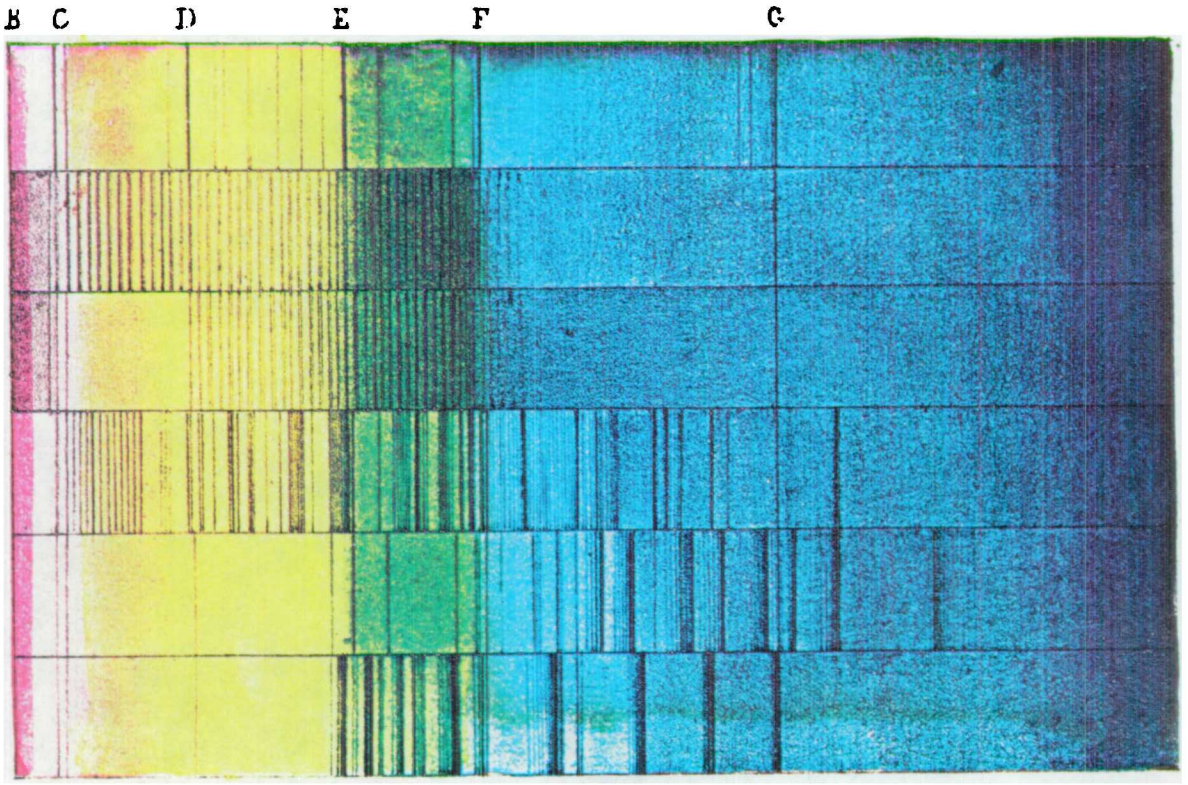
By the early 1840s this was as far as chemical spectroscopy could go. By using spectra scientists could distinguish with a considerable degree of certainty between two otherwise similar substances, but the method could not be utilised generally to analyse a sample where there was no fore-knowledge of its composition. Thus Talbot could distinguish between lithium and strontium and Daniell between nitrous acid gas and bromine, but a spectrum could not be used to determine the composition of a compound. Chemical spectroscopy was indeed useful; it was both theoretically and experimentally valid; but it had not been perfected to the degree of generality of which Talbot thought it was capable.

The extension of this technique was a project undertaken by W. A. Miller in the mid 1840s. He firmly believed that it could be extended and he directed his efforts to so doing, by continuing the experimental work which W. H. Miller and Daniell had initiated of passing light through various gaseous substances and examining their spectra. By comparing the absorption spectra of bromine and of iodine with the solar spectrum he discovered that the refrangibilities of the lines caused by each gas was different - an observation which appears not to have been made before his work (131). He also discovered that the various oxides of chlorine each possessed a set of common lines. This did not imply to him that this set of common lines was produced by either oxygen or chlorine since he had observed that these gases, in their free states, did not absorb light. In the case of the recurrence of the lines in the oxides of chlorine W. A. Miller commented that "chemical considerations... may assist in explaining the cause" (132) and left it at that. This illustrates the problem which existed for those chemists who took an interest in spectro-chemical analysis in the 1840s, namely that they attempted to isolate the spectra of chemical compounds as opposed to concentrating on chemical elements. This

was due to two reasons: firstly the way in which they conducted some of their investigations by analysing prismatically light which had been passed through a gas, at normal temperatures, meant that the individual atoms of the elements could not produce their characteristic spectra. Secondly it would appear that it had not been made sufficiently clear by either Brewster or Talbot that they thought that it was the chemical elements which were uniquely responsible for the cause of the lines, not the chemical compounds on which the chemists concentrated their attention.

The papers which had been written by the participants in the debate had a curious effect on the subsequent development of spectro-chemical analysis. On the one hand most of the theories of absorption did suggest that spectro-chemical analysis was a theoretical possibility. On the other hand these theories were ambiguous as to where their authors thought the cause of absorption lay. The reason for this ambiguity, I would suggest, was that these papers had been written with the object of explaining absorption in one way or another. They had not been written with the object of establishing a method of spectro-chemical analysis. The declared object of the papers could be undertaken without explicit mention of the nature of matter, since most of the debate centred on analogical arguments; there was therefore no need for the participants in the debate to be particularly explicit about where they thought the cause of the lines lay in terms of the structure of matter. Brewster and Talbot in the papers they wrote, after the debate, on the possibility of using spectra as a method of chemical analysis, were not successful in establishing a general system of spectro-chemical analysis. Neither Brewster not Talbot, who both had precise views about the origin of the lines, made their ideas explicit in these papers; both of them examined the spectra of chemical compounds as well as chemical elements without appearing to distinguish between them. Those chemists who did take an interest in spectro-chemical analysis were attempting to turn an ill-defined theory in physics into a method of chemical analysis; it is not particularly surprising that they were unsuccessful.

Spectra of Daylight through Coloured Gases & Vapours.



Phil. Mag. S. 3. Vol. XI. Pl. III.

fig.5

W.A.Miller's spectra of light transmitted through various gases and vapours

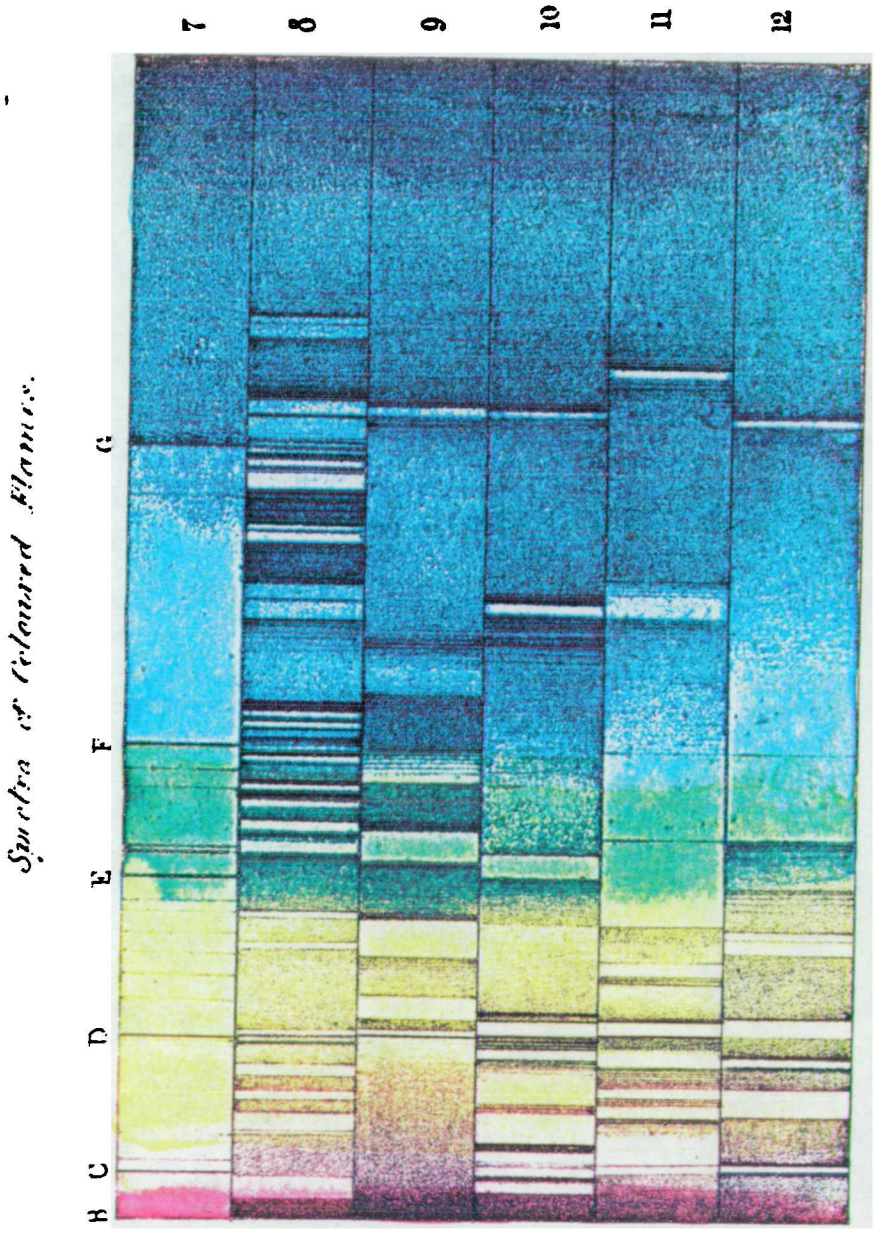
1. Solar spectrum
2. Iodine
3. Bromine
4. Nitrogen peroxide
5. Chlorine peroxide
6. Perchloride of manganese

fig.6

W.A.Miller's spectra of coloured flames

7. Solar spectrum
8. Copper chloride
9. Boric acid
10. Strontium nitrate
11. Calcium chloride
12. Barium chloride

Phil Mag. S 3 Vol XXVII Pl II.



Spectra of Coloured Flames.

J Bas n ...

It was difficult for chemists such as W. A. Miller to decide what they should investigate experimentally in so far as spectra were concerned. Therefore W. A. Miller examined spectra in all the possible ways which he could imagine. Thus, following Daniell (133), he investigated the possibility of establishing links between substances which produced similar absorption spectra:

> I was in hopes of discovering, amongst other bodies, and particularly amongst compounds of similar nature and properties, a correspondence, if not in colorific position, at least in the general arrangement of the lines...This hope, however, I have not been able to realise to any considerable extent (134).

Again his failure to devise satisfactory links between substances by way of their absorption spectra can be attributed to the theories of spectra with which he and his contemporaries were working. The theories suggested that line spectra were unique to chemical substances but it was apparently not clear that the theorists actually meant elements. Further, there was no consistency between Talbot's undulatory hypothesis and Brewster's particulate hypothesis about how the lines were caused. So it was not clear to either Daniell or W. A. Miller what they should look for in terms of links between line spectra and ponderable matter. The experiments which they performed on line spectra gave apparently inconsistent results which did not enable them to sort out any of the problems relating to the cause of the lines.

When W. A. Miller came to investigate the spectra of flames he again ran into experimental difficulties. He explained that he

> had sought to ascertain if any relation could be found between the chemical characters of the bodies under examination and their properties of exhibiting Fraunhofer lines; but as yet [he added] no such relation could be detected (135).

All that he could do was to describe the flame spectra of various substances which he examined: in particular he described the spectra of numerous chlorides (136) as well as boric acid, strontium nitrate and the metals zinc, iron and platinum (figs. 5 and 6). In these metals he only observed the bright yellow line as he had done in some of the salts of chlorine.

He did not specify precisely why these results were unsatisfactory, but it may be easily imagined that the ubiquity of the yellow line in so many flames presented severe problems in the context of the theoretical understanding of spectra, since it should have only belonged to one substance (either a chemical element or compound). If spectra were supposed to be unique to particular substances how could the yellow line be caused by so many substances? Again this can be attributed to the failure of the theorists to make it clear that they thought that chemical elements were solely responsible for producing the lines; this would have then ensured that chemists would look for evidence of contamination. W. A. Miller appears not to have realised (or if he did, he did not mention it) that the yellow line was being caused by the contamination by sodium of the samples under investigation. This was something which was not taken into account by the physical theories of spectra, and the chemists were unable to go beyond what the physicists had offered. Such was the situation even ten years later in 1855 when W. A. Miller described some of these results in his text book "Elements of Chemistry" (137). Here he stated that the

> chemical nature of the substance has a very important influence on the kind of light which it emits. Each of the metals, in burning, gives out light of a peculiar and distinctive colour; and in each case certain portions of the spectrum are wanting (138).

In spite of this statement he recorded the spectra of only five substances and did not utilise the method as a practical technique of qualitative chemical analysis.

Yet despite the fact that the experiments conducted by chemists on spectro-chemical techniques produced highly unsatisfactory results and certainly did not produce a practical means of analysis, it was still believed that the theoretical work on absorption ensured that spectral lines were unique to chemical substances. The difficulty was that none of the theories had clearly located where the cause of the lines lay thus giving rise to considerable confusion when chemists attempted to put the theory into practice. We can thus perceive that there was a recognition by both physicists and

chemists that line spectra could be used for the purpose of chemical analysis. But for various reasons the practical implementation of a general system of chemical analysis using spectra was not possible. Chemists such as Daniell and W. A. Miller must have realised that an immense amount of experimental work would be necessary in order to establish such a system of chemical analysis. But for these chemists there also existed the problem that the physicists who had concerned themselves with the interaction of matter and light did not agree amongst themselves about whether spectra belonged uniquely to chemical elements or not. Both Brewster and Talbot had appeared to argue that spectra were unique to chemical compounds, despite the fact that they had largely assumed that spectra were unique to chemical elements; but both had based their final arguments on totally different theories of the interaction of matter and light. To add to the confusion Herschel had argued, albeit from acoustical analogies, that absorption revealed a complex structure of matter, which could imply, though he did not say so explicitly, that spectra were not unique to chemical compounds.

There were, therefore, as many theories of absorption, as there were scientists advancing theories to explain absorption. It is not surprising that those chemists who tackled the problem of spectro-chemical analysis were not very successful. But the important thing is that the idea of using light for chemical analysis had been conceived and established as a theoretically valid idea, and because of the debate on absorption it had been widely disseminated.

Chapter Four

THE STUDY OF SPARK SPECTRA 1835-1859

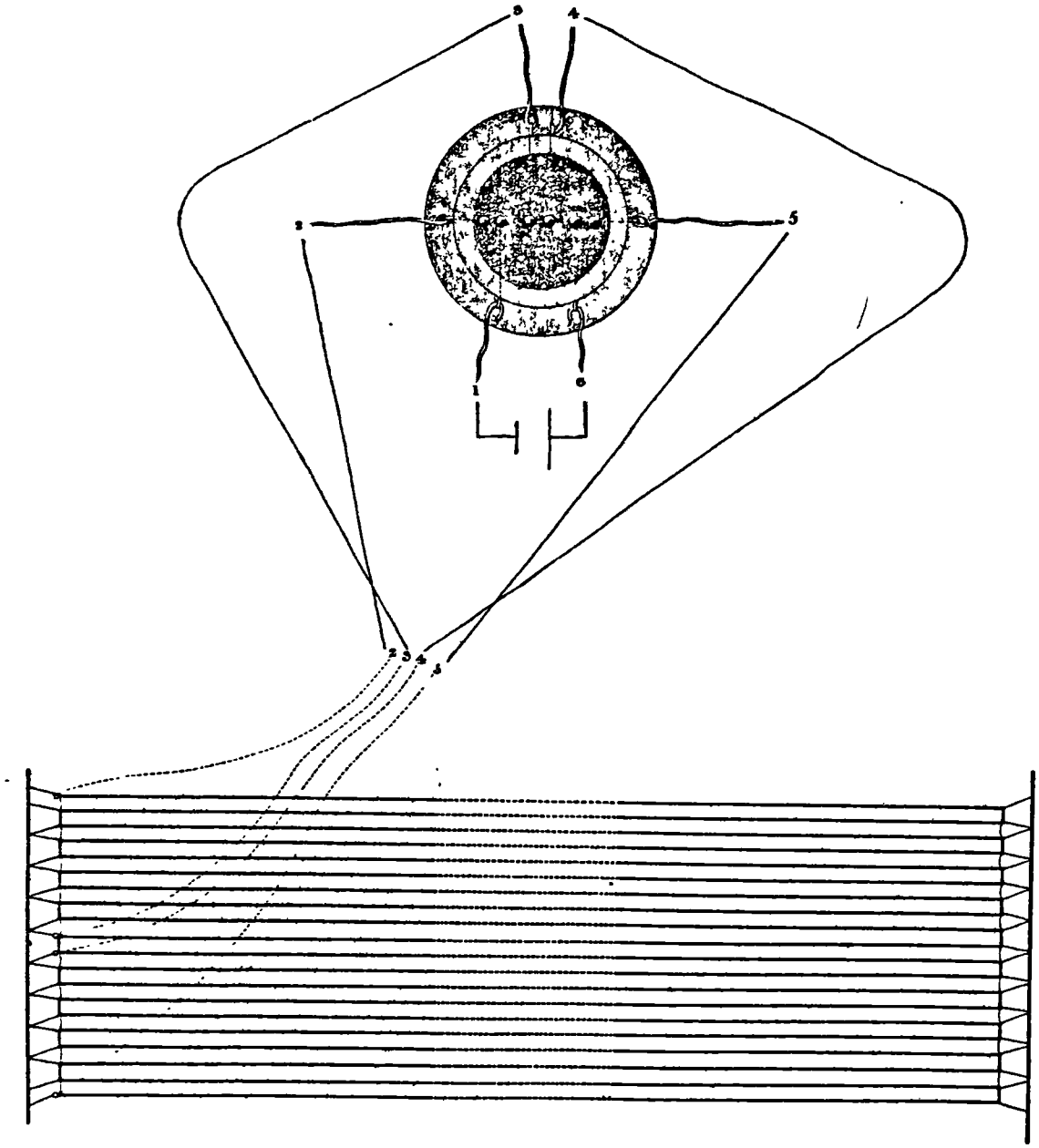
The study of electrical phenomena in the nineteenth century raised numerous questions concerning the nature of both matter and electricity. One of the main problems which scientists faced was the relationship between matter and electricity. For example much of Michael Faraday's (1) work especially on electro-chemistry was directed towards the elucidation of this relationship (2). One of the forms which this problem took in the work of both Faraday and other scientists was the question of the nature of electric light. In other words how did electricity and matter interact to produce light? In this chapter I shall concentrate on one approach which scientists adopted between 1835 and 1859 towards this problem, namely the prismatic analysis of the light produced by sparks. This particular approach arose out of Charles Wheatstone's (3) investigation into the nature and velocity of electricity, which involved the examination of the behaviour of sparks, and Faraday's theoretical interpretation of Wheatstone's work. It was thus ensured that from the outset the study of spark spectra was closely related to problems concerning the nature of electricity and its interaction with matter.

Wheatstone considered that the problems of the nature and velocity of electricity were closely related, and that they could be solved by examining the behaviour of the spark passing between two electrodes under certain conditions. As he put it in a lecture which he wrote, but which was delivered by Faraday to the Royal Institution in March 1833 (4)

> The object is to ascertain whether the time occupied by the passage of the electric spark is appreciable; if it be, then the existence of an electric fluid, or of two fluids, and the direction of the passage may be determined (5).

Wheatstone thus thought that if he could show that it took a perceptible period of time for the electricity to cross from

fig. 1



Wheatstone's apparatus to measure the velocity of electricity.

one electrode to the other to form a spark, this would provide more information than merely enabling a determination of its velocity to be made. In particular he thought that he would discover whether or not electricity was composed of one or two fluids and, if it was one fluid, the direction of its propagation. Wheatstone thought that he could do this because in order to measure the velocity of electricity crossing between two electrodes he employed a revolving mirror by which he observed the spark, hoping to "slow" it down sufficiently to watch its journey across the gap. No doubt he was expecting to see the spark emerge from one electrode if electricity was a single fluid, or from both electrodes if it was composed of two fluids. Unfortunately for Wheatstone the velocity of the spark was too great for any such effect to be perceived even using the revolving mirror and he was forced to abandon this approach (6).

In his next attempt to determine the nature and velocity of electricity he passed electricity through a length of wire half a mile long. The results of his spark experiment must have convinced him that the velocity of electricity was such that it must travel a considerable distance before its speed could be made apparent even using his revolving mirror. In his half mile circuit he in effect placed three spark gaps at equal distances along the wire (fig. 1) (7). He argued that the order in which the sparks flashed would indicate whether the electricity was flowing from one pole of the battery or from both. If the sparks flashed one after the other along the wire then electricity would be a single fluid flowing from one pole of the battery to the other. When he conducted this experiment he observed that the middle spark was measurably retarded compared with the other two sparks which flashed at exactly the same time. He therefore argued that the electricity must have reached these two spark gaps simultaneously from their respective poles of the battery. After passing through the first two spark gaps the electricity from both would proceed to the middle spark gap to cause the spark there. He therefore concluded that electricity was composed of two fluids flowing round the circuit; and, incidentally, that its

speed was 288,000 miles per second (8).

Although Wheatstone did not express any dissatisfaction with this interpretation of his experimental work, a problem which may well have presented itself to him was how did the electricity propagate itself across the spark gaps? Whether he actually had such a question as this in mind or not, the following year (1835) he read a paper to the Dublin meeting of the British Association in which he was very much concerned with examining the nature of the electric spark and how electricity could be transmitted across a spark gap (9). In order to do this he prismatically analysed the light produced by the spark. Quite what led Wheatstone to employ this particular type of analysis is not clear. He was aware that Fraunhofer had reported, in passing, that electric light produced by a friction machine produced singularities in its spectrum (10). Also in a pamphlet which Wheatstone published maintaining that he was the inventor of the electric telegraph (11), on which he had worked more or less contemporaneously with his work on the nature and velocity of electricity, he stated that the electrical impulses which he had sent along a wire had been originally made visible by creating a spark. To determine the period of duration of the gaps in the spark which would carry the message he had attempted to use a "revolving prism" (12); though whether this would have shown the spectral lines is problematical. Nevertheless the fact is that Wheatstone did analyse prismatically the light produced by the spark.

Wheatstone originally appears to have analysed sparks which were produced by electricity originating from an electromagnetic induction machine. I would suggest that he chose this method of producing the electricity for the spark as one which gave a sustained source of current even though the spark it produced was not particularly bright. To brighten the spark he dipped one of the electrodes into a bowl of mercury before passing the electricity through it (13). When he prismatically analysed the spark so produced he observed

> a few definite lines of light, separated by very wide dark intervals from each other, some of great brightness (14).

When he repeated the experiment, substituting for the mercury fluid zinc, cadmium, bismuth, tin and lead (all of which have a fairly low melting point) he discovered that they possessed spectra similar to that produced when using mercury but with their lines in different positions. He concluded

> the appearances [of the spectra] are so different that by this mode of examination, the metals may be readily distinguished from each other [fig. 2] (15).

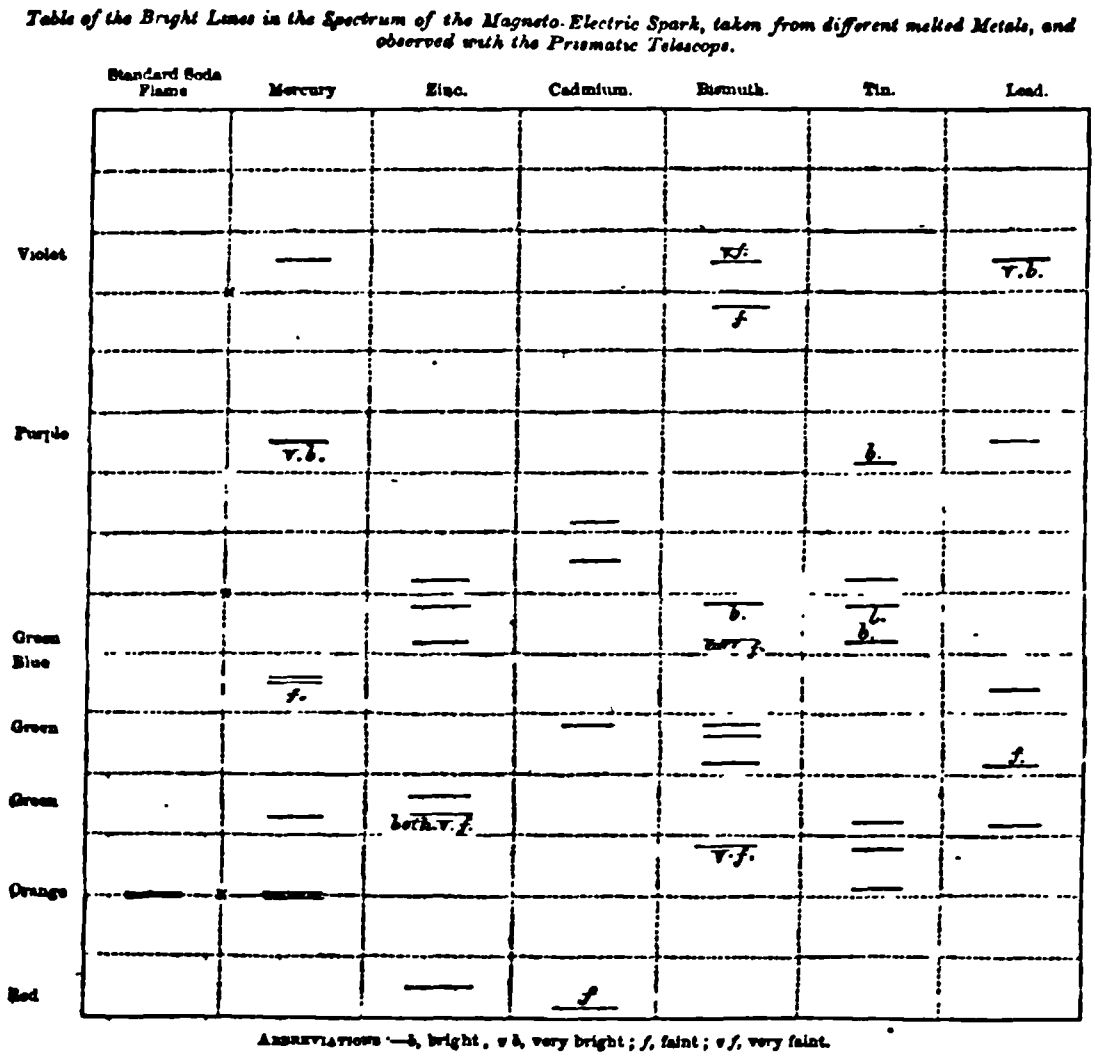


fig.2

Wheatstone must have spent a considerable amount of time and effort in order to obtain the spectra of these metals and this implies that he had an a priori idea of what he would find. He was apparently aware of some of the work conducted by scientists on flame spectra since in the diagram of the electric spectra which he provided he referred the position of the lines of the spark spectra to the "standard soda flame" (16). Further Wheatstone commented that

> The peculiar luminous effects produced by electrical action of different metals, depend, no doubt, on their molecular structure; and we have hence a new optical means of examining the internal mechanism of matter, in addition to those which Sir D. Brewster and other philosophers have already placed at our disposal (17).

It would appear that Wheatstone was acquainted with earlier work on flame spectra and that he accepted the fundamental proposition which had emerged from this work that spectra were dependent on the internal structure of matter which produced them. But beyond this it is not clear what rôle this earlier work on flame spectra played in the development of Wheatstone's work. His idea that line spectra were dependent on the structure of matter need not necessarily imply that he thought that spectra were characteristic of the chemical elements; Brewster had affirmed this, but others, such as Herschel, had not. Therefore in order to be able to examine the nature of the spark, Wheatstone had to confirm, for himself, that spectra were uniquely characteristic of the chemical elements.

That line spectra were characteristic only of the elemental metals Wheatstone confirmed by examining the spark spectra of alloys of the various metals the individual spectra of which he had already investigated. He observed that

> When the metals differed much in volatility the lines appertaining to the most volatile metal only was observed; in other cases lines belonging to both were seen (18).

Wheatstone had here established that it did not matter whether or not the metals occurred individually or in combination,

it was the metals acting individually which caused the spectral lines. No further lines other than those which each metal produced individually were seen when two metals were sparked together. Although the intensity of the lines of one metal might possibly be greater than those of another metal no doubt these were also present but impossible to observe. Wheatstone was able therefore to experimentally establish to his own satisfaction that the spectral lines were uniquely characteristic of the elemental metals which composed the electrodes. Wheatstone was in no doubt about where the cause of the lines lay. This he could establish experimentally without referring to any of the existing theories of line spectra and indeed Wheatstone did not speculate about why the lines should exist, which had been one of the main problems concerning those scientists who had worked on absorption and flame spectra.

Although Wheatstone had the germ of the idea of spectrochemical analysis, it was not his prime object to develop such an idea. It was a tool to be used to establish the nature of the spark. All that Wheatstone had done was to establish that each metal when placed on the electrodes generated unique spectra when the electricity produced by electro-magnetic induction was passed across the gap. This was not sufficient for him in his examination of the nature of the spark, since sparks could also be produced by electricity originating from other sources. He therefore examined the mercury spark produced by electricity originating from a voltaic pile, the spectra of which he found possessed the same lines as when the spark was produced by electricity originating from electro-magnetic induction. However, when he analysed prismatically the mercury spark produced by "ordinary" electricity (presumably from the leyden jar) he discovered that in addition to those lines which had been produced by the voltaic pile, there were many other lines. It is not clear what Wheatstone had observed here, mainly because the observational information he provided is inadequate. However, the new lines could have been caused by a change in potential between the electrodes; alternatively, there may have been sufficient increase in the

current to produce lines caused by the atmosphere. This would explain why there were no common lines in Wheatstone's spectral diagrams of sparks produced by electro-magnetic induction (and the voltaic pile) since the current may not have been strong enough to produce the atmospheric lines. But Wheatstone did not speculate on where these extra lines came from.

Curiously Wheatstone had considered the idea that some lines of the voltaic spark spectrum might be caused by the medium in which the spark was exploded; this implies that he did not really have any idea about what to look for, so far as atmospheric lines were concerned. After determining that the spark spectrum of mercury was the same in the ordinary atmosphere as in a vacuum (presumably the vacuum was not total), carbon dioxide, or oxygen he concluded that the medium in which the spark was exploded "had no influence on the nature of the light" (19). When he examined the mercury spark under water, in alcohol and in oil, he discovered that its spectrum was still the same. Further some black powder which had been precipitated in these liquids "proved to be pure mercury, in a very finely-divided state" (20). He therefore argued that the spark was not a "consequence of combustion" (21) i.e. the mercury had not oxidised. To confirm that the metals placed on the electrodes had not been burnt he placed in turn iron, copper, bismuth, lead and tin on heated charcoal towards which he directed an oxygen jet to facilitate combustion; when the light so produced was prismatically examined he found that the spectra of these metals were continuous. This confirmed for Wheatstone, as he had no doubt expected, that the light given off by burning the metals was different from that produced by sparking them. Presumably the temperature of the metals had not been sufficiently high for them to emit their characteristic spectrum.

Wheatstone's method of obtaining the spectra of metals by igniting them is interesting since his predecessors when they had attempted to obtain flame spectra of metals had been prepared to deduce metallic spectra from the spectra

produced by their salts. Wheatstone it appears was not prepared to accept that this was indeed the characteristic combustion spectrum of each metal and he therefore wanted direct experimental verification of the spectrum of each metal in order to establish that combustion was not the cause of the spark. This illustrates the minimal influence which the earlier work on flame spectra exercised on Wheatstone's work. He had to examine every aspect of the problem of spark spectra which had been discovered. The object of the earlier work on absorption and flame spectra had been to reconcile these phenomena with the undulatory theory of light; the object of Wheatstone's work on the other hand was to gain an understanding of the spark. Between these two fields of study different questions would necessarily have to be asked of the spectral phenomena. In the earlier case the problem was to discover how line spectra were caused; in Wheatstone's case it was to discover how line spectra could be utilised for the study of sparks. It should therefore not be found surprising that despite the fact that both approaches dealt with ostensibly the same phenomenon - line spectra - there was in fact very little influence by the earlier work on flame and absorption spectra on the study of spark spectra. This dichotomy in approach was, as we shall see, very widespread so far as those who worked on spark spectra were concerned.

Using his spectral studies Wheatstone was able to demonstrate the insufficiency of earlier theories of the spark. For example Biot had proposed, in 1805, that the spark was caused by the pressure of electricity in the electrodes causing it to eventually propagate itself through the air (22). Wheatstone said that this could not be the true explanation of spark phenomena because

> if any change should be observable in the character of the spark, it should depend on the medium which is supposed to produce the light by its compression, and not on the conducting substances from which the electricity escapes; where we find the direct contrary to be the case (23).

Wheatstone's observation that there were no lines caused by the

medium in which the spark was propagated immediately invalidated, for him, Biot's hypothesis. He presumably thought that if this was what happened then surely the behaviour of spark spectra would also be dependent on the media, which was certainly not the case. In a similar manner Wheatstone dealt with the theory of sparks (originally proposed by Ritter and subsequently developed by Davy, Oersted and Berzelius) which suggested that they were caused by the transmission of the innate electricity belonging to the atoms of ponderable matter into the atmosphere. This process, Wheatstone commented, was insufficient to explain why the light given off by the spark should be different for different metals, although he did not specifically reject this as a mechanism.

Instead of these hypotheses Wheatstone postulated his own:

> I am strongly induced to believe that it [the electric spark] results solely from the volatilization and ignition of the ponderable matter of the conductor itself. The difference between the appearance of the prismatic spectra of the same metal electrically ignited and ignited by ordinary combustion, I conceive to consist in this, - in the first case the particles are by volatilization attenuated to the highest possible degree; while in the second, that of ordinary combustion, the light is occasioned by incandescent particles of sensible magnitude (24).

In this he consciously followed the work of the Venetian physicist Ambrogio Fusinieri (1773-1853) who had suggested that the electric spark in passing from one electrode to the other took some of the ponderable matter of the electrodes with it (25). This accorded perfectly with Wheatstone's assertion that the spectra were produced only by the metal of the electrodes and no other agent, and with his observation that the precipitate produced by the sparking process in a fluid was the metal of the electrodes.

Wheatstone had thus devised an explanation of spark phenomena which I would speculatively suggest could account for his observations of the behaviour of the three sparks in his experiment on the velocity of electricity; it could now be conceived that sparks might be self-propagating from one electrode to the other which did not necessarily have any

electricity on its side, since this would be done via the transmission of ponderable matter across the gap. Presumably Wheatstone thought that once sufficient electricity was in an electrode then it must be able to escape by the volatilization of the particles of the electrodes, attracted towards the nearest conductor.

In Wheatstone's work there is a dichotomy in the problem of spark spectra which was common to nearly all those who worked on the subject. Those who worked on sparks per se naturally asked what the nature of the spark was; those who analysed the spark prismatically were able like Wheatstone to use the spectra so produced as a tool to analyse the spark. But there was no necessity, as the work of Wheatstone illustrates, for this latter group to ask the question what caused the spectrum of the spark; it was simply required that the spectra of individual chemical elements were uniquely characteristic of those elements so that they could be utilised for the purpose of understanding the spark.

Although Wheatstone took no further research interest in the theory of sparks or their spectra until after 1860 when he joined in the polemics regarding the early history of spectroscopy, his work greatly interested Faraday who did pursue it. As early as November 1835 Faraday had realised the importance of Wheatstone's work in the theory of electricity:

> The retardation of the middle spark in Wheatstone's three sparks is probably a connecting link between conduction and induction. [I] must consider it in relation to induction in metals (26).

This interest in sparks grew and Faraday's diary reveals that it was one of his main research interests in late 1835 and most of 1836. He published the results of this work in the twelfth series of his "Experimental Researches in Electricity" (27) in early 1838.

Faraday found that if one of the wires connecting the electrodes in Wheatstone's circuit was removed and replaced by water, glass or some such bad conducting substance then the amount of retardation of the middle spark was increased (28). He therefore argued that there must be a gradual build up in

the charge of these substances before what we would now call the potential difference existing between either side of the spark gap was sufficient to permit the spark to cross.

Faraday was therefore concerned to discover what it was between the electrodes which caused the spark. He recorded in his diary early in his investigation that it might "have reference to the nature of the substance of which the points are made" (29). In other words, though he did not explicitly say so, he considered that Wheatstone's hypothesis concerning the transmission of electricity across the spark gap might be an explanation of the phenomenon. Faraday however did not examine the differences in the light of the spark caused when the electrodes were made of different materials, instead he pursued the differences caused by sparking electrodes in different gases. Faraday had found that when a spark was exploded in different gases its colour depended on the nature of the gas; further he observed that each gas had its own characteristic colour. Although he did not perform the detailed chemical analyses which Wheatstone had done, it is evident that Faraday considered that the colour of the light produced by the spark in the various gases which he examined was peculiar to each gas: "the characters of the electric spark in <u>different gases</u> vary" (30). In other words he implicitly disagreed with Wheatstone's contention that the medium in which a spark was exploded had no effect on its light. On the other hand Faraday did not deny Wheatstone's assertion that spark spectra depended on the chemical nature of the electrodes.

Faraday's aim in his theoretical consideration of the nature of the spark was to include spark phenomena within his theory of electricity. The passage of electricity along a wire was, according to Faraday's theory of induction "an action of contiguous particles consisting in a species of polarity" (31). The transmission of electricity would therefore depend on the particular particles involved in transmitting electricity. Since there existed this specific relationship between the particles of a conductor and the electricity which it carried then there must also be a "specific relation of the

particles [of the spark] and the electric forces" (32). This was evinced experimentally by the colour of the spark in different gases. He concluded therefore that

> the ultimate effect is exactly as if a metallic wire had been put into the place of the discharging particles; and it does not seem impossible that the principle of action in both cases, may, hereafter, prove to be the same (33).

In other words when electricity was passed across the gap between two electrodes the matter between the gap had been conditioned to behave as if a metal wire had been put in its place; the spark was therefore dependent on the matter in the gap. Although Faraday did cautiously assign the cause of the colour differences of the spark to the characteristic relationship between electricity and the gas in which it was sparked, he did not make it clear where he thought the matter in the gap originated. To a certain extent the question of the origin of the matter between the electrodes was not important for Faraday since, wherever the origin lay he had shown that spark phenomena could be fully included within his theory of induction. He had therefore devised a theory of sparks, i.e. that they were caused by electricity passing between the two electrodes, which fully accorded with his theory of electricity.

According to Faraday's theory, electricity and matter must have characteristic relationships for each type of matter. It would therefore be difficult to imagine that light produced by the interaction of electricity and matter was not characteristic of the matter. That such relationships existed Faraday had effectively shown so far as gaseous substances were concerned; but equally well it must also apply to metals which transmitted electricity. This relationship would be expressed in the characteristic emission spectra belonging to each material. While Faraday had not been specifically concerned with spectral problems, he had effectively laid the theoretical foundations for the study of spark spectra in which each element would be guaranteed a characteristic spectrum. The idea that line spectra produced by sparks indicated the presence of a particular metal in or on the electrodes was one which was present in a paper of Léon Foucault's (34) of

January 1849 (35) although it is not clear what the theoretical antecedents of Foucault's assertion was. However, Foucault had been interested in spark phenomena for some time being the first person with A.-H.-L. Fizeau (1819-1896) to photograph the spark in order to compare its intensity with other light sources (36).

Foucault undertook the prismatic examination of the spark produced between two charcoal electrodes. He observed the presence of the double yellow line which "recalled [to him] by its form and situation the line D of the solar spectrum" (37). In order to confirm this apparent similarity, he passed sun light through the spark and observed that the

> arc, placed in the path of a beam of solar light, absorbs the rays D, so that the above-mentioned line D of the solar light is considerably strengthened when the two spectra are exactly superposed. When, on the contrary, they jut out one beyond the other, the line D appears darker than usual in the solar light, and stands out bright in the electric spectrum, which allows one easily to judge of their perfect coincidence. Thus the arc presents us with a medium which emits the rays D on its own account, and which at the same time absorbs them when they come from another quarter.
>
> To make the experiment in a manner still more decisive, I projected on the arc the reflected image of one of the charcoal points, which, like all solid bodies in ignition, gives no lines, and under these circumstances the lines D appeared to me as in the solar spectrum (38).

In other words Foucault had observed what would later be termed reversal: that a source emitting light of a particular wave-length could also absorb light of that same wave-length thus causing dark absorption lines to be observed in its spectrum. This observation effectively dealt with one of the problems which Herschel had had to contend with in his work on the solar spectrum, viz how could the hot solar atmosphere not emit light of certain wave-lengths. Herschel had supposed that molecules of the solar atmosphere were unable to vibrate at certain wave-lengths when hot; Foucault had observed that light coming from a stronger source was quite capable of being absorbed by a medium which emitted light which would thus cause absorption lines. This observation led Foucault to suggest that the study of stellar spectra (including the sun) would in all probability lead to an understanding of the

chemical nature of the stars (39).

It seems therefore that Foucault was convinced that line spectra were uniquely characteristic of chemical substances, but he was unable to determine which lines belonged to which substance. For example in the case of the double yellow line he had not only observed its presence in the spectrum of spark between two charcoal electrodes, he had also observed it to occur in cases where the electrodes were made out of iron or copper (40). In the latter two cases he found that the yellow lines could be intensified by placing salts of sodium or potassium on one of the electrodes (41). But he was unable to draw any positive conclusions about the location of the origin of the lines.

It seems clear that Foucault subscribed to the idea that line spectra, at least when produced by sparks, could be utilised for the purpose of qualitative chemical analysis. Although Foucault did not discuss the origin of the Fraunhofer lines, he must have thought that they were due to an absorption process in the stars themselves since he had argued that the lines he had created on earth were absorption lines. Therefore there must be a causal link between the emission and absorption of light at the same wave-length.

Foucault had suggested two properties appertaining to the Fraunhofer lines: firstly that they were caused by the stars themselves and secondly that they could be uniquely characteristic of the chemical composition of the stars. Both these assumptions appear to have been implicit in a paper by Fizeau which he had presented a month before Foucault had presented his (42). In this paper Fizeau argued, using the analogy of sound and light, that the frequency of a ray of light would be affected by the relative velocity of its point of emission and the observer. Christian Doppler (43) had suggested this a few years earlier and had established it satisfactorily for sound although not for light (44); it would appear however that Fizeau was in ignorance of Doppler's work. Fizeau thought that the only way in which the change in frequency of a moving body emitting light could be detected would be by looking for a displacement in the position of its line spectra

when compared with the position of the lines when a source of light emitting the same lines, was stationary. Thus he said that the D lines belonging to Venus should be displaced 2",56 from their normal position when the prism was made of flint glass with an angle of 60^{o}. In this Fizeau assumed that the same substance which caused the D line on earth must also cause it on Venus, since otherwise any apparent displacement could simply be due to another material causing similar lines close by. He also assumed that the D lines of Venus were caused by Venus herself and not by, for example, the terrestrial atmosphere. Unfortunately there were considerable observational difficulties in making this measurement, as Fresnel pointed out, although he thought that they could be overcome.

For Fizeau as well as for Foucault the study of both emission and absorption lines presented considerable opportunities not only for the study of terrestrial chemistry, but also for ascertaining information concerning the stars. That they did not take advantage of the opportunity can really only be ascribed to lack of exact knowledge concerning the precise origin of the lines. But neither Foucault nor Fizeau felt inclined to pursue the matter; they were more concerned with problems such as determining the speed of light.

This lack of precise information concerning the spectral lines together with the idea that once this information had been elicited, answers to many other physical problems such as the chemical nature of the stars, and the physical nature of the spark, would follow, ensured that research into spectral phenomena would continue. It was the problems surrounding the nature of the spark to which Antoine-Philibert Masson (45) addressed himself. Masson had begun his work on sparks in the mid 1840s by investigating what was required to produce an electric spark and quantitively relating its photometric intensity to the various causal agents which he found were concerned in its production: that is the area and thickness of the condensers of the battery, the width of the spark gap and so on. By 1845, on the basis of this research he had established several quantitative laws relating sparks

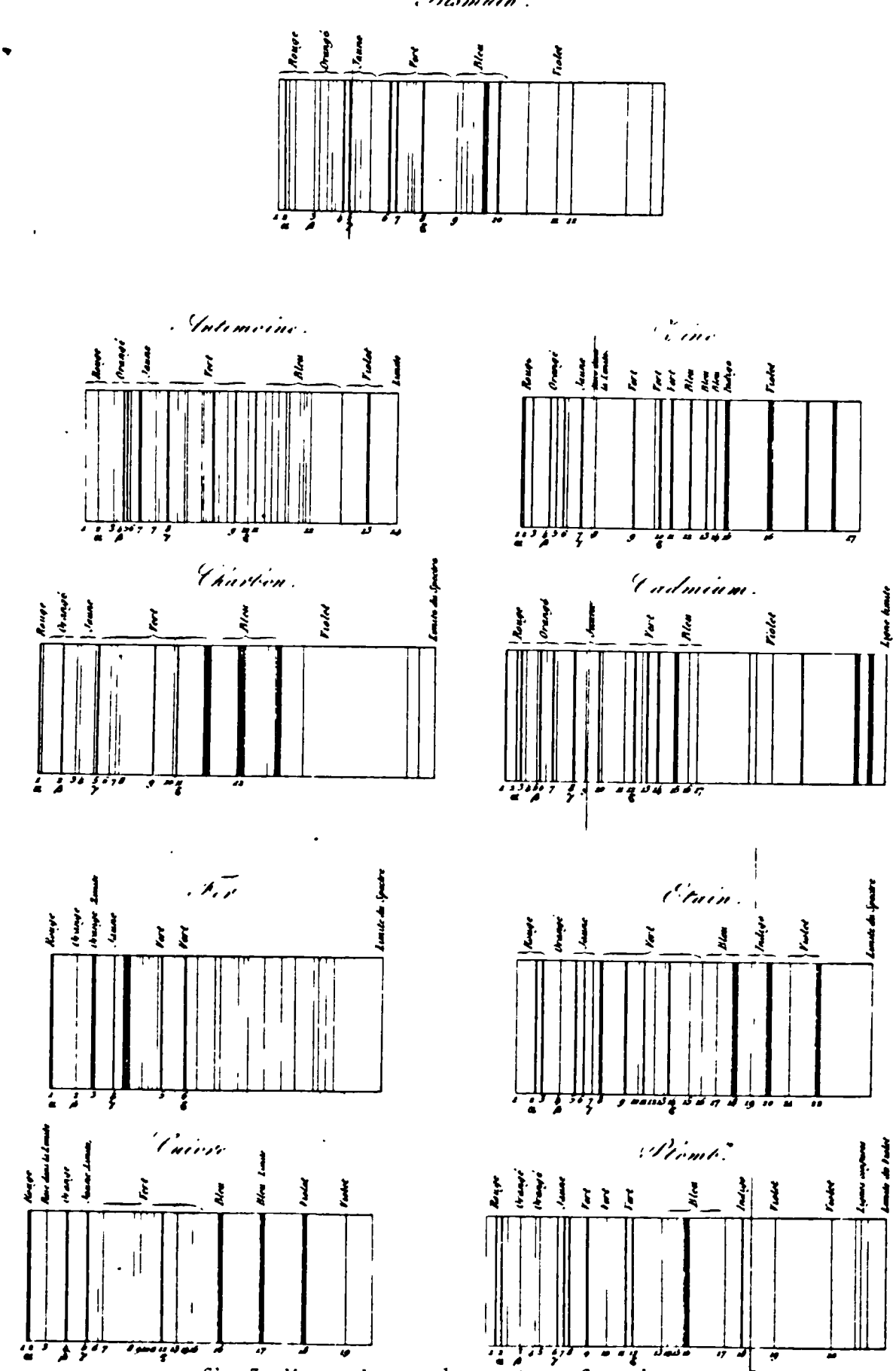


fig.3 Masson's spark spectra of various metals

to the electrical agents which produced them (46).

By 1851 Masson had undertaken a systematic study of spark phenomena produced by using electrodes made of different metals. Like Wheatstone, of whose work he was aware (47), Masson used spectra to help analyse the nature of the spark. Masson noted that "when the nature of the poles is changed, the character of the spectrum is altered" (48). But he had also noted that among the lines of each spark spectrum which he examined there were four lines which he called "raies communes" (49) which existed in every spark spectrum. Masson seems to have thought that these lines, which he designated α, β, γ, and δ (50), belonged to the metals, since he included them in his list of lines which characterised the individual spark spectra of carbon, cadmium, antimony, bismuth, lead, tin, iron, zinc and copper (fig. 3) (51). Since he made his electrodes out of the metals concerned, and therefore did not need to dip them in the fluid metal as Wheatstone had done, he was able to extend the number of metals the spark of which could be examined prismatically.

This work decisively showed Masson that the spark spectrum of each metal was different. It also showed him where the origin of the lines lay: i.e. with the metal of the electrodes, but it did not enable him to explain why the lines should exist. It was reasonable for him to suppose, as he did, that it was the particles from the metals of the electrodes in the spark gap which caused the differences in the electric spectra. As he put it:

> The electric spark is produced by a current which is propagated by, and traverses the ponderable matter [of the spark] and it heats it in the same manner and following the same laws as does a voltaic current which heats and renders luminous a metallic wire (52).

Masson acknowledged that this was fully in agreement with Faraday's view of the nature of the electric spark. Masson had experimentally verified Faraday's suggestion that the electricity passing between the electrodes of a spark gap obeyed the same laws as those of electricity in a wire. It followed that Masson had also verified Faraday's contention that between electricity and matter there subsisted unique

relationships for each variety of matter, this for Masson being evinced by the characteristic spectrum emitted by each metal. The only difference between Masson and Faraday, so far as this work was concerned, was that the former explicitly located where the origin of the matter of the spark lay, a question which Faraday had left open.

Masson adduced further evidence for his contention concerning the origin of the material which carried electricity across the spark gap by investigating the behaviour of sparks passing through gaseous and liquid media. To confirm positively that matter was transmitted by a spark, Masson examined the spectrum produced by sparking the electrodes in alcohol. The sparks showed the same metal spectra as when they were sparked in the ordinary atmosphere. When he collected the precipitate which had been produced by the spark in the alcohol he found that it was the oxides of each of the various metals of the electrodes (53). Therefore, he argued, there was a definite transfer of matter in the spark between the two electrodes.

When he passed a spark through rarefied air and examined its spectrum, he observed that although the intensity of its light was diminished when compared with a spark in the ordinary atmosphere, the position of the lines for a particular metal remained the same (54). This showed for Masson that even though the spectral lines originated with the metal, the medium in which the spark occurred must have some effect on the transmission of the metal of the electrodes since the intensity of the lines had decreased. The implication of this experiment was that the intensity of a spark diminished as the pressure of the medium was lowered; in the ultimate case where there would be no matter between the electrodes i.e. a vacuum, electricity could not flow. Masson performed several experiments in which he attempted to pass electricity across a gap placed in a vacuum, but he discovered, as he no doubt expected, that this was impossible. He therefore concluded that

> In all possible cases, ponderable matter is necessary for the propagation of currents and for the induction of statical electricity in the vacuum (55).

This he claimed was also in full agreement with Faraday's view of the transmission of electricity through matter (56). In fact Faraday had been very cautious in dealing with the problem of transmission of electricity in a vacuum, writing:

> In experiments I think I have observed the luminous discharge to be principally on the inner surface of the glass; and it does not appear at all unlikely, that, if the vacuum refused to conduct, still the surface of the glass next it might carry on that action (57).

But

> My theory, as far as I have ventured it, does not pretend to decide upon the consequences of a vacuum (58).

In other words Faraday thought that the fact that electricity flowed through matter did not necessarily preclude the possibility that electricity could flow in a vacuum. Masson on the other hand thought it did preclude such a possibility and he showed experimentally that this was the case. For Masson the medium in which a spark was created played a rôle in the creation of a spark since it was necessary for a medium to exist in order that matter from the electrodes could be transmitted across the spark gap. Quite why Masson, following this, did not realise that the raies communes were caused by the atmosphere is not clear. Perhaps he was influenced by Wheatstone's assertion that the medium had no influence on the spectra of the spark; perhaps his observation that the same lines occurred when he sparked electrodes in alcohol convinced him that the medium could have no influence on the spectrum.

To sum up: the problem to which Masson had addressed himself was what was the spark? In the context of this question he had followed Faraday's theoretical ideas and largely verified them. Masson had shown that the matter of the electrodes was responsible for the spark spectrum and therefore this was the material which transmitted the electricity across the gap. He had shown that electricity could not pass across a vacuum; ponderable matter was required and this was all that Masson needed to do to justify Faraday's work. Masson was not interested in spectro-chemical analysis beyond what was required to justify his interpretation of

Faraday's work. He could therefore quite happily not pay any attention to the fact that four lines repeatedly recurred in all spark spectra; he had used the spectra to make his own point and he need go no further,

In spite of this Masson realised that he had not discovered "the real cause of the phenomena [which] remains to be explained" (59) i.e. why should particular metals always emit a characteristic spectrum. In other words he realised that he had only examined the nature of the spark and not gone beyond that to investigate the cause of the spectrum. Masson thus recognised and implicitly supported the distinction between studying spark spectra in order to understand the spark, and studying spark spectra in order to understand the spectrum; that is between the electrical and optical approaches. But these two approaches were connected in that it would be difficult, if not impossible, to understand how the spectrum was produced if there was no understanding of the spark. This was realised by Anders Jonas Ångström, assistant professor of astronomy at the University of Uppsala (60) who, although he was primarily interested in the study of spectra (61), (as I shall discuss in the following chapter), thought that before he could begin to understand the nature of the light emitted by the spark, he first had to investigate the nature of the spark itself, and in particular to discover where the cause of the lines lay.

In the course of his investigation he discovered that there existed two over-lapping spectra in the spark spectrum. One of these he found was due to the medium in which the spark was exploded, and the other due to the metal which formed the electrodes. He had observed, no doubt aided by Masson's observation of four common lines (62), that there were several lines which were common to all spark spectra and these he thought were caused by the atmosphere; this was confirmed for Ångström by his observation that the intensity of these lines varied with the humidity of the atmosphere (63). Consequently he concluded that these lines must be due to the medium in which the spark was produced. These atmospheric lines were, Ångström commented, easily distinguishable from the lines caused by the metal electrodes

since these latter lines did not completely traverse the spectrum from side to side when a weak battery was used as a source of the electricity. Instead, these lines, Ångström observed, tapered from either side of the spectrum. To have observed this Ångström must have held a side of the prism vertically towards the spark. By doing this he could observe where the origin of the light occurred at any particular point in the spark gap. Near the electrodes he observed emission lines which were caused by the metal of the electrodes, but they did not extend all the way across the gap; across the whole gap he observed lines, in different positions, which originated from the medium in which the spark was exploded, since the medium necessarily extended across the whole gap. Therefore a line which was common to all spark spectra, but tapered, Ångström assigned to the metal (64). Actually this line was the sodium R line so Ångström's supposition that this was not an atmospheric line was perfectly correct. He effectively argued that any line which completely traversed that spectrum when there was a low charge must necessarily be caused by the medium in which it was sparked.

Ångström said that the lines caused by the atmosphere were, as he put it, quoting Masson

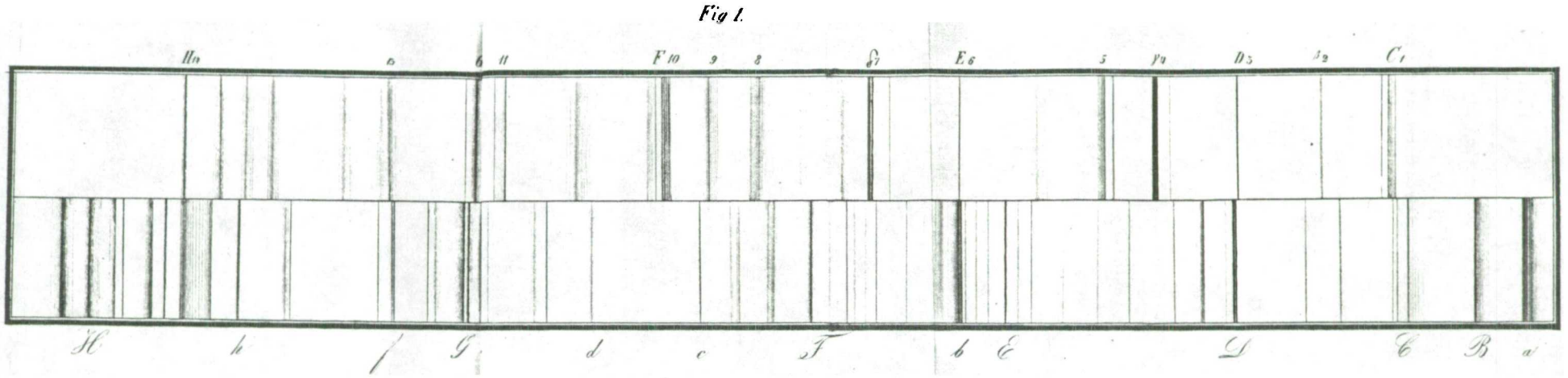
> produced by a current which propagates itself across, and by means of ponderable matter, which it heats in the same manner, and according to the same laws, as a voltaic current heats a metallic wire (65).

Ångström had assumed the same cause for the sparks as Masson and Faraday had done, that is they were due to the ponderable matter existing between the gap of the electrodes, but he had shown experimentally that the metal from the electrodes could not be the cause of all the emission lines and that some must be caused by the atmosphere. Thus he differed from Masson's view that the lines were caused entirely by the metal of the electrodes. But, as Masson had done, Ångström fully concurred with Faraday's view of the relationship between matter and electricity. Both Masson and Ångström working within Faraday's theoretical structure were able to ensure for themselves that line spectra were uniquely

Wilhelm K. Vet. Akad. Handl. 1852.

fig.4

Ångström's atmospheric spectrum



solar spectrum

(reduced by one quarter linearly)

Ångström's spark spectra of various substances

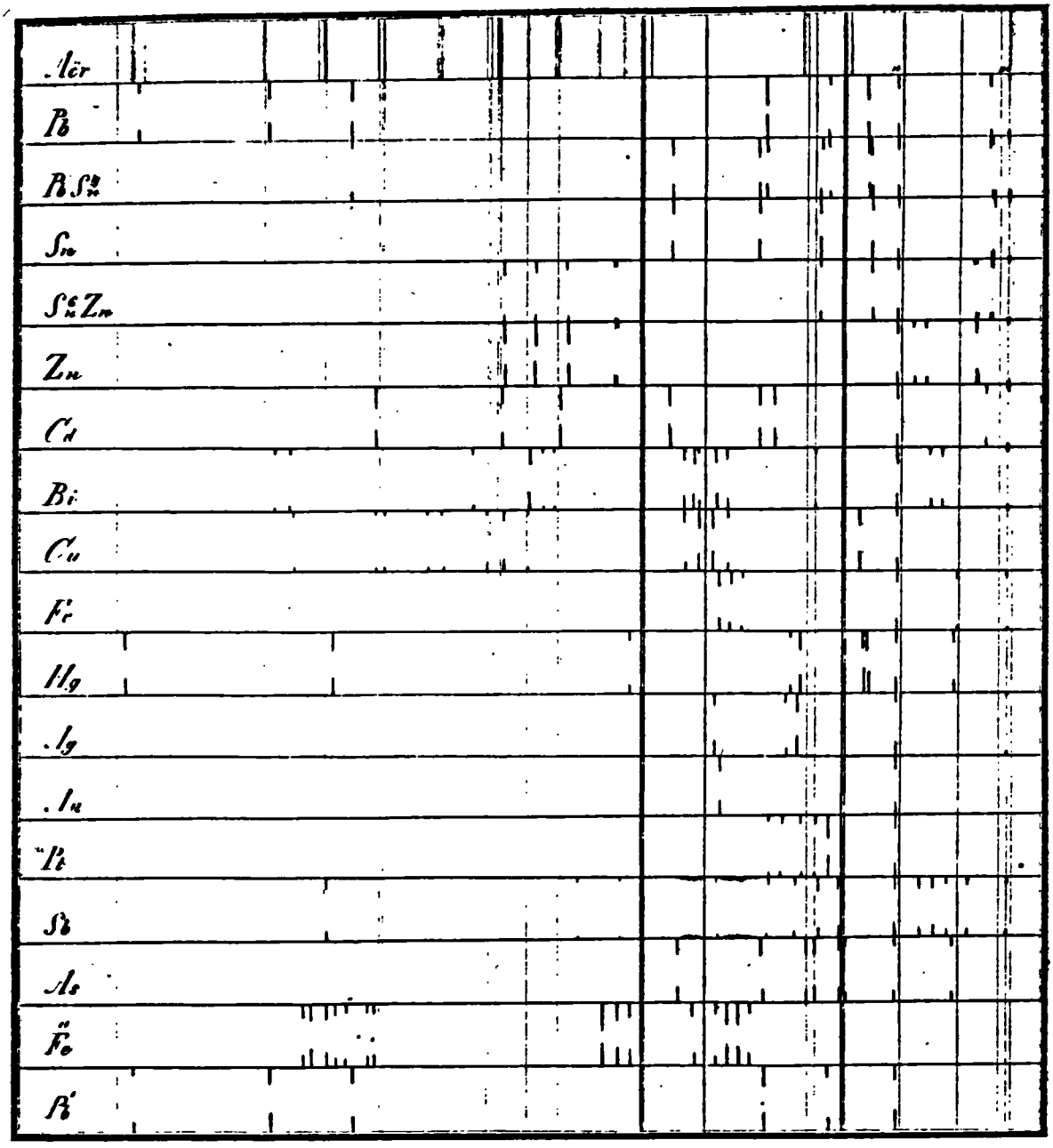


fig.5

characteristic of the chemical elements. The only matter of dispute between them concerned where exactly each spectral line originated.

Since the atmospheric lines were common to all spark spectra, irrespective of the material of the electrodes, their position could be easily determined using only a few spark spectra. Ångström performed this operation using the spectra of tin, lead, zinc and platinum (66). He labelled the atmospheric lines with his own numbers and also used Masson's and Fraunhofer's labelling systems to aid identification. A line might therefore be labelled δ7 where δ was one of Masson's raies communes and 7 Ångström's number or G12 where the line had the same refrangibility as Fraunhofer's G line in the solar spectrum (fig. 4).

As well as determining the position of the atmospheric lines Ångström also mapped the spark spectra of metals to include, in addition to those which he had already used to map the atmospheric spectrum, cadmium, bismuth, iron, mercury, silver, gold, platinum, antimony and arsenic (fig. 5). Like his predecessors Wheatstone and Masson, Ångström had no difficulty in saying that these lines were "peculiar to each metal" (67). This he further confirmed by examining the spectrum of the spark produced by passing electricity through a spark gap, one electrode of which was made of pewter (in Ångström's case this meant $PbSn^4$) and the other of charcoal. He observed that the spectra of both lead and tin were present in the spectrum so produced and no other additional metallic lines were present. Ångström therefore concluded that the elemental metals possessed unique spectra irrespective of how they were combined.

Ångström's investigation emphasises the fundamental difference between the work on flame and absorption spectra and that on electric spectra. In the former case although some theories had suggested unique relationships between elements and their spectra, observationally this had not been successfully substantiated. One cause of this was that observations of absorption spectra had been conducted at normal temperatures thereby failing to allow the individual elements to exhibit their characteristic spectra. In the case

of spark spectra the temperatures reached would always be sufficient to permit the line spectra of the electrodes and the medium in which the spark took place to exhibit their characteristic spectra. There would therefore be no question of the observational conditions affecting this aspect of the problem. In addition there was really only one accepted theory of sparks: Faraday's. And this despite the different interpretations it received at the hands of Masson and Ångström guaranteed for them that a unique relationship existed between the light produced by sparks and the matter, whatever its origin, which carried the electricity across the spark gap. It must have seemed inconceivable to them, though they did not say so explicitly, that a theory which stated that there existed unique relationships between matter and electricity did not imply that there must also be a unique relationship between the matter which had been activated by the electricity and the light which it produced. The theoretical problems which applied to flame and absorption spectra such as how precisely the ponderable matter of the flame interacted with light need not necessarily concern those interested in spark spectra, since their theoretical basis which guaranteed the uniqueness of spectra to ponderable matter emerged from a different, and for them, a more certain direction. This, I would suggest, is one reason why there appears to have been so little influence exercised by the earlier work on flame and absorption spectra on the spark spectra work of the 1840s and '50s. Those scientists who did work on spark spectra did not have any of the observational or theoretical problems which had beset those who had worked on flame and absorption spectra.

The idea that the study of the behaviour of spark spectra could be used to investigate the chemical and physical structure of matter in the spark gap was one which appears to have gained wide acceptance in the 1850s. David Alter, an American physician (68), Volkert Simon Maarten van der Willigen (1822-1878), a Dutch physicist and Julius Plücker (1801-1868), professor of physics at the University of Bonn all in their disparate ways took up the study of spark spectra with the idea that such studies could be used to

elucidate the nature of matter within the spark. Alter and Willigen continued the work of Masson and Ångström in that they were both concerned with the nature of the spark; Plücker, on the other hand, changed the emphasis of the work on spark spectra to suggest, for the first time, that they could be utilised as a method of qualitative chemical analysis. So far as I can ascertain spark spectral analysis had not made any appearance in chemical text books as a means of chemical analysis either as a theoretical or practical proposition as flame spectra had done. This I would suggest was due to the fact that those scientists who had studied spark spectra had not been primarily concerned with chemical analysis per se. They had been concerned with studying the nature of the spark for which the chemical uniqueness of line spectra was a tool - nothing more.

In the work of Alter this attitude found a quite definite expression; the more so since so far as I can make out he did no original work and his main interest lay in what might possibly be discovered using spark spectra. He examined exactly the same metals as Ångström had done, arriving at the same conclusions as he had on where the cause of the lines lay (69). But as with his predecessors Alter used this work not as a method of chemical analysis, but as a possible method of answering questions concerning the nature of matter and electricity:

> Is there such a fluid as electricity? Or, are the phenomena, commonly reputed electrical, the result... of chemical affinity? If so, are there only two poles ...to each molecule - or, are there as many poles or combining surfaces as are indicated by the number of bright bands of its refracted light? And... would not these bands give an indication of the size of those surfaces or poles? (70)

These questions reiterate the point that it was thought by those scientists who studied spark spectra that such spectra were to be used for the purpose of examining the nature of the spark. The problems which interested them followed the assertion that line spectra were uniquely characteristic of the chemical elements. However, the type of questions which Alter proposed could not be answered simply by spectroscopic analysis; one would have to know a good deal more about both

spectra and electricity before these could be answered. Spectroscopic analysis had already been a very useful tool in elucidating Faraday's theory of the spark, and because of its success it was thought that its application could be extended. But it had been applied to a theory and could only work in terms of that theory. Without Faraday's work there would have been no guarantee of the uniqueness of electricity to matter and the consequent assertion that light produced by electricity and matter was unique to the matter could not have been sustained. The whole theory of sparks and their spectra depended on the theory of electricity, not on the uniqueness of spark spectra to chemical elements. But by the 1850s it would appear that the idea of using spectroscopic analysis of sparks was thought of as one of the main methods by which new information could be gathered about sparks. Yet at the same time it was realised that not all the questions concerning the spark had been answered using spectral analysis; Alter had only asked them, not answered them.

Similarly the Dutch Society of Sciences must have realised the unsatisfactory state of spark studies since it asked more or less the same question as Alter had been concerned with: "[What is] the true nature of light produced by electricity?" (71). Willigen responded to this question with a series of papers entitled "Over Het Electrisch Spectrum" entirely on spark spectra. But he could not go beyond what had already been done by Masson and Ångström and indeed he thought that the "question, regarding the actual sparks, was answered by Masson" (72). What Willigen did do was to analyse the spectra produced by different gases and metals, allocating, describing and mapping their lines with a degree of accuracy previously unknown. In other words Willigen thought that by gaining precise knowledge of spark spectra he would be able to answer the question in detail. What was required was a new approach to sparks which could overcome the problems; but Willigen following Masson and Ångström was unable to achieve it. Nor because they were primarily interested in the theory of the spark were these three scientists

able to devise an explicit method of chemical analysis beyond what they required for the purpose of examining the nature of the spark.

It was the problem of spectro-chemical analysis using electric sparks on which Plücker eventually concentrated (73). He had originally become interested in the study of spark phenomena when he had examined the phenomena which occurred in the discharge tube. Although Wheatstone, Masson, Ångström and Willigen had all prismatically studied the phenomena of sparks in a tube they had done this with the purpose of determining where the cause of the lines lay. But the phenomena of sparks in a nearly complete vacuum had been studied non-prismatically throughout the 1850s by scientists such as Rühmkorff (74), Quet (75), Grove (76), and Gassiot (77). This work had produced numerous interesting observations concerning the light produced by what was termed an "electric egg". The most interesting of the observations was the stratifications which occurred when a spark was passed through such an egg. But it was not until Johann Geissler (78), chief "mechanic" (technician) at the University of Bonn made the discharge tube in the form of a long thin narrow cylinder, that the phenomena of the electric discharge could be studied in detail.

Plücker studied the various phenomena which occurred in Geissler's tubes. For example he investigated the behaviour of the stratifications in the tube when placed in a magnetic field and informed Faraday that it

> enable [me] by means of electric light, to render luminous your lines of magnetic force (79).

It was not until some time later that he thought of examining the discharge in Geissler tubes with a prism. From that moment his work on discharge tube phenomena took two independent directions. Firstly he studied the spectral lines produced by substances in the discharge tube. And secondly he continued his ordinary work on discharge tube phenomena with apparently very little influence coming from his spectral studies (80). This dichotomy illustrates the point that spectral studies had ceased to be able to provide any new and useful information concerning the nature of the spark; spark

spectra had therefore to be studied for reasons other than this.

At the commencement of his spectral studies Plücker observed, as he fully expected, that the prism elongated the lines of stratification (81). He also discovered that when prismatically analysed

> such tubes show beautiful spectra of the most varied kind, according to the nature of the traces of gases or vapours which they contain...Each gas... has a characteristic spectrum (82).

This he had established by examining the spectra of hydrogen and of fluoride of boron (BF_3) which he found to be "totally different" (83) from each other. Therefore since the spectrum altered when a different gas was placed in the tube the spectral lines must belong to the gas involved, not to the metal of the electrodes. This, he noted, was different from the case of the spark in the ordinary atmosphere where the material of the electrodes also contributed to causing the spectrum which, as he said, had been observed by Masson (84).

From this work he thought that the study of discharge tube phenomena was

> one belonging, if I may use the expression, to Micro-chemistry. Conditions occur in it [the discharge tube] which differ from those under which chemical actions usually take place. It is only on the successful solution of these questions, that many not unimportant points for the molecular theory will be satisfactorily solved, such as -
>
> How may the spectrum of a mixed gas be derived from the spectra of its constituents?
>
> How are the spectra of a compound gas related to one another before and after its chemical decomposition by the current?
>
> How does the chemical combination which the gas effects with the electrode influence the spectrum?
>
> Do isomeric gases give rise to similar spectra? (85)

This is a complete contrast with the work on spark spectra that had gone before. Previously the centre of attention had lain with determining the nature of the spark; in Plücker's work the centre of attention was chemical analysis. Plücker effectively wanted to turn line spectra from being a tool for the study of spark phenomena to being a chemical analytical technique.

By use of this technique Plücker hoped to discover not only an optical method of identifying a particular substance, but also what occurred during the process of a chemical reaction:

> The most difficult question which arises on the discharge of electricity through rarefied gases, is the chemical nature of the ponderable substance which gives rise to so infinitely varied phenomena of light (86).

In other words it was difficult to determine the precise course of a chemical reaction which occurred in a discharge tube. But he thought that

> This question can only be safely discussed in connexion with the prismatic analysis of light which is produced, - the more so as by this means every sudden or gradual chemical change in the substance is recognised (87).

In effect Plücker said that the only way to discover what occurred in the discharge tube which gave rise to optical phenomena was to study the spectra produced by these phenomena. This was a reasonable position for Plücker to hold since he already had an idea of what spectra represented in terms of chemical elements. Presumably he thought that if he could establish a consistent system of prismatic analysis then his ideas on the use to which spectro-chemical analysis could be put would be validated.

Plücker illustrated his contention concerning the chemical use of spectra by utilising the changes which occurred in the spectrum of oxygen in a discharge tube. When electricity was first passed through the oxygen tube the spectrum of the light so produced showed a red band, two orange bands and a few in the green. As the experiment progressed Plücker observed that

> The violet became more intense, black streaks appearing in it; the bright line to which the red was originally confined, became paler and paler. Bright red bands appeared over a wider space, alternating with dark ones...The light in the narrow tube became continually greener, increasing in brightness (88).

Eventually the light turned violet and finally disappeared entirely. He explained this change by assuming that the original spectrum was that of oxygen which "evidently loses

gradually its free condition" (89); the second spectrum was caused by traces of other gases which, as there was less oxygen, were then able to assert their spectra. Consequently when all the free oxygen had been disposed of there was nothing left through which the spark could pass. This, he thought, fully concurred with the work of Faraday and Masson, who he said had shown that a spark could not travel in a vacuum (90). Plücker accounted for these oxygen tube phenomena by saying that the gas had combined with the platinum of the electrode eventually creating a vacuum (91); but he did not suggest what had happened to the other gases in the tube.

Plücker continued his work on electric spark spectra in order to provide additional evidence for his hypothesis that the light of the discharge tube was caused by the particles of gas. He had become aware of the work of Gassiot (92) who had shown that no particles of metal passed from one electrode to the other as they would surely do if they caused the light of the discharge tube. Plücker also prismatically analysed the discharge tube light of hydrogen, arsenic hydride (AsH_3) and antimony hydride (SbH_3) (93). The light of these tubes showed only the hydrogen spectrum; Plücker therefore concluded that the other two gases had decomposed when the spark was passed through them into the metal, arsenic or antimony, and hydrogen which had then produced its characteristic spectrum. In other words he showed that his hypothesis concerning the use of spectra to investigate chemical reactions which occurred within the discharge tube was valid.

When Plücker mixed hydrogen and carbon dioxide together in a discharge tube and examined the behaviour of their combined spectrum when they were sparked he discovered that both their individual spectra were present. He therefore concluded that

> If two different gases are mechanically mixed in a tube, and the two spectra of the separate gases are known, it is easy to see how the spectra of the separate gases overlap one another, forming the spectrum of the mixed gas (94).

He had therefore established that it was the individual chemical elements which caused the spectra, irrespective of

how they might combine; this he also found was true for chemical combination of gases.

In addition to the spectra of the gases he had already described he worked on nitrogen, ammonia (95), various oxides of nitrogen, water vapour, iodine, bromine and chlorine (96). In those gases which were a chemical combination of other chemical gases Plücker found that each gas had decomposed into its component gases and these consequently produced their own individual spectra. In the case of carbon dioxide he was forced to conclude that the carbon must have been deposited in the tube as its spectrum displayed only the oxygen lines.

In spite of his formulation of the theoretical principles of the subject Plücker had not provided detailed listings of the lines by which the spectrum of various substances might be recognised. This gap he filled in his third and final paper on the subject (97). He naturally reiterated the views which he had expressed in his previous papers on the subject adding "the presence of a gas is shown with certainty by one of its lines" (98). This was a decidedly bolder statement than he had made hitherto; all that now had to be done to identify the substance under investigation was to measure the refrangibility of one line of its spectrum. That Plücker could have made such an assertion was largely due to the experimental apparatus which he used for making these measurements; and in particular his addition of a collimator clarifying the spectrum (99) enabled him to achieve the certainty of identification of the spectral lines which he required.

Plücker calculated the refrangibilities of the lines of the following substances: hydrogen, water vapour, oxygen, nitrogen, mercury, sodium, bromine, chlorine, zinc chloride ($ZnCl_2$), silicon tri-chloride (probably Si_2Cl_6) , carbon dioxide, anhydrous acetic acid, sulphur, bisulphate of carbon (100), iodine and phosphorous (101). To isolate the spectra of sodium and phosphorous he sparked these substances in hydrogen gas and observed that the lines of the latter were present; therefore the remaining lines, Plücker said, must belong to sodium or to phosphorous. He observed that the sodium

spectrum was essentially a yellow line of the same refrangibility as Fraunhofer's D line (102), but he did not make any further comment on this observation.

Plücker had fully justified his hypothesis that the spectral lines were unique to the gases in the discharge tube. He could therefore write

> [that] every gas being characterised by its spectrum (even by one of the bands of the spectrum, the position of which is measured), we get a new kind of chemical analysis (103).

Plücker fully recognised that in his work he had developed a new method of chemical analysis. His work was different from that of his predecessors who had worked on spark spectra in that they had not consciously attempted to develop a system of chemical analysis, whereas Plücker had. His predecessors had been concerned with using spectra as a tool to elucidate the nature of the spark; they had therefore not emphasised the chemical utility of the lines. They were certain because of Faraday's theory of sparks that the light produced by the spark must be unique to the material agent which produced it. Plücker in his work concentrated on the chemical utility of spectra and consciously ennunciated a system of chemical analysis using spectra. Because he too could rely on Faraday's theory of the spark he was not beset with the theoretical problems which had concerned those scientists who had previously worked on absorption and flame spectra; Plücker could therefore state, quite simply, the principles of spectro-chemical analysis, without the need to either devise or state any theory of line spectra.

This lack of theoretical necessity illustrates the crucial difference between work on absorption and flame spectra and the work on spark spectra. In the former cases the origin of the work lay in the debate on the nature of absorption; as I showed in the previous chapter, to preserve the physical validity of the undulatory theory of light it was necessary to show that absorption was compatible with the theory. To this purpose work on the understanding of absorption and flame spectra was directed, by the supporters of the undulatory theory at least. With spark spectra the

problem which was tackled was to discover the nature of the spark. It was found that spark spectra were uniquely characteristic of the chemical elements and could be therefore utilised in determining the chemical composition of the spark and thereby aid the understanding of the spark. These were the different contexts in which early spectral studies were conducted and it should therefore not be found surprising that there was not much overlap (except perhaps in the case of Wheatstone) between those who studied absorption and flame spectra and those who studied spark spectra; they were after all attempting to answer different questions. The study of spectral phenomena should therefore be viewed not as a continuous process, with one worker building on the results of his predecessor, but as what could be termed 'development in context' in which workers sought to find solutions to different problems by using spectra. It would not be ignorance of earlier spectral work which caused those who worked on spark spectra to take very little notice of that work (who in the scientific world could have failed to notice the debate on absorption?), but that to these later workers, the earlier work would have appeared irrelevant to their own pursuits.

Chapter Five

THE CONSERVATION OF ENERGY, THEORIES OF SPECTRA AND RESONATING MOLECULES 1851-1854

The discovery of the principle of the conservation of energy in the 1840s was one which eventually wrought profound changes in the attitudes of mid-nineteenth century scientists towards mechanical explanations of physical phenomena which had been hitherto adopted. Heat, light, electricity, magnetism etc, previously only qualitatively connected, could now be quantitively defined, in theory at least, in terms of each other. In every physical process which converted one form of energy to another exactly the same quantity of energy must be present in the physical system (assuming it was closed) at each stage of a mechanical process. No energy could be created and, equally important, no energy could be destroyed. This is not the place to examine how this principle was developed (1); rather I shall concentrate on the effects which the application of the principle had on optical theories, and in particular on the study of spectral phenomena.

That light and heat were varieties of the same phenomenon, i.e. vibrations in an all pervading aether, came to be widely accepted in the 1840s and '50s (2). It followed naturally that if heat energy had to be conserved then so must the energy belonging to light. Therefore explanations of optical phenomena where light was involved in a mechanical process necessarily had to be considered in terms of the principle of conservation of energy. Two scientists who considered optical phenomena in such a way were George Gabriel Stokes (3), Lucasian Professor of Mathematics at Cambridge and Anders Jonas Ångström

The theories of line spectra which had been devised in the 1830s were rooted in the ideas of how ponderable matter and the luminiferous aether interacted. These were mechanical processes and it was to such processes that the principle of conservation of energy could be easily applied. As Stokes

pointed out in 1852

> The only theory of absorption, so far as I am aware, in which an attempt is made to deduce its laws from a physical cause is that of Baron von WREDE, who attributes absorption to interference. The Baron's paper is in many respects very beautiful, but it has always appeared to me to be a fatal objection to his theory that it supposes vibrations to be annihilated (4).

Wrede had supposed that some of the incident light in an absorption medium was reflected back to interfere with and thus annihilate some of the light following. This is perfectly reasonable as a geometric proposition; but as a physical proposition it does not conform with the principle of the conservation of energy, since it assumed that some of the energy belonging to the aetherial molecules had been destroyed. For Stokes there was no question of being able to modify Wrede's theory; it did not conform to the principle of conservation of energy and must therefore be false. This was less than Wrede had hoped for; he had thought that while his physical hypothesis might be incorrect, the numbers which he had generated from it, and which did accurately describe a number of absorption phenomena, must have some meaning. But despite Stokes's view that Wrede's theory was "beautiful" (presumably meaning its descriptive ability) he could not reconcile it with the conservation of energy and it therefore had to be jettisoned as an explanation of absorption.

Ångström on the other hand was not as explicit as Stokes had been in his arguments concerning the role of the conservation of energy in explaining optical phenomena. Nevertheless he was careful to take into account the energy requirements demanded by the conservation principle. For example when he discussed the vibrations of ponderable molecules under the influence of a ray of light he commented that

> the molecular motions produced by the action of light are not infinitely small, and hence, in accordance with what has been adduced, a higher order, such as the octave, may be communicated to the aether-vibrations as long as the body is illuminated, but that on the withdrawal of the latter they become insensible. In such a case the medium would, however, have its temperature increased (5).

When the light was no longer incident on an absorptive medium then the vibrating molecules of that medium would cease to transmit light but, simultaneously, they would have to release the energy which they had possessed in order to vibrate. This energy Ångström thought would take the form of an increase in temperature of the absorbing medium; the increase so caused would be miniscule, and indeed Ångström made no attempt, nor suggested any method by which it could be recorded. But he had explicitly ensured that the energy of the system would be conserved.

Although not mentioned by either Stokes or Ångström, John Herschel's theory of absorption was also falsified by the principle of the conservation of energy. Herschel had considered that if light was assumed undulatory then it "may be divided, and the divided parts made to oppose and, in effect, destroy each other" (6) and thus cause absorption lines. As with Wrede's theory this failed to conform with the principle of conservation of energy and would, if they had examined it, also been falsified by Stokes and Ångström.

By the early 1850s therefore the status of absorption phenomena was again the same as it had been before the debate on absorption twenty years earlier, that is, there was no valid theory which reconciled the phenomena with the undulatory theory. This was part of a greater feeling of dissatisfaction with the mechanisms by which optical phenomena involving the interaction of ponderable matter and light were explained according to the undulatory theory. As Ångström expressed it:

> The dispersion, absorption, and diffusion of light, are effects, the complete solution of which, it may be assumed, is still very distant from us (7).

But in addition to these phenomena which concerned the interaction of matter and light Stokes was to add another phenomenon with apparent similarities to absorption, when, early in 1851, he appears to have heard that there was "something peculiar" (8) about a solution of quinine in tartaric acid and water. (Quinine in the natural sulphate is $C_{20}N_{24}N_2O_2HSO_48H_2O$). He obtained a sample of the substance (actually a solution of sulphate of quinine) and read the two

papers by Herschel in the Phil. Trans. of 1845 (9) in which were contained the discovery (10) and the description of the phenomenon Stokes was later to name fluorescence (11).

Herschel's two papers to the Royal Society were separated by a period of some five weeks. In his first communication he stated that when ordinary sunlight was passed, at particular angles, through an apparently clear solution of sulphate of quinine, the solution was perceived to emit a blue light (12); at the same time ordinary light was apparently still transmitted through the solution without hindrance. Herschel continued this paper by describing the angle at which the incident light should enter the solution of quinine to give the most advantageous view of the resulting blue colour.

In this first paper Herschel restricted himself to the reporting of the observation; in his second communication however, he attempted to examine the nature of the light dispersed by the solution of quinine - a phenomenon to which he had attached the name "epipolic" dispersion (13). Herschel assumed that the blue portion of the spectrum had somehow become detached from the rest of the incident light and he thought, for reasons which he did not state, that the colour of the remaining incident light ought to be orange (14); presumably he thought that the combined colour of the light remaining after the blue had been taken out of the spectrum should be that (15). The reason why the transmitted beam did not display this expected orange colour was, he argued, because ordinary white light was intermingled with the transmitted beam and would consequently restore the missing blue light to the beam (16). However, Herschel discovered that when he attempted to ensure the complete removal of the blue light from the transmitted beam, by passing it through another test tube of the solution, he could not; further he found that the dispersed blue beam was not repeated. He therefore concluded that the transmitted beam was, as he said "incapable of further undergoing epipolic dispersion" (17). From this he deduced that the light of the transmitted beam could not be

exactly the same as the incident light since it lacked some quality which the incident beam possessed (18).

When Herschel came to analyse the dispersed blue beam prismatically he discovered that it was composed of light starting faintly in the green and becoming increasingly intense towards the violet; he consequently concluded that:

> no one prismatic ray in particular is selected for epipolic dispersion, but that a certain small per-centage of rays extending over a great range of refrangibility are subject to be so affected (19).

In this interpretation of the phenomenon Herschel effectively assumed that by an unusual process of dispersion, some of the light of the incident beam had been made to change direction.

Herschel had discovered that this phenomenon was produced by three substances: sulphate of quinine, green fluor of Alston Moor and Esculine (20). It was with this information and Herschel's decidedly limited interpretation of the phenomenon that Stokes began his investigation in early 1851. At first Stokes used sulphate of quinine and for a while, according to his account, adopted the hypothesis that the phenomenon was a combination of absorption and dispersion:

> At first I thought that some rays of particular refrangibility had been absorbed (in the sense of taken out of the incident light) and that these rays were given out by scattering (21).

In other words Stokes adopted Herschel's suggestion that part of the incident light had been made to change direction. But Stokes defined the process more precisely by suggesting that absorption must have first occurred to the part of the incident light which was to be dispersed. However, when Stokes analysed the transmitted beam passing through the solution he could not discover the dark bands in its spectrum which should have been present had parts of the incident light been absorbed. Stokes evidently did not consider that Herschel's suggestion that the incident light continually replaced the dispersed blue light was a satisfactory explanation for the absence of absorption bands in the transmitted beam, though why he did not do so Stokes did not state. He consequently dismissed Herschel's supposition

concerning the origin of the blue beam, but came to the same conclusion, that is that the nature of the light had been changed qualitatively by the action of the solution (22).

Stokes however, unlike Herschel, did not leave it at that, but went on to investigate the possible nature of this qualitative change in the light. Stokes, as a firm believer in the undulatory theory of light, which he had adapted to help account for the existence of an elastic solid aether (23), naturally considered that

> According to the undulatory theory, light is completely defined by two things, its refrangibility, ...and its state of polarisation. To a change of one of these then we are to look for the explanation of the phenomenon (24).

At first Stokes took it as axiomatic that the dispersed rays possessed the same refrangibility as the rays of the incident light from which they had arisen (25). Since light was passing through a fluid, he thought that the phenomenon might have been connected with a possible change of direction in the circular polarisation of the incident light. On this hypothesis Stokes thought that one direction of polarisation might be left unchanged, whilst the other might be selected for dispersion. However, this he was inclined also to dismiss since again absorption bands ought to have been produced in the beam selected to cause the dispersed beam; of these bands Stokes had seen no trace in his original investigational experiments but he was preparing to look for them again when an explanation due to the other defining factor of light occurred to him:

> What if light [he wrote] should have changed its refrangibility in the process of dispersion? (26).

The phenomenon on this supposition was, for Stokes, easy to explain since he had only

> To suppose that the chemical rays [ultra-violet light] have given rise by interior dispersion to light of a refrangibility wh[ich] brings it within the limits of the visible spectrum (27).

From the supposition that light could change its refrangibility Stokes deduced that it must be the ultra-violet light which had given rise to the dispersed beam. He had already established that the transmitted beam when passed through the

solution showed no absorption bands; therefore he concluded that the light of the transmitted beam was the same light as the incident beam where it had not been affected by the solution of sulphate of quinine. Now, since the transmitted beam had remained unchanged, the dispersed beam must have been produced by an agency outside the visible spectrum; hence it was reasonable for Stokes to postulate that the ultra-violet light was the cause of the beam. In other words Stokes considered that the solution of quinine had increased the wave-length and thus lowered the refrangibility of the ultra-violet light, consequently rendering it visible as blue light.

To prove this supposition Stokes first sought a piece of glass which would absorb the causal agent of the dispersed beam. He discovered that a pale smoked coloured glass when placed in the path of the incident light prevented the formation of the dispersed beam (fig. 1).

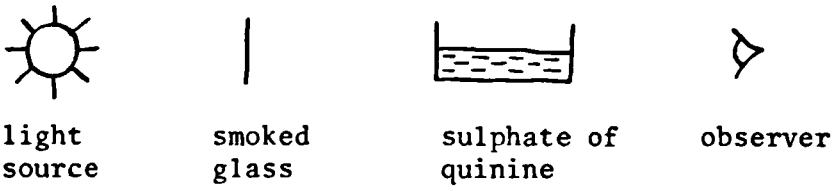


fig.1

If, on the other hand, he placed the glass between the test tube and the eye (fig. 2)

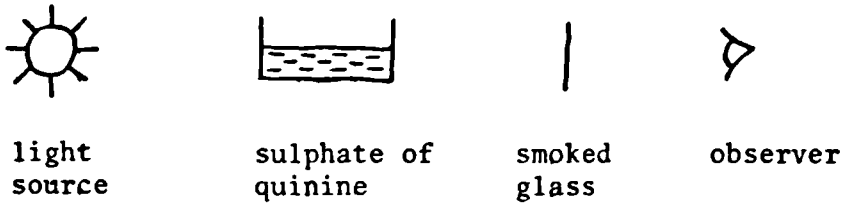


fig.2

he could see the blue light of the dispersed beam through the glass. In the first position the glass absorbed light of particular refrangibilities causing the dispersed beam to

disappear; in the second position the light of the blue beam passed through the same piece of glass. Since according to the undulatory theory the same glass must absorb the same amount of light at the same refrangibility, the refrangibility of light reaching the glass must be different in the first position compared to the second; consequently the refrangibility of the light affected by the solution of quinine must have changed (28).

Stokes's next confirmatory experiment was to pass ordinary light through a prism and then move a test tube containing sulphate of quinine in front of the prism so that the tube would be bathed in each prismatic colour in turn. As the light of the visible parts of the spectrum passed through the tube, no fluorescent light was emitted by the sulphate of quinine. However, when ultra-violet light entered the tube Stokes observed the sulphate of quinine to emit the dispersed blue colour, thus confirming his hypothesis that sulphate of quinine changed only the refrangibility of the ultra-violet light (29).

When Stokes discovered that sulphate of quinine actually changed the refrangibility of ultra-violet light, he had made one of the major discoveries concerning the phenomenon. The other empirical fact which was fairly obvious following this initial discovery was that the refrangibility of the part of the incident beam which was affected by fluorescent substances was always lowered (30).

Throughout 1851 and early 1852 Stokes worked on over fifteen different substances which displayed fluorescent phenomena (31). Though some of these substances produced dispersed beams of different colours (for instance a red beam was produced in some cases), they did not produce phenomena which differed in a qualitative manner from the phenomena which Stokes had observed in sulphate of quinine. The rules which he had established for sulphate of quinine, viz that a fluorescent substance changed and always lowered the refrangibility of a portion of the incident light, were strongly confirmed. These were both experimentally derived rules and Stokes wanted them to be accepted as such; he was therefore careful to distinguish between his experimental work and his theoretical considerations, which he admitted were mainly

conjectural. Thus as he wrote to Herschel:

> I had from the first a particular view of the nature of the process; but wishing to avoid all theory, and speak only as an experimentalist, I chose for the title of my paper the change of refrangibility of light, as being simply an expression of an observed fact (32).

This was despite the fact that on his own admission he had discovered the causal agent of the dispersed beam by considering how light waves would have to behave to produce such a phenomenon. What Stokes meant was that he wanted to establish, as an experimental fact, that certain substances possessed the property of being able to lower the refrangibility (a term whose meaning was independent of either theory of light) of some incident light. Therefore while the theory directed him in making his observations and confirmatory experiments, it did not obtrude into his description of his experimental work.

Stokes thought that in dealing theoretically with fluorescence he was concerning himself with a subject which was "associated with the inmost structure of chemical molecules" (33). Therefore to provide a satisfactory physical explanation of fluorescence would involve, as he realised, immense complications. However, his task was easier than it might have been since he had determined two qualitative rules which were the same for all fluorescent substances.

Stokes, as a believer in the undulatory nature of light, assumed that light was the result of the transmission of vibratory motions of the ultimate particles of a self-luminous body to the aether (34). It was therefore reasonable for him to argue, as he did, that the phenomenon of fluorescence was caused by the vibrations of the molecules of fluorescent substances which had been activated by the incident light (35). Thus ultra-violet light must, in some manner, affect the molecules and start them vibrating. Stokes in a letter, some years later, told Herschel that he had

> always been of [the] opinion that [fluorescence] was due to the self-vibrations of the molecules, that is, the molecules in their vibrations are to be regarded as free, and by no means as forming with the aether one compressed vibrating system (36).

This is quite reasonable for as soon as Stokes had shown experimentally that light could change its refrangibility he had destroyed what had been previously regarded as one of the basic axioms of the undulatory theory· that no matter what processes light may go through it always retained the same wave-length (37). Therefore he considered that a new mode of explanation was required in order to explain the phenomenon of fluorescence. Thus when he said that he had always rejected the idea that the aether and fluorescent matter formed one compressed vibrating system he had in effect rejected the possibility that fluorescence could be caused by refraction or reflection, These phenomena were caused, according to the undulatory theory, by the aether which was compressed into the particular refracting or reflecting material and not by the ponderable matter itself (38).

He realised that he was being controversial in suggesting the hypothesis that the ponderable matter of fluorescent substances could change the periodic time of the vibrations of the aether; he was stating that non self-luminous matter could alter the refrangibility of light. Now although Stokes had suggested as a consequence of the analogy between sound and light, which he considered to be of immense use (39), that ponderable matter might impress its velocity on the aether (40) and had accepted the usual explanations for refraction, reflection, etc, he had not suggested that any of these phenomena could affect the refrangibility of light; nor had he suggested that the aether could affect the motion of ponderable matter. Therefore to suggest even the possibility that there could exist a mechanism whereby ponderable matter could directly affect the refrangibility of light was a radical departure from previous work both by himself and others.

Indeed Herschel in a footnote to his proof of the principle of forced vibrations whereby any system already vibrating or with the potential to vibrate, will adopt, after a time, the period of any incident vibrations (or will cancel them out) had commented that one of the consequences of this principle would be that

> rays [of light] of one refrangibility can never excite by any combination of their own vibrations with those of the bodies they may traverse or impinge on, any resultant rays of a different refrangibility (41).

While Stokes may, or may not, have read this passage, it is certain from the importance which he attached in his paper to showing that this view could in certain circumstances be untenable, that he thought this was the prevailing attitude at that time. Stokes argued that the view that matter could not interact with the aether in the way he was proposing was dependent on the application to the aether-matter system of a "certain dynamical principle relating to indefinitely small motions" (42). This principle which Stokes curiously failed to name was in fact (as Herschel pointed out (43)) the principle of forced vibrations from which Herschel's assertion concerning the invariability of the length of light waves followed.

Stokes pointed out that the proof and therefore the applicability of the principle depended on whether or not the vibrations were indefinitely small:

> the excursions of the atoms [Stokes wrote] may be, and doubtless are, excessively small compared with the length of a wave of light; but it by no means follows that they [the vibrations of the atoms] are excessively small compared with the linear dimensions of a complex molecule (44).

The vibrations of the atoms being therefore sensible, they could reach a point where the disruption of the molecule occurred. Stokes pointed out that it was well known that chemical changes occurred under the influence of light, which implied that total molecular disruption had taken place. Therefore under such circumstances or potential circumstances, the principle of forced vibrations need not be applicable; this was all Stokes desired to show at this point.

After establishing that the interaction which he envisaged between non self-luminous matter and the aether was a theoretical possibility, Stokes turned to the problem of explaining the specific phenomenon of fluorescence. In a letter to Herschel some years later Stokes said that he had considered the theory of forced vibrations in explaining

fluorescence, but could not arrive at a method which would describe vibrations of a different refrangibility

> so long as the forces acting were supposed proportional to the displacements, and the disturbing forces were supposed periodic and going on indefinitely (45).

Stokes gave Herschel the equations which would have resulted, showing that under such circumstances there would be no change in the periodicity of the emitted light. In other words if he retained the hypothesis that the forces of restitution were strictly proportional to the molecular displacements then the molecules

> could only be excited by etherial vibrations having almost exactly the same period, but would be powerfully excited by such (46).

If Stokes retained this hypothesis then the dispersed beam could only be produced by light of the same refrangibility as that of the incident beam, which was observationally not the case. Therefore to obtain a satisfactory qualitative theory of fluorescence, Stokes had to abandon the hypothesis that the forces of restitution of the displaced molecules were proportional to their displacements. This meant, as Stokes pointed out, that if the forces of restitution of the molecules were not proportional to their displacements then the principle of forced vibrations ceased to be applicable even for indefinitely small molecular disturbances (47). The dropping of this assumption meant that Stokes could begin to reach towards a qualitative description of the phenomenon:

> it seems evident that a sort of irregular motion must be produced in the molecules, periodic only in the sense that the molecules retain the same mean state; and that the disturbance which the molecules in turn communicate to the ether must be such as cannot be expressed by circular functions of a given period (48).

In other words Stokes had abandoned all hope of a quantitative description of fluorescence derived mathematically from the undulatory theory.

Before Stokes could continue to explain in greater detail his conjectures regarding the nature of fluorescence he had to consider other aspects of the problem. In the course of his experiments he had discovered that the chemical nature

of the fluorescent materials did not change when they fluoresced; therefore it was necessary in his theoretical considerations to have chemically stable molecules, i.e. such that an atom from one molecule did not attach itself to another molecule. In other words the inherent internal forces of the molecule and those created by the vibrations of the aether must together be greater than any force attempting to disrupt the molecule (49). This did not contradict Stokes's earlier hypothesis that the forces of restitution could not be proportional to their displacements, since, he argued, there were still forces proportional to second and higher orders of displacements which would ensure that the atoms forming complex molecules remained together.

Stokes had also observed that fluorescent phenomena recurred consistently for each fluorescent substance which he had examined, e.g. sulphate of quinine always emitted a blue light; the fluorescent light was therefore characteristic of each substance which produced it. This meant that the cause of fluorescence must be due to the individual molecules of the substance itself, not to any combination of molecules since this would not necessarily ensure that the light was always the same for each substance. He therefore concluded that the molecular vibrations were due, not to the interaction of the molecules, since this would render them chemically unstable, but to vibrations

> among the constituent parts of the molecules themselves, performed by virtue of the internal forces which hold the parts of the molecules together (50).

Stokes visualised these internal forces as causing the molecules to perform a sort of "swinging" action;

> the incident vibrations of the luminiferous ether produce vibratory movements among the ultimate molecules of sensitive substances, and that the molecules in turn, swinging on their own account, produce vibrations in the luminiferous ether, and thus cause the sensation of light. The periodic times of these vibrations depend upon the periods in which the molecules are disposed to swing, not upon the periodic time of the incident vibrations (51).

Since Stokes had dropped the hypothesis that the forces of restitution of the molecules were proportional to their displacements a particular molecule no longer strictly oscillated about its centre of vibration; the centre moved according to the internal forces of the molecules and consequently would vibrate around what would in effect be an instantaneous centre. The location of the instantaneous centre with respect to the rest of the molecule would depend on the particular fluorescent substance and the position it occupied within that substance.

Stokes viewed the phenomenon not as occurring the instant the incident light entered the fluorescent substance but in a time which could be made sensible experimentally. Indeed writing to William Thomson, later Lord Kelvin, professor of natural philosophy at the University of Glasgow (52) in November 1851, Stokes commented that the experimental difference between phosphorescence, which was known not to be an instantaneous phenomenon, and fluorescence may not be great since

> Theoretical reasons lead me to believe that the commencement and assertion of the ill[u]m[ination] (in my exper[imen]ts) really occupies a time which is large compared with the period of a luminous vibration though whether it can be made sensible in experiment is altogether another question (53).

Stokes, before the publication of his paper did not perform the experiment required to make this determination (54) and in his published theoretical considerations he did not overtly consider this point. Stokes did however implicitly assume that this was the case; this can best be illustrated by the following analogy which Stokes gave to Herschel to help him understand the theory:

> Suppose a number of ships moored together, or simply placed near each other, on a perfectly still ocean, the assemblage extending in two directions laterally, and not being merely a line. Imagine a series of waves now to be propagated along the surface of the ocean. These would set the ships swinging in an irregular manner, and would then pass on. The ships would of course act as a sort of breakwater, so that as the series passed on the water would be comparatively calm behind them. The ships however, having been set swinging, would in turn become centres of disturbance, and waves would spread from them in all directions (55).

Fluorescence appears to commence immediately light enters a sensitive substance; in the analogy, the ships (analogous to the fluorescent substance) would take some time relative to the period of the incident waves before they reached their own period of vibration. Therefore, according to Stokes's theory, the period between the light entering the fluorescent substance and the emission of the dispersed beam would occupy a sensible time.

The analogy also explained what happens to the ultra-violet light in the period between it entering the sensitive substance and fluorescent light being emitted. Stokes stated that the ships act as a form of breakwater preventing the incident waves from passing through; hence the ultra-violet light - which we are only discussing here - is totally absorbed by the vibrations of the molecules which the ultra-violet undulations had initiated and when there was sufficient energy within the molecules they began to emit light of their own.

In his consideration of why ultra-violet light should have this effect while visible light does not, Stokes examined the two possibilities that either the aetherial vibrations were faster than the potential vibrations of the molecules or they were slower. In the latter case Stokes demonstrated that the motion of the molecules would cease because too little energy was being put into the system to keep the molecules vibrating. In other words the molecules would not have any ultra-violet light impinging on them. This also explained why ordinary light could pass through undisturbed since such light did not provide sufficient energy to make the fluorescent particles vibrate.

In the former case Stokes showed that

> It is only when the periodic time of the etherial vibrations is less than that of the molecular, that the latter vibrations can be kept going by the former (56).

In other words incident light imparted energy to the molecules; the molecular vibrations in their turn increased thus absorbing energy in performing their vibrations and consequently emitted light of a lower refrangibility than the

incident light. They could not emit light of a higher refrangibility as this would have contradicted the principle of conservation of energy. This accorded well in a qualitative way with Stokes's observations, since as fluorescent substances were "black" to ultra-violet light, it must be possible for light to break off sharply at the more refrangible boundary.

To account for the observed fact that the dispersed beam showed light of all colours, though progressively fading in intensity away from the ultra-violet end of the spectrum, Stokes used his assumption that the forces of restitution of the fluorescent molecules were not proportional to their displacements since this meant that

> when vibrations are performed under the action of forces which vary in a higher ratio than the displacements, the periodic times are not constant, but depend upon the amplitudes of vibration [of the molecules] (57).

Therefore Stokes obtained a description of the spread of fluorescent light: each molecule could have its own amplitude of vibration since the movement of a particular molecule would be restricted by its neighbours, and therefore every molecule could emit light at a different wave-length. Since each molecule had the same structure, and consequently if left to itself would emit light at a wave-length peculiar to that particular substance, most of the light would tend to occur at, or very near that particular wave-length, while there would be a small scattering effect from those molecules which were very restricted in their movements; this therefore accounted for the predominant colour of a fluorescent substance. Further molecular vibrations could decrease indefinitely and thus there could never be a sharp breaking off point at the lower limit of refrangibility, which again accorded well with observation (58).

With these self-admitted conjectural hypotheses Stokes had devised an explanation of fluorescence which largely conformed with the observations he had made. He had employed explicit energy arguments in constructing a mechanism by which the ponderable molecules and the aetherial molecules could interact. For Stokes the application of this principle was not only a method which falsified previous theories

of the interaction of matter and light, it was also, and more importantly, a tool with which new theories of the interaction of matter and light could be constructed. The identification of heat and light as undulatory motions propagated in the same aether, differing only in wave-length, ensured that the energy in optical systems would have to be investigated by scientists in the mid-nineteenth century when they turned their attention to such problems.

Although Stokes had, for the time being, concentrated on explaining fluorescence, which implicitly involved considering the nature of absorption, Ångström, on the other hand, was primarily concerned to explain the absorption of light per se. Stokes had argued that the absorption of light took place by an increase in the internal energy of a molecule before it was re-emitted as fluorescent light. Ångström adopted what on the surface appeared to be a very similar explanation for absorption based on Euler's theory of resonance which had been used to account for the colour of non self-luminous bodies (59). Euler had supposed that the particles of the surface of a non self-luminous body were capable of emitting light of particular wave-lengths, but did not do so until light of those same wave-lengths was incident upon them; as Ångström put it:

> the colour of a body is produced by the resonance of the oscillations, which can be assumed by the particles themselves (60).

Ångström, although he adopted this principle of Euler's, did not claim as much for it as Euler had done; he considered that it

> explains, not so much the colour which a body actually exhibits, as that which it is unable to assume, because most of the oscillatory motions which bodies assume in consequence of absorption, make no impression on our organs of sight, but fall in the domain of feeling (61).

According to Ångström when a ray of light passed through an absorptive medium most of its wave-lengths passed through unimpeded, transmitted by the aether within the molecules of the medium. However some of the light was able to activate the ponderable molecules of the medium to vibrate so that they

could not transmit the light through the medium. Instead these wave-lengths made the molecules vibrate at rates which were not perceptible to the eye (thus causing absorption lines); these vibrations caused a sensation of "feeling", i.e. heat, in order to ensure that the input of the light energy was balanced by the energy output from the absorbing medium, thus conforming with the principle of conservation of energy.

After outlining these limits of Euler's principle of resonance, Ångström deduced the following hypothesis from it:

> According to the fundamental principle of Euler, a body absorbs all the series of oscillations which it can itself assume, it follows from this that the same body, when heated so as to become luminous, must emit the precise rays which, at its ordinary temperature, is absorbed (62).

The molecules of the medium had quite specific rates of vibration with which they could absorb light of those wave-lengths, but not transmit them since they were unable to freely vibrate at those wave-lengths. Ångström therefore thought that when the molecules of that body were free to vibrate - i.e. when they were self-luminous - they would necessarily emit light of the same wave-lengths as they absorbed. However, he realised that "the proof of the correctness of this proposition is...surrounded with great difficulties" (63). He therefore required a body such that he could study its absorption properties at low temperatures and its emission properties at high temperatures.

If Ångström was to confirm his deduction he would need to be certain that line spectra were uniquely characteristic of chemical substances, so that any comparison he made between spectra would be valid. Ångström's comment on the inadequacy of previous theories of the interaction of matter and light suggests that he realised that there were considerable theoretical problems surrounding the nature of flame and absorption spectra. But in the case of spark spectra there was no doubt that the line spectra were uniquely characteristic of the chemical elements and therefore spark spectra were ideally suited to his purpose.

It is not clear from his account whether in the course of his examination of spark spectra Ångström originally investigated the spectra of sparks in order to discover the characteristic emission spectra of the metals of the electrodes, or whether he was expecting to discover an atmospheric spark emission spectrum. It is hard to imagine what Ångström could have thought an absorption spectrum of a metal would be, whereas he was aware that it was

> generally assumed [that the lines in the solar spectrum], are not only due to the action of the [terrestrial] atmosphere, but also to be referred to the action of the sun itself. For the present we are not in a position to separate the two systems of lines from each other (64).

As evidence for this he cited the work of Brewster (65), W. A. Miller (66), and O. J. Broch (67), all of whom had argued, from observation, that a considerable number of the Fraunhofer lines were produced by the terrestrial atmosphere. It was reasonable therefore, according to his hypothesis, that if there existed terrestrial atmospheric absorption lines, then there should also exist emission lines caused by the atmosphere when it was hot enough. Whether Ångström consciously adopted this argument is not clear, but his discovery of the emission spectrum of air gave him the opportunity he needed to study both the emission and absorption spectrum of the same body.

Ångström when he calculated the wave-length of five of the lines of the atmospheric emission spectrum found that two of the Fraunhofer lines, D and b, coincided very closely with two of these lines. But when he performed a "direct experiment" (68) to compare the dark D line with what he thought was its equivalent in the atmospheric spark spectrum, he discovered that they did not exactly coincide (69). Presumably he had not realised that he had already allocated the yellow emission line belonging to sodium as being caused by the metal of the electrodes rather than by the atmosphere (70). He continued by analysing some of the other differences which existed between the atmospheric emission spectrum and the Fraunhofer lines, pointing out where there appeared to be lines of identical refrangibility in the two spectra,

Despite Ångström's denial that the terrestrial atmospheric Fraunhofer lines had not yet been properly distinguished from those caused by the sun it seems that he was convinced that he knew which Fraunhofer lines were caused by the terrestrial atmosphere:

> The analogy between the two spectra [atmospheric absorptive and emissive] may, however, be more or less complete when abstraction is made from all the minuter details. Regarded as a whole, they produce the impression that one of them is a reversion of the other. I am therefore convinced that the explanation of the dark lines in the solar spectrum embraces that of the luminous lines in the electric spectrum (71).

Although Ångström did not say so explicitly, presumably because of the lack of conclusive experimental evidence concerning the origin of the Fraunhofer lines, we can see that this is in full agreement with his deduction from Euler's theory of resonance Ångström had deduced from the theory that a body when heated would emit light of the same refrangibility as that light which it absorbed at a lower temperature. In this case when the spark spectrum of air was examined its emission lines possessed more or less the same refrangibility as some Fraunhofer lines which Ångström had therefore effectively assigned to the air at normal temperature. But beyond this Ångström could not go. He had provided evidence for his deduction which linked emission and absorption, but not in the strictly causal way which Stokes had done with fluorescence. Ångström did not realise this for he thought that Stokes's theory of fluorescence was similar to his own theory of absorption:

> I see with satisfaction that Stokes's explanation of the remarkable phaenomena of dispersion in the green colours of plants, in sulphate of quinine, and in an infusion of horse-chesnut bark, namely, that the medium, when illuminated by the sun, becomes itself luminous, is exactly the same as that which I have given in the foregoing pages of the same phaenomenon (72).

Ångström clearly thought that the optical phenomena which he had discovered were produced by the electric spark were the same as fluorescent phenomena. He appears not to have realised the differences between the phenomena, possibly because since

he perceived his and Stokes's theories of the interaction of matter and light to be similar, the phenomena they explained must be the same.

Indeed the theories were similar though not identical: they both depended ultimately on the vibrations of ponderable molecules. But beyond this they differed considerably. Ångström's idea of linking emission and absorption depended on his interpretation of Euler's principle of resonance; for Ångström there was no mechanism beyond this which linked these two phenomena. On the other hand Stokes had devised a mechanism whereby the incident light was absorbed by the molecules and eventually re-emitted at a lower refrangibility, with energy being conserved at all points. Herein lies the difference between Ångström's and Stokes's work in that the former assumed that energy would be conserved and circumvented this boundary condition by suggesting that there would be small increases in temperature to compensate for apparent energy loss, whereas Stokes had to show, to his own satisfaction at least, that energy was conserved throughout the whole process of fluorescence.

This energy approach Stokes again adopted when he tackled the problem of the absorption of light per se. In his discussion of the relationship between the vibrations of incident light and the vibration of the fluorescent molecules Stokes had primarily examined the cases of when the vibrations were greater or less than each other. He had also briefly discussed the phenomena which would result should these vibrations be isochronous (73). Under such circumstances he thought that the molecular vibrations would be powerfully excited by the incident vibrations since the forces of restitution of the molecules would, in this case, be strictly proportional to the molecular displacements; therefore the principle of forced vibrations would be applicable (74). When Stokes had considered the t eory and principle of forced vibrations in attempting to explain fluorescence he may well have realised, though there is no direct evidence for this statement, that he had devised a mechanical explanation of absorption (75). It is not unreasonable to suppose this, since according to his theory of fluorescence

the incident light was first absorbed by the molecules before being re-emitted; his theory of fluorescence therefore implicitly included a theory of absorption.

Although we do not have any explicit statement by Stokes on absorption spectra until some two years after his paper on fluorescence, there is little doubt that the work on spectra discussed by Stokes and Kelvin in their correspondence of 1854 and 1855 (76) was conducted by Stokes at the time he was working on fluorescence (77). In one of these letters Stokes outlined his mechanical explanation of the identical refrangibility of the bright yellow R line and the dark D line of the solar spectrum which had been established by W. H. Miller (78)

> It seemed to me that a plausible physical reason [for the coincidence of the lines] might be assigned for it by supposing that a certain vibration capable of existing among the ultimate molecules of certain ponderable bodies, and having a certain periodic time belonging to it, might either be excited when the body was in a state of combustion, and thereby give rise to a bright line, or be excited by luminous vibrations of the same period, and thereby give rise to a dark line by absorption (79).

Stokes argued that when the vibrating molecules were excited by the luminous vibrations, the internal energy of each molecule increased in order to absorb the luminous vibrations and thus conserve the total vis viva of the system. This was a point which he was to make strongly in 1860 when he discussed a physical explanation of Foucault's and Kirchhoff's independent observations of the reversal of the bright R line into the dark D line when the former was observed in front of a more powerful light source (80). Stokes resorted to the analogy of light and sound to make his point:

> We know that a stretched string which on being struck gives out a certain note (suppose its fundamental note) is capable of being thrown into the same state of vibration by aërial vibrations corresponding to the same note. Suppose now a portion of space to contain a great number of such stretched strings, forming thus the analogue of a "medium". It is evident that such a medium on being agitated would give out the note above mentioned, while on the other hand, if that note were sounded in air at a distance, the incident vibrations would throw the strings into vibration, and consequently would themselves be gradually extinguished, since otherwise there would be a creation of vis viva (81).

Stokes made the point both here and in his earlier work that the wave-lengths of the incident light must be isochronous with those of the vibrating molecules for absorption to occur. This is well in line with the view expressed in his paper on fluorescence regarding the phenomenon which would result from isochronous vibrations of the aether and molecules, that the molecular vibrations would use their energy to absorb the incident vibrations and thus cause absorption lines since they had stopped emitting their own light. In other words Stokes had, in 1854, provided a physical explanation of the reversal phenomenon though he did not, of course, realise it then. He had consciously provided a theory of absorption, which happened also to explain the peculiarities of reversal. He had informed Kelvin that he knew of no experiment which justified his hypothesis (82); when he published his physical explanation of Foucault's and Kirchhoff's work, he no doubt thought that he had obtained the required experimental confirmation.

Though Stokes did not think in 1854 that he had any experimental justification for his hypothesis, this did not mean that he had no experimental evidence to work on. Indeed in a letter to Kelvin (83), he had referred him to the work of W. A. Miller (84). In particular Stokes discussed W. A. Miller's observation of the dark lines in the spectrum of the flame of nitrate of strontia $Sr(NO_3)_2$, since Kelvin had asked, a later self-admitted "lapsus pennae" (85) "Are all artificial lights subject to dark lines?" (86). Stokes replied that the flame of the nitrate of strontia did display dark lines in the red, but that the phenomenon was exceptional; however he continued:

> these same dark lines are found in the spectrum of common light transmitted across the flame, so that they appear to be due, not to the non-production of light of definite or almost definite refrangibility, but to its absorption by a certain gas or gases produced by combustion (87).

This description of the phenomenon added nothing material to W. A. Miller's account (88); indeed Stokes failed to mention the condition which W. A. Miller had stipulated, namely that the common light must not be too intense. Although Stokes

failed to state whether or not he had conducted this experiment, his adoption of W. A. Miller's experiment was in line with his theoretical ideas on the nature of absorption. He concluded explicitly, as W. A. Miller had not, that around the flame of this particular substance a gaseous atmosphere had been formed and that it absorbed light from the luminous centre of the flame, thus producing the dark absorption lines. Neither W. A. Miller, nor Stokes through W. A. Miller, could have perceived the reversal effect, since this required a bright emission line to be reversed into an absorption line. Stokes's theory of the absorption of light - by vibrating molecules increasing their own internal energy in order to absorb the energy received from the light - precluded his expecting the common light to obscure the dark lines of this flame. His theory stated that the molecules, already vibrating to absorb light from the flame, would continue to vibrate and thus absorb sun light at those wave-lengths. Thus Stokes could not regard this experiment as a justification for his hypothesis.

Kelvin in his reply to Stokes (89) described an experiment he had performed, though he was ambiguous as to when he had conducted it, in which he had passed the light of the sun through a slit, on the other side of which he had placed a spirit lamp (fig. 3).

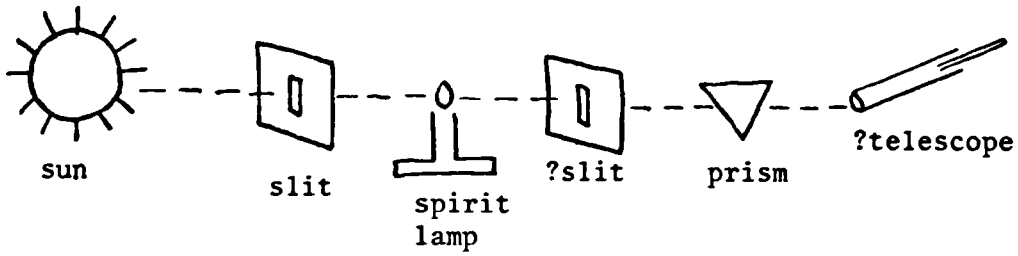


fig.3

When he observed this through a prism, presumably with another slit and observing telescope, he saw that the dark D lines were visible at the point of the spirit lamp; above and below that

the R line of the lamp was visible. Though Kelvin had seen the reversal effect, he had not observed it, as he could have done by decreasing the intensity of the incident sunlight. Nor had he noticed that the flame had intensified the original D line of the sun. Kelvin seems to have considered that the effect of the lamp was minimal, since he wrote that

> It was curious to observe, the dark line not sensibly illuminated by the full light of the sp[irit] lamp coming through it, (the brightness on each side was so great) but a line of light above and below the solar spectrum appeared as an exact continuation of the dark D line (90).

That is, for Kelvin the D line was coming through the flame and not being absorbed so that he was observing the D line of the sun, not of the flame.

Now this interpretation, or lack of it, must be viewed in terms of the fact that Kelvin was interested in establishing that the R and D lines both occurred only when sodium was present; he took it for granted, following W. H. Miller's proof of the identical refrangibilities of the R and D lines, that there must be some physical agency connecting them (91). His experiment was designed to confirm the coincidence of the lines; this he had done in a way which prevented him from perceiving the reversal of the lines. It is ironical that, despite their correspondence, which gave Stokes the experiment which would have justified his hypothesis, they could not arrive at a satisfactory theory of line spectra. Thus the phenomenon of reversal, which could be explained accurately according to Stokes's theory, was not satisfactorily explained by him in 1854 because of his lack of experimental knowledge. As Stokes commented in a letter written some years later to Kelvin remonstrating with him for suggesting that he had devised a full theory of spectra in the 1850s:

> I perceived that the connection between D-emission and D-absorption was explicab e in dynamical principles, but I did not perceive that it was necessary (92).

In other words he had explained absorption but could not have predicted reversal. His theory could not direct him to new experiments because it explained all the phenomena of which

he was then aware.

Another difficulty with Stokes's theory of absorption was that it demanded that the fundamental particles of matter possess the ability to vibrate at certain rates, That is, one type of particle could emit only its own characteristic light. The difficulty with this was that the yellow R line occurred in what appeared to be a wide variety of circumstances. Kelvin said that the problem of the ubiquity of the R line prevented his making any certain statement about a causal relationship between chemical elements and particular flame spectra (93). However, if such a statement were possible he considered that a qualitative chemical analysis of the solar atmosphere would follow, since Stokes's theoretical ideas on absorption would guarantee that the dark solar lines were caused by the same elements. Stokes in his discussion of the problem of the ubiquity of the R line told Kelvin that he was "not aware that there is any pure substance known to produce the bright line D [R] except soda" (94). However, he said in a postscript referring to this passage that both Foucault, using an electric spark with several different metals, and W. A. Miller, using a spirit lamp with various salts, had observed the R line to occur fairly consistently (95), implying that either sodium had contaminated these other metals or that the R line was caused by some other agent.

In a later letter (96) Stokes said that he thought that Foucault's results required confirmation; however, he continued, if they were borne out, then it was possible that the various metallic atoms could be made out of particles more elementary than the chemical atoms. One of these particles could be responsible for the production of the R line, and be included in the composition of many metals which would then all produce the R line. This hypothesis would continue to ensure that one substance could only produce one spectrum which was what Stokes required for his theory (97).

There Stokes's and Kelvin's correspondence on the subject of spectra ceased for over a year until Foucault visited England in the November and December of 1855 to receive the Royal Society's Copley medal (98). Stokes later

recollected that in a conversation which took place at Dr. Neil Arnott's house (99), Foucault had given him a reference to his original paper on spectral work (100). Stokes when he informed Kelvin of the conversation (101) told him that apart from Foucault's observation that the R line consistently occurred in the spark spectrum, which they already knew, Foucault had discovered that "the voltaic arc produces by absorption the fixed line D in light in wh[ich] it did not before exist" (102). Stokes was later to write that this observation had struck him with all the "freshness of originality" (103). Ten days later Stokes again reported to Kelvin on Foucault's work (104) informing him that Foucault had found that arc usually produced the bright line R; however, when viewed with a brighter source behind it, the dark D line was seen in place of R. Kelvin in his reply (105) said that he was disappointed that sodium appeared not to be essential for the production of the R line (though he still had his doubts); however he thought that this was

> a minor point compared to the great fact that the same medium giving rise to the light D [R] when generated in itself and absorbing the same kind of light passing through it (106).

In other words Stokes had obtained the proof which he had said he had lacked for his hypothesis; but here they left their work in unpublished form until Kirchhoff published his work at the end of the decade (107), though both Kelvin and Stokes lectured on the subject in their own universities, as was reported by some of their students (108).

The application of the principle of conservation of energy to optical systems not only falsified earlier theories of the interaction of matter and light, it also aided, in Stokes's case at least, the formulation of new theories. The study of the energy involved in optical phenomena reinforced the idea that light could be used to study the internal constitution of matter. By an understanding of spectra Stokes was able to begin to devise theories of matter based on energy considerations; but as in earlier spectral work experiments were unable to justify the theory. But again there was the over-riding theoretical belief that light could be used to

determine the structure of matter. Stokes was after all prepared to postulate an internally structured chemical atom on the basis of spectral studies. Fresnel's assertion that light held the key to the understanding of matter was being substantiated with the development of the principle of the conservation of energy.

Chapter Six

THE CONSERVATION AND DISSIPATION OF ENERGY, AND SOLAR THEORIES 1846-1862

The principle of the conservation of energy was not only something which altered scientists' perceptions of mechanical processes, it was also a principle which had immediate cosmological implications. If it was assumed that the universe was finite then it followed from the principle that the amount of energy in the universe was finite. Every material body had a pre-determined amount of energy belonging to it; for example a lump of coal could only produce so much heat and light and no more. The implication of this was that a body even as large as the sun, being finite, was capable of producing only a limited amount of heat and light and that it would eventually cease emitting this energy. Julius Robert Mayer (1) using solely his version of the principle of the conservation of energy drew this conclusion as did William Thomson, later Lord Kelvin and Herman von Helmholtz (2) (independently of Mayer) using, in addition, the second law of thermodynamics.

That they arrived at this conclusion is not surprising since they were all well aware that the rate at which the sun was emitting energy had been experimentally determined independently by John Herschel (3) and C-S-M Pouillet (4). The latter had found (assuming that there was no terrestrial atmosphere to absorb the solar heat) that in one minute the sun would raise the temperature of one gramme of water placed on the surface of the earth 1.7633^{o}C (5). This implied that in one minute, one square centimetre of the solar surface emitted enough heat to raise the temperature of a gramme of water on the solar surface 84888^{o}C (6).

Mayer thought that this vast rate of emission of heat meant that "in terms of human conceptions the sun is an inexhaustible source of physical energy" (7). But according to his work on the conservation of energy

> Every incandescent and luminous body diminishes in temperature and luminosity in the same degree as it radiates light and heat, and at last, provided it be not repaired from some other source of these agencies, becomes cold and non-luminous (8).

The implication was that the sun was running down. Mayer, using Pouillet's data (9), computed the rate at which the sun was emitting radiation and arrived at the conclusion that unless there was no replenishment, the sun ought to cool 1,8°C annually. That is, in a period of 5000 years the sun should have cooled 9000°C (10). He thought that

> This amazing radiation ought, unless the loss is by some means made good, to cool considerably even a body of the magnitude of the sun (11)

and according to his views derived from the conservation of energy, the sun would ultimately become cold.

This would have disastrous consequences for the earth since, as Mayer noted

> The stream of this [solar] energy which...pours over our earth is the continually expanding spring that provides the motive power for terrestrial activities (12).

This sentiment concerning the source of energy available for use on earth was common, in its different forms, to all those who dealt with the problem of solar heat. The investigation of the source of the sun's energy was therefore not only a very interesting scientific problem, but also one which was perceived as being fundamental to the very existence of man himself. It was the examination of the question of the origin of solar heat to which Mayer turned his attention in an unpublished paper which he sent to the Académie des Sciences in Paris in 1846 (13), and which he had privately published two years later as "Beiträge zur Dynamik des Himmels".

In addition to explaining how such an enormous amount of energy could be generated, any theory of the sun also had to take into account two other observational constraints. Firstly during the period in which human records had been kept (since Hipparchos say) the sun had not been observed either to contract or expand. And, secondly, the rate at which this radiation had been emitted had to be fairly constant over a significant period of time to conform to the historical,

biological and geological record. These were the minimum criteria to be fulfilled by any solar theory which sought to account for the production of solar heat.

Within the context of these observational constraints Mayer examined the various mechanisms for the production of solar heat which had been advanced in the past. For example he calculated that even on the most favourable supplementary hypotheses the heat of the sun could not be sustained for even 5000 years by chemical processes (14). Similarly he showed that the sun could not be a heated body steadily losing heat as it would soon cease to emit light and heat (15). Therefore theories which had in the past been advanced to account for solar heat were rejected by Mayer since they failed to explain satisfactorily how the heat was produced. Possible new causes of solar heat which Mayer postulated included the rapid rotation of the sun on its axis, but this he also rejected since he could not think of any frictional agent for the sun's surface to resist against.

Energy considerations provided a test by which it could be ascertained whether or not it was possible for a particular mechanism to provide sufficient solar heat within the necessary observational constraints. But these considerations could not provide a solution to the problem of how the sun's energy could be generated and sustained; this had to be done by finding another source of energy by which the sun was fueled and then checking to see if the new theory fulfilled the required energy and observational constraints.

Mayer proposed the hypothesis that the sun's heat was due to the continual impact of meteorites on its surface, whereby they turned their energy (derived from motion) into heat and light. In an earlier paper Mayer had calculated the energy of bodies falling from an infinite distance to the surface of the earth (16). Using his estimate of the mechanical equivalent of heat, Mayer had realised that the impact of such bodies would produce a considerable quantity of heat. The possibility that meteoric impacts might be the source of solar heat may well have occurred to him when faced with the problem of accounting for the sun's energy. Alternatively

Mayer may have applied the equivalence of heat and mechanical energy to an idea contained in a passage in Book III of Newton's Principia in which Newton had suggested that comets falling into a star might refuel what had otherwise been a dying star (17).

Whether Mayer devised what would later be termed the "meteoric hypothesis" by one or other of these routes, or by some different route, he did devise it. The proposition which Mayer wished to prove was whether or not

> the wonderful and permanent evolution of light and heat be caused by the uninterrupted fall of cosmical matter into the sun (18).

At no stage did Mayer consider the possibility that the meteorites fell in straight lines from space to the sun's surface, since, in his view, even though the sun's attraction acted throughout space, there was also a resisting medium forcing bodies attracted to the sun to follow a spiral orbit (19). Therefore, since these bodies must be approaching the sun radially at a very small velocity compared to their actual velocity, it followed that there must be a conglomeration of small bodies near the sun, the existence of which was evinced by the zodiacal light (20).

According to Mayer, because smaller bodies fell towards the sun faster than larger bodies, the planets would remain in the same position, their movements being imperceptible, while meteors would be attracted quickly towards the sun (21). Now the smallest velocity at which such a body could hit the sun's surface would be $1/\sqrt{2}$ of the sun's escape velocity, while the greatest would be the escape velocity itself. After performing the calculations to determine the amount of energy released by the impact of a meteorite on the sun, Mayer concluded that

> An asteroid, therefore, by its fall into the sun developes[sic] from 4600 to 9200 times as much heat as would be generated by the combustion of an equal mass of coal (22).

Mayer therefore drew the conclusion that material cannot descend to the sun's surface to help in the chemical generation of solar energy, since the very act of augmentation released more energy than any chemical reaction which he could

possibly imagine (23).

Mayer assumed that material was still, at the present time, coming from outside the solar system to replenish the zodiacal light; this, for Mayer, was evinced by the meteors seen in the earth's atmosphere. A much greater number of meteors must consequently be by-passing the earth on their way to the zodiacal light, since the earth occupied, at any one time, only a very small fraction of the space through which the meteors had to pass. Mayer realised that there would be two consequences of what was effectively the meteoric augmentation of the sun from outside the solar system. Firstly there would be an increase in the volume of the sun, which he calculated would amount to an increase in apparent solar diameter of at most one second of arc in 33000 years, i.e. an unobservable quantity over the historic period (24). The second, more serious, consequence was that such meteoric augmentation would increase the mass of the sun due to a constantly replenished zodiacal light. He calculated that such a fall of meteorites would shorten the siderial year from between three eighths to three quarters of a second annually (25), which would be observable. Mayer pointed out that although, according to the undulatory theory, light did not have mass, yet

> An undulating motion proceeding from a point or a plane and excited in an unlimited medium, cannot be imagined apart from another simultaneous motion, a translation of the particles [of aether] themselves; it therefore follows, not only from the emission, but also from the undulatory theory, that radiation continually diminishes the mass of the sun (26).

In other words he suggested that matter from the sun forms the luminiferous medium which then spreads out through space. This emission of aether from the sun is, in terms of mass, exactly balanced by the input of meteoric matter:

> The radiation of the sun [Mayer wrote] is a centrifugal action equivalent to a centripetal motion (27)

which

> harmonizes with the supposition that the vis viva of the universe is a constant quantity (28).

For Mayer the sun was constantly replenished by meteors coming in from outside the solar system and this was exactly counter-balanced by the emission of heat and light energy from the sun.

There was no possibility of determining when the sun would cease to emit energy since this depended on the cessation of the meteors about which Mayer possessed no information. He was not interested in cosmogonical problems; he was more concerned with what was happening now, for which evidence could be adduced, than in considering the origin of the solar system or how it had evolved:

> we shall leave, however, all suppositions concerning subjects so distant from us both in time and space, and confine our attention exclusively to what may be learnt from the observation of the existing state of things (29).

This emphasises the point that to Mayer the meteoric sustention of the sun was not an hypothetical abstraction, but a theory based on physical reasoning for which observational evidence, such as the zodiacal light, could be produced in support. He further suggested that other solar phenomena such as sun spots and faculae could be accounted for by supposing that they were caused by the "most powerful meteoric processes" (30) (i.e. large meteorites landing on the sun) creating disturbances in the solar atmosphere.

Mayer had provided a solution to the problem of the sustention of solar heat, which conformed with the observational constraints required of any solar theory. He did admit, however, that the theory had problems, such as the fact that it appeared that the meteors did not approach the sun from all directions but only in the plane 30^{o} on either side of the solar equator because this was the sun spot belt, where the meteoric action could be observed. This meant that it was difficult to explain how the sun emitted heat and light uniformly over its whole surface (31) Mayer never returned to deal with this problem or any other connected with solar heat; after 1848 his own personal tragedy - the death within the previous two years of three of his children, and the continuing lack of recognition of his work - increased to the point of causing temporary insanity,

his original scientific work ceased. Indeed this 1848 paper was his last major contribution to science.

It was not until Kelvin's 1851 ennunciation of what would later be called the second law of thermodynamics (32) that he, unaware of Mayer's work (33), turned his attention to the problem of solar heat. Kelvin's version of the second law stated that

> It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature (34).

Once he had formulated this he quickly followed it by a strong interest in the sources of terrestrial energy. He realised that the sun ultimately supplied virtually all terrestrial energy. Writing to Stokes in early 1852, he commented that

> I think that, with the exception of what might be got from tide mills, or the combustion of meteoric stones or other native metals, all [vis viva] is derived from the sun, and is merely part of the mechanical nature of the undulations which he has sent us from the epoch of the creation of the planets (35).

Kelvin's realisation that the sun was almost the sole provider of energy for the earth, a sentiment he had in common with Mayer, started him on a path which was to lead to a life long interest in solar theories (36). Kelvin was not, at this time, aware of any quantitative work on solar radiation: in the same letter he had asked Stokes if there was any experimental data available to determine the amount of heat emitted by the sun. Unfortunately we do not have Stokes's reply; however, two weeks later in February 1852, Kelvin read a paper to the Royal Society of Edinburgh in which he was aware of Pouillet's estimate of solar heat (37). The main conclusion which Kelvin drew in this paper was the same as in his letter to Stokes:

> Heat radiated from the sun...is the principal source of mechanical effect available to man (38).

It was hence natural for Kelvin to attempt to discover the source of the sun's heat.

This process he began in a paper which he read also to the Royal Society of Edinburgh a couple of months later entitled "On a Universal Tendency in Nature to the Dissipation

of Mechanical Energy" (39). In this Kelvin effectively defined the problem: he discussed particular consequences of his version of the second law and showed that whenever and by whatever process energy was dissipated from a source in a closed system, total restoration of that energy to that source was impossible, i.e. in every mechanical act which liberates heat it is impossible to fully derive from that heat the original quantity of mechanical effect. This is a consequence of the fact that after heat has been dissipated from a source some independent outside mechanism is required to restore it. From this he deduced the startling but reasonable conclusion that

> within a finite period of time past the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject (40).

Though Kelvin's statements regarding the dissipation of heat apply to the universe as a whole, there can be no doubt, bearing in mind this passage and remembering that he regarded the sun as virtually the sole supplier of energy for the earth, that he had the sun specifically in mind. In other words the sun, being a finite body, was losing energy at a rate which he knew to be immense. Further, according to this view, the sun in the past had emitted more energy than it was doing now, and in the future it would emit less; both states being highly undesirable for the continuation of life on earth, and the former inconsistent with the biological and historical record.

A little calculation would have shown Kelvin that the hypothesis that the sun was a hot body steadily losing heat was untenable, since such a body could not, even on the most favourable supplementary hypotheses, have permitted the existence of life on earth for the biblical 6000 years (41) let alone for longer. While Kelvin did not then accept (he never did accept) the age of the earth proposed by geologists such as Lyell, and later Darwin (42), he knew that the length of time for which the sun had been emitting

radiation at its present level was considerably longer than six thousand years. Indeed in a letter to Stokes a couple of years later Kelvin indicated that he must have made some such calculation then since he said that he "had always inclined to the primitive heat theory till rather more than two years ago" (43). So it seems that Kelvin's thermodynamic work led him almost immediately to reject, for the reasons outlined above, the theory of solar heat which he had up to that time held (44). He was therefore in a frame of mind which would enable him to search for, or accept an alternative hypothesis, if one were provided, to account for the production of solar heat.

It was not long before an alternative hypothesis was proposed. At the 1853 meeting of the British Association in Hull, at which Kelvin was not present (45), John James Waterson (46) read a paper entitled "On Dynamical Sequences in Kosmos" (47) in which he proposed a solution to the problem of solar radiation. This paper, though not printed in the Report of the British Association, was fully reported in the Athenaeum and this is presumably where Kelvin read it.

In this paper Waterson argued, without going through the preliminaries of showing that previous solar theories must be false, that if enough aerolites, i.e. meteorites (48), fell onto the surface of the sun, converting their energy due to motion into heat, this would account for the enormous quantities of heat which Pouillet had shown to be emitted by the sun. Waterson showed, presumably in order to conform to the observational constraints imposed on any solar theory, that, assuming the meteors had reached their maximum velocity, i.e. the sun's escape velocity, the consequent annual expansion of the radius of the sun due to these meteoric impacts would be about 14.6 feet (49). In other words this would not be an observable increase even over the historic period of astronomical observations - say 2100 years (50).

Waterson summed up his fundamental idea by saying that

> [since] gravitation...generates heat centripetally, radiation may be viewed as the escape of vis viva centrifugually (51).

That is, meteors approach the sun, and radiation is emitted from the sun in perpendicular directions from all over the sun's surface. The meteors in order to reach their maximum velocity had to approach the sun perpendicularly to its surface. This implied that they must originate from outside the solar system, which, for Waterson, was evinced by the great number of meteors observed in the earth's atmosphere; this implied, though he did not say so explicitly, that it was reasonable to suppose that a far larger number of meteorites were falling onto the sun.

Waterson, like Mayer, did not consider where the origin of these meteors lay; he did say however that his theory conformed with Laplace's nebular hypothesis of the formation of the solar system from the collapse of a gaseous nebula, but he did not make it clear how this was so (52). I would speculate that Waterson may have thought that following the formation of the sun and planets there must have been some material left in the form of meteors throughout the whole solar system; evidence for the existence of such meteors would come from the observation that some meteors coming to the earth appeared to originate from beyond its orbit. Waterson's postulation that the meteors originated from outside the earth's orbit indicates that he had not realised that the increase of mass of the sun would have an observable effect on the motion of the earth. Despite these omissions Waterson had provided an answer to the question, which following the foundation of the principles of the conservation and dissipation of energy, was increasingly exercising the attention of mid nineteenth century physicists: what was the cause of the sun's heat? One of the cornerstones in the development of the principle of the conservation of energy was the determination of the mechanical equivalent of heat: a kn wn quantity of motion generated a pre-determined amount of heat, no more and no less. I would suggest that while thermodynamics did not, indeed could not, provide a solution to the problem of solar heat, the idea that motion could be converted into heat may well have provided the initial idea that the source of solar heat was caused by moving bodies landing on the sun's surface. Beyond this

I can offer no explanation for the apparently independent formulations of the meteoric hypothesis by Mayer and Waterson and its subsequent adoption by Kelvin.

Kelvin gave high praise to Waterson's suggestion that the sun's energy came from meteoric impacts. He commented that the theory

> may have occurred at any time to ingenious minds, and may have occurred and been set aside as not worth considering; but it was never brought forward in any definite form, so far as I am aware, until Mr WATERSON communicated to the British Association, during its last meeting at Hull, a remarkable speculation on cosmical dynamics, in which he proposed the Theory that solar heat is produced by the impact of meteors falling from extra-planetary space, and striking his surface with velocities which they have acquired by his attraction (53).

This was the highest praise Kelvin gave Waterson's work; the paper in which Kelvin proposed his version of the meteoric theory ("On the Mechanical Energies of the Solar System"), was, as we shall see, written with caution. Indeed in it Kelvin noted many fallacies which occurred in Waterson's work, proceeding to construct his own theory to take account of them. A possible reason for caution was that Kelvin's ex-supervisor at Cambridge, and president of the Association for that year, William Hopkins (1793-1866), commented that while Waterson's paper suggested "important hints and valuable lines of inquiry" (54), caution should be exercised in regarding Waterson's work as representing "determined scientific truth" (55).

Kelvin heeded Hopkins's warning admirably. In presenting his own theory of solar heat Kelvin used a form of the reductio ad absurdum argument by discussing three possible theories of solar heat and then showing that two of them could not supply sufficient energy for the sun, implying that the third did. Besides Waterson's meteoric hypothesis the other two theories which Kelvin discussed were first, that the sun was a hot body losing heat, and secondly that chemical reactions within the sun were causing the heat (56). Kelvin maintained - as he had effectively done in his second 1852

paper (57) - that the former proposition was untenable for the long period of time for which the sun was known to have been emitting heat (58). The second proposition he showed to be false because of the enormous amount of matter required, assuming similar chemical reactions to those observed on earth, for the sun to emit heat for any significant period of time (59).

Kelvin's rejection of both these hypotheses illustrates the extent to which thermodynamic reasoning dominated his thought on the subject. Until the laws of thermodynamics had been established, there had been no reason to suppose that the sun was running down and such theories as those which Kelvin refuted could be easily advanced. But when he applied the laws of the conservation and dissipation of energy to the primitive heat and chemical reaction theories of solar heat, taking into account the finite size and mass of the sun, it became clear that, according to these two theories, the sun would soon be exhausted of its supply; indeed according to such theories it should already have been exhausted. The second law also precluded what Kelvin called "anti-radiation" (60) (i.e. heat coming to the sun from some other source) from restoring energy to the sun, for he argued, there was no other body in the solar system at a higher temperature than the sun, and therefore no heat could pass to the sun from anywhere else in the solar system. Consequently it became necessary to devise a new mechanism by which the sun could be supplied with energy.

It was this necessity which enabled Kelvin to adopt Waterson's meteoric hypothesis with apparent ease, since it did, after all explain the production of solar heat. Kelvin thought that <u>some</u> heat must be generated by meteors falling onto the sun's surface, since Joule (61) had shown that they generated heat in passing through the earth's atmosphere (62). Kelvin therefore argued from this that the meteoric hypothesis

> is in fact not only proved to exist as a cause of solar heat, but it is the only one of all conceivable causes which we know to exist from independent evidence (63).

This did not prove that meteors were the sole cause, but since

he had shown that the other "conceivable causes" were entirely insufficient to supply the necessary amount of solar heat, it followed that the meteoric hypothesis must be sufficient. Indeed writing to Stokes in March 1854, Kelvin expressed himself in a manner which leaves no doubt that he firmly believed in the truth of the hypothesis:

> There must be a great deal of...[iron] about the sun, seeing we have so many iron meteors falling in [the earth's atmosphere], and there must be immensely more such falling in to the sun. I find the heat of combustion of a mass of iron w[ou]ld be only 1/34000 of the heat derived from potential energy of gravitation, in approaching the sun. Yet it w[ou]ld take 2000 pounds of meteors per sq. foot of the sun, falling annually to account for his heat by gravitation alone (64).

At this time Kelvin evidently accepted Waterson's original version of the theory in which the meteors came from outside the earth's orbit, since 2000 pounds of meteors was the mass required only if the meteors had achieved their maximum velocity when they reached the sun's surface. Kelvin was further beginning to formulate a theory of meteoric impact which he would ultimately use to destroy any possibility that the sun's heat was chemical in origin. As regards this latter point he argued that the energy produced by the burning of meteoric material was insignificant compared with the heat produced by the conversion of the meteorite's energy due to motion into heat and light which it generated on impact (65).

Stokes's response to Kelvin's theory, after some prodding by Kelvin (66), was to say that he knew no objection against it. He added that he had never been able to "believe in the luminous atmosphere that Herschel talks about" (67). Stokes had thus rejected William Herschel's (1738-1822) suggestion made in 1795 (68) that the sun possessed an atmosphere which alone produced the solar light and heat. Stokes continued that he had always been "in the habit" of assuming that the sun was

> an enormous body in a state of intense heat, emitting continually a portion of its original heat; as in fact "growing dim with age" (69).

This reaction is to a certain extent puzzling since Stokes

seems to have adhered to the theory of primitive heat even after Kelvin had shown in 1852, albeit implicitly, that the theory was untenable. I have shown in the previous chapter that Stokes and Kelvin were not in contact during this period (70) and I would suggest that Stokes's statement that he was "in the habit" of holding this theory implies that he had not been particularly concerned with this problem. There is, therefore, nothing unreasonable in Stokes accepting Kelvin's theory once Kelvin had explained it to him (71).

However, Stokes was rather more cautious than Kelvin appears to have been in accepting the possibility that meteoric impacts might produce the requisite amount of solar heat. He pointed out that Kelvin's version of the theory (which only altered the numbers from Waterson's version in order to take account of an arithmetical error which Waterson had made) - whereby material came to the sun from outside the earth's orbit - would result in an increased mass of the central body of the solar system. This in turn implied, Stokes argued, that there would have been, over a comparatively short period, an observable augmentation of the Earth's motion and a consequent retardation of the Moon's motion, neither of which had been observed to occur (72).

Kelvin replied to Stokes's criticism by writing:

> I think I can prove that the sun's light is due to parts of the zodiacal light (which is merely a whirling cloud of stones acc[ordin]g [to] Herschel) falling in (73).

John Herschel had said that according to the laws of dynamics the zodiacal light must be composed of many solid particles rotating as individual planetlets round the sun; and by their mutual interaction, Herschel continued, some must fall onto the sun and inner planets (74). The zodiacal light was observed to be entirely within the orbit of the earth and therefore could not exercise any perturbatory influences on the motions of the earth-moon system other than those which it already did. If it could be shown that there was enough material within the zodiacal light to provide sufficient meteors to keep the sun fueled, then there would be no need to posit material coming from outside the solar system to provide the source of energy for the sun.

This Kelvin had argued for in his paper on the meteoric hypothesis which he had read to the Royal Society of Edinburgh, slightly before writing to Stokes (75). Though praising Waterson's fundamental idea, Kelvin rejected his version of the theory, replacing it with his own version which took account of Stokes's criticism. Here Kelvin suggested that the origin of the meteors falling into the sun lay in fact in the zodiacal light (76).

In addition to Stokes's criticism Kelvin was also led to modify Waterson's theory that the meteors originated from outside the earth's orbit by the fact that he had been, before he read the paper

> trying to make out what share of meteors the earth w[oul]d take, if the sun gets enough to produce his heat, &c I think it possibly reconcilable with what we have of falling stars, &c (77).

Kelvin must have been trying, in a way which is not clear, to calculate the quantity of meteors hitting the sun from the number observed in the earth's atmosphere. However, by the time he read his paper he had decided that a reconciliation between the two figures was not possible since he said that if the meteors originated from outside the solar system the earth would be struck much more copiously by meteors than it was observed to be (78). It would appear that it was this difficulty together with Stokes's criticism which led Kelvin to place the origin of the meteors in the zodiacal light.

Kelvin pointed out that the new hypothesis in which the meteors circled the sun as the zodiacal light, meant that the velocity of impact of the meteors on the sun would be that of a planet at a distance of the sun's radius from its centre - i.e. $1/\sqrt{2}$ of the sun's escape velocity. Thus the amount of matter required to keep the sun going had to be doubled. Even so this would not, over the historic period, result in an observable increase of the sun's volume (79).

Kelvin had therefore established a theory which successfully conformed to constraints imposed on any solar theory:

> According to this form of the gravitation theory, a meteor would approach the Sun by a very gradual spiral, moving with a velocity very little more than that corresponding to a circular path at the same

> distance, until it begins to be much more resisted, and to be consequently rapidly deflected towards the Sun; then the phenomenon of ignition commences; after a few seconds of time all the dynamical energy the body had at the commencement of the sudden change is converted into heat and radiated off; and the mass itself settles incorporated in the Sun (80).

From this it is clear that Kelvin had considered that he had shown the solar atmosphere to exist as a result of the mechanism of heat creation which he proposed. According to this mechanism meteors circled slowly in decaying orbits round the sun, which implied the existence of a resisting medium in the form of a solar atmosphere. Kelvin was not very clear as to precisely what he thought the solar atmosphere was, though he certainly thought it existed (81). As a suggestion I would speculate that Kelvin's calculation of the density of the luminiferous aether, made at this time, which showed that it must necessarily be denser near the sun than it was in the vicinity of the earth (82), may have led him to identify the dense aether with the solar atmosphere; he did think that the aether was probably an extension of the earth's atmosphere (83) and therefore this identification may not be too unreasonable.

I have so far discussed how Kelvin formulated his theory of solar heat, but not how he attempted to establish its validity. He had ensured that this theory conformed to the observational constraints which were the minimum criteria for any solar theory; if any of these constraints were transgressed by a solar theory then that theory would be false. However, merely satisfying these constraints was not sufficient since more than one theory may satisfy three constraints. Kelvin seems to have been aware that in order to establish the validity of his theory he should provide both explanatory and predictive evidence to justify it, since this is what he proceeded to do.

He showed that his theory provided simple explanations of phenomena which previously had had complicated explanations, or none at all. For example, he declared

> The meteoric theory affords the simplest possible explanation of past changes of climate on the earth. For a time the earth may have been kept melted by the heat of meteors striking it. A

> period may have followed when the earth was not too hot for vegetation, but was still kept, by the heat of meteors falling through its atmosphere, at a much higher temperature than at present (84).

Other phenomena which could be accounted for included novae which might be caused by a dark body entering a cloud of meteors (85). This is particularly interesting since it implies that Kelvin's view of the sun and stars was non-evolutionary at that time, i.e. there was no necessity for the stars and the meteors, which supplied them with energy, to have been created together.

Kelvin not only offered explanations for known phenomena, but further, and more importantly, predicted phenomena which would necessarily be a consequence of his theory if it was true. His main inference was that the zodiacal mass should cause perturbations in the motions of the planets (86). The zodiacal light, being a flattened disc in the plane of the sun's equator, would naturally exert varying influences on the planets as they moved above and below the plane of the zodiacal light. The most extreme case of this phenomenon would be, as Kelvin pointed out, that Mercury would gradually move towards the sun, ultimately falling into its atmosphere; alternatively he considered that it might be slowly dissipated in the solar atmosphere as its orbit decayed (87).

Secondly the existence of Kelvin's 1854 correspondence with Stokes on the nature of emission and absorption, a correspondence which Kelvin initiated, can only be sensibly interpreted in the context of Kelvin's desire to establish a satisfactory solar theory. Kelvin no doubt remembered the conversation which he had had with Stokes in 1852 when the latter had mentioned the possibility that the existence of chemical elements in the sun might be inferred from the presence of their spectral lines if these could be determined. Kelvin, in 1854, asked Stokes particularly if the iron spectrum was present in the solar spectrum (88). It was well known that iron was the main constituent of the meteorites which landed on earth and it was therefore reasonable to suppose that iron was the chief

element in the meteors falling into the sun's atmosphere. If this was the case then the iron spectrum should be present in the solar spectrum. Although Stokes had devised a theory which showed that there was a physical connection between the solar absorption lines and flame emission spectra and had assumed that a particular spectral line was caused uniquely by one type of matter, he was far from sure what this matter was. Foucault and W. A. Miller had independently shown, for example, that the double yellow R lines were apparently produced by a number of different metals. Stokes was therefore not prepared to make any definite statement concerning the origin of the dark D lines in the solar spectrum beyond that it was caused by the same agency as the R lines. Stokes told Kelvin that Brewster had observed that Fraunhofer lines A and B had the same refrangibility as the emission lines belonging to potassium nitrate (KNO_3) (89); he also thought that Brewster had identified group a of the solar spectrum (90). But Stokes was not prepared to commit himself to saying that the spectral lines were indicative of the existence of these or any other chemical substances in the solar atmosphere. And he certainly could not supply Kelvin with any information concerning the iron spectrum.

Both Stokes and Kelvin agreed that the Fraunhofer lines were potentially usable to determine the chemical constitution of the sun but they were unable to put this into practice. Kelvin had attempted to use this hypothesis, which after all was not new, in a new manner. Whereas Brewster had sought to establish a chemical analysis of the sun, based on an understanding of the spectral lines, Kelvin sought to use the spectral lines as a justification of his solar theory. Where Brewster had implied that there must be, for example, deflagrating nitre in the solar atmosphere because the solar absorption lines possessed the same refrangibility as the emission spectrum of that compound, Kelvin said that the iron lines must be present in the solar spectrum because there were iron meteorites falling into the sun. This was a new approach to the Fraunhofer lines in that Kelvin was attempting to use them in a confirmatory

rôle rather than an investigative rôle. But because of Stokes's lack of experimental knowledge of spectra this approach could not be successfully pursued by Kelvin.

To a certain extent this seems not to have bothered Kelvin, since he appears to have made very little attempt to investigate any of the predictions which he made For Kelvin it was sufficient to present his work in a rigorous methodological mode, that is, as an hypothesis which conformed to the rule of greatest simplicity and from which verifiable inferences were possible. If either of these inferences proved false, that the motions of the planets were not perturbed, or that the iron spectrum was not found in the solar spectrm, then the theory would necessarily be falsified. I would suggest that because Kelvin was convinced of the validity of his theory he felt that there was no need for him to verify these predictions; they would only be important to the theory if it was shown that these phenomena did not occur.

Kelvin made one final modification to his theory before it was published. He seems to have realised that if there was a solar atmosphere with meteors rotating around and falling into the sun, then there must exist friction between what he now called the "vortex" of the meteors and the solar atmosphere; and friction creates heat and light (91). Despite this modification so that the immediate cause of solar heat was the friction between the whirling mass of meteors round the sun and the solar atmosphere, the ultimate cause of solar heat was still contained in the dynamical energy derived from gravitational attraction existing between the sun and the meteors.

Kelvin's thermodynamic work acted not as an historical cause which led him to the meteoric theory, but as a context in which he rejected previously held theories of the sun, and which, when presented with Waterson's theory, he could accept and with advice modify it in accordance with constraints imposed on any solar theory. Two of the founders of thermodynamics, Mayer and Kelvin, were able using this new tool to dispense with many mistaken ideas concerning the nature of

the sun. What is interesting following that, is that in place of chemical and primitive theories of solar heat, they both, independently of each other, and with different approaches, proposed remarkably similar theories, differing only in details. Thus it seems that the constraints which observation had imposed on the sun led them to a theory which, although the fallacies would become apparent within a very few years, satisfied the requirements of that time.

It was not long before an alternative to the meteoric hypothesis was advanced; indeed at the exact time that Kelvin had been working on his theory Helmholtz had proposed a different theory of solar heat in a lecture delivered in Königsberg entitled "Ueber die Wechselwirkung der Naturkräfte und die drauf bezüglichen neuesten Ermittelungen der Physik" (92). In this Helmholtz proposed that the sun's heat originated in the gravitational contraction of the sun.

Like Kelvin, Helmholtz was also concerned with the consequences of the second law which Kelvin had drawn from it in 1852:

> We must admire the sagacity of Thomson [wrote Helmholtz], who, in the letters of a long-known little mathematical formula, which speaks only of the heat, volume and pressure of bodies, was able to discern consequences which threatened the universe, though certainly after an infinite [unendlich] period of time, with eternal death (93).

Here no doubt Helmholtz was referring to Kelvin's 1852 paper on the dissipation of energy (94). Helmholtz drew the same conclusion as Mayer and Kelvin, namely that

> the life of man, animals, and plants, could not of course continue if the sun had lost his high temperature, and with it his light (95).

A realisation that the sun was the ultimate source of all energy for man, and that it is therefore important to discover its source, was a common thread in this work on solar theories throughout the 1850s.

The premises from which each man begun were different: while Kelvin and Mayer started from differing thermodynamic viewpoints with which to make the leap, in their different ways, to the idea of bodies falling into the sun to cause its heat, Helmholtz, starting from the same thermodynamic

viewpoint as Kelvin, thermodynamically analysed the behaviour of the gaseous nebula which had been postulated by Kant and Laplace to account for the formation and evolution of the solar system - the so-called "nebular hypothesis" (96). He pointed out that "with regard to the origin of heat and light this view [the nebular hypothesis] gives us no information" (97). On the other hand Helmholtz believed the nebular hypothesis was a substantially correct account of the formation of the solar system and that it was the only hypothesis which he posited in his work (98). It followed that the contraction of the nebula must have affected the formation of the sun and consequently the manner in which it now sustains itself. According to Helmholtz we can only gather empirical evidence for the latter but not for the former. So far as the creation of the solar system is concerned we can only posit hypotheses, such as the nebular hypothesis. But from this hypothesis deductions according to the known physical laws can be made to discover how such a nebula developed into the solar system, ending with what we now perceive, with which comparison can be made to justify the original hypothesis. One of the results of the contraction of the nebula, Helmholtz argued, was that it must account for the production of the sun's heat.

Helmholtz demonstrated that in order for the sun and planets to have coalesced as recognisable independent entities, the nebula in the process of contracting must have dissipated most of its original energy due to gravitation as heat into the universe (99). However, by setting the potential of the sun equal to the amount of energy required to raise its temperature a specified amount, he showed that there would be enough energy left within the solar system

> to raise a mass of water equal to the sun and planets taken together, not less than 28 millions of degrees of the Centigrade scale (100).

From this it followed that a contraction of $1/10000^{th}$ of the radius of the sun, where most of the energy was located, would raise the temperature of a body of the same mass as that of the sun $2861^{\circ}C$ (101). Helmholtz had calculated from Pouillet's

data that the sun must be cooling one and a quarter degrees Centigrade per year (102), this meant that the solar contraction which he had envisaged would account for the maintainance of solar heat for 2289 years (103). Helmholtz considered that "such a small change...would be difficult to detect even by the finest astronomical observations" (104) and added that for at least 4000 years the sun had emitted heat without sensible change. In other words Helmholtz's contraction hypothesis, which permitted the sun to emit radiation at the same level over a long period of time, fulfilled the constraints incumbent upon any solar theory.

Helmholtz examined the behaviour of meteors to provide empirical evidence for the hypothesis that the original nebula when collapsing had dissipated heat and, that by the contraction of the sun, the nebula was effectively still emitting heat. He said that meteors - the remains of the nebula - generated a large quantity of heat when they entered the earth's atmosphere, which was then dissipated:

> Thus has the falling of the meteoric stone, the minute remnant of processes which seem to have played an important part in the formation of the heavenly bodies, conducted us to the present time, where we pass from the darkness of hypothetical views to the brightness of knowledge (105).

In other words, the fact that the meteors dissipated heat when brought to rest was evidence, albeit in a very much reduced scale, of the process of coalescence of the nebula which had gone on in the past. Because the nebula must have in the past behaved in this way, the sun, having been formed out of the nebula, must continue to produce its heat by contracting. Further since meteorites were made of the same chemical materials as found on earth this must imply that the sun was made out of the same materials since all - sun, earth, meteors - had been created out of the original nebula (106).

Helmholtz had thus devised a theory of solar heat which conformed to the observational constraints, and which was an integral part of the evolutionary process of the solar system. In this meteors played a purely evidential rôle and not the crucial heat supplying rôle assigned to them

by Mayer, Waterson and Kelvin. Helmholtz's position was that the contraction of sun was simply a continuation of the contraction of the nebula which had, under gravity, been going on since the nebula was formed. In other words the application of the laws of the conservation and dissipation of energy to the nebula produced, immediately, a theory of solar heat which conformed to the constraints and which did not require the formulation of any additional hypotheses. The three others who had worked on solar theories had deliberately not concerned themselves with cosmogonical problems. Mayer had said that it was impossible to provide certain evidence for cosmogonical hypotheses; Waterson had said that his theory conformed to Laplace's hypothesis but didn't say how, and Kelvin regarded the nebular hypothesis as a "mere hypothesis" (107). These three had then proceeded to devise theories of meteoric impact on the solar surface without considering how the sun, or the meteors which supplied it, had come to exist or how the relationship which subsisted between them had been created.

Kelvin's antipathetical attitude towards the nebular hypothesis precluded him from adopting a favourable attitude towards Helmholtz's theory. At the Liverpool meeting of the British Association in September 1854 Kelvin rejected all the conclusions reached by Helmholtz (108). He rejected the nebular hypothesis on the grounds that if the present motions of the solar system were traced then, he declared, that all "the bodies now constituting our solar system have been at infinitely greater distances from one another in space than they are now" (109). According to Kelvin therefore the solar system could not have originated from a gaseous nebula as Helmholtz had postulated. That Kelvin then proceeded to reject Helmholtz's theory of solar heat which was, after all, based on the nebular hypothesis, is not surprising:

> It is quite certain that it cannot, as the nebular theory has led some to suppose it may, be the energy of gravitation effecting any continued condensation of the sun's present mass, since without increased pressure, it is only by cooling that any condensation can be taking place (110).

Helmholtz had only been concerned with a straightforward theory

in which it was the motion of the particles of the sun towards the solar centre which caused a constant quantity of heat to be emitted by the sun without apparent lowering of temperature; Helmholtz had not taken any account of the change in velocity of the particles or of the density and pressure of the sun at different distances from the centre. Kelvin made no attempt to show whether, when these variables were taken into account, it would produce a theory of the sun which would account for the production of solar heat. I would suggest that Kelvin thought that the fact that his theory of meteoric impact which he reaffirmed as true (111) had already accounted for the production of solar heat precluded the possibility that there existed valid alternative theories. For Kelvin this lack of validity would be especially strong when the alternative theory depended on the nebular hypothesis about which he had severe reservations. He rejected Helmholtz'z solar theory not solely for the reasons which he advanced, but because such a theory must be false since he had devised the true theory of solar heat.

There Kelvin left the problem of solar heat until 1859 (112), in which year U. J. J. Leverrier (1811-1877) announced his discovery of the advance of perihelion of Mercury (113). It is not necessary to discuss here how Leverrier made this discovery; suffice it to say that he made it in the context of his normal work on celestial mechanics (114). What is important here are the explanations of the phenomena which Leverrier offered. Firstly he said that an increase of $1/10^{th}$ in the mass of Venus would account for the advance of Mercury's perihelion; but this he rejected since it would cause all sorts of perturbations in the motion of the earth with the theory of which he was already satisfied. He also showed that the same phenomenon would be caused by the existence of a planet of the same size as Mercury in an orbit interior to Mercury at half its distance from the sun. This he also had to reject since he thought that such a planet would have been observed previously. However, he said that the disturbing mass could be the result of a large number of "corpuscles" circling the sun interior to Mercury's orbit. Whether this suggestion was influenced by Kelvin's 1854 work

is not clear, though it should be pointed out that Kelvin's paper on the meteoric hypothesis had been translated into French (115).

Kelvin said that this discovery of Leverrier's was similar to his and Adam's 1846 discovery of Neptune, in that Leverrier had discovered that Mercury also was affected by "planetary matter" not previously recognised (116). Kelvin continued by asking if this matter was "unseen" answering himself thus:

> Surely, on the contrary, it is it that we see as the Zodiacal Light, long before conjectured to consist of corpuscles circulating round the Sun (117).

Kelvin, as can be imagined drew the obvious conclusion by saying that Leverrier's discovery provided

> that kind of evidence of the existence of matter circulating round the Sun within the earth's orbit, which, more than five years ago, in publishing his theory of meteoric vortices to account for the Sun's heat and light, he [Kelvin] had called for, from perturbations to be observed in the motions of the known planets (118).

However, Kelvin's enthusiasm was to be very short lived, for a month later he published results which would ultimately refute the meteoric hypothesis. He showed that according to his calculations the motion of Mercury should have displayed, over the previous one hundred and fifty years, a geocentric difference of eight and a half seconds of arc from its calculated position if enough matter was to be present to cause the heat of the sun (119). He pointed out that this difference, if it existed, would have been detected by Leverrier in the course of his very precise work on Mercury's perihelion. Kelvin was not, at that time, prepared to conclude that there were not enough meteors within Mercury's orbit to cause the sun's heat since he argued that

> it may be concluded that if matter has been really falling in at the rate supposed by my dynamical theory of the solar radiation, the place from which it has been falling must be either nearer the Sun or more diffused from the plane of Mercury's orbit than we have supposed in the preceding example (120).

Although Kelvin suggested means of verifying this suggestion,

it is fairly obvious that he was beginning to add supplementary hypotheses to his original theory in order to account for this discovery. He presumably realised that the meteoric hypothesis was now unsatisfactory for within two years he was to abandon his original form of the theory and effectively adopt Helmholtz's theory of solar heat, with some alterations (121).

Kelvin, since he had raised, in 1854, objections to Helmholtz's theory of solar contraction, had to deal with them himself before he could reasonably accept it. This was not possible in the early sixties because the mathematical description of such a mass as the sun had not yet been tackled, and Kelvin apparently made no attempt to do so then (122). To deal with the problem he took limits on either side of possible specific heats and the possible increases in density towards the sun's centre to arrive at the limits of the rate of contraction. Within these limits Kelvin was prepared to admit Helmholtz's theory:

> The meteoric theory of solar heat...in the form in which it was advocated by Helmholtz...is adequate, and it is the only theory consistent with natural laws which is adequate to account for the present condition of the sun (123).

Kelvin effectively made Helmholtz's theory a meteoric theory, but instead of the continuing process which Kelvin had originally envisaged, he placed the meteoric action far back in time when the sun had originally coalesced. It is very noticeable in this work that Kelvin made no mention of the nebular hypothesis and I would suggest that although he now accepted Helmholtz's theory of the sustention of solar heat he could not bring himself to believe in the nebular hypothesis from which Helmholtz had derived his theory.

In their examination of the problem of solar heat and the hypotheses which they had proposed to account for it, Mayer, Waterson, Kelvin and Helmholtz had placed the study of the sun on an entirely new theoretical basis. Indeed Helmholtz's theory of the sun was to gain such a hold on nineteenth century thought that Agnes Clerke was able to write near the end of the century that his "theory of solar

energy [is] now generally regarded as the true one" (124). It did after all fulfil all the requirements of a solar theory and while arguments were to continue all through the century and beyond about the physical constitution of the sun (125), and for how long it had supplied its energy (126), the basic problem of how such an enormous amount of energy could be generated by a finite body had been solved. And it was now known that the sun was not going to cease emitting energy in the near future.

Of the four scientists who had concerned themselves with the theory of solar heat in the 1840s and '50s, all but one - Waterson - had been concerned in formulating the principles of the conservation and dissipation of energy. Mayer, Kelvin and Helmholtz had all discovered as a result of their thermodynamic work that the sun was running down and until they had formulated their theories of solar heat there was no indication about how long the sun might continue to emit radiation; and in the case of Mayer this even then was not certain. In the course of their work each of these scientists had realised that the sun was and had been virtually the sole supplier of energy to the earth; the basic sources of energy on earth: coal, winds, wood, oil, all ultimately emanated from the sun (127). But more than this it was realised that if the sun were to cease to emit radiation then it would be impossible for life on earth to continue. Because the sun was the sole supplier of energy and was running down, it followed that man's period of habitation on earth was distinctly limited. I would suggest therefore that those scientists who by their thermodynamic work had condemned life on the planet to so unfortunate an end, felt it incumbent upon themselves to attempt an explanation of solar heat, which was after all also a very interesting scientific problem. This they had done and man could be assured of a considerable further period of residence on the earth.

Chapter Seven

SPECTRO-CHEMICAL ANALYSIS 1854-1861

By 1854 it was thought by a considerable number of scientists that the study of line spectra could be used to examine the structure of ponderable matter. It naturally followed that it was theoretically possible to use spectra for the purpose of chemical analysis. The problem was that it had proved difficult, with flame spectra at least, to determine where the cause of the lines lay. Did they originate in the molecule of a chemical compound, or in the atom of a chemical element, or, as Stokes had privately suggested, in particles more fundamental than the chemical atom (1)? Despite numerous attempts to solve this problem nobody had provided a satisfactory answer.

The reason why spectro-chemical analysis was a theoretical possibility was also why it had failed to make any significant impact on the practice of chemical analysis. The theories of spectra which suggested that such a method of analysis was possible had not been made sufficiently rigorous for there to be no uncertainty about the source of the lines. This meant that when observations were made of the same line caused by apparently different chemical elements, there was no necessity to suppose, according to the existent spectral theories, that impurities were present in an individual substance under investigation. A point had thus been reached where spectro-chemical analysis was a theoretical possibility but an experimental impracticability. Further it was realised by scientists such as Stokes that the effort required to work out a system of spectro-chemical analysis would be considerable, and there was no certainty that any useful chemical analytical method would be developed as a result. But more than this: those scientists who had in the past worked on spectral phenomena had directed their work towards solving physical problems and they had not concentrated

specifically on attempting to utilise spectra for chemical analysis beyond what had emerged from their solutions to these problems. By the early 1850s therefore, a point had been reached where the theories of spectra could not solve the problem of obtaining a system of spectro-chemical analysis. Further it would appear at that time that there was hardly any motivation to establish such a system.

It was perceived, however, that the ordinary methods of qualitative chemical analysis inherently involved long and tedious chemical processes. As John Hall Gladstone (2) put it in 1858:

> The ordinary methods of qualitative analysis depend on a system of exclusion. We first determine that the substance analysed does not contain any member of certain large groups, but consists of one or more members of certain other groups: and these we subdivide, excluding one division after another, till we arrive at the individual member or members, and these are at length distinctly recognized by special characteristics, or perhaps, special tests (3).

This was what was required just to identify the chemical constituents of a sample. Following this the quantities of each chemical element present in a compound had to be determined. A method of qualitative chemical analysis which would simplify and shorten the principle of exclusion was something which was greatly to be desired. The development and utilisation of an optical method of chemical analysis to do this was one which commended itself to a number of chemists in the latter half of the 1850s. Gladstone, for example, thought

> that chromatic phenomena may be relied on in analysis to an extent, which I think has been rarely, if ever, suspected (4).

However, the execution of this idea, which was not new, was much more difficult than its statement.

Those scientists who did attempt to put the idea into practice met with only limited success. For example William Crookes (1832-1919) was in no doubt that the bright yellow line which was present in so many flame spectra was caused by sodium (5) and he seems also to have identified the blue line belonging to calcium (6). He published neither of these observations although the former was mentioned by Gladstone in

a lecture to the Royal Institution in 1857 (7). Apart from these observations Crookes appears to have taken very little interest in using spectral lines as a means of chemical analysis in the 1850s; he was more concerned with examining the effect that the different spectral colours had on photographic plates (8). But his work and Gladstone's acceptance of it does show that chemists were beginning to assume that spectra were caused uniquely by the chemical elements and that questions concerning how precisely spectra were produced were ceasing to be of great importance.

This attitude was also present in the work of William Swan (9), who during an examination of the spectra produced by hydrocarbons (10) was obliged to investigate the cause of the yellow lines which were present in a number of spectra which he examined. He found that a "portion of chloride of sodium, weighing less than $\frac{1}{1,000,000}$ of a grain is able to tinge a flame with bright yellow light" (11). From this he concluded that "much caution is necessary in referring the phenomena of the spectrum of a flame to the chemical constitution of the body undergoing combustion" (12). Bearing this in mind Swan investigated the emission spectra produced by fifteen hydrocarbons (13) and reached the conclusion

> that, in all the spectra produced by substances, either of the form C_rH_s or of the form $C_rH_sO_t$, the bright lines have been identical (14).

In other words the proportions of hydrogen and carbon in a particular compound did not affect the spectrum which was produced by the hydrocarbons; nor did it matter whether or not oxygen was present as this had no effect on the spectra produced by such compounds. He had therefore established that the lines were caused not by the molecules of the individual hydrocarbons, since different molecules would no doubt produce different spectra, but that they must be caused by the individual atoms of hydrogen and carbon. However, he could not determine which lines were caused by which element. Swan expressed no opinion on what the cause of the spectra was, but concerned himself exclusively with discovering where the cause of the lines lay.

Despite this confidence of Swan, Gladstone and Crookes in the uniqueness of flame spectra to particular chemical elements they had not been able to extend the method beyond sodium, calcium and the hydrocarbons which Swan had investigated. This led Gladstone to suggest that "this plan of procedure, [chemical use of flame spectra], though doubtless very accurate in certain cases, is of limited and difficult application" (15). In other words while he accepted the validity of the principle of spectro-chemical analysis, he did not think it could be satisfactorily extended to become a general method of chemical analysis. He preferred to concentrate on analysing the spectra of light passing through solutions of chemical substances which he thought would be uniquely characteristic of those solutions. He therefore examined the transmitted spectra of some twenty solutions and concluded that

> as a general rule...all the compounds of a particular base, or acid, have the same effect on the rays of light (16).

This, as he pointed out, provided a test which showed that some substances could not be present in a particular solution (17), a result which he admitted was negative and which was effectively merely a continuation of the principle of exclusion in chemical analysis. But he also thought that there would be occasions when a fluid transmitting light might present "some familiar spectral appearence,...which cannot be mistaken, and is at once distinctive" (18).

Although, as he admitted, Gladstone had not developed a complete method of chemical analysis, since this would require "regular tables of comparison" (19), he had shown experimentally that the prismatic analysis of transmitted light was a useful and valid method of chemical analysis. But like some of his predecessors Gladstone had realised that an extraordinary amount of rather tedious work would have to be undertaken in order to determine the characteristic spectrum of each substance. The basic trouble with Gladstone's method was that if it were to be used on the scale which he envisaged then it would require an extensive process of comparing the spectrum of the sample which was to be identified, with maps

of the spectra known to be produced by a large number of compounds, since the spectra were characteristic of compounds, not of the chemical elements.

This work of Crookes, Swan and Gladstone in the latter part of the 1850s shows that by this time there existed a desire to establish a method of chemical analysis using light, More importantly this desire had been established within a chemical context: that is the physical problems which had been paramount in spectral studies up to the mid-1850s did not play a role in formulating either the question of how could light be used for chemical analysis, or in providing the answers. These three scientists had used chemical methods to establish to their own satisfaction that the light produced by the substances which they had investigated was uniquely characteristic of those substances. But they had not developed the hoped for general system of chemical analysis using light. Even when Robert Bunsen, professor of Chemistry at the University of Heidelberg (20), turned his attention to the idea of using light for chemical analysis, the practical problems which this involved did not disappear immediately.

According to his friend and colleague Gustav Kirchhoff, the professor of physics at Heidelberg (21), Bunsen originally directed (22) one of his British students, Rowlandson Cartmell (23) to investigate the colours imparted to a flame when particular chemical substances were present (24). As Cartmell pointed out in his 1858 paper on the subject it was well known that some substances imparted characteristic colours when they were present in a flame (25); for instance sodium when placed in an ordinary flame produced a very strong yellow colour (26). The object of Cartmell's work was to devise a method of chemical analysis using light in which the effects of impurities would be minimised. To this end he searched for light filters which would obscure the characteristic colour of chemical substances already known to be present in a flame. This would then make visible the characteristic colours of any other chemical substances which also happened to be present in the flame. For example Cartmell found that a solution of indigo would obscure the yellow colour caused

by salts of sodium, whilst allowing the characteristic red rays due to salts of lithium and of potassium to pass through (27). This method of using light for chemical analysis ensured that the light produced by any impurities in the substance being investigated would be eliminated by the filters. For example the yellow light produced by sodium would always be eliminated provided the appropriate filter was used. There would therefore be no question that impurities would cause problems in the identification of particular substances by means of the light it emitted. It would appear therefore that Cartmell was certain that each element emitted light which was uniquely characteristic of it, and of no other element or compound.

The difficulty with Cartmell's method was that it was necessary for him to discover a filter which would obscure the light of each chemical element. This, in turn, meant that a table of the influence each filter had on the light emitted by each chemical element would have to be prepared. Therefore when the identification of an unknown substance was called for, a potentially lengthy process of spectral comparisons might be required. Indeed Cartmell examined the problem of using light in this way for chemical analysis where only the alkali metals were concerned and, although he said that he would like to extend the method to the heavy metals (28), he never did so.

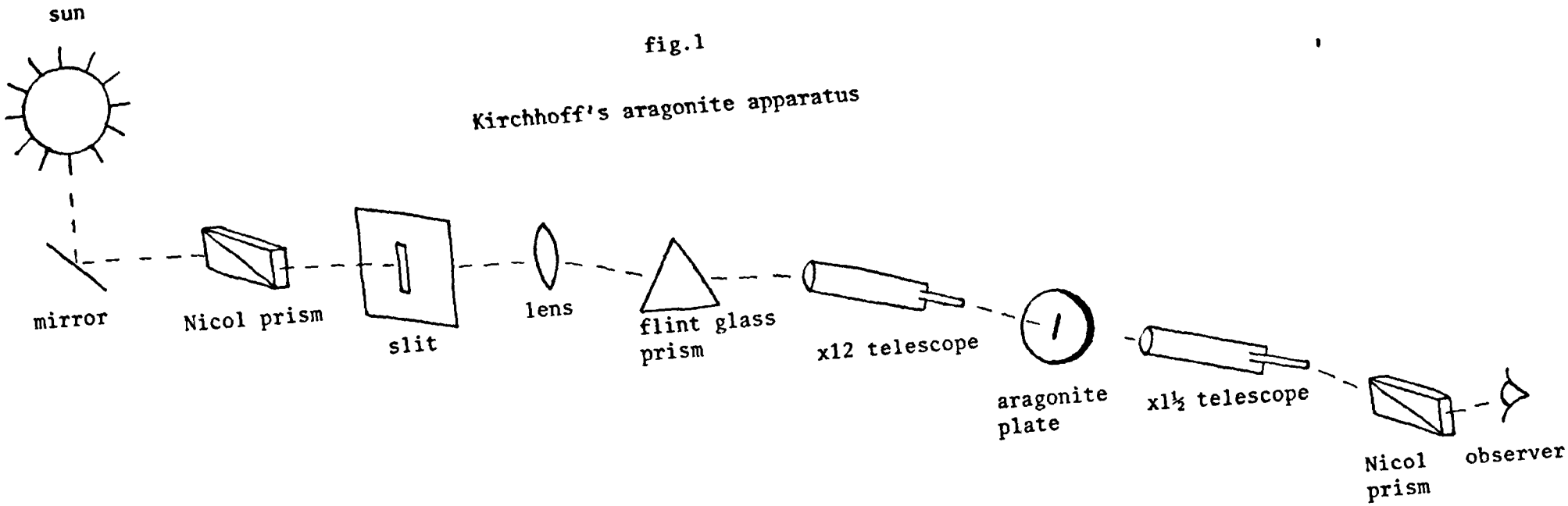
Since Cartmell needed to identify the refrangibilities of the light which was absorbed by particular filters, he turned to Kirchhoff to carry out the necessary optical measurements for him (29). Kirchhoff found, for example, that when light from a flame was passed through

> the solution of indigo used to distinguish the alkalies, [it] allow[ed] those rays to pass extending from A to B and from E to G...of Fraunhofer's lines of the spectrum (30).

Quite how Kirchhoff carried out these measurements, or what type of apparatus he used in 1858 is not clear, but the following year, and at the latest by September, he was using a fairly sophisticated optical arrangement to determine the optical axes of a plate of aragonite crystal (31) for

fig.1

Kirchhoff's aragonite apparatus



differently refrangible light (32). He described the apparatus he employed as follows

> The light rays are reflected horizontally by a mirror, pass[ing] through a Nicol prism [thus polarising the light] and fall[ing] onto a narrow vertical slit situated at the focus of a lens; after passing through this lens, they fall onto a flint glass prism with a refracting angle of about 45°, with its refracting edge vertical; then through an astronomical telescope having a magnification of about 12 and, on leaving the eyepiece of the telescope, pass through the aragonite plate and then into a second astronomical telescope having a magnification of about $1\frac{1}{2}$, and then a second Nicol prism [so that the intensity of light passing through could be easily controlled] before entering the eye of the observer (33).

Unfortunately Kirchhoff did not include a diagram of the apparatus, but it is possible to make a reconstruction following his description (fig. 1). Between the first Nicol prism and the plate of aragonite is essentially the spectroscope which Bunsen and Kirchhoff used in their spectral work (34). In this arrangement Kirchhoff used the lens as a collimator, rendering the rays of light leaving the lens parallel. Whether he knew of Plücker's spectroscope at this time is not clear (35), but besides Plücker there were several other scientists who had earlier used optical devices, not necessarily single lenses, to render light parallel (36). Kirchhoff was therefore in possession of an optical arrangement which with very little adaption could be used to undertake spectral studies per se.

Bunsen during the first half of 1859 had been continuing Cartmell's work on optical methods of chemical analysis (37). He replaced Cartmell's light filter with a hollow prism filled with indigo solution (38), saying that the discrimination between the chemical substances which Cartmell had analysed would be

> more easily effected by observing the succession of changes of colour which the mixed flame produced by these substances experiences when the rays reach the eye after passing through gradually thicker layers of an indigo solution (39).

In other words he observed the light source through the prism which was moved horizontally in front of the flame. Bunsen could therefore detect the change in colour caused both by the absorption of light in the fluid and by the refraction of the light by the prism, both of which changed as the prism was moved across in front of the flame. Using this method Bunsen was able to determine the characteristic light produced by calcium, sodium, potassium and lithium; he described the changes in colour which occurred to these elements as they were viewed through progressively thicker portions of the liquid. These colour changes were, he said, uniquely characteristic of the presence, or otherwise, of these elements in the flame.

Apart from the process of the identification of the characteristic colours produced by these chemical elements, I have found only one other practical application of this method of chemical analysis using light filters. This was by another of Bunsen's students, a Dr. Folwarczny (40), who in a paper published in 1860 (41), described his use of a thick blue glass filter to show that potassium was present in a sample of ash which he had placed in a flame (42). But despite this single success of the method Bunsen felt, as he wrote to one of his British ex-students Henry Roscoe (43), that he had "squandered" the Easter vacation working to devise an optical method of chemical analysis (44). Presumably Bunsen meant that his and Cartmell's work had only produced a method of very limited application, and not the hoped for general method of chemical analysis using light.

The fundamental problem with both Cartmell's method and Bunsen's development of it was that they were both cumbersome; these methods would ultimately require, if they were to be of any practical utility, a full tabulation of the behaviour of the light produced by at least the chemical elements, passing

through a large number of different filters. The checking then required to identify the constituents of an unknown compound using either method would have been at least as formidable a task as the standard methods of qualitative analysis. But this work does show that for a number of chemists in both England and Germany in the latter half of the 1850s it was important to discover a means of optical chemical analysis to try to simplify the process of qualitative chemical analysis. For Bunsen the fundamental problem was to obtain a practical method of chemical analysis using light. The solution to this problem still eluded him in mid-1859.

Following this failure Bunsen appears to have discussed the problem of optical chemical analysis with Kirchhoff who suggested that if the light emitted by a flame was subjected to prismatic analysis, then it might be possible to devise a system of chemical analysis using line spectra (45). It is curious that it was not until this time that Kirchhoff suggested the use of spectrum analysis for the purpose of chemical analysis. He must have been aware through his contribution to Cartmell's work that Bunsen was searching for a general method of chemical analysis using light, but yet he apparently did nothing to help Bunsen with his problem until the latter had failed to devise a suitable method. Kirchhoff, in the first few papers he published on his and Bunsen's spectral work showed that he was acquainted with some of Brewster's work on the subject (46); he noted that Brewster had described the characteristic spectrum of burning saltpetre (nitre) on coal, and that the D line was missing from the spectra of some of the fixed stars (47), but he did not give the source for these observations. It is not unreasonable, but by no means certain, to suppose therefore that Kirchhoff may have gained the idea of using spectra for chemical analysis from Brewster's work. Apart from Brewster his knowledge of other

workers on spectra appears, at that time, to have been minimal (48), although he may have known of Swan's work on the sodium line (49).

On the other hand there was really no necessity for Kirchhoff to have consciously adopted the idea that line spectra were uniquely characteristic of the chemical elements from either Brewster or Swan for Bunsen, from his and Cartmell's work on using light filters, already had the idea that the chemical elements emitted characteristic light; what was required was a suitable method by which this could be made apparent. Kirchhoff suggested that emission lines might do this, and in this he was correct. Since Bunsen already had the idea from his own work that the light emitted by the chemical elements was uniquely characteristic of them, it followed that it was inconceivable that when subjected to prismatic analysis the spectra produced by the light of the chemical elements should not also be characteristic of those elements. Thus the theoretical problems which had at one time beset spectral analysis did not trouble Bunsen and Kirchhoff, not because they had been solved (on the contrary they had not) but because Bunsen and Kirchhoff asked different questions of the phenomena.

Despite this uncertainty about how Kirchhoff arrived at the idea that spectral analysis could be used for chemical analysis, he did at some point in the summer of 1859 suggest it to Bunsen as a solution to the latter's problem. Immediately they set about its elucidation and by the twentieth of October Kirchhoff was able to write that he and Bunsen could

> recognize the qualitative composition of complicated mixtures from the appearence of the spectrum of their blowpipe-flame (50).

He and Bunsen had identified the spectra of the alkalies: sodium, lithium and potassium, and he mentioned Brewster's observation of the spectrum of the latter metal (51). It would appear therefore that by October 1859 they had not advanced chemical analysis by means

of optical methods, using spectral analysis, beyond what had already been made possible by Cartmell and Bunsen using light filters. Cartmell and Bunsen had, to their own satisfaction, established that the light emitted by these metals was uniquely characteristic of them; Bunsen and Kirchhoff should therefore have been able to feel some confidence that the spectra produced by these elements would also be uniquely characteristic of them. By extension if the spectral lines for these metals were indeed characteristic of them, then all other spectral lines should be caused uniquely by a particular element, and no other.

In the process of identifying the flame spectra of these elements they decided to compare them with the solar spectrum. Possibly they wanted to do this in order to check Brewster's assertion that the emission lines characteristic of potassium had the same refrangibility as the lines A, a and B of the solar spectrum (52). Alternatively they may have wanted to establish a system of identification of the lines using the solar spectrum with its Fraunhofer lines of fixed refrangibility as the basic measure of the position of the lines of the emission spectra. Besides Brewster's assertion concerning the identical refrangibility of the potassium lines, and Fraunhofer's A, a and B lines, Bunsen and Kirchhoff were also well aware that Fraunhofer had said that the double yellow R line produced by the sodium flame possessed the same refrangibility; it was this that they decided first to confirm.

In order to do this they

> formed a solar spectrum by projection, and allowed the solar rays concerned, before they fell on the slit, to pass through a powerful salt-flame. If the sunlight were sufficiently reduced, there appeared in the place of the two dark lines D two bright lines [fig. 2] (53).

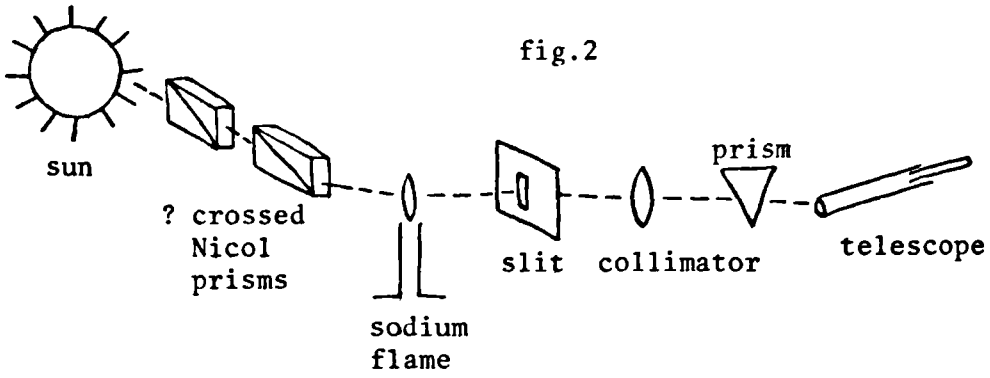


fig.2

Now Kirchhoff commented, albeit in a later paper, that they had "reduced the brightness of the sunlight, in order that it should not prevent us from perceiving the fainter light of the salt flame" (54). Otherwise, they thought, the light of the sodium flame would be overwhelmed and rendered invisible by the solar light, and consequently useless for the purpose of comparison. When they did pass the reduced sunlight through a sodium flame, Bunsen and Kirchhoff observed, as they fully expected, that the yellow R lines of the sodium flame occurred in place of the dark D lines of the solar spectrum (55). Had there not been an exact coincidence, the dark D lines would have been observed against the rest of the sunlight, as usual, to the side of the R lines of the flame. This work suggests that they must have been using the same, or similar, apparatus as that which Kirchhoff had used in his aragonite work, since by using the two crossed Nicol prisms they could have easily controlled the intensity of the sunlight being passed through the apparatus.

Kirchhoff next decided (56) "to find the limit at which the sodium [R] bands were still perceptible" (57), expecting that there would come a point when the sunlight would be of the same intensity as the sodium flame, thus rendering the emission lines invisible in the background of the sunlight. As he increased the amount of sunlight passing through the sodium flame, presumably by using the crossed Nicol prisms, he perceived, to his great astonish-

ment, that the yellow R lines turned into the dark D lines (58); in other words Kirchhoff had observed the "reversal" effect. Further he observed that the D lines now seen in the flame were stronger than those caused by the sun alone; this he confirmed by respectively removing and replacing the flame several times to observe the resulting diminution and increase in intensity of the D lines (59).

Kirchhoff had made two observations in this experiment: firstly the actual reversal of the lines themselves and secondly the intensification of the phenomenon by the sodium flame. Kirchhoff's next move was to see if he could recreate in the laboratory the former phenomenon. This he did by performing a second experiment (fig. 3)

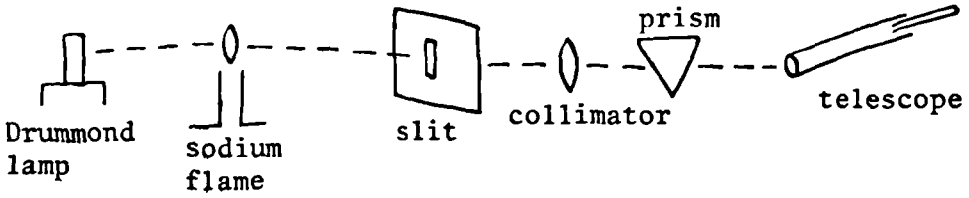


fig.3

in which he passed the light of a strong Drummond lamp (60), (which did not emit the sodium lines) through a sodium flame and subsequently a spectroscope; he observed, as he expected, that the R lines of the sodium flame reversed into the dark D lines (61).

The fact that Kirchhoff carried out this particular experiment on the sodium flame gives us some indication of what he considered the nature of the reversal phenomenon to be. His observation that the sodium flame in the first

experiment intensified the D lines of the sun evidently led him to conclude that the cause of the intensification must lie in the absorption of light by the flame. Therefore a similar causal agent must exist to create the D lines per se; in other words Kirchhoff thought that the Fraunhofer lines must be caused by the absorption of light by an incandescent body, i.e. the solar atmosphere, which Kirchhoff, like his contemporaries, assumed to exist (62). Thus Kirchhoff's interpretation of his first experiment was entirely dependent on the assumption of the existence of an incandescent solar atmosphere which absorbed light from below. While most nineteenth century theories of the sun, including those of Kelvin and Helmholtz, (who was then at Heidelberg (63)) did provide the sun with an atmosphere, it was by no means certain that it was the cause of the Fraunhofer lines. For example at exactly the same time as Kirchhoff was doing this work in Heidelberg Brewster and Gladstone in Britain were attempting to discover the influence of the terrestrial atmosphere on the Fraunhofer lines, and they stated in effect that the lines were caused not by the solar but by the terrestrial atmosphere (64).

Kirchhoff wanted to be certain that his interpretation of reversal was correct and this demanded a terrestrially based experiment. He had already been wrong once in interpreting the behaviour of the lines when he had assumed that the emission lines would cease to be observed when the sunlight was sufficiently intense. A terrestrial experiment would provide evidence for the soundness of his absorption interpretation and incontrovertible evidence, for others, that such an interpretation was valid. The logical step would be to attempt to recreate artificially the process which Kirchhoff believed to be happening in the solar atmosphere. This he had done in his second experiment where the solar atmosphere is analogous to the sodium flame, while the Drummond light took the rôle of the central mass of the sun (65).

Indeed this interpretation of reversal as being due to

the absorption of light in the solar atmosphere/flame was the one which Kirchhoff postulated from his interpretation of his second, terrestrially based, experiment. He concluded from this experiment that the

> coloured flames in the spectra of which bright sharp lines present themselves, so weaken rays of the colour of these lines, when such rays pass through the flames, that in place of the bright lines dark ones appear as soon as t ere is brought behind the flame a source of light of sufficient intensity, in the spectrum of which these lines are otherwise wanting (66).

In other words whenever a singularity occurred in an emission spectrum it would "weaken" (67) light at that wave-length from a source (of sufficient intensity) behind it. However, it is not clear in this context, what Kirchhoff meant by "weaken". The idea that the sodium flame only weakened the sun light probably came from the observation, in his first experiment, that the sodium flame intensified the D lines of the solar spectrum, i.e, there must still be some light in the D lines left to be absorbed. Therefore, by extension, the light of the D lines after passing through the sodium flame must also contain some light, albeit further reduced in intensity.

In his second experiment Kirchhoff had shown that the emission lines belonging to a chemical element, in this case sodium, were reversed into the absorption lines when a stronger light source was passed through it. This implied that where absorption lines were caused by an incandescent body, they must also be indicative of the presence of chemical elements in that body. Kirchhoff argued that the Fraunhofer lines could be used to determine the presence or otherwise, of chemical elements in the solar atmosphere. And indeed in his first paper, he had outlined how these results could be used to do this, saying that sodium and potassium must be present in the solar atmosphere, but not lithium, because none of its lines were present in the solar spectrum (68).

To provide further confirmatory evidence that the Fraunhofer lines were caused by the solar atmosphere and could

therefore be used to determine its chemical composition, Kirchhoff examined the emission spectrum of an iron flame. According to Helmholtz when Kirchhoff compared this spectrum with the solar spectrum he found that "the E lines and the most refrangible of the three b lines [are] from iron" (69) and he consequently concluded that "the sun's atmosphere contains iron" (70). It will be recollected that the principal theories of solar energy in the 1850s - Kelvin's and Helmholtz's - both supposed, for different reasons, that iron must be an important constituent of the sun (71). It was therefore natural for Kirchhoff, once he had realised that the Fraunhofer lines could be used to provide a chemical analysis of the solar atmosphere, for him to look for the existence of chemical elements in the solar atmosphere which he had reason to believe to be present. By showing that there was iron in the solar atmosphere Kirchhoff not only helped to provide supporting evidence for current solar theories but also confirmed his interpretation of the nature of the Fraunhofer lines, i.e. that they were caused by the absorption of light in the solar atmosphere.

In his second communication on spectra (72) Kirchhoff considered, more precisely, his ideas on the nature of the Fraunhofer lines and the phenomenon of reversal. In the case of the solar spectrum, Kirchhoff declared that the phenomena he had observed in his first experiment could only be understood by supposing

> 1) that, of the [solar] rays which pass through the sodium chloride flame, it is precisely those [solar rays] having the same colour as those rays which the flame itself emits, which are weakened by it [the flame]; and
> 2) that the dark lines of the solar spectrum do also contain light, but much fainter than the light in their vicinity (73).

The first supposition is a tighter statement of Kirchhoff's previous conclusion, and therefore is also an explanation of his second, terrestrially based, experiment; however, he still did not define what he meant by "weaken" and he continued to use colour as the determining factor as opposed to wave-length. His second assumption, however, helps, in a

qualitative way, to define "weaken". Kirchhoff must have reasoned, as he seems to have done in his first paper, that the intensification of the D lines, caused by the sodium flame, indicated that there must still be some light remaining in the D lines of the sun which would be subject to a diminution in intensity and his second assumption therefore followed.

Bunsen, Helmholtz and Kelvin were all satisfied that Kirchhoff's experiments by themselves were sufficient to establish the chemical analysis of the solar spectrum on a secure causal basis (74); they pointed out, as Kirchhoff had done, that he had shown in his terrestrial experiment that the element concerned had to be present in the flame which absorbed light, for reversal of its emission spectrum to occur. Consequently they argued that whenever a set of Fraunhofer lines appeared in the solar spectrum, the element which normally produced an emission spectrum at those points must be present in the solar atmosphere (75). Therefore by discovering the characteristic spectrum of each of the chemical elements they would not only be developing a new chemical analytical technique, but also discovering the chemical composition of the atmosphere.

Kirchhoff was naturally concerned to ensure that this solar chemical analysis was valid and he therefore undertook a theoretical examination of the reversal phenomenon. In the last two months of 1859 he developed two mathematical theories to explain the phenomenon, but it is not clear whether he developed them concurrently or sequentially. The title of his first mathematical paper, dated 11 December 1859, is revealing in its own right: "On the relation between emission and absorption of light and heat" (76). Kirchhoff presumably extended his work to include radiant heat so that he could analyse the problem of absorption according to "the general premises of the mechanical theory of heat" (77), that is according to the laws of the conservation and dissipation of energy.

The proposition which Kirchhoff wished to prove was that

> for rays of the same wave-length at the same temperature, the ratio of the emissivity [$\underline{e}$] to the absorptivity [$\underline{a}$] is the same for all bodies (78).

In other words the ratio of emissivity to absorptivity, e/a, is a function, for all bodies, of wave-length and temperature. From this proposition Kirchhoff deduced, that if a body, at a given temperature, emitted light of particular wave-lengths, as in the case of a flame spectrum, then the body could only absorb light at those particular wave-lengths at that temperature. From this the reversal phenomenon must necessarily be a consequence (79).

To prove this proposition Kirchhoff assumed, for the sake of simplicity in proof, the existence of two infinite plates, the outer faces of which were covered with perfect mirrors (fig. 4).

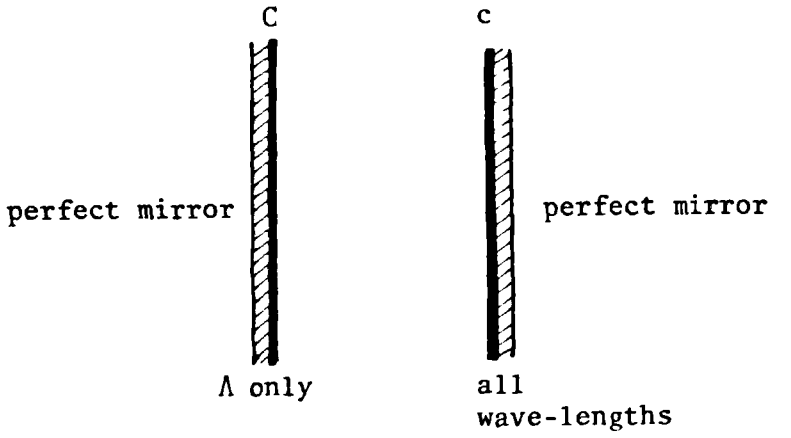


fig.4

This ensured a closed system to which energy arguments could be applied. One of the plates C, could emit and absorb radiation only at one particular wave-length Λ, while the other plate, c, could emit and absorb radiation at all wave-lengths. After dismissing the case of all wave-lengths not equal to Λ by saying that all such rays emitted by c would eventually be reabsorbed by c, he considered those rays emitted by both plates which were of wave-length Λ. Kirchhoff showed what portion of a ray emitted by C would be absorbed by c, and it followed, by the principle of conservation of energy, since the system was closed, that the remainder would be returned to C and so on. Kirchhoff derived expressions for the amount of radiation absorbed by each body if the process was assumed to continue for an infinite time (since this involved summing geometric

progressions to infinity) (80). He then proceeded to apply a similar treatment to a ray of wave-length λ, emitted by c. When the exchange of radiation had been completed, both plates, he argued, must have reached the same temperature, and therefore, by the second law of thermodynamics, the flow of heat must have ceased. The thermodynamic condition for the heat flow to have ceased was that the amount of radiation emitted by one plate, say c, was equal to the total amount of radiation which had been absorbed by C, plus that which had been reabsorbed by c; a similar argument applied to radiation emitted by C. From this condition it followed that e/a was identical for both plates at the same temperature and wave-length (81). He then argued that if c was replaced by another body the same result would still follow; he therefore maintained that the law held for all bodies (82).

In the space of about seven weeks Kirchhoff had devised a thermodynamic analysis of his observations in such a way that the phenomenon of reversal, though not its intensity, was shown to be a consequence of the general proposition that e/a was the same for all bodies at the same temperature and wave-length (83). In his first two papers he had concentrated on a qualitative attempt to explain all the reversal phenomena (i.e. both the intensity and the position of the lines). In this third paper he was content to state and prove his proposition and thus show that if a singularity existed in an emission spectrum of an element then a singularity must, of necessity, exist at the same wave-length and temperature in the absorption spectrum of that element.

In his first paper Kirchhoff had made the observation that the Drummond lamp had to be of a higher temperature than the sodium flame for the dark D lines to appear in the former flame (84). In other words Kirchhoff had described in his second experiment what would nowadays be termed the higher and lower energy states of the flames, necessary for a successful observation of the phenomenon to be made. He considered that this observation was of "great importance" (85), though he did not specify why he thought this, and in his second

paper he did not emphasise the point. Bearing in mind the importance which he attached to temperature in his theoretical analysis of reversal, it seems reasonable to suppose that this observation may have suggested to him a thermodynamic analysis once he had realised that it was the position (i.e. the wave-lengths) of the lines which mattered and not their intensity. The intensity, he could have concluded from his experiments, would be dependent not only on the particular element, but also on temperature, and the thickness of the flame/atmosphere through which the non-absorbed portions of light had to pass, and these were not easily amenable to theoretical analysis.

There is an analogy, which Kirchhoff did not draw, between the system of twin plates and the sodium flame/Drummond lamp in his second experiment (and consequently with the solar atmosphere and interior). Plate c may be the representation of the non-sodium flame in that it emits and absorbs radiation at all wave-lengths, while plate C is analogous to the sodium flame in that it can only absorb and emit radiation at given wave-lengths, of which Kirchhoff considered one (Λ) in his analysis. It must be emphasised that the flame system in the second experiment is not closed as the plate system is; but analogy is not the same as equivalence. Kirchhoff required a closed system to analyse the radiation from c which C did not absorb and which would otherwise continue into space as occurred in the second experiment. Therefore for the radiation to be amenable to thermodynamic analysis C must have a perfect mirror to reflect the non-absorbed radiation back to c. Since c similarly cannot absorb all the radiation returned to it by C, it too must have a perfect mirror to prevent radiation dispersing into space. Therefore a closed system was ensured to which thermodynamic arguments could be applied and, from which the analysis, discussed above, swiftly followed.

Despite the fact that Kirchhoff had argued in this analysis that the materials used were arbitrary, it would appear that he was not satisfied since the following month, January

1860, he gave a more general proof of his proposition which dispensed with the special properties of the plates and mirrors (86). In this second analysis he employed a "black body" (87), defined by stating that all radiation impinging on such a body is absorbed by the body by conversion into heat; when enough radiation has been absorbed, Kirchhoff said that the black body would then emit a continuous spectrum (88). Plate c may thus be taken as an ill defined example of a black body (89). He then analysed the behaviour of radiation in a box containing a black body, concluding, as he had done from his analysis of the system of two plates, that the function e/a was the same for all bodies at the same temperature and wave-length.

Kirchhoff then proceeded to examine the possible nature of this function which he could only do by considering specific examples, since, as he admitted, he could not determine it mathematically (90). He showed that when the temperature remained constant, i.e. when e/a was dependent only on wave-length, the

> function I [e/a] can have no strongly marked maxima and minima for waves of different lengths. Hence it follows that if the spectrum of a red-hot body presents discontinuities or strongly marked maxima or minima, the power of absorption of the body, regarded as a function of the waves, must present similar discontinuities or strongly marked maxima and minima (91).

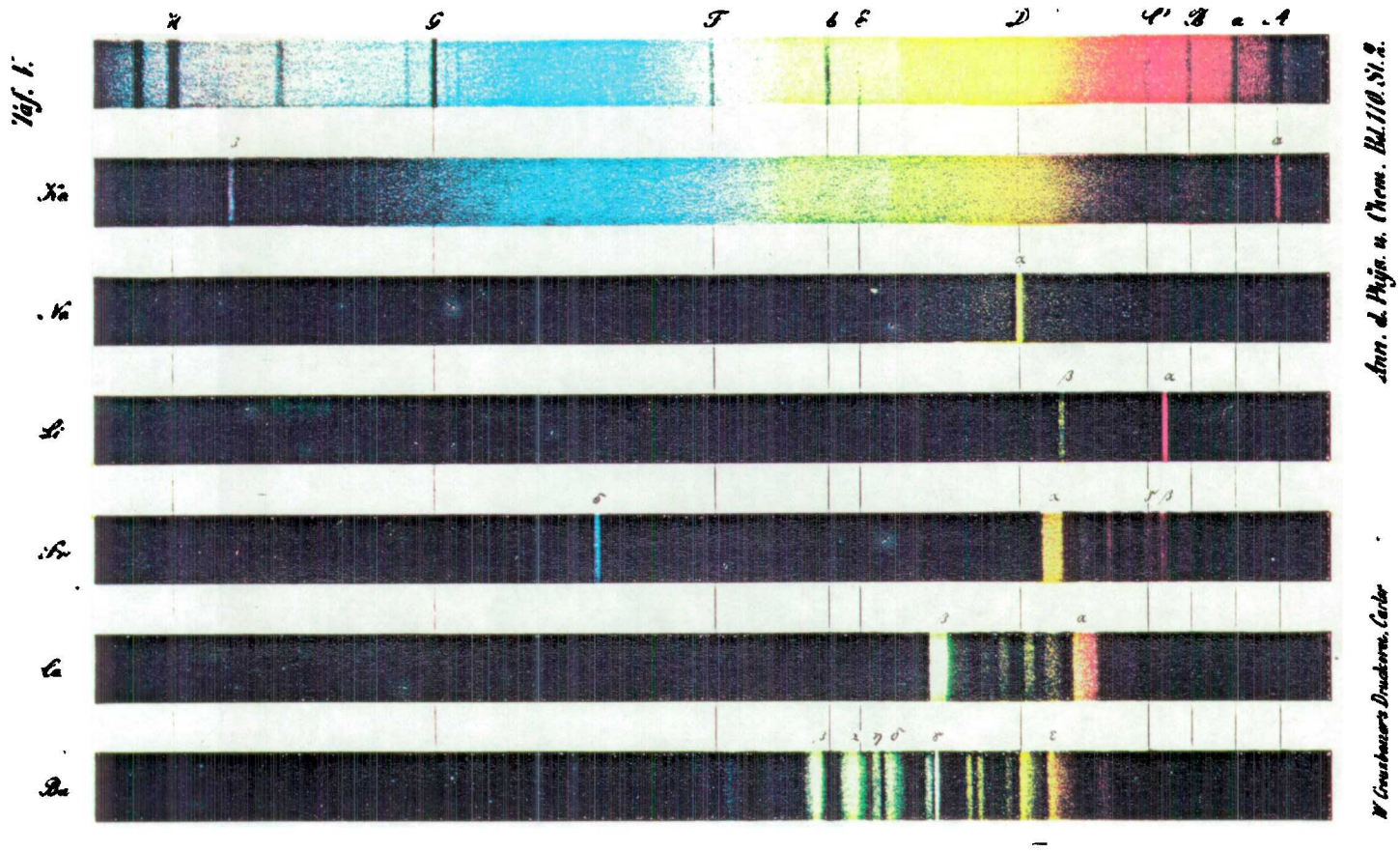
Hence we have come full circle: from his original observation of the reversal of the spectral lines, Kirchhoff had devised his ratio law. From this, by deduction, he had shown the connection between emission and absorption and consequently accounted for the phenomenon of reversal.

However, this did not explain the existence of the lines. It merely stated that if a set of emission lines belonged to a chemical element, then, under suitable circumstances, its absorption spectrum must also be a set of lines of the same wave-length and vice versa. Kirchhoff admitted, to a certain extent, the problems posed by this fact:

> The wave-lengths which correspond to maxima of the radiating and absorbing powers are...altogether independent of the temperature; and moreover, in the case of salts which produce flames having such maxima, it is the metal that determines the nature of the spectrum (92).

In other words, apart from the statement derived from his and Bunsen's spectral observation that the metal of a salt determined the spectrum, Kirchhoff revealed nothing about what he thought spectra represented in physical terms. In none of his published papers on the subject did he give any hint of even having considered the problem, let alone suggest solutions. For Kirchhoff it was not necessary to discover why reversal occurred; he had established the result which he required: the Fraunhofer lines were caused by the solar atmosphere, and they could consequently be used for analysing the chemical composition of the atmospheres of the sun and stars. Kirchhoff had considered the theory of the lines independently of any matter theory and had therefore not attempted to discover how they were produced. He had achieved a firm understanding of how the various spectral phenomena were related. The assumptions which Kirchhoff made in his proof, especially of the relationship between light and heat, implied the existence of some form of vibrating particle which caused the emission and absorption of heat and light. But for Kirchhoff thermodynamics had come to dominate the subject; light and heat were only required to be forms of energy in order that he might account for the reversal phenomenon. It was no longer necessary to suggest matter theories to account for the links between emission and absorption; such links were implicit in the laws of thermodynamics and Kirchhoff had made them explicit.

Kirchhoff had therefore established the chemical analysis of the solar atmosphere using the Fraunhofer lines, not only on an experimental basis but on a theoretical basis also. This provided a further impetus, if one was needed, for Bunsen and Kirchhoff to concentrate on determining which spectral lines belonged to which chemical elements. This Bunsen had been doing while Kirchhoff had been working on his understanding of the reversal phenomena. In their joint paper on spectrochemical analysis Bunsen and Kirchhoff added the spectra of strontium, calcium, and barium (93) to those which they



Bunsen and Kirchhoff's spectral maps

fig.5

had described (fig. 5), although curiously in this paper they omitted all mention of the spectrum of iron.

Because Kirchhoff's work did not deal specifically with the problem of where the cause of the emission lines lay (i.e. with the molecules, atoms, etc.), in their joint paper he and Bunsen had to advance reasons why line spectra were uniquely characteristic of the chemical elements. Firstly they said that

> As the result of...somewhat lengthy experiments, the details of which we here omit, it appears that the alteration of the bodies with which the metals employed were combined, the variety in the nature of the chemical processes occurring in the several flames, and the wide differences of temperature which these flames exhibit, produce no effect upon the position of the bright lines in the spectrum which are characteristic of each metal (94).

In other words once they had had the idea of utilising emission spectra for chemical analysis, they, that is, presumably, Bunsen, had checked to see if the spectral lines of particular elements always occurred no matter what other circumstances were pertaining. The second piece of evidence which they advanced to show that spectra were uniquely characteristic of the chemical elements stemmed from a suggestion made by Kirchhoff, when after citing the work of Wheatstone, Masson and Ångström on spark spectra, he said that

> it may be assumed that these [electric spectral] lines coincide with those which would form in the spectrum of a flame at a very high temperature if the same metal, in suitable form, were placed in it (95).

By the time they published their joint paper they had confirmed the identical refrangibility of the emission lines of flame and electric spectra so far as sodium, potassium, lithium, strontium, and calcium were concerned (96). The implication was that since the lines produced by the electric spark, which were known both theoretically and experimentally to be characteristic of the chemical elements, had the same refrangibility as the emission lines produced by the flame spectra of the same elements,

it followed that flame spectra must also be uniquely characteristic of the chemical elements. The previous work on electric spectra thus served in a confirmatory rôle for Bunsen and Kirchhoff; it did not serve as an idea which led them to conclude either that spectra could be used for chemical analysis, or that spectra were uniquely characteristic of the chemical elements. They were not concerned with the problem of elucidating the nature of the spark using spectra, but with using the experimental observation, which had been conclusively demonstrated, that electric spectra were uniquely characteristic of the chemical elements. By doing this they demonstrated, for others, that flame spectra must also be uniquely characteristic of the chemical elements, a result which they were already convinced of from an early point in their researches.

Bunsen must have realised that in order to gain adequate and accurate knowledge of the spectrum of each metal, every sample he examined would need to be as pure as possible, since as Swan had shown the smallest impurity of, for example sodium, would cause the characteristic lines to appear. In fact for some substances Bunsen carried out the purification process up to ten times for a single sample (97). Processes of this nature take a good deal of time and it was several months before he could be certain that he had located all the spectral lines of the elements he was investigating.

During this process of determining which lines were caused by which element, Bunsen discovered that some elements such as lithium and strontium, previously thought rare, occurred quite widely. He had found them to occur in samples of mineral waters which he had investigated (98) and by a process which I can only describe as extrapolation Bunsen decided to see if there were any unknown elements in these mineral waters (99). He found what he was looking for: a blue emission line which did not belong to any known element. As he wrote to Roscoe:

> I have obtained full certainty, by means of spectrum analysis, that besides Ka, Na & Li, a fourth alkali must exist, and all my time has been occupied in endeavouring to isolate some compounds of the new substance (100).

Since all the other lines of the mineral water spectra had been allocated by Bunsen to known metals the blue line must, he argued, be caused by an hitherto unknown element. This type of argument was to lead many a scientist astray in the future (101), but for Bunsen, on the ground floor, it proved sound. Indeed so confident was he of his spectroscopic discovery of a new element that in his and Kirchhoff's joint paper of April 1860 its existence was referred to solely on the grounds of its spectrum (102).

There was a problem however: the quantities of this new element which Bunsen had detected occurred in such minute quantities as to be very difficult to isolate chemically. The new element was mentioned three times in April 1860 (103) and again in early May (104), by which time Bunsen had been able to determine, to a certain extent, some of its chemical properties:

> The chloride of the new alkali metal differs from sodium chloride and lithium chloride in that, like potassium chloride, it forms a yellow deposit with platinum chloride. It differs from potassium in the solubility of its nitric salt in alcohol (105).

While these properties cannot be called detailed chemical knowledge, this is definitely an advance since Bunsen had detected the element and showed from independent chemical evidence that he was not mistaken in his assumption that he had discovered a new chemical element. Bunsen thus had the confidence to order the distillation of forty four thousand kilogrammes of Durkheim mineral water (106) in order to obtain a sufficient quantity of this new element, which he named caesium (107), to be chemically useful.

This discovery of Bunsen's opened the way for the discovery of further hitherto unknown chemical elements both by himself and others. Indeed Crookes was so confident

of the existence of unknown chemical elements that he could write to his friend and collaborator C. H. Greville Williams (108) in February 1861 that he

> should like to commence our joint labors [sic] with a new element to work upon, there seem to be plenty of them waiting to be found out, I have seen several suspicious looking spectra (109)

and the following month referring to his spectral work of the 1850s, he commented that he had then observed "other unknown lines also, so there are new elements waiting for us" (110). This seems to have been a fairly common attitude existing towards line spectra and chemical elements in early 1861, since in the first three months of that year, four new chemical elements were "detected" spectroscopically.

Bunsen's diligence in distilling the large amount of mineral water which he had done was well rewarded with the discovery, sometime during the first two months of 1861 (111), of another emission line, this time lying in the red, which did not belong to any known element (112). Bunsen being, by now, very familiar with line spectra was able with some confidence to say that he had discovered yet another new element, as indeed he had, later naming it rubidium (113). But those other scientists who thought that there were other chemical elements waiting to be discovered had little practical experience of working with spectra and could only use for guidance the spectral maps which Bunsen and Kirchhoff had provided with their paper.

Thus using Bunsen and Kirchhoff's spectroscopic method and their maps the brothers F. W and A. Dupré (114) in January 1861, announced that they had discovered a blue line which appeared not to belong to any known element, and this element they ascribed to the calcium group of metals (115). A couple of months later Crookes, using as a guide his previous observati n of the calcium spectrum, discovered, using a new sample of calcium, that this line was in fact one of the characteristic lines of

calcium (116). This line had not been included in the map which Bunsen and Kirchhoff had provided of the calcium spectrum and their maps were consequently attacked by Crookes as being inadequate (117).

Before Crookes had shown that F. W. and A. Dupré had not discovered a new element, he too had been on the "track of a new element" and had been looking for

> something which would give me decided evidence of it. It is not caesium, nor is it the new metal of Dupré's (118).

Indeed so confident was he that he had detected a new element that he even had "the name decided on" (119), but it turned out that

> the lines are formed by internal reflection from the different surfaces of the prism and lenses (120).

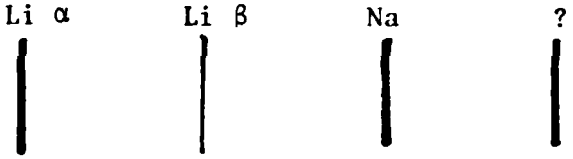
These failures appear to have had very little effect on the development of spectro-chemical analysis. By 1861 the method had been so well accepted as a valid means of chemical analysis that it could actually fail on occasions without its validity being questioned. I would suggest that the spectro-chemical method developed by Bunsen and Kirchhoff fitted in so well with the desire for such a method of analysis, previously expressed in the work of Crookes, Gladstone, and Swan, that it could now withstand the effects of the occasional failure. Crookes might severely criticise the spectral maps provided by Bunsen and Kirchhoff, but there was nothing that would induce him to abandon the method. The idea that spectra were uniquely characteristic of the chemical elements was firmly established, and those extra elem nts were simply teething troubles in the process of elaborating the method.

Thus Crookes kept looking for unascribed spectral lines which might indicate the existence of hitherto unknown chemical elements. His persistence was rewarded in early March with his observation of an hitherto unnoticed green line. As he asked Williams:

> Have you ever noticed a single bright green line, almost exactly as far from Na α on one side as Li α is on the other. If not, I have got a new element (121)

and two days later

> I really think I have caught the "line" at last. It is a sharp distinct green line situated thus (122)



This time Crookes was not wrong in his supposition that he had discovered a new chemical element. He provisionally named it "A" (123) and later thallium (124) and by March 8th he had established that its chemical reactions were unlike those of any other known element (125). Towards the end of March he was "hurried into print by the information, privately given, that another was close at my heels" (126). To whom Crookes is here referring is not clear. Lamy (127) in France did not independently discover the green line until the following year (128), so it would appear that there was some other scientist who was also attempting to discover new elements using spectral lines.

This search for new elements using spectro-chemical techniques, whether successful or unsuccessful, shows that by 1861, Bunsen and Kirchhoff were perceived by other chemists to have placed spectro-chemical analysis on a secure basis. Bunsen had been determined to discover an optical method of chemical analysis; in this he was not alone. But it was his perseverance, after failing twice, and in the face of what turned out to be a very tedious process, which brought success. And because Bunsen and Kirchhoff were working at a time when there was an apparent desire among chemists for an optical method of chemical analysis, their success was immediately recognised.

A large amount of work remained to be done, but the search for an optical method of chemical analysis was over.

The method had been shown to be successful and in the main reliable. In the past scientists had only theories of spectra upon which to rely, and these had not provided sufficient incentive for them to do the necessary work. This was especially so since these theories of spectra had been unable to reach any consensus as to where the origin of the lines lay with respect to the structure of the ponderable matter from which they emanated. Those scientists who worked on spectral phenomena in the latter half of the 1850s and early '60s were not concerned with the theoretical problems associated with spectra. They were solely concerned with utilising spectra for chemical analysis for which spectral theories were not, as it turned out, necessary. The study of spectral phenomena depended on the questions which were being asked. In the latter half of the 1850s the question was how could light be utilised for chemical analysis? It was to this question that Bunsen and Kirchhoff had addressed themselves. Neither Bunsen nor Kirchhoff were concerned with how line spectra were caused, they were only concerned with how they could be utilised. As a result Bunsen had discovered two new chemical elements and Kirchhoff had established the chemical analysis of the solar atmosphere on a secure basis. There was no need for them to postulate how the lines were caused; for them it had become inconceivable that a chemical element should emit different spectra at different times or that different elements should emit the same lines.

They had worked in a context in which the main problem was how to devise a system of chemical analysis using light. Apart from possibly taking the idea that line spectra might be characteristic of the chemical elements, they took nothing from earlier work on spectra. In each context in which spectra were studied - the undulatory theory, the electric spark, and chemical analysis - it was necessary, because the questions being asked in each context were different, for each group of scientists to work through the problems inherent in studying spectral

phenomena. Very little knowledge of spectral phenomena could be exchanged between contexts, since earlier work was, on the whole, not relevant to later work. The context in which Bunsen and Kirchhoff did their work, led them to ask questions of spectra which had not, hitherto, been explicitly asked, and within their own context they had placed spectro-chemical analysis on a secure basis, valid not only for light produced on earth, but for light produced by the stars.

Conclusion

THE EARLY HISTORIOGRAPHY OF SPECTROSCOPY

There had existed in the latter part of the 1850s a desire on the part of some chemists to establish a system of qualitative chemical analysis using light. This was not put into effect until Bunsen and Kirchhoff's sustained effort of 1859-60 conclusively showed that by analysing the spectrum of the light produced from a flame it was possible to identify the chemical elements which were present in that flame. As I showed in the previous chapter, the chemical utilisation of spectra was one among a number of contexts in which spectral phenomena were studied during the first sixty years of the nineteenth century. Earlier spectral studies had been conducted in the context of attempts to reconcile the phenomenon of the absorption of light by ponderable matter with the undulatory theory of light, and in the context of attempting to elucidate the nature of the electric spark.

One of the consequences of this work on absorption and spark spectra was that some scientists thought that qualitative chemical analysis using both emission and absorption lines was a theoretical possibility, but they did not put this into practice to any great extent before 1859. Even in the case of spark spectra, where a method of qualitative chemical analysis would have been easy to develop, the possibility was not explored until the late 1850s. Those scientists who worked on spark spectra were interested in the nature of the spark and they directed their attention towards this topic rather than towards chemical analysis.

The situation was more complicated in the case of absorption spectra (which for most scientists included emission spectra), since it was far from clear where the

cause of the spectral lines lay in terms of the structure of matter from which the light emanated. Those scientists who had examined the problem of spectro-chemical analysis were so confused by the numerous conflicting theories of spectra which had been developed, and by their own inconsistent observations of spectral phenomena, that none of them had made much progress in turning spectral theories into a practical method of chemical analysis. But besides these difficulties the main point of their work had been to reconcile the absorption of light with the undulatory theory, not to devise a method of spectro-chemical analysis.

In addition to the utilisation of spectra for chemical analysis, it had also been thought by a number of scientists that the Fraunhofer lines could be employed to determine the chemical composition of the sun, planets and stars. But to the problems which had beset terrestrial chemical analysis was added the difficulty, in this case, that because there was no agreement about the nature of the sun, there was no certainty about the cause of the Fraunhofer lines.

These original studies of line spectra proceeded from attempts to solve problems which had arisen as a result of various developments in the physical sciences during the first half of the nineteenth century. To a scientist during this period an unexplained gap in an otherwise successful physical theory could not be tolerated, and had to be included within the theory. Thus the absorption of light had to be reconciled with the undulatory theory; the spark had to be explained according to Faraday's theory of electricity; and the source of solar energy had to be accounted for, since thermodynamic analysis had shown the sun to have been unable to have maintained its energy output for even the period of recorded history, without some mechanism of heat production. A considerable amount of effort was spent in providing solutions to each of these problems. The development of a method of spectro-chemical analysis must

have appeared as a minor problem to those scientists who worked on absorption or on sparks. Spectro-chemical analysis did not have the theoretical importance which these other problems possessed and consequently little attention was paid to it.

This was where Bunsen and Kirchhoff's spectral work differed from that of their predecessors. They, or at least Bunsen originally, had sought to devise a system of chemical analysis using light. For them there was no other purpose to their work; they were not seeking the cause of spectra, they were not seeking to discover the nature of matter; they were simply concerned to devise a method of chemical analysis. They were not familiar with the physical uses for which spectra had been previously employed; Kirchhoff was acquainted with Brewster's idea that certain spectra were characteristic of some chemical elements, but it is not clear how important this was to the development of his and Bunsen's spectro-chemical work. They appear to have used the earlier spectro-chemical work of which they were aware as a justification of the validity of their own work, rather than as a foundation on which they based their own research. In the process of their research Bunsen and Kirchhoff essentially studied spectral phenomena from a chemical point of view; that is they asked chemical questions of spectral phenomena, rather than physical questions. By doing this they in effect ignored the physical questions concerning the nature of spectra. Kirchhoff also established a causal relationship between emission and absorption lines without having to assume or devise any structure of matter, which up to that time had been necessary in order to explain why some emission and absorption lines had identical refrangibilities. Kirchhoff therefore could analyse the chemical constitution of the solar atmosphere with as much certainty as he and Bunsen could identify the chemical elements present in a flame using spectral analysis;

Kirchhoff was aided in doing this by the new theories of the sun which Kelvin and Helmholtz had devised to explain its heat production.

Bunsen and Kirchhoff's work on spectro-chemical analysis consequently represented to them, because of the different context in which it was conducted, a self-perceived break with the past. That this was their position Kirchhoff made quite clear in his discussion of Swan's work:

> Swan...made a most valuable contribution towards the solution of the proposed question as to whether the bright lines of a glowing gas are solely dependent upon its chemical constituents; but he did not answer it positively, or in its most general form...
>
> No one, it appears, had clearly propounded this question before Bunsen and myself; and the chief aim of our common investigation was to decide this point. Experiments which were greatly varied, and were for the most part new, led us to the conclusion upon which the foundations of the "chemical analysis by spectrum-observations" now rest (1).

While Kirchhoff could acknowledge the value of the work of earlier scientists on spectral phenomena, he thought that it was the questions that he and Bunsen had asked of the phenomena which made their spectral work different from that of their predecessors. They had not deliberately shifted the emphasis of the study of spectral phenomena away from physical theories towards chemical utility; rather they had studied line spectra in a context different from those which had gone before. This time the context was provided by chemical studies, rather than physical studies.

Although Bunsen and Kirchhoff thought that their spectral work was different from that of their predecessors, it was not generally admitted, at that time, that this was the case. As Crookes put it:

> Now the attention of scientific men is being drawn to the method of [chemical] analysis by means of spectrum observations, our readers will feel an interest in knowing that many of the observations which are now being followed by Continental savans, have been investigated in a more or less perfect manner by English experimentalists (2).

He continued by citing Talbot and Wheatstone as examples of such English experimentalists. In this Crookes implicitly admitted, but failed to recognise, that the chemical significance of Talbot's and Wheatstone's work was realised only after Bunsen and Kirchhoff had explicitly made clear the significance of spectral analysis for chemical analysis. But Crookes insisted that all of Bunsen and Kirchhoff's predecessors should be given credit in what he thought was a continuous development of the method of spectro-chemical analysis stretching back to Fraunhofer. To this end he republished in the Chemical News, which he edited, Wheatstone's 1835 paper (both the abstract (3) and, for the first time, the full text (4)), Talbot's 1826 paper (5) and various of his notes following that (6), and W. A. Miller's 1845 paper (7). Crookes thus ensured that the source material for histories of spectroscopy was easily available.

Roscoe quickly challenged Crookes's view of the development of spectroscopy. In a lecture to the Chemical Society in mid-1861, apparently with Bunsen and Kirchhoff's approval, he commented that

> I ought...to mention that Bunsen and Kirchhoff were by no means the first to observe the particular lines of metals. In their paper they begin by saying it is well known that certain bodies when placed in a flame produce spectra containing brightly-coloured bands. They were acquainted with the researches that had gone before. I have their own authority for saying this. In our own country, Talbot, and Wheatstone and, Dr. [W. A.] Miller observed closely the same thing; at all events, they observed some of the points which were noted by Bunsen and Kirchhoff, but to Bunsen and Kirchhoff belongs the honour of having first brought the subject to a definite issue and made it a distinct and prominent branch of chemical analysis (8).

While Roscoe could in public be to some degree conciliatory in attitude towards this earlier spectral work, in private he was much more explicit:

> The real importance of...[a] discovery is not to be measured by the first imperfect notices which have been made on the subject,...the discovery is really made when the true importance of these observations in shown, & when they are connected together in a scientific & exact manner (9).

Then after a passage criticising the work of W. A. Miller, Talbot and Wheatstone, Roscoe continued

> I believe that my position, viz. that B[unsen] & K[irchhoff] did the thing first, that they first observed the phenomenon with the due care & exactitude necessary in order that it might become the basis of a new system of analysis is perfectly correct (10).

Roscoe maintained that even though Bunsen and Kirchhoff knew of the work of their predecessors (a doubtful statement, in fact) it had not influenced their work since it had been full of errors and mistakes.

W. A. Miller implicitly objected to this account in an address to the 1861 meeting of the British Association in Manchester when he commented that

> like all other great discoveries, it [spectro-chemical analysis] was not the work of one individual. It was a work in which, he [Miller] was proud to say, their own countrymen had taken a prominent part, and many of the members of the British Association had laid the foundations of our knowledge of this point (11).

He then proceeded to give an account of the numerous scientists, modestly omitting himself, who had worked on line spectra in one way or another prior to Bunsen and Kirchhoff. W. A. Miller was well aware of the existence of the different types of spectra which had been studied. He suggested in this address, and, much more explicitly in a later lecture (12), that the study of spectra had been undertaken in four distinct areas: the study of the Fraunhofer lines, absorption spectra, flame spectra and spark spectra. He discussed, sometimes at great length, the contributions made by individual scientists to each of these studies; in all cases he emphasised the rôle that each scientist had played in recognising which spectral lines belonged to which

chemical element. This he did at the cost of ignoring what each scientist had wanted to achieve by his study of spectra.

This concentration on only spectro-chemical analysis when discussing the history of spectroscopy by both Crookes and W. A. Miller is understandable when it is remembered that their own contributions to spectral studies prior to 1859 had been in this field. They did not perceive that other early spectral studies had been directed towards reconciling the undulatory theory of light with the phenomena of absorption, or in examining the nature of the spark, but not towards devising a method of chemical analysis. Although W. A. Miller's spectral work had been bound up with the theoretical problems surrounding the interaction of matter and light, he had attempted to devise a system of chemical analysis using spectra. But the theories with which he had to work had not been sufficiently explicit or consistent for him successfully to devise a practical method of spectro-chemical analysis. He had had the idea of spectro-chemical analysis and he thought, quite naturally, that Bunsen and Kirchhoff's work was the ultimate step in a process of spectro-chemical studies stretching back forty years.

It was this view that Kirchhoff repudiated in his own paper on the history of spectro-chemical analysis (13). By the time Kirchhoff published this paper he must have thought that the whole debate on the history of spectroscopy had got out of hand, since he went through the work of most of his predecessors, so far as spectro-chemical analysis was concerned, pointing out, in no uncertain manner, where they had gone 'wrong'. For example, in the case of W. A. Miller's spectral drawings; which had been highly praised by Crookes at Bunsen's expense (14), Kirchhoff said that he had

> laid Prof. [W. A.] Miller's diagrams before numerous persons conversant with the special spectra, requesting them to point out the drawing intended to represent the spectrum of strontium, barium, and calcium respectively, and that in no instance have the right ones been selected (15).

There were in effect two views of the history of spectro-chemical analysis. These were the W. A. Miller-Crookes version which said that Bunsen and Kirchhoff's work was the culmination of forty years of continuous effort, and the Roscoe-Kirchhoff view which maintained that Bunsen and Kirchhoff's work had been more or less completely independent of the work of their predecessors, because this had contained so many errors as to be useless. The fundamental difference between Roscoe and Kirchhoff and their protagonists therefore lay in their assessment of this early work on spectra. Was it full of mistakes which rendered this work useless, or were these mistakes necessary steps in the development of the method? I would suggest that W. A. Miller and Crookes adopted the latter approach for two reasons. Firstly they had both done work on spectro-chemistry before 1859, although Crookes did not emphasise his work, in which the idea that chemical elements possessed uniquely characteristic spectra was certainly present. They therefore felt that Bunsen and Kirchhoff had simply shown that this idea would work in practice. Secondly there were distinct nationalistic overtones to both Crookes's and W. A. Miller's comments on earlier work: British scientists had done it first. Although W. A. Miller had received his chemical training in Germany, and Crookes had effectively received a German chemical training in Britain, neither of them had the loyalty towards Heidelberg which Roscoe did, and consequently they could put forward the claims of British scientists at the expense of Bunsen's work, which Roscoe would not do. Despite these differences in approach, both sides in the debate assumed that because Bunsen and Kirchhoff had established that spectro-chemical analysis was the important aspect of spectral studies, then those scientists who had in the past worked on line spectra must have also been searching for a method of qualitative chemical analysis.

This priority debate shows that it was realised at that time that Bunsen's and Kirchhoff's work had placed spectro-chemical analysis on a secure footing - there would obviously have been no necessity to claim priority over them if their work was not perceived to be important and successful. This historical debate did not play a rôle in persuading scientists to accept the validity of Bunsen and Kirchhoff's work; the fact that it took place at all indicates that their work was already fully accepted and that their predecessors were attempting to take some share of the credit for their discovery. The fact that it took place also indicates that it was perceived by both sides that Bunsen and Kirchhoff's work represented some sort of discontinuity in the development of spectral studies. To the supporters of Bunsen and Kirchhoff their work represented the establishment of spectro-chemical analysis on a secure basis upon which all future spectral work could be conducted. The attitude of those who opposed this view was that while Bunsen and Kirchhoff had placed spectro-chemical analysis on a secure basis, their work had been the culmination of forty years of effort towards this goal and that they had finally achieved what had been sought for so long. Thus this historical debate signalled, in the clearest possible manner, that the study of spectra had undergone a fundamental change, but it was not perceived by the participants in the debate what precisely this change was.

In the process of the debate the participants, on both sides, had shifted some of the earlier work on line spectra out of the context of the physical problems in which such studies had been conducted, into the context of spectro-chemical analysis. In other words the debate effectively rewrote the history of spectroscopy by changing the emphasis of the study of line spectra from physics, which it had been, to chemistry, which it had not been. Such was the effect that this debate had on people's perception of the development of spectral studies that line spectra were almost thought of as a tool which had been available

to chemists for some considerable time, but not used. As Edward Frankland put it:

> I have recently read, with very great interest, the beautiful researches which Dr. [W. A.] Miller made some sixteen years ago upon this very subject. It is really wonderful that sixteen years ago we had the real pith of the whole of this matter thrown before us, but up to the present time we have been unable to use it (16).

In the final sentence Frankland effectively admitted, but failed to perceive that he had done so, why W. A. Miller's work had not been successful: "we have been unable to use it". It was the utilisation of spectral lines which ultimately counted as far as chemistry was concerned, not the theory. It was the chemical context in which Bunsen and Kirchhoff conducted their spectral research, i.e. the desire for an optical method of chemical analysis, which manifested itself in the 1850s, which led Bunsen and Kirchhoff to ask the appropriate questions of the phenomena. Their work was not the transfer of a body of physical knowledge to chemistry, as W. A. Miller's work was. Their problem arose from chemistry and they solved it largely within their chemical context.

As a result of the debate, by the early 1860s spectroscopy was perceived as a topic which had belonged to chemistry as well as to physics. But the accounts of its developments were initiated by chemists, and they were therefore biased towards the chemical side of the subject. The implication was that the development of spectroscopy had been the development of spectro-chemical analysis. In the accounts of the development of the spectro-chemical analytical technique the rôles which the physical problems had played were therefore ignored. Thus those scientists who wrote on the history of spectroscopy - Crookes, W. A. Miller, Roscoe, Kirchhoff - could take passages out of context from earlier work and then wonder why spectro-chemical analysis had not been developed years earlier. They did not perceive that those scientists who had worked on, for example, the problem of the absorption of light in the 1830s had concerned themselves successfully

(on their own terms) with a problem which was not chemical in nature. These scientists who wrote the history of spectroscopy as the history of spectro-chemical analysis therefore characterised this earlier work as a 'failure' because those earlier scientists had not attempted to answer the questions concerning spectra which the historians were interested in (17).

One reason, I would suggest, apart from natural chemical bias, that these historians did not realise the significance, or even the existence of the physical problems which spectra had been originally used to solve, was that by the 1860s scientists were so used to thinking in terms of the undulatory theory or in terms of thermodynamics that they failed to perceive the profound changes which these subjects had wrought in the study of spectra. Similarly they did not appreciate the rôle which solar theories had played in guiding the development of spectral theories. Without the realisation of the rôles which each of these subjects had played in the development of spectroscopy it was almost inevitable that the chemical view of the development of spectroscopy would come to predominate.

The sciences of spectroscopy and astrophysics did not suddenly make their appearance in 1859 with Bunsen and Kirchhoff's work. Nor did they emerge as a result of a continuous process of elaboration of spectral studies stretching back to Fraunhofer and developing independently of any but a self-contained scientific context, as the early historians of spectroscopy would have us believe. Rather these sciences were a response to problems caused by the developments in physical theories during the first half of the nineteenth century (i.e. the undulatory theory, the theory of electricity and thermodynamics). Spectra had been used in a variety of ways to solve these problems and they had provided answers to questions which had been asked. What was the structure of an absorbing medium? What was the nature of the spark? And so on. Thermodynamics affected the study of spectra in two ways. Firstly thermodynamics had led to the establishment of new theories of spectra,

and ultimately to Kirchhoff's radiation law, and secondly, it had forced scientists to view the sun in a completely different way, so that new solar theories were devised which in turn had their own effect on spectral studies.

All this was missed by the early historians of spectroscopy because they were interested in only one aspect of the problem: spectro-chemical analysis. Chemists had taken spectra to be part of their own subject in a comparatively short period of time (some two years) and they wanted to provide a history of the subject. This they did and the physicists, such as Kirchhoff, acquiesced in the basic assumption that the history of spectroscopy was the history of spectro-chemical analysis. Even Stokes, usually very perceptive in these matters, accepted this assumption in a letter to Plücker, before the debate had got under way:

> Chemists must learn to deal more with optical methods than has hitherto been the case (18).

This implies that Stokes thought that it had been possible for chemists to use spectroscopic analysis before Bunsen and Kirchhoff. This was not so, for it was not until the latter half of the 1850s that the questions which could produce a method of qualitative chemical analysis using light were asked; after that time chemists could, and did, successfully use an optical method of chemical analysis.

This was the best possible answer which could be given to Brewster's criticism that the undulatory theory of light was not a physically valid representation of optical phenomena. Line spectra had been shown to be uniquely characteristic of ponderable matter. According to Brewster, who was one of the few people who kept silent during the historical debate, this should not have been possible if the undulatory theory was physically invalid. But it had been done and the undulatory theory was, once again, vindicated. It is difficult to assess how large a rôle work on spectra played in changing the undulatory theory from the mathematically abstract theory of Fresnel's into the physical theory it became, since there were so many other optical researches in the first half of the

nineteenth century which also tended to show that the theory was physically valid. But the study of spectra was an area where it became apparent that light waves were 'real' and could therefore be used, as Fresnel had predicted they would be, to examine the nature of matter.

Appendix

THE MATHEMATICAL PROOF OF KIRCHHOFF'S LAW OF RADIATION

Kirchhoff let e & a and E & A be the emissivity and absorptivity of c & C respectively at wave-length Λ. Now if C emits an amount E of radiation, this will be absorbed and emitted between the two plates in ever diminishing quantities. The amount absorbed by c & C is in turn:

c	C
aE	
$a(1-A)(1-a)E$	$A(1-a)E$
$a(1-A)^2(1-a)^2E$	$A(1-A)(1-a)^2E$
$a(1-A)^3(1-a)^3E$	$A(1-A)^2(1-a)^3E$
.	.
.	.
.	.

which sum to

$\frac{aE}{1-k}$	$\frac{A(1-a)E}{1-k}$

where $k = (1-a)(1-A)$

Now if c emits an amount e of radiation, then the consequent absorption of it by C & c is as follows

c	C
	eA
$e(1-A)a$	$e(1-A)(1-a)A$
$e(1-A)^2(1-a)a$	$e(1-A)^2(1-a)^2A$
$e(1-A)^3(1-a)^2a$	$e(1-A)^3(1-a)^3A$
.	.
.	.
.	.

which sum to

$\frac{e(1-A)a}{1-k}$	$\frac{eA}{1-k}$

In the case of c: when the system is in equilibrium, the condition that it remains at constant temperature is

$$e = \frac{aE}{1-k} + \frac{e(1-A)a}{1-k}$$

$$\therefore \frac{e}{a} = \frac{E}{A}$$

In the case of C: when the system is in equilibrium, the condition that it remains at constant temperature is

$$E = \frac{eA}{1-k} + \frac{A(1-a)E}{1-k}$$

$$\therefore \frac{E}{A} = \frac{e}{a}$$

NOTES AND REFERENCES

When a paper or a book is first cited full bibliographic details are given. In subsequent citings short titles are employed with partial bibliographic information.

For journal abbreviations I have generally adopted the conventions used in the "Royal Society Catalogue of Scientific Papers" (12 vols, London, 1867-1902) and in M. Whitrow (ed) "ISIS Cumulative Bibliography" (5 vols, London, 1971-).

Manuscript abbreviations are as follows:

DM		Deutsches Museum, Munich
GUL		Glasgow University Library
RS		Royal Society
	HS	John Herschel's papers
	Ph	Photostats
	PT	Manuscripts of Phil. Trans. papers
	RR	Referees reports
RSC		Royal Society of Chemistry
SM		Science Museum
ULC		University Library Cambridge

NOTES AND REFERENCES TO CHAPTER ONE

The physical interpretation of the undulatory theory of light

1 D. Brewster "Observations on the absorption of specific rays, in reference to the undulatory theory of light" Phil. Mag. 1833, 2:360-63, p361 Brewster's emphasis.

2 David Brewster (1781-1868). No modern biography, scientific or otherwise exists of Brewster. But for a philosophical and methodological analysis of his views on the undulatory theory of light see E. W. Morse "Natural Philosophy, Hypotheses and Impiety: Sir David Brewster Confronts the Undulatory Theory of Light" (University of California (Berkeley) Ph.D. thesis, 1972). For a shorter discussion of Brewster's attitude towards hypotheses see R. Olson "Scottish Philosophy and British Physics 1750-1880" (Princeton 1975) especially p177-88.

3 George Biddell Airy (1801-1892), later Astronomer Royal. The main source for Airy's life is W. Airy (ed) "Autobiography of Sir George Biddell Airy" (Cambridge, 1896).

4 G. B. Airy "Remarks on Sir David Brewster's paper "On the Absorption of Specific Rays &c"" Phil. Mag. 1833, 2:419-24.

5 G. B. Airy to J. F. W. Herschel 16 July 1833 RS MS HS 1.49. Brewster was editor of the Edinburgh Journal of Science. The book to which Airy referred was D. Brewster "A treatise on optics" (1st ed, London, 1831). Richard Potter (1799-1886) was later professor of natural philosophy and astronomy at University College, London.

6 It is not the purpose of this discussion either to give a detailed account of the development of the undulatory theory of light, or to examine the long and bitter debate between the supporters of the undulatory and the particulate theories. For a discussion of these aspects see V. Ronchi "The nature of light" (London, 1970; first published in Italian in 1939) esp. chapter 7. G. Cantor "The history of 'Georgian' optics" Hist Sci. 1978, 16:1-21 and "The reception of the wave theory of light in Britain: A case study illustrating the role of methodology in scientific debate" Hist. Stud. Phys. Sci. 1975, 6:109-132. E. Frankel "Corpuscular optics and the wave theory of light:

Notes and references to Chapter 1 (cont.)

The science and politics of a revolution in physics" Social Stud. Sci. 1976, 6:141-84. E. Mach "The principles of physical optics: An historical and philosophical treatment" (London, 1926).

7 Leonhard Euler (1707-1783). Most of Euler's writings are published in "Leonhardi Euleri Opera Omnia" (3 series Berlin, Göttingen, Leipzig, Heidelberg, Zürich, 1911-). This will be cited as Opera Omnia.

8 Thomas Young (1773-1829). Most of Young's writings are published in G. Peacock & J. Leitch (eds) "Miscellaneous Works of the Late Thomas Young" (3 vols London 1855). This will be cited as Works. The best life of Young remains G. Peacock "Life of Thomas Young" (London 1855). For a valuable discussion of Young's early optical work see K. A. Latchford "Thomas Young and the Evolution of the Interference Principle" (University of London (Imperial College) Ph.D. thesis, 1974). For a discussion of Young's aether see G. Cantor "The Changing Role of Young's Ether" Brit. J. Hist. Sci. 1970, 5:44-62.

9 Augustin Jean Fresnel (1788-1827). Most of Fresnel's writings are published in H. de Senarmont, E. Verdet & L. Fresnel (eds) "Oeuvres Complètes d'Augustin Fresnel" (3 vols Paris 1866-1870; New York 1965). This will be cited as Oeuvres. For a study of Fresnel and his effect on science see R. H. Silliman "Fresnel and the Emergence of Physics as a Discipline" Hist. Stud. Phys. Sci. 1974, 4:137-162.

10 It was not until the 1830s that the spelling of aether became standardised in this form; until that time both aether and ether were used interchangeably. There appears to be no particular significance attached when one spelling was used in preference to the other. In my discussion I will use aether consistently except where necessity dictates in quotations.

11 L. Euler "Lettres a une Princesse d'Allemagne" Opera Omnia 3rd series, vols 11 & 12 ed by A. Speiser (Zürich 1960). Originally published St. Petersburg 1758. Translated into English by H. Hunter as "Letters of Euler to a German Princess" (2 vols London 1795). Letter 20, I, 89. Euler's emphasis.

12 L. Euler "Nova Theoria Lucis et Colorum" Opera Omnia 3rd series, volume 5, "Commentationes Opticae" volume 1 ed by D. Speiser (Zürich 1962) p1-45. Originally published in L. Euler "Opuscula Varii Argumenti" 1746, 1:169-244.

Notes and references to Chapter 1 (cont.)

13 ibid art 113. Quemadmodum ergo corda tensa a sono ei, quem ea edit, aequali vel consono concitatur, ita particulae illae minimae in superficie corporis opaci sitae, a radiis eiusdem vel similis indolis contremiscere pulsusque undique diffundendos producere valebunt. Radii itaque lucis, quoniam omnis generis pulsus, ratione frequentiae, involvunt, omnes corporum opacorum particulas ad motum ciebunt; etiamsi enim non eadem pulsuumfrequentia in radiis insit, tamen dummodo fuerit duplo, triplove maior vel minor, tremorem etsi debiliorem inducet.
Translated by Prof. A. R. Hall.

14 T. Young "Outlines of Experiments and Enquiries respecting Sound and Light" Phil. Trans. 1800: 106-50; Works I: 64-98.

15 ibid 78-83

16 ibid 79

17 ibid 79-83

18 T. Young "On the Theory of Light and Colours" Phil. Trans. 1802: 12-48; Works I: 140-169. His first Bakerian lecture was "On the Mechanism of the Eye" Phil. Trans. 1801: 23-88; Works I: 12-63.

19 T. Young "On the theory of light"
1st hypothesis Works I: 142
2nd hypothesis Works I: 143
3rd hypothesis Works I: 144
4th hypothesis Works I: 147

20 T. Young "Experiments and calculations relative to physical optics" Phil. Trans. 1804: 1-16, Works I: 179-191, p188.

21 T. Young "An Account of some cases of the Production of Colours not hitherto described" Phil. Trans. 1802: 387-397; Works I: 170-78, p170.

22 See K. A. Latchford "Thomas Young" esp p130-3 & 169-70.

23 T. Young "Dr. Young's reply to the Animadversions of the Edinburgh Reviewers, on some papers published in the Philosophical Transcations" (London 1804) Works I: 192-215, p202.

24 T. Young "Outlines of Experiments" Works I: 83-5

Notes and references to Chapter 1 (cont.)

25 T. Young "Production of Colours" Works I: 172-3

26 T. Young "On the Theory of Light" Works I: 160-3

27 ibid 163

28 T. Young "Production of Colours" Works I: 173-4

29 T. Young "On the Theory of Light" Works I: 164-6. For a discussion of this aspect of Young's work see K. A. Latchford "Thomas Young" p180-5.

30 A. J. Fresnel "Mémoire sur la Diffraction de la Lumière" Mém. Acad. Sci. 1821-2 [published 1826] 5: 339-475; Oeuvres I: 247-382.

31 For an account of the award of the prize and of the publication of Fresnel's paper see R. Fox "The rise and fall of Laplacian Physics" Hist. Stud. Phys. Sci. 1974, 4: 89-136, p112-4 and the notes contained therein.

32 A. J. Fresnel "Diffraction" Oeuvres I: 278-80. The reference to Berthollet and Malus has not been traced.

33 ibid 287-8

34 Siméon-Denis Poisson (1781-1840). See R. Fox "Laplacian Physics" Hist. Stud. Phys. Sci. 1974, 4: 113-4 for Poisson's possible rôle as a judge of Fresnel's paper.

35 Dominique François Jean Arago (1786-1853). Most of Arago's papers were collected in J. A. Barral (ed) "Oeuvres complètes de François Arago" (17 vols, Paris, 1854-62). This will be cited as Oeuvres.

36 See D. F. J. Arago "Rapport fait par M. Arago à l'Académie des Sciences, au nom de la Commission qui avait été chargée d'examiner les Mémoires envoyés au concours pour le prix de le diffraction" Ann. Chim. 1819, 11: 5-30; A. J. Fresnel Oeuvres I: 229-37. This is Arago's report on Fresnel's paper for the prize commission of which he was a member. On ibid 236 he reports Poisson's prediction and his experimental verification.

Notes and references to Chapter 1 (cont.)

37 A. J. Fresnel and D. F. J. Arago "Mémoire sur l'Action que les rayons de lumière polarisée exercent les uns sur les autres" Ann. Chim. 1819, 10: 288-306; Fresnel Oeuvres I: 509-22, p521 Dans les mêmes circonstances où deux rayons de lumière ordinaire paraissent mutuellement se détruire, deux rayons polarisés en sens contraires n'exercent l'un sur l'autre aucune action appréciable. Fresnel's and Arago's emphasis.

38 A. J. Fresnel "Second Mémoire sur la Double Réfraction" (written 1822) Mém. Acad. Sci. 1827, 7: 45-176; Oeuvres II: 479-596. Translated into English (by A. W. Hobson) as "Memoir on double refraction" Taylor's Sci. Mem. 1852, 5: 238-333, p244

39 Young had privately proposed in 1817 that light had a "minute" transverse component which would account for polarisation. See Young to Arago 12 January 1817 Works I, 380-4, where he further commented that "in a physical sense, it [the transverse component] is almost an evanescent quantity, although not in a mathematical one". Young published this suggestion in his article "Chromatics" in "Supplement to the fourth, fifth and sixth editions of the Encyclopaedia Britannica" (6 vols, Edinburgh, 1824) III, 141-63, Works I: 279-342, p332-3. This was written in September 1817 (Works I, 279.)

40 A. J. Fresnel "Double Refraction" Taylor's Sci. Mem. 1852, 5: 243-4.

41 ibid 249

42 ibid

43 ibid 243

44 ibid

45 ibid 258

46 ibid 261

47 ibid 262

48 T. Thomson "A System of Chemistry" (5th ed. 4 vols London, 1817). Translated into French, with a supplement, (by J. Riffault) as "Système de Chimie" (5 vols, Paris 1818-1822). Fresnel's essay in the

supplement was "De la Lumière" Oeuvres II: 3-146. This was translated into English (by Thomas Young; see footnote A. J. Fresnel "Double Refraction" Taylor's Sci. Mem. 1852, 5: 264) as "Elementary view of the Undulatory Theory of Light" Quart. J. Sci. 1827, 23: 127-141, 441-454; 24: 113-135, 431-448; 1828, 25: 198-215; 26: 168-191, 389-407; 1829, 27: 159-165.

49 ibid 1829, 27: 162

50 D. F. J. Arago "Notice sur la Polarisation de Lumière" Oeuvres VII, 291-449. This appears not to have been published in French until it was published here. However, Young translated a manuscript copy as "Refraction, double, and Polarisation of Light" in "Addenda et Corrigenda" to the "Supplement to the fourth, fifth and sixth editions of the Encyclopaedia Britannica" VI, 838-863. Young's addition was entitled "Theoretical investigations intended to illustrate the phenomena of polarisation" ibid 860-3, Works I, 412-17.

51 ibid 415 Young's emphasis

52 ibid 416-7

53 See H. Lloyd "On the Phenomena presented by Light in its Passage along the Axes of Biaxial Crystals" Phil. Mag. 1833, 2: 112-120, 207-10 where he reports Hamilton's prediction and his own experimental verification of it. Hamilton app ars to have made this prediction by considering mathematically how a ray of light obeying Fresnel's equations would behave on entering various crystals. For details see R. P. Graves "Life of Sir William Rowan Hamilton" (3 vols, Dublin, 1882-9) I, 623-38 and G. Sarton "Discovery of conical refraction by William Rowan Hamilton and Humphrey Lloyd (1833)" ISIS 1932, 17: 154-71.

54 For a discussion of this point see E. W. Morse "Natural philosophy, hypotheses and impiety".

55 D. Brewster "Observations on the absorption of specific rays" Phil. Mag. 1833, 2: 361

56 D. Brewster to H. Brougham 21 February 1849 University College, London, Brougham papers 26, 638.

Notes and references to Chapter 1 (cont.)

57 John F. W. Herschel (1792-1871). In this thesis mention of any other Herschel will always be signified by the use of their initials. For an account of Herschel's life see G. Buttmann "The shadow of the telescope: A biography of John Herschel" (London, 1970)

58 J. F. W. Herschel "Preliminary discourse on the study of natural philosophy" (London, 1831) art. 291. For a somewhat hostile criticism of Herschel's philosophical position see J. Agassi "Sir John Herschel's philosophy of success" Hist. Stud. Phys. Sci. 1969, 1: 1-36.

59 The title "Essay on light" is now so prevalent that I will continue to use it. The proper title is "Light" and the article appeared in the Encyclopaedia Metropolitana 1828, 2: 341-586. Herschel dated the Essay "Slough December 12, 1827".

60 ibid art. 952.

NOTES AND REFERENCES TO CHAPTER TWO

Experiments on, and observations of, emission and absorption spectra to 1830

1 See, for example, A. J. Fresnel "Diffraction" Oeuvres I: 264, where he describes the necessity to use homogeneous light in diffraction experiments.

2 Joseph von Fraunhofer (1787-1826). There is a considerable amount of literature on Fraunhofer mainly concerned with his work on practical optics. In particular the following are useful: Gunter D. Roth "Joseph von Fraunhofer" (Grosse Naturforscher 39) (Stuttgart 1976); Anon. (but probably D. Brewster) "Memoir of the Life of M. Le Chevalier Fraunhofer, the Celebrated Improver of the Achromatic Telescope, and Member of the Academy of Sciences at Munich" Edinb. J. Sci. 1827, 7:1-11. Reprinted in Am. J. Sci. 1829, 16: 304-13.

3 J. v. Fraunhofer "Bestimmung des Brechungs- und Farbenzerstreuungs - Vermögens verschiedener Glasarten, in Bezug auf die Vervollkommnung achromatischer Fernröhre" Denksch. königl. Akad. Wiss. München 1814-15 [published 1817] 5: 193-226. Translated into English as "On the Refractive and Dispersive Power of different Species of Glass, in reference to the improvement of Achromatic Telescopes, with an Account of the Lines or Streaks which cross the Spectrum" Edinb. Phil. J. 1823, 9: 288-99; 1824, 10: 26-40.

4 Pierre Guinand (c. 1748-1823). For an account of his life see E. R. "Notice sur feu Mr. Guinand, Opticien" Bib. Univ. Gen. 1824, 25: 142-58, 227-36. Translated into English (by C. P. d. B.) as "Some account of the late M. Guinand and of the important discovery made by him in the manufacture of flint glass for large telescopes" (London, 1825). Reviewed (anonymously) in Edinb. J. Sci. 1825, 2: 348-54.

5 Joseph von Utzschneider (1763-1840). For an account of the firm, see W. H. S. Chance "The Optical Glassworks at Benediktbeuern" Proc. Phys. Soc. 1937, 49: 433-43.

6 J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. J. Sci. 1823, 9: 290

Notes and references to Chapter 2 (cont.)

7 ibid 290-1

8 ibid 291

9 ibid

10 It is not clear which particular foot Fraunhofer used, but since he did employ the Paris inch it seems reasonable to suppose that he used here the French foot = 12.8 English inches.

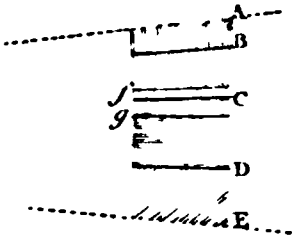
11 J. v. Fraunhofer "Refractive and dispersive power" Edinb. J. Sci. 1823, 9: 291-5

12 ibid 295

13 ibid 293

14 ibid 296 Fraunhofer's emphasis. This was not the first time that the dark lines in the solar spectrum had been observed. William Hyde Wollaston (1766-1828) had in 1802 reported his observation of a few of them in "A method of examining the refractive and dispersive powers by prismatic reflexion" Phil. Trans. 1802: 365-80, particularly p378-80. He labelled them as in fig. 1 below

fig.1



He interpreted the existence of lines A, B, C, D, E as being the boundaries between what he regarded as the four primary colours of the spectrum. Despite this paper having been translated into German as "Neue Methode die brechenden

Notes and references to Chapter 2 (cont.)

und zerstreuenden Kräfte der Körper vermittelst prismatischer Reflexion zu erforschen" Gilbert Ann. 1809, 31: 235-51, 398-416 there is no indication in any of Fraunhofer's work that he was aware of it. For a near contemporary identification of the lines observed by Wollaston see D. Brewster "Report on the recent progress of optics" Rep. Brit. Ass. 1832: 308-22, p320.

15 J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. J. Sci. 1823, 9: 296

16 ibid 298

17 J. v. Fraunhofer "Kurzer Bericht von den Resultaten neuerer Versuche über die Gesetze des Lichtes, und die Theorie derselben" Gilbert Ann. 1823, 74: 337-78. Translated into English as "A short account of the results of recent Experiments upon the Laws of Light, and its Theory" Edinb. J. Sci. 1827, 7: 101-13, 251-262; 1828, 8: 7-10, p108.

18 ibid 7

19 See J. v. Fraunhofer "Ueber die Construction des so eben vollendeten grossen Refractors" Astr. Nachr. 1824, 4: 17-24, 35-8. Translated into English as "On the construction of the large refracting telescope just completed" Phil. Mag. 1825, 66: 41-7.

20 J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. J. Sci. 1823, 9: 298

21 ibid 1824, 10: 37-8

22 J. v. Fraunhofer "Neue Modification des Lichtes durch gegenseitige Einwirkung und Beugung der Strahlen, und Gesetze desselben" Denksch. königl. Akad. Wiss. München 1821-2, 8: 1-76. (Each paper in this volume is individually paginated)

23 ibid 76. Dass dieselben Prinzipe eine Erklärung der Ursache der Entstehung der Linien und Streifen, die in dem durche ein Prisma gebildeten Farbenspectrum gesehen werden, zulassen.

24 J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. Phil. J. 1824, 10: 38

25 ibid 39

26 J. v. Fraunhofer "Experiments upon the Laws of Light" Edinb. J. Sci. 1828, 8; 7 & 9 respectively.

Notes and references to Chapter 2 (cont.)

27 ibid 9-10

28 J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. Phil. J. 1824, 10: 39

29 ibid 40

30 By June 1822 Herschel was aware of Fraunhofer's paper on diffraction (J. v. Fraunhofer "Neue Modification" Denksch. könig. Akad. Wiss. München 1821-2, 8: 1-76). Von Littrow had sent a copy of this to Herschel for which he was thanked (Herschel to v. Littrow, 25 June 1822 RS MS HS 20.145). In the July edition of the Edinburgh Philosophical Journal (partly edited by Brewster) there appeared three short reports of Fraunhofer's work Edinb. Phil. J. 1822, 7: 178-80. The following year Brewster published a translation of Fraunhofer's first paper (J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. Phil. J. 1823, 9: 288-99; 1824, 10: 26-40). From which date every paper of importance on the spectrum contains mention of Fraunhofer's work. It therefore seems reasonable to assume that Fraunhofer's work was known to neither Brewster nor Herschel until mid-1822.

31 D. Brewster "Description of a monochromatic lamp, with observations on the composition of different flames as modified by reflexion, refraction and combustion" Edinb. Phil. J. 1822, 7: 163. Fully published as "Description of a monochromatic lamp for microscopical purposes, &c. with remarks on the absorption of the prismatic rays by coloured media" Trans. Roy. Soc. Edinb. 1822, 9· 433-44.

32 J. F. W. Herschel "On the absorption of light by coloured media, and on the colours of the prismatic spectrum exhibited by certain flames; with an account of a ready mode of determining the absolute dispersive power of any medium by direct experiment" Trans. Roy. Soc. Edinb. 1822, 9: 445-60. Read on 18 November 1822, dated 24 July 1822.

33 This is not the place to give a detailed account of the development of the achromatic microscope. Suffice it to say that such microscopes had been in existence since 1791 and were produced by a large number of opticians. But they appear not to have been very good and had nly a low resolving power. In 1818 Amici built a catadioptric microscope which was achromatic; but it was not until 1837 that he built an achromatic microscope with a resolving power that was greater than that of simple microscopes. See S. Bradbury "The evolution of the microscope" (Oxford, 1967) especially chapter 5.

Notes and references to Chapter 2 (cont.)

34 D. Brewster "Observations on vision through coloured glasses, and on their application to telescopes, and to microscopes of great magnitude" Edinb. Phil. J. 1822, 6: 102-7, p103. Brewster's ignorance of Fraunhofer's work is further evinced by his citation (D. Brewster "Description of a monochromatic lamp" Trans. Roy. Soc. Edinb. 1822, 9: 441) of Wollaston's observation of the dark lines in the solar spectrum (W. H. Wollaston "Refractive and Dispersive Powers" Phil. Trans. 1802: 378-80; Brewster would have presumably referred to Fraunhofer's observations instead of, or as well as, Wollaston's observations had he known of the former.

35 D. Brewster "Description of a monochromatic lamp" Trans. Roy. Soc. Edinb. 1822, 9: 438

36 ibid 440

37 For an account of these aspects of Brewster's work see P. D. Sherman "Problems in the theory and perception of colour: 1800-1860" (University of London (Imperial College) Ph.D. thesis 1971).

38 Thomas Melvill (1726-1753) was a Scottish experimental philosopher who studied at the University of Glasgow. For a short account of his life see Patrick Wilson "Biographical Account of Alexander Wilson, M.D., Late Professor of Practical Astronomy in Glasgow" Edinb. J. Sci. 1829, 10: 1-17, p5-8.

39 D. Brewster "Description of a monochromatic lamp" Trans. Roy. Soc. Edinb. 1822, 9: 435. T. Melvill "Observations on light and colours" read to the Medical Society of Edinburgh 3 Jan & 7 Feb 1752 in Essays and Observations, Physical and Literary 1756, 2: 12-90. The relevant observation being on p35.

40 D. Brewster "Description of a monochromatic lamp" Trans. Roy. Soc. Edinb. 1822, 9: 435-6.

41 ibid 437

42 D. Brewster "Account of a New Monochromatic Lamp depending on the combustion of Compressed Gas" Edinb. J. Sci. 1829, 1: 108.

43 J. F. W. Herschel "On the action of crystallized bodies on homogeneous light, and on the causes of the deviation from NEWTON'S scale in the tints which many of them develop on exposure to a polarized ray" Phil. Trans. 1820: 45-100.

Notes and references to Chapter 2 (cont.)

44 D. Brewster "Description of a monochromatic lamp" Edinb. Phil. J. 1822, 7: 163

45 J. F. W. Herschel "On the absorption of light" Trans. Roy. Soc. Edinb. 1822, 9:446

46 ibid 454

47 ibid 455-8

48 W. H. Fox Talbot (1800-1877). For an account of his life see H. J. P. Arnold "William Henry Fox Talbot: Pioneer of Photography and Man of Science" (London, 1977)

49 W. H. F. Talbot "Some experiments on coloured flames" Edinb. J. Sci. 1826, 5: 77-81; reprinted in Chem. News. 1861, 3: 261-2.

50 W. H. F. Talbot "Some experiments on coloured flames" Edinb. J. Sci. 1826, 5: 81.

51 Talbot to Herschel 27 March 1833 RS MS HS 17.270.

52 Talbot, although he had visited Fraunhofer, does not seem to have been aware of the double nature of the yellow line.

53 W. H. F. Talbot "Some experiments on coloured flames" Edinb. J. Sci. 1826, 5: 81.

54 ibid 79

55 ibid

56 ibid Talbot's emphasis

57 ibid

58 ibid 81

59 ibid Talbot's emphasis

60 ibid Talbot referred to Herschel's work so far as strontium was concerned

61 ibid

62 Talbot to Herschel 22 May 1827 RS MS HS 17.263; he did not publish this observation until some time later "Facts relating to optical science No. I" Phil. Mag. 1834, 4: 112-4, art 6 "On the flame of cyanogen" p114.

Notes and references to Chapter 2 (cont.)

63 Unfortunately we do not have an explicit statement of Herschel's view on the nature of the sun until 1834 (J. F. W. Herschel "A treatise on astronomy" (London, 1834) arts 330-7). But it seems from his comments in his "Essay on Light" that the views he expressed in 1834 were not dissimilar from those which he held at this period.

64 J. F. W. Herschel "Astronomy" art 334

65 J. F. W. Herschel "Essay on Light" art 505

66 Herschel knew of Talbot's paper because he had communicated it to Brewster for publication. Talbot to Herschel July 1826 RS MS HS 17.261.

67 J. F. W. Herschel "Essay on Light" art 524. Those flame colours which had not been published by others or himself prior to their appearance in his "Essay" Herschel later said had been discovered by himself (see Herschel to Tyndall 21 July 1861 RS MS HS 23.335). It is curious that in this list Herschel omitted the flame of sulphur; this may well have been due to Talbot's suggestion about the respective specific gravities of water and sulphur. Lithium was not isolated until 1855 (by Bunsen), but various of its salts had been noted by 1827.

68 J. F. W. Herschel "Essay on Light" art 524.

69 ibid

70 ibid art 814

71 ibid art 746 Herschel's emphasis

72 ibid art 755 Herschel's emphasis

73 ibid

74 T. Young "Théorie des couleurs observées dans les expériences de Fraunhofer" Ann. Chim. 1829, 40: 178-83. Translated into English as "Theory of the colours observed in the experiments of Fraunhofer" Edinb. J. Sci. 1829, 1: 112-6. Apart from discussing the problem in this paper Young also discussed it in a set of letters to Herschel in mid-1828 the following of which are of interest:

4 May 1828	RS MS HS 18.343
13 May 1828	RS MS HS 18.339
late May 1828?	RS MS HS 18.342

The last letter is merely dated "Thursday night" but its contents follow in sequence the other two letters the dates of which can be established from the postmarks. Unfortunately no replies from Herschel have been traced.

75 Young to Herschel late May 1828? RS MS HS 18.342, Young's emphasis.

76 Young to Herschel 13 May 1828 RS MS HS 18.339. Quite what Young had read of Fourier is not clear. But functions such as the one which Young proposed were common in Fourier's work.

77 T. Young "Theory of the colours" Edinb. J. Sci. 1829, 1: 115-6.

NOTES AND REFERENCES TO CHAPTER THREE

The debate on the nature of absorption 1830-1835 and its chemical consequences

1 A. J. Fresnel "Elementary View" Quart. J. Sci. 1829, 27: 161

2 See chapter 2, p31 and P. D. Sherman "Problems in the Theory and Perception of Colour"

3 D. Brewster "Observations on the Lines of the Solar Spectrum, and on those produced by the Earth's Atmosphere, and by the action of Nitrous Acid Gas" Trans. Roy. Soc. Edinb. 1834, 12: 519-30, p519

4 ibid 520

5 ibid 520/1

6 ibid 521 Brewster's emphasis

7 D. Brewster "Report on the recent progress of optics" Rep. Brit. Ass. 1832: 308-22, p321. Here should be noted a curious discrepancy in Brewster's observational technique. In the case of nitrous acid gas he observed the existence of the absorption lines, whereas in the case of iodine, where there also exists a large number of lines, he only noted that the middle of the spectrum tended to be absorbed. Brewster might well have used a different prism for his latter observations; I can think of no other experimental reason.

8 See Talbot to Herschel 27 March 1833 RS MS HS 17.270 where Talbot comments that it was a "twelvemonth" since Brewster had told him about the discovery.

9 D. Brewster "Observations on the lines of the solar spectrum" Trans. Roy. Soc. Edinb. 1834, 12: 521.

10 D. Brewster "Report" Rep. Brit. Ass. 1832: 319

11 See for example D. Brewster "On the laws of the Polarisation of Light by Refraction" Phil. Trans. 1830: 69-84, 133-44.

12 D. Brewster "A treatise on Optics" (1st ed London, 1831)

13 ibid p135

14 See E. W. Morse "Natural Philosophy, Hypotheses, and Impiety" p189-90 for a discussion of this point.

Notes and references to Chapter 3 (cont.)

15 See chapter 1

16 D. Brewster "Report" Rep. Brit. Ass. 1832: 321 Brewster's emphasis.

17 ibid 321-2

18 Talbot to Herschel 27 March 1833 RS MS HS 17.270

19 ibid Talbot makes it quite clear that Brewster had informed him. Whether Brewster had informed Herschel is problematical since by that time Herschel and Brewster had seriouly disagreed over the decline of science question (see Herschel to Daubeny 25 February 1832 RS MS HS 21.102 and S. F. Cannon "Science in culture: The early Victorian period" (New York, 1978) chapter 6) from which time Brewster's and Herschel's correspondence effectively ceased.

20 John Frederic Daniell (1790-1845), professor of chemistry at King's college London between 1831 and 1845.

21 William Hallowes Miller (1801-1880), professor of mineralogy at Cambridge.

22 A week after Brewster had announced the name of the gas to the Royal Society of Edinburgh on 15 April 1833 (see note 3) W. H. Miller read to the Cambridge Philosophical Society on 22 April a paper detailing the work he and J. F. Daniell had done on absorption spectra of light passing through bromine vapour, iodine vapour, chlorine, euchlorine (Cl_2O_7) and vapour of indigo ("On the effect of light on the spectrum passed through coloured gases" Phil. Mag. 1833, 2: 381-2). He made it quite clear that their work was derived from Brewster's work and that they knew the name of the gas in which Brewster had observed the phenomena. It would thus appear that they held back their work until they knew that Brewster had announced his.

23 See Talbot to Herschel 9 & 27 March 1833 RS MSS HS 17.269/70 and 31 May 1833 RS MS HS 17.272 where Talbot states that the substance was iodine vapour.

24 W. H. Miller "On the effect of light" Phil. Mag. 1833, 2: 381-2 reported that he and Daniell had observed that the spectrum of iodine vapour had equidistant lines. In fact, Talbot had observed (Talbot to Herschel 31 May 1833 RS MS HS 17.272) that the lines became more and more numerous towards the blue end of the spectrum.

Notes and references to chapter 3 (cont.)

25 D. Brewster "Observations on the lines of the solar spectrum" Trans. Roy. Soc. Edinb. 1833, 12: 519-30.

26 ibid 521-3

27 ibid 521

28 ibid 528

29 ibid 529

30 [D. Brewster] review of W. Whewell "Astronomy and General Physics considered with reference to Natural Theology" (3rd Bridgewater Treatise) (London 1833) Edinb. Rev. 1834, 58: 422-57, p456 where Brewster suggests that this is the case.

31 D. Brewster "Optics" p142

32 ibid and ibid 87 where he describes Fraunhofer's observations of stellar spectra. See chapter 2, p29.

33 D. Brewster "Observations on the lines of the solar spectrum" Trans. Roy. Soc. Edinb. 1833, 12: 529.

34 D. Brewster & J. H. Gladstone "On the lines of the solar spectrum" Phil. Trans. 1860: 149-60. On p158-9 they reported that Gladstone had attempted this experiment at Beachy Head but that he had not detected any lines.

35 D. Brewster "Observations on the lines of the solar spectrum" Trans. Roy. Soc. Edinb. 1833, 12: 530.

36 D. Brewster "Report" Rep. Brit. Ass. 1832: 308-22 mentions both these aspects of Brewster's work on absorption.

37 D. Brewster "Observations of the absorption of specific rays" Phil. Mag. 1833, 2: 360-3.

38 ibid 361

39 ibid 362 Brewster's emphasis

40 ibid

41 ibid 363 This passage illustrates Olson's thesis "Scottish Philosophy and British Physics 1750-1880" of the grip which analogical reasoning had on the common sense school of Scottish philosophy in which Brewster was trained.

Notes and references to Chapter 3 (cont.)

42 G. B. Airy "Remarks on Sir David Brewster's Paper" Phil. Mag. 1833, 2: 419-24

43 ibid 422

44 W. Whewell "Address to the 1833 British Association" Rep. Brit. Ass. 1833: xi-xxvi

45 ibid xv-xvii

46 ibid xvi

47 ibid xvii

48 Talbot to Herschel 31 May 1833 RS MS HS 17.272

49 ibid

50 ibid

51 ibid

52 J. Dalton "A New System of Chemical Philosophy" (2 vols, London 1808-27) I, 143-4

53 J. F. W. Herschel "On the absorption of light by coloured media, viewed in connexion with the undulatory theory". Abstract in Rep. Brit. Ass. 1833: 373-4. Full paper in Phil. Mag. 1833, 3: 401-12.

54 ibid 406

55 Robert John Kane (1809-90) then lecturer in natural history at the Royal Dublin Society. In 1845 he became director of the Museum of Economic Geology in Dublin, later the Royal College of Science for Ireland.

56 R. J. Kane "Case of interference of Sound" Rep. Brit. Ass. 1835, pt 2: 13-14

57 J. F. W. Herschel "On the absorption of light" Phil. Mag. 1833, 3: 406

58 ibid

59 J. F. W. Herschel "Essay on Light" art 505

60 J. F. W. Herschel "On the absorption of light" Phil. Mag. 1833, 3: 406-9

Notes and references to Chapter 3 (cont.)

61 ibid 407 Herschel's emphasis

62 J. F. W. Herschel "Sound" Encyclopaedia Metropolitana 1830, 2: 747-825 dated "Slough, Feb 3, 1830" This will be cited as "Essay on Sound".

63 J. F. W. Herschel "On the absorption of light" Phil. Mag. 1833, 3: 409 Herschel's emphasis. This refers to his "Essay on Sound" art 205. Herschel stated in his paper that since writing his essay he had discovered that Charles Wheatstone had made the same observation in "On the resonances or reciprocated vibrations of columns of air" Quart. J. Sci. 1828, 1: 175-83 in "The scientific papers of Sir Charles Wheatstone" (London, 1879) p36-46.

64 J. F. W. Herschel "Essay on Sound" art 323. He also restated it in "Astronomy" art 526.

65 J. F. W. Herschel "On the absorption of light" Phil. Mag. 1833, 3: 402

66 ibid 410

67 ibid

68 ibid 402 There can be little doubt that this refers to Herschel's 1822 graphs on absorption.

69 W. Whewell "Suggestions respecting Sir John Herschel's Remarks on the Theory of the Absorption of Light by Coloured Media" Rep. Brit. Ass. 1834: 550-2

70 ibid 550-1

71 ibid 551

72 ibid

73 ibid

74 ibid 552

75 Fabian Jakob von Wrede (1802-1893). I have not been able to discover much biographical detail about Wrede. He joined the army in 1818 and by 1838 was a major. He later became chief of staff of the artillery. He represented Sweden at the international metrication commission in Paris. In 1835 he was elected to the Stockholm Academy.

Notes and references to Chapter 3 (cont.)

76 F. J. v. Wrede "Försök att härleda Ljusets absorbtion från Undulations-Teorien" Kongl. Veten. Acad. Handl. 1834: 318-52. Translated into English (by W. Francis) as "Attempt to explain the absorption of light according to the undulatory theory" Taylor's Sci. Mem. 1836, 1: 477-502.

77 F. J. v. Wrede "Attempt to explain the absorption of light" Sci. Mem. 1836, 1: 478

78 ibid 476. Wrede would not have known at this time of Whewell's comments.

79 ibid 478

80 ibid 478-9

81 ibid 479-80

82 ibid 479

83 ibid

84 ibid 485

85 ibid 480-1. See chapter 1, p14 for details of Fresnel's work.

86 F. J. v. Wrede "Attempt to explain the absorption of light" Sci. Mem. 1836, 1: 485

87 ibid 487

88 D. Brewster "Observations on the lines of the solar spectrum" Trans. Roy. Soc. Edinb. 1833, 12: 521-3.

89 F. J. v. Wrede "Attempt to explain the absorption of light" Sci. Mem. 1836, 1: 488-9

90 ibid 489

91 ibid 489 & 490-1 respectively

92 ibid 501

93 ibid 489

94 ibid 489-90

95 ibid 491

96 ibid

Notes and references to Chapter 3 (cont.)

97 ibid 492

98 ibid 494

99 ibid

100 ibid 502

101 ibid

102 ibid 490

103 F. J. v. Wrede "Versuch, die Absorption des Lichts nach der Undulationstheorie zu erklären" Pogg. Ann. 1834, 33: 353-89

104 J. F. W. Herschel "On the absorption of light" Phil. Mag. 1833, 3: 410

105 W. H. Miller "On the effect of light" Phil. Mag. 1833, 2: 381-2

106 Talbot to Herschel 31 May 1833 RS MS HS 17.272

107 W. H. F. Talbot "On the nature of light" Phil. Mag. 1835, 7: 113-8, p117

108 ibid

109 ibid 117-8

110 ibid 117 Talbot's emphasis

111 W. H. F. Talbot "Facts relating to optical science No. III" Phil. Mag. 1836, 9: 1-4. "On prismatic spectra" ibid p3

112 Talbot to Herschel 31 May 1833 RS MS HS 17.272

113 W. H. F. Talbot "Facts relating to optical science. No. I." Phil. Mag. 1834, 4: 112-4 art 5. "On the flame of lithia" ibid 114

114 ibid 112-4

115 J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. J. Sci. 1823, 9: 298

116 W. H. Miller to G. G. Stokes, undated ULC MS add 7656, M561. This letter was dated by Joseph Larmor as having been written on 8 March 1854, since he placed it in the context of the Stokes-Kelvin correspondence

on spectroscopy of 1854 (see chapter 5). I would suggest that a date of 4 July 1871 was more likely since on 5 July 1871, Stokes informed Kelvin of the exact contents of W. H. Miller's letter (ULC MS add 7656, NB21, letter 42).

117 Stokes to Kelvin 7 March 1854, ULC MS add 7342, S 367, Stokes's emphasis

118 Stokes to Kelvin 8 March 1854, ULC MS add 7342, S 368

119 D. Brewster "On the luminous bands in the spectra of various flames" Rep. Brit. Ass. 1842, pt 2: 15-16, p16.

120 D. Brewster "On luminous lines in certain flames corresponding to the defective lines in the sun's light" Rep. Brit. Ass. 1842, pt 2: 15. W. H. F. Talbot "Some experiments on coloured flames" Edinb. J. Sci. 1826, 5: 81

121 D. Brewster "On luminous lines" Rep. Brit. Ass. 1842, pt 2: 15

122 D. Brewster "A treatise on optics" (4th ed, London, 1853)

123 ibid 177-9

124 ibid 178

125 D. Brewster "Observations sur le spectre solaire" Comptes Rendus 1850, 30: 578-81, p581

126 W. Whewell "Suggestions" Rep. Brit. Ass. 1834: 552

127 William Allen Miller (1817-1879) was Daniell's successor as Professor of Chemistry at King's College. For an account of some of his work see F. Trusell "William Allen Miller: Pioneer Stellar Spectroscopist" J. Chem. Ed. 1963, 40: 612-3. The similarity in name with W. H. Miller has given rise to some confusion in the history of spectroscopy despite at least one attempt to sort it out. See C. W. Adams "William Allen Miller and William Hallowes Miller" ISIS 1943, 34: 337-9

128 J. F. Daniell "An introduction to the study of chemical philosophy" (2nd edition, London, 1843)

129 ibid 336, 385 & 388 respectively

130 ibid 385

Notes and references to Chapter 3 (cont.)

131 W. A. Miller "On the action of gases on the prismatic spectrum" Rep. Brit. Ass. 1845, pt 2: 28-9

132 W. A. Miller "Experiments and observations on some cases of lines in the prismatic spectrum produced by the passage of light through coloured vapours and gases, and from certain coloured flames" Phil. Mag. 1845, 27: 81-91, p83.

133 J. F. Daniell "Introduction" p388

134 W. A. Miller "Experiments and observations" Phil. Mag. 1845, 27: 82

135 W. A. Miller "On the action of gases" Rep. Brit. Ass. 1845, pt 2: 29 Miller's use of the term "Fraunhofer lines" was idiosyncratic.

136 These were: copper, calcium, barium, sodium, magnesium, iron, zinc, cobalt, nickel, mercury.

137 W. A. Miller "Elements of chemistry" (3 vols, London 1855-7) vol. 1 "Chemical Physics"

138 ibid p136

NOTES AND REFERENCES TO CHAPTER FOUR

The study of spark spectra 1835-1859

1 Michael Faraday (1791-1867). For an account of his life and work see L. P. Williams "Michael Faraday" (London 1965). Faraday's electrical papers were collected in "Experimental Researches in Electricity" (3 vols, London, 1839-55). This will be cited as Researches followed by the series and article number. His research diary was published as "Faraday"s Diary" (7 vols and index, London, 1932-6). This will be cited as Diary followed by entry date, volume and entry number. Some of his letters were published in L. P. Williams (ed) "The selected correspondence of Michael Faraday" (2 vols, Cambridge, 1971). This will be cited as Correspondence.

2 See L. P. Williams "Michael Faraday" chapters 6 & 7 for an account of this work.

3 Charles Wheatstone (1802-1875). Professor of Experimental Philosophy at King's College London from 1834. For an account of his life and work see B. P. Bowers "The life and work of Sir Charles Wheatstone (1802-1875) with particular reference to his contributions to electrical science" (Universtiy of London (external) Ph.D. thesis 1975), which was published (minus footnotes) as "Sir Charles Wheatstone FRS 1802-1875" (London 1975). For an account of his telegraphic work see G. Hubbard "Cooke and Wheatstone and the invention of the electric telegraph" (London 1965). Most of Wheatstone's papers were collected in "The scientific papers of Sir Charles Wheatstone" (London 1879). This will be cited as Papers

4 This was a common procedure for Wheatstone to adopt (see L. P. Williams "Michael Faraday", p331). The lecture was "On the velocity and nature of electricity" Lit. Gaz March 9, 1833, p152.

5 ibid Wheatstone's emphasis

6 C. Wheatstone "An account of some experiments to measure the velocity of electricity and the duration of electric light" Phil. Trans. 1834: 583-91; Papers 84-96, p85

Notes and references to Chapter 4 (cont.)

7 ibid 90 The engraver of the circuit appears to have made an error in showing the wire to be continuous. Wheatstone makes it quite clear (ibid) that the wire was disconnected in the middle.

8 ibid 93 E. Whittaker "A history of theories of aether and electricity" (Edinburgh 1962) maintains, on p228, that this high velocity was due to the way in which Wheatstone wound the wire causing cross-induction between different parts of the wire. Dr. K. Dawson (private communication) thinks it more likely that Wheatstone's method of calculating the number of revolutions per second of the mirror from the pitch of the note which it produced was the cause of the error.

9 C. Wheatstone "On the prismatic decomposition of electrical light" Rep. Brit. Ass. 1835, pt 2: 11-12; Phil. Mag. 1835, 7: 299; Papers 223-4. This was an abstract of the paper which Wheatstone read to the Association. William Crookes reprinted this abstract in Chem. News 1861, 3: 185 adding that he would print, for the first time, the full text of Wheatstone's paper, without alteration (ibid). This Crookes did as C. Wheatstone "On the prismatic decomposition of the electric, voltaic, and electro-magnetic sparks" Chem. News 1861, 3: 198-201. The points which Wheatstone made in this full paper are the same which occur in the abstract, although they are made at considerably greater length. It seems reasonable to suppose that the paper Wheatstone published in the Chem. News was the same as that read to the 1835 British Association.

10 J. v. Fraunhofer "Refractive and Dispersive Power" Edinb. J. Sci. 1824, 10: 39

11 The pamphlet entitled "The case of Professor Charles Wheatstone in the arbitration between himself and Mr. William Fothergill Cooke" was printed in W. F. Cooke (ed) "The electric telegraph: was it invented by Professor Wheatstone?" (2 vols, London, 1856-7) II: 81-114.

12 ibid 83

13 C. Wheatstone "Prismatic decomposition" Chem. News 1861, 3: 198

14 ibid

15 C. Wheatstone "Prismatic decomposition" Phil. Mag. 1835, 7: 299.

Notes and references to Chapter 4 (cont.)

16 C. Wheatstone "Prismatic decomposition" Chem. News 1861, 3: 199

17 ibid 201

18 ibid 200

19 ibid

20 ibid

21 ibid

22 J.-B. Biot "Sur le formation de l'eau par le seule compression, et sur la nature de l'étincelle électrique" Ann. Chim. 1805, 53: 321-7. Translated into English as "Note on the formation of water by mere compression; with reflections on the nature of the electric spark" J. Nat. Phil. 1805, 12: 212-5.

23 C. Wheatstone "Prismatic decomposition" Chem. News 1861, 3: 201

24 ibid

25 A. Fusinieri "Sopra il trasporto di materia ponderabile nelle folgori" Gior. Fis. Chim. 1827, 10: 353-369. Translated into English as "On the transport of ponderable matter which occurs during electrical discharges" Elec. Mag. 1844, 1: 235-47.

26 M. Faraday Diary 3 November 1835; 2, 2554

27 M. Faraday Researches 12, 1318-1479. Read to the Royal Society on 8 February 1838.

28 ibid 1329-30.

29 M. Faraday Diary 5 January 1836; 2, 2799

30 M. Faraday Researches 12, 1421. Faraday's emphasis.

31 M. Faraday Researches 11, 1165

32 M. Faraday Researches 12, 1421

33 ibid 1406

Notes and references to Chapter 4 (cont.)

34 Jean Bernard Léon Foucault (1819-1868). For an account of Foucault's life see J. A. Chaldecott "The scientific works of Léon Foucault" (University of London (University College) M.Sc. thesis, 1949). Most of Foucault's papers are published in "Recueil des travaux scientifiques de Léon Foucault" (2 vols, Paris, 1878).

35 This paper was published under the heading "Physique. Lumière électrique" in L'Institut 1849-50, 17: 44-6 as part of the procès-verbaux of the Société Philomatique de Paris of 20 January 1849. Portions of this paper were later republished in French as "Note sur la lumière de L'Arc Voltaique" Ann. Chim. 1860, 58: 476-8. Different portions of the paper were translated into English (by G. G. Stokes) as "On the simultaneous emission and absorption of rays of the same definite refrangibility" Phil. Mag. 1860, 19: 194.

36 A.-H.-L. Fizeau and J. B. L. Foucault "Recherches sur l'intensité de la lumière émise par le charbon dans l'expérience de Davy" Comptes Rendus 1844, 18: 746-54; "Addition à une précédente Note concernant l'application des procédés daguerriens à la photographie" ibid 860-2. Translated into English as "Researches on the intensity of light emitted by the charcoal in Davy's experiment" Elec. Mag. 1845, 1: 325-32, and "Addition to a preceding note concerning the application of the Daguerrien Process to Photometry" ibid 333-5.

37 J. B. L. Foucault "Simultaneous Emission and Absorption" Phil. Mag. 1860, 19: 194.

38 ibid

39 J. B. L. Foucault "Lumière électrique" L'Institut 1849-50, 17: 45

40 ibid

41 ibid

42 A.-H.-L. Fizeau "Acoustique et optique" L'Institut 1849-50, 17: 11 was read to the Société Philomatique de Paris on 23 December 1848.

Notes and references to Chapter 4 (cont.)

43 Christian Doppler (1805-1853). For an account of Doppler's life and work see E. N. da C. Andrade "Doppler and the Doppler effect" Endeavour 1959, 18: 14-19.

44 C. Doppler "Ueber das farbige Licht der Doppelsterne und einiger anderer Gestirne des Himmels" Abh. Königl. Böhm. Ges. Wiss. 1843, 2: 465-82. In this Doppler had suggested that the colour of all stars was white, but that some appeared coloured because they were travelling towards or away from us. In this Doppler did not take into account ultra-violet and infra-red light which would have simply taken the place of any visible light of the stars which had been displaced.

45 Antoine-Philibert Masson (1806-1860) was professor of physics at the Collége Louis-le-Grand and the École Centrale des Arts et Manufactures. He wrote a set of papers in the 1840s and '50s on spark phenomena under the general title "Études de photometrie Électrique" Ann. Chim. 1845, 14: 129-95; 1850, 30: 5-55; 1851, 31: 295-326; 1855, 45: 385-454. The articles of these papers were numbered in sequence respectively 1-75, 76-106, 107-170, 171-330.

46 A.-P. Masson "Études" Ann. Chim. 1845, 14: 129-95.

47 Wheatstone's paper had been translated into French to be part of A.-C. Becquerel's "Traité Expérimental de L'Électricité et du Magnétisme et de leurs rapports avec les phénomènes naturels" (6 vols, Paris 1834-40) IV, 34-5.

48 A.-P. Masson "Études" Ann. Chim. 1851, 31: 295-326, art 119. Lorsqu'on change la nature des pôles de l'étincelle, la caractère du spectre est altéré.

49 ibid Masson's emphasis

50 ibid art 121

51 ibid art 122

52 ibid art 159. L'étincelle électrique est produite par un courant qui se propage à travers et par le matière pondérable, et l'échauffe de la même manière et suivant les mêmes lois qu'un courant voltaïque échauffe et rend lumineux un fil métallique.

Notes and references to Chapter 4 (cont.)

53 ibid art 171 footnote 1

54 ibid art 149

55 ibid art 151. Dans tous les cas possibles, la metière pondérable est nécessaire à la propagation des courants et à l'induction statique de l'électricité dans la vide. Masson's emphasis.

56 ibid. In particular he said that this agreed with M. Faraday Researches 14, 1667/8, where Faraday re-emphasised his point about the need for material entities for the transmission of electricity.

57 M. Faraday Researches 13, 1613.

58 ibid 1615

59 A.-P. Masson "Études" Ann. Chim. 1851, 31: 295-326 art 169. Le cause réelle d'un phénomène resté jusqu'ici sans explication.

60 A. J. Ångström (1814-1874). For a short account of his life see A. Beckman "Anders Jonas Ångström" in S. Lindroth (ed) "Swedish Men of Science 1650-1950" (Stockholm 1952) p193-203.

61 A. J. Ångström "Optiska Undersökningar" Kongl. Veten. Akad. Handl. 1854: 335-360. Translated into German as "Optische Untersu chungen" Pogg. Ann. 1855, 94: 141-165. Translated into English by John Tyndall see p202 of his "Six lectures on light" (5th ed, London, 1895) as "Optical Researches" Phil. Mag. 1855, 9: 327-42.

62 ibid 330

63 ibid 329

64 ibid 333

65 ibid 330

66 ibid 331

67 ibid 330

68 David Alter (1807-1881). For biographic details see W. A. Hamor "David Alter and the discovery of spectro-chemical analysis" ISIS 1935, 22: 507-10.

Notes and references to Chapter 4 (cont.)

69 D. Alter "On certain physical properties of light, produced by the combustion of different metals in the electric spark, refracted by a prism" Am. J. Sci. 1854, 18: 55-7.

70 D. Alter "On certain physical properties of the light of the electric spark, within certain gases as seen through a prism" Am. J. Sci. 1855, 19: 213-4, p214.

71 V. S. M. v. d. Willigen "Over Het Electrische Spectrum" Versl. Meded. Akad. Weten. 1858, 7: 209-32, 267-73, 274-80, 362-7; 8: 32-51, 189-208, 308-15; 9: 300-6. The first paper of this was translated into German as "Ueber das elektrische Spectrum" Pogg. Ann. 1859, 106: 610-32, p610. Das eigentliche Wesen des durch Elektricität hervorgebrachten Lichtes verlangen.

72 ibid Frage über den eigentlichen Funken wurde beantwortet durch Masson.

73 Although Plücker's papers on discharge tube phenomena did not have a common title they were numbered in sequence as follows:
"Ueber die Einwirkung des Magneten auf die elektrischen Entladung in verdünnten Gasen" Pogg. Ann. 1858, 103: 88-106, 151-7 (arts 1-38, 39-46); "Fortgesetzte Beobachtungen über die elektrische Entladung durch gasverdünnte Räume" ibid 1858, 104: 113-28 (arts 47-75); "Ueber einen neuen Gesichtspunkt, die Einwirkung des Magneten auf den elektrischen Strom betreffend" ibid 1858, 104: 622-30 (arts 76-86); "Fortgesetzte Beobachtungen über die elektrische Entladung" ibid 1858, 105: 67-84 (arts 88-117 (no art 87)); "Fortgesetzte Beobachtungen über die elektrische Entladung in gasverdünnten Räumen" ibid 1859, 107: 77-113 (arts 118-173); "Ueber die Constitution der elektrischen Spectra der verschiedenen Gase und Dämpfe" ibid 1859, 107: 497-539 (arts 174-214); "Nachtrag zu der Abhandlung über die Constitution der elektrischen Spectra der verschiedenen Gase und Dämpfe" ibid 1859, 107: 638-43 (arts 215-7). Articles 1-117 were translated into English by Frederick Guthrie (1833-1886) as "On the action of the magnet upon the electrical discharge in rarefied gases" Phil. Mag. 1858, 16: 119-135 (arts 1-46); "Observations on the electrical discharge through rarefied gases" ibid 1858, 16: 408-18 (arts 47-75); "Observations

on the electric discharge" ibid 1859, 18: 1-20 (arts 76-117). Plücker also wrote an abstract of these papers specifically for the Royal Society "Abstract of a series of papers and notes concerning the electric discharge through rarefied gases and vapours" Proc. Roy. Soc. 1860, 10: 256-69.

74 See J. Plücker "On the action of the magnet" Phil. Mag. 1858, 16: 119-35 art 5 for details of Rühmkorff's work. There are no papers of his listed in the Royal Society Catalogue of scientific papers.

75 J. A. Quet "Sur quelques faits relatifs au courant et à la lumière électriques" Comptes. Rendus. 1852, 35: 949-52.

76 W. R. Grove "On the electro-chemical polarity of gases, including the striae in electrical discharges" Phil. Trans. 1852: 87-102; "On the striae seen in the electrical discharge in vacuo" Phil. Mag. 1858, 16: 18-22.

77 J. P. Gassiot "On the stratifications and dark bands in electrical discharges as observed in Torricellian vacua" Proc. Roy. Soc. 1858, 9: 146-50; Phil. Trans. 1858: 1-16.

78 Johann H. W. Geissler (1815-1879). See J. Plücker "On the action of the magnet" Phil. Mag. 1858, 14: 119-35 art 2 for details of Geissler's work on Geissler tubes (a term coined by Plücker).

79 Plücker to Faraday 27 December 1857 in M. Faraday Correspondence 2. 675. Plücker's emphasis.

80 J. Plücker "Ueber einen neuen Gesichtspunkt" Pogg. Ann. 1858, 104: 622-30

81 J. Plücker "Observations on the electrical discharge through rarefied gases" Phil. Mag. 1858, 14: 408-18 art 66.

82 ibid

83 ibid art 71

84 ibid art 74

85 ibid art 75

86 ibid art 72

87 ibid

88 ibid art 73

89 ibid

90 ibid

91 J. Plücker "Observations on the electric discharge" Phil. Mag. 1859, 18: 1-20, art 117.

92 ibid art 89

93 ibid art 91

94 ibid art 105 Plücker's emphasis

95 ibid arts 106/7

96 ibid art 116

97 J. Plücker "Ueber die Constitution der elektrischen Spectra" Pogg. Ann. 1859, 107: 497-539; "Nachtrag zu der Abhandlung" ibid 638-43. Respectively dated 8 May and 11 June.

98 J. Plücker "Ueber die Constitution der elektrischen Spectra" Pogg. Ann. 1859, 107: 497-539, art 174. Das Vorhandenseyn eines Gases durch eine seiner Linien mit Bestimmtheit.

99 ibid art 175

100 ibid arts 187-214.

101 J. Plücker "Nachtrag zu der Abhandlung" Pogg. Ann. 1859, 107: 638-43 arts 215-7.

102 J. Plücker "Abstract" Proc. Roy. Soc. 1860, 10: 267

103 ibid 267-8.

NOTES AND REFERENCES TO CHAPTER FIVE

The conservation of energy, theories of spectra and resonating molecules 1851-1854

1 For accounts of the development of the principle of the conservation of energy see W. L. Scott "The conflict between atomism and conservation theory 1644-1860" (London 1970); Y. Elkana "The discovery of the conservation of energy" (London 1974); T. Kuhn "Energy conservation as an example of simultaneous discovery" in M. Claggett (ed) "Critical problems in the history of science" (Madison, 1969) p321-56.

2 See S. G. Brush "The wave theory of heat: a forgotten stage in the transition from the caloric theory to thermodynamics" Brit. J. Hist. Sci. 1970, 5: 145-67; R. J. McRae "The origin of the conception of the continuous spectrum of heat and light" (University of Wisconsin Ph.D. thesis 1969).

3 G. G. Stokes (1819-1903). The main collection of Stokes's manuscripts is kept in the University Library Cambridge (ULC MS add 7656) and has been catalogued by D. B. Wilson in "Catalogue of the manuscript collections of Sir George Gabriel Stokes and Sir William Thomson, Baron Kelvin of Largs in Cambridge University Library" (Cambridge, 1976). Stokes's scientific papers were collected in "Mathematical and Physical Papers" (5 vols, Cambridge, 1880-1905); vols 1-3 were edited by Stokes and vols 4-5 were edited by J. Larmor. These will be cited as Stokes Papers. In the three volumes of papers which Stokes edited he consciously suppressed papers of his which had been of a deliberately controversial nature (see ULC MS add 7656, NB 27). Some of Stokes's correspondence was published in J. Larmor (ed) "Memoir and Scientific Correspondence of the Late Sir George Gabriel Stokes" (2 vols, Cambridge, 1907). This will be cited as Stokes Memoir.

4 G. G. Stokes "On the Change of Refrangibility of Light" Phil. Trans. 1852: 463-562; Papers III, 267-409; RS MS PT 45.2, art 238. This paper will be cited as Stokes CRL.

5 A. J. Ångström "Optical Researches" Phil. Mag. 1855, 9: 342.

Notes and references to Chapter 5 (cont.)

6 J. F. W. Herschel "On the absorption of light" Phil. Mag. 1833, 3: 403.

7 A. J. Ångström "Optical Researches" Phil. Mag. 1855, 9: 327.

8 G. G. Stokes Memoir I, 8 and "Fluorescence" in "Science lectures at South Kensington" (London, 1876) 22-43, p26. Both accounts say that it was mentioned by a friend. It is unusual that Stokes did not name him since it was his normal practice to do so.

9 J. F. W. Herschel "'Αμόρφωτα, No. I. On a case of superficial colour presented by a homogeneous liquid internally colourless" Phil. Trans. 1845: 143-5; " 'Αμόρφωτα, No. II On the epipolic dispersion of light, being a supplement to a paper entitled "on a case of superficial colour presented by a homogeneous liquid internally colourless" " ibid 147-53.

10 David Brewster had observed similar phenomena both in sulphate of quinine and other substances. D. Brewster "On the Colours of Natural Bodies" Trans. Roy. Soc. Edinb. 1834, 12: 538-45; "On a new phenomenon of colour in certain specimens of fluor spar" Rep. Brit. Ass. 1838, pt 2: 10-12. Brewster noted in "On the decomposition and dispersion of light within solid and fluid bodies" Phil. Mag. 1848, 32: 401-12 that Herschel's observations were similar to his own published in the two papers cited above. It would appear that Herschel was unaware of Brewster's previous work, since the experimental conditions of each worker were different.

11 G. G. Stokes CRL footnote to art 27. Stokes considered that fluorescence had similarities with opalescence, and hence the name, derived from fluor spar, one of the substances which exhibited the phenomenon.

12 J. F. W. Herschel "'Αμόρφωτα, No. I" Phil. Trans. 1845, 144.

13 J. F. W. Herschel "'Αμόρφωτα, No. II" ibid 147. This comes from the Greek ἐπιπολῆ, a surface of a body, since he had observed that the dispersion occurred near the surface of the solution.

Notes and references to Chapter 5 (cont.)

14 ibid

15 Herschel held that all colours could be made out of three primary colours, "Essay on Light" arts 509-19. Though he did not specify which three colours he considered to be primary, the fact that he thought this may well have enabled him to make such an assertion about the colour of the beam after the blue had been removed.

16 J. F. W. Herschel " 'Αμόρφωτα, No. II" Phil. Trans. 1845: 147.

17 ibid 148

18 ibid

19 ibid 152

20 These last two substances are: Esculine $C_{15}H_{16}O_9$ and fluor spar CaF_2; the green colour is due to lead deposits in the area (Cumberland).

21 ULC MS add 7656 NB28, p1. This is a note book in which Stokes copied his observations up to June 3rd 1851 on which day he wrote that he had "written [them] out, partly from memory and partly from notes"(p9). One of these notes headed "A Discovery" is printed in G. G. Stokes Memoir I, 9/10; the manuscript version has not been located. It is dated Monday April 28 1851 (the transcription reads 1852, but this must be an error made by Larmor; Stokes's 1s and 2s can be difficult to distinguish). In it Stokes says that he had discovered that "in the phenomenon of interior dispersion a ray of light actually changes its refrangibility" (transcription's emphasis).

22 ULC MS add 7656 NB28, p1.

23 See the optical papers of Stokes in Papers I.

24 ULC MS add 7656 NB28, p3.

25 ibid

26 ibid

27 ibid

Notes and references to Chapter 5 (cont.)

28 ibid p4. See also G. G. Stokes CRL arts 7-9. The document "A Discovery" (Memoir I, 9/10) does not refer to this experimental detail. Therefore presumably this refers only to Stokes's deduction which as he said he "felt considerable confidence that it would turn out true" ULC MS add 7656, NB28, p3.

29 ibid p7, see also G. G. Stokes CRL art 10.

30 ibid art 80.

31 See ULC MS add 7656, NB28, p63 and G. G. Stokes CRL art 239 for lists of these substances.

32 Stokes to Herschel 27 June 1856 RS MS HS 17.31.

33 G. G. Stokes CRL art 229

34 ibid art 226.

35 ibid

36 Stokes to Herschel 12 November 1859 RS MS HS 17.40.

37 G. G. Stokes CRL art 5

38 ibid art 226.

39 See, for example, G. G. Stokes "On the dynamical theory of diffraction" Trans. Camb. Phil. Soc. 1849: 1-62; Papers II: 243-328, p250.

40 G. G. Stokes "On the theories of the internal friction of fluids in motion, and of the equilibrium and motion of elastic solids" Trans. Camb. Phil. Soc. 1845, 8: 287-319; Papers I: 79-129, p127.

41 J. F. W. Herschel "Essay on Sound" footnote to art 328.

42 G. G. Stokes CRL art 227

43 J. F. W. Herschel "Report on Prof Stokes' paper on the change of refrangibility of light" 21 June 1852, RS MS RR 2.230.

44 G. G. Stokes CRL art 227

45 Stokes to Herschel 9 July 1856 RS MS HS 17.34.

Notes and references to Chapter 5 (cont.)

46 G. G. Stokes CRL art 234

47 ibid art 227

48 ibid

49 ibid art 230

50 ibid art 228

51 ibid art 226

52 William Thomson, Lord Kelvin (1824-1907) will always be cited as Kelvin, though he did not obtain his peerage until 1892, to avoid confusion with the many other Thomsons and Thompsons active in the scientific world in the 19th and 20th centuries. This is also advantageous since his papers at the Cambridge University Library are catalogued under Kelvin (see note 3) as ULC MS add 7342. There is also a collection of his manuscripts at Glasgow University Library catalogued in "Index to the manuscript collection of William Thomson, Baron Kelvin in Glasgow University Library" (ULP 6) (Glasgow 1977). Most of Kelvin's papers were collected in "Mathematical and Physical Papers" (6 vols, Cambridge 1882-1911); vols 1-3 were edited by Kelvin and vols 4-6 were edited by J. Larmor. These will be cited as Kelvin Papers. Kelvin's "Popular Lectures and Addresses" (3 vols, London 1889-94) will be cited as Kelvin Lectures. The correspondence between Stokes and Kelvin will be published in D. B. Wilson "The correspondence between Sir George Gabriel Stokes and Sir William Thomson, Baron Kelvin of Largs" (Cambridge, forthcoming). This will be cited as Wilson Correspondence followed by the number of the letter involved. I am very grateful to Dr. Wilson for providing me with a pre-publication list of the letter numbers. Where there is a printed version of a letter this will be cited, unless the manuscript has not been traced, only when the letter is first referred to; in later citations only the MS number will be used. The standard biographies of Kelvin remain S. P. Thomson "The life of William Thomson, Baron Kelvin of Largs" (2 vols, London, 1910) and Andrew Gray "Lord Kelvin: An Account of his Scientific Life and Work" (London, 1908; New York 1973).

53 Stokes to Kelvin 15 November 1851 ULC MS add 7342, S365, D. B. Wilson Correspondence 88 Stokes's emphasis.

Notes and references to Chapter 5 (cont.)

54 G. G. Stokes CRL art 224

55 Stokes to Herschel 27 June 1856 RS MS HS 17.31. The analogy was published in G. G. Stokes "Fluorescence" p39-40.

56 G. G. Stokes CRL art 231

57 ibid

58 ibid art 234

59 Ångström quoted Euler's principle in "Optiska Undersökningar" Kongl. Veten. Akad. Handl. 1854: 336 (footnote). For a discussion of Euler's principle see chapter 1, p11.

60 A. J. Ångström "Optical Researches" Phil. Mag. 1855, 9: 327.

61 ibid 327/8 Ångström's emphasis.

62 ibid 329

63 ibid

64 ibid 332

65 D. Brewster "Observations on the lines of the solar spectrum" Trans. Roy. Soc. Edinb. 1833, 12: 528/9.

66 W. A. Miller "Experiments and Observations" Phil. Mag. 1845, 27: 85.

67 O. J. Broch "Ueber die Fraunhofer'schen Linien *im Sonnenspectrum; wie sie sich dem unbewaffneten* Auge zeigen" Pogg. Ann. Engänz 1853, 3: 311-6

68 A. J. Ångström "Optical Researches" Phil. Mag. 1855, 9: 332

69 ibid

70 See chapter 4, p106.

71 A. J. Ångström "Optical Researches" Phil. Mag. 1855, 9: 332.

72 ibid 341

73 G. G. Stokes CRL art 234

Notes and references to Chapter 5 (cont.)

74 ibid

75 Although some writers (see, for example, M. A. Sutton "Spectroscopy and the structure of matter: A study in the development of physical chemistry" (University of Oxford D. Phil. thesis, 1972) p185/6 and R. T. Glazebrook "Sir George Gabriel Stokes, FRS" Good Words 1901: 312-6, p315) have pointed out the existence of a relationship between Stokes's work on fluorescence and his work on line spectra, the connection has not hitherto been investigated. Stokes himself hinted that there was a connection when he commented that his mechanical explanation of line spectra fell in "very well with certain conjectures which I have made in my paper On the Change of Refrangibility of Light (art 230 &c)". Stokes to Kelvin 28 March 1854, ULC MS add 7342, S369, D. B. Wilson Correspondence 104, partly printed in G. G. Stokes Papers IV: 372-3.

76 The letters of interest are the following:
Kelvin to Stokes 20 February 1854, ULC MS add 7656, K62, transcript by Larmor K63, D. B. Wilson Correspondence 98, partly printed in G. G. Stokes Papers IV 367.
Stokes to Kelvin 24 February 1854, ULC MS add 7342, S366, D. B. Wilson Correspondence 99, partly printed in G. G. Stokes Papers IV 368-9.
Kelvin to Stokes 2 March 1854 ULC MS add 7656, K64, transcript by Larmor K65; D. B. Wilson Correspondence 100, partly printed in G. G. Stokes Papers IV 369-70.
Stokes to Kelvin 7 March 1854, ULC MS add 7342 S367, D. B. Wilson Correspondence 101, partly printed in G. G. Stokes Papers IV 370-1.
Stokes to Kelvin 8 March 1854 ULC MS add 7342 S368, D. B. Wilson Correspondence 102, partly printed in G. G. Stokes Papers IV 372.
Kelvin to Stokes 9 March 1854, ULC MS add 7656, K66, transcript by Larmor K67, D. B. Wilson Correspondence 103, partly printed in G. G. Stokes Papers IV 371-2.
Stokes to Kelvin 28 March 1854 ULC MS add 7342, S369.
Stokes to Kelvin 26 November 1855, ULC MS add 7342, S383, D. B. Wilson Correspondence 140, printed in G. G. Stokes Papers IV 374.
Stokes to Kelvin 6 December 1855 ULC MS add 7342 S384, D. B. Wilson Correspondence 141, partly printed in G. G. Stokes Papers IV 374.
Kelvin to Stokes 14 December 1855 ULC MS add 7656, K88, D. B. Wilson Correspondence 142.

To put these letters into context: Kelvin, who initiated this correspondence, was concerned at the time with, among other things, formulating his meteoric hypothesis of solar heat and setting up a course of experimental physics at Glasgow University (for details of the latter see draft of Kelvin to the Furguson Fund 4 February 1858, GUL Kelvin papers T154). Spectral experiments being relatively inexpensive Kelvin with his limited resources at that time must have welcomed such experiments. The rôle of the meteoric hypothesis will be discussed in the next chapter.

77 Kelvin recalled (Kelvin to Stokes 9 March 1854, ULC MS add 7656, K66) that he had a conversation with Stokes a "long time ago" in which Stokes had told him of his work on line spectra. In Kelvin to Stokes 1 July 1871 (ULC MS add 7656, K174; D. B. Wilson Correspondence 275) Kelvin says that it was prior to the summer of 1852 and two letters later (Kelvin to Stokes 7 July 1871 ULC MS add 7656, K176, transcript by Larmor K177, D. B. Wilson Correspondence 279, partly printed in G. G. Stokes Papers IV 374-5) Kelvin added that he was not in Cambridge from that time till 1866. Stokes said (Stokes to Kelvin 24 February 1854 ULC MS add 7342, S366) that he had "hardly" any "communication" with Kelvin since his wedding i.e. 15 September 1852. (There is only one letter from Kelvin to Stokes between his wedding and 1854 (Kelvin to Stokes 21 December 1852 ULC MS add 7656, K61, D. B. Wilson Correspondence 97) and none from Stokes). Kelvin was definitely in London in June-July 1852 (Kelvin to Stokes ULC MS add 7656 K58-60, D. B. Wilson Correspondence 94-6) so he might well have gone to Cambridge then. Kelvin would not have had the chance (apart from the unlikely time of his wedding) from then until this correspondence of 1854 to discuss Stokes's spectral work. However, it should be pointed out that writing some years later to Stokes (Kelvin to Stokes 7 July 1871) Kelvin said that he had taught Stokes's work on spectra in the 1852-3 session. It is therefore curious that Kelvin should write in 1854 to ask Stokes about the subject, if he had already been teaching it. According to Andrew Gray "Lord Kelvin" p84-5, a student note-book dated 1854 (it is not made clear whether this was 1853-4 or 1854-5) shows "the whole affair of spectrum analysis was in his [Kelvin's] hands" (p84). Unfortunately this note-book has been lost since 1908; the nearest in date now surviving is that of William Jack of 1852-3 (GUL MS gen 130), where there is no mention of any spectroscopic work. I would

therefore suggest that the most likely sequence of events was that Stokes in the course of conversation about fluorescence told Kelvin about his ideas on line spectra; that Kelvin remembered it in early 1854 and asked Stokes for details; and that he subsequently taught the subject to his natural philosophy class.

78 See chapter 3 p73.

79 Stokes to Kelvin 7 March 1854, ULC MS add 7342 S367.

80 J. B. L. Foucault had observed the reversal phenomenon before January 1849, when he published it in "Lumière électrique" L'Institut 1849-50, 17: 44-6 (see chapter 4 p97-100). Parts of this paper were translated into English by Stokes and published together with a translation of G. Kirchhoff's paper containing his observation of reversal ("Ueber die Fraunhofer'schen Linien" Berlin Monatsber. 1859: 662-5) as "On the simultaneous emission and absorption of rays of the same definite refrangibility; being a translation of a portion of a paper by M. Léon Foucault, and of a paper by Professor Kirchhoff" Phil. Mag. 1860, 19: 193-7. At the end of this paper Stokes added his physical explanation of the phenomenon. It will be shown that Stokes was not aware of Foucault's work on reversal until 1855, i.e. after his correspondence with Kelvin on spectra.

81 ibid 197

82 Stokes to Kelvin 7 March 1854 ULC MS add 7342, S367.

83 Stokes to Kelvin 24 February 1854 ULC MS add 7342, S366.

84 W. A. Miller "Experiments and Observations" Phil. Mag. 1845, 27: 81-91. Stokes referred to Miller through F. Moigno (ed) "Répertoire d'Optique Moderne" (4 vols, Paris 1847-50). This is essentially a collection of texts, summaries and abstracts of work on optics and light in the first half of the nineteenth century; though there is some eighteenth century material. Moigno's method of referring is erratic to say the least since references, when they are given, only occur in the author index in volume 4. Miller's paper was translated almost entirely by Moigno in "Répertoire" III, 1237-43.

85 Kelvin to Stokes 2 March 1854, ULC MS add 7656, K64.

Notes and references to Chapter 5 (cont.)

86 Kelvin to Stokes 20 February 1854, ULC MS add 7656 K62.

87 Stokes to Kelvin 24 February 1854, ULC MS add 7342, S366.

88 W. A. Miller "Experiments and Observations" Phil. Mag. 1854, 27: 89-90.

89 Kelvin to Stokes 2 March 1854, ULC MS add 7656, K64.

90 ibid

91 Kelvin to Stokes 9 March 1854 ULC MS add 7656, K66. Kelvin said that Stokes had told him about W. H. Miller's experiments.

92 Stokes to Kelvin 5 July 1871 ULC MS add 7656, NB 21, letter 42 D. B. Wilson Correspondence 277. Stokes's emphasis.

93 Kelvin to Stokes 9 March 1854, ULC MS add 7656, K66.

94 Stokes to Kelvin 24 February 1854, ULC MS add 7342, S366.

95 ibid. Foucault published his results on the ubiquity of the R lines in the same paper as his observation of reversal "Lumière électrique" L'Institut 1849-50, 17: 44-6. Stokes referred to this aspect of Foucault's work through Moigno "Répertoire" III 1243-4. Moigno did not publish Foucault's observation of reversal, but said that the coincidence between the dark and bright lines was striking. Nor did Moigno give a reference to Foucault's paper in vol. IV.

96 Stokes to Kelvin 28 March 1854 ULC MS add 7342, S369.

97 W. McGucken "Nineteenth century spectroscopy: Development of the understanding of spectra 1802-1896" (Baltimore, 1969) in his limited discussion of Stokes's work (p22/3) ignores this part of the correspondence in pursuit of his thesis that the lack of the idea of one spectrum, one element was the cause of the "slowness" of the development of spectroscopy.

98 Which Foucault received on 30 November 1855 Stokes was the seconder of Wheatstone's proposal that Foucault should be awarded the medal (see "Minutes of the Council of the Royal Society 1846-1858"

(London 1858), p325). Stokes later said (Stokes to Kelvin 11 January 1876 ULC MS add 7342, S405, D. B. Wilson Correspondence 315, printed in G. G. Stokes Papers IV 375-6) that he wrote the address for the presentation (delivered by Lord Wrottesley) Proc. Roy. Soc. 1855, 7: 571-4 for which Stokes to Kelvin 10 November 1855 (ULC MS add 7342 S380, D. B. Wilson Correspondence 134) is evidence since there he reported some of Foucault's electromagnetic work which indicates that he was working on the address.

99 Stokes to Kelvin 5 July 1871 ULC MS add 7656, NB21, Letter 42.

100 J. B. L. Foucault "Lumière électrique" L'Institut 1849-50, 17: 44-6.

101 Stokes to Kelvin 26 November 1855 ULC MS add 7342, S383.

102 ibid Stokes's emphasis.

103 Stokes to Kelvin 5 July 1871 ULC MS add 7656, NB21, letter 42.

104 Stokes to Kelvin 6 December 1855 ULC MS add 7342, S384.

105 Kelvin to Stokes 14 December 1855 ULC MS add 7656, K88.

106 ibid. M. Sutton "Spectroscopy and the Structure of Matter" p179 and 183 attempts to make something of Kelvin's visit, in 1850, to France where he met both Moigno and M. Duboseque-Soleil (a maker of optical instruments, from whom Kelvin purchased a number of instruments in 1851 (see Fischer to Kelvin 4 November 1851 ULC MS add 7342, F100)) and saw a number of optical experiments. Now S. P. Thompson "Kelvin" says (I, 300), without evidence, that Kelvin saw Foucault's reversal experiment and talked to Stokes about it. But in the 1854 correspondence there is no mention of Foucault's reversal work, and in the 1855 correspondence the work came as new to Kelvin as to Stokes. Sutton tends to disagree with Thompson's statement but does suggest that Kelvin may have seen it but forgotten it by 1854; which would be very surprising since Kelvin had described an experiment, not Foucault's, which showed reversal.

107 It should not be found surprising that Stokes neglected to publish his work then, since he had just become secretary of the Royal Society, a position in which he was most conscientious. Indeed it was a contemporary complaint that Stokes was wasted being secretary when he could have been working on science. See P. G. Tait "Scientific Worthies V George Gabriel Stokes" Nature 1875, 12: 201-3. Also Stokes was well aware that there was a vast amount of work to be done on spectral phenomena Stokes to Kelvin 24 February 1854 ULC MS add 7342, S366.

108 For John Ferguson's account of Kelvin's 1859 lecture on spectra see J. Ferguson "Lord Kelvin: A recollection and an impression" Glasg. Univ. Mag. 1908, 20: 276-82, p279. For R. B. Clifton's account of Stokes's lectures on spectra see ULC MS add 7656, PA249.

NOTES AND REFERENCES TO CHAPTER SIX

The conservation and dissipation of energy, and solar theories 1846-62

1 Julius Robert Mayer (1814-1878). For an account of his life and English translations of most of his papers see R. B. Lindsay "Julius Robert Mayer: Prophet of Energy" (Oxford 1973).

2 Hermann von Helmholtz (1821-1894) was professor of physiology at the universities of Königsberg (1849-1855), Bonn (1855-1858) and Heidelberg (1858-1871). The standard biography of Helmholtz remains L. Koenigsberger "Hermann von Helmholtz" (3 vols, Braunschweig, 1902-3). Translated into English (by F. A. Welby) (Oxford, 1906).

3 J. F. W. Herschel "Outlines of Astronomy" (2nd edition, London 1849) (This will be the only edition used in this chapter) art 397; "Results of Astronomical Observations, made during the years 1834, 5, 6, 7 , 8 at the Cape of Good Hope, being a completion of a telescopic survey of the whole surface of the visible heavens commenced, in 1825" (London 1847).

4 Claude-Servais-Mathias Pouillet (1790-1868) "Mémoire sur le chaleur solaire, sur les pouvoirs rayonnants et absorbants de l'air atmosphérique, et sur la température de l'espace" Comptes Rendus 1838, 7: 24-65. Translated into English as "Memoir on the solar heat, on the radiating and absorbing powers of atmospheric air, and on the temperature of space" Taylor's Sci. Mem. 1846, 4: 44-90.

5 ibid 50

6 ibid 53

7 J. R. Mayer "Die organische Bewegung in ihiem Zusam enhang mit dem Stoffwechsel. Ein Beitrag zur Naturkunde" (Heilbronn 1845). Translated into English (by R. B. Lindsay) as "The motions of organisms and their relation to metabolism. An essay in natural science" in R. B. Lindsay "Mayer" 75-145, p99.

8 J. R. Mayer "Beiträge zur Dynamik des Himmels, in populärer Darstallung" (Heilbronn 1848). Translated into English as "On celestial Mechanics" Phil. Mag. 1863, 25: 241-8, 387-409, 417-28; p241.

Notes and references to Chapter 6 (cont.)

9 ibid 244-5

10 ibid 245. In performing this calculation Mayer assumed that the material of the sun had the same specific heat as water and that the sun emitted its heat uniformly from its whole mass. In his paper he did not specify the solar radius of the sun which he used, but from my calculation he appears to have assumed the radius to be 712,200 kilometres. This agrees (approximately) with his statement (ibid 246) that the sun's diameter is nearly 112 times larger than the earth's.

11 ibid 245

12 J. R. Mayer "The motions of organisms" in R. B. Lindsay "Mayer" p99.

13 The part of the paper which was published was entitled "Sur la transformation de la force vive en chaleur, et réciproquement" Comptes Rendus 1848, 27: 385-7. This makes clear, on p385, that the title of Mayer's paper, presented on 27 July 1846, was "Sur la production de lumière et de la chaleur du soleil". The published portion deals with Mayer's work on the mechanical equivalent of heat. It was this paper which first attracted the hostile attention of Kelvin and Joule to Mayer's work (see Joule to Kelvin correspondence ULC MS add 7342 J61-7) and provoked Joule's highly critical response "Sur l'équivalent mécanique du calorique" Comptes Rendus 1849, 28: 132-5.

14 J. R. Mayer "On celestial dynamics" Phil. Mag. 1863, 25: 245.

15 ibid 246

16 J. R. Mayer "The motions of organisms" in R. B. Lindsay "Mayer" p88.

17 J. R. Mayer "On celestial dynamics" Phil. Mag. 1863, 25: 397. I. Newton "The Mathematical Principles of Natural Philosophy" (translated from the Latin by A. Motte) (3 vols, London, 1803) II, 307-9. This aspect of Newton's work is discussed by D. Kubrin "Newton and the cyclical cosmos: providence and the mechanical philosophy" J. Hist. Ideas 1967, 28: 325-46.

18 J. R. Mayer "On celestial dynamics" Phil. Mag. 1863, 25: 387.

Notes and references to Chapter 6 (cont.)

19 ibid

20 ibid 389

21 ibid. Mayer did not have the problem of dealing with the asteroids since by 1848 only eight had been discovered. These being comparatively large bodies they would not fall towards the sun particularly quickly.

22 ibid 392

23 ibid 395

24 ibid 399

25 ibid

26 ibid 397. In a footnote to this passage Mayer suggested that this was the reason why comet's tails pointed away from the sun.

27 ibid

28 ibid 400

29 ibid 388

30 ibid 402

31 ibid

32 Kelvin "On the dynamical theory of heat with numerical results deduced from Mr. Joule's equivalence of a thermal unit, and M. Regnault's observations on steam" Trans. Roy. Soc. Edinb. 1851, 20: 261-98, 475-82; 1854, 21: 123-71; Papers I: 174-291.

33 See Kelvin to Joule 25 April 1851 ULC MS add 7342, J78

34 Kelvin "On the dynamical theory of heat" Papers I, 181, Kelvin's emphasis.

35 Kelvin to Stokes 13 January 1852 ULC MS add 7656, K53, D. B. Wilson Correspondence 89.

36 Indeed almost the last problem which Kelvin worked on was the theory of the sun "The problem of a spherical gaseous nebula" Phil. Mag. 1908, 15: 687-711; 16: 1-23; Papers V: 254-83.

Notes and references to Chapter 6 (cont.)

37 Kelvin "On the mechanical action of radiant heat or light: on the power of animated creatures over matter: on the sources available to man for the production of mechanical effect" Proc. Roy. Soc. Edinb. 1852, 3: 108-113. He mentions Pouillet's work on p109, of which Stokes had, presumably, informed him.

38 ibid 113 Kelvin's emphasis.

39 Kelvin "On a universal tendency in nature to the dissipation of mechanical energy" Proc. Roy. Soc. Edinb. 1852, 3: 139-42.

40 ibid 142

41 Kelvin "On the mechanical energies of the solar system" Trans. Roy. Soc. Edinb. 1854, 21: 63-80; p64 where Kelvin makes this point implicitly.

42 For an account of Kelvin's changing attitudes to the problem of the age of the earth see J. D. Burchfield "Lord Kelvin and the age of the earth" (New York 1975).

43 Kelvin to Stokes 26 April 1854 ULC MS add 7656, K69.

44 J. D. Burchfield "Lord Kelvin" p23, states that the chemical origin theory of solar heat was the generally accepted one until the 1850s. Not only Kelvin, but as we shall see, Stokes, thought, at one stage, that the sun was a body emitting primitive heat. This would imply that the two views were both held quite widely at that time.

45 Kelvin to Stokes 20 February 1854 ULC MS add 7656, K62 and Kelvin to Helmholtz 24 July 1855 (in S. P. Thompson "Kelvin" I, 309) make it clear that Kelvin was not at the Hull meeting.

46 John James Waterson (1811-1883) is now chiefly remembered for his anticipation of the kinetic theory of gases. For further information see J. S. Haldane "The collected scientific papers of J. J. Waterson" (Edinburgh, 1928). This contains a biographical sketch by Haldane of Waterson, but does not contain his paper on the meteoric hypothesis. See also S. G. Brush "The development of the kinetic theory of gases II Waterson" Ann. Sci. 1957, 13: 273-82 and R. Olson "Scottish Philosophy" esp. p236-51.

Notes and references to Chapter 6 (cont.)

47 J. J. Waterson "On dynamical sequences in Kosmos" Athenaeum 1853: 1099-1100. Both J. D. Burchfield "Lord Kelvin" p23 and D. H. DeVorkin "An astronomical symbiosis: stellar evolution and spectral classification (1860-1910)" (Leicester University Ph.D. thesis, 1978) p13, say that Kelvin heard Waterson. This impression seems to have prevented them from looking for a text of Waterson's paper. Burchfield refers to Waterson via another of his 1853 papers ("On a law of mutual dependence between temperature and mechanical force" Rep. Brit. Ass. 1853, pt 2: 11-12) which contains no mention of his meteoric hypothesis. Burchfield also states (again p23) that Joule had devised a meteoric hypothesis, and refers to his "On the mechanical equivalent of heat, as determined by the heat evolved by the friction of fluids" Phil. Mag. 1847, 31: 173-76 which contains nothing about the subject. Joule, as we shall see, did write about the heat evolved by meteors in the earth's atmosphere. DeVorkin (p13) follows Burchfield in his assertion concerning Joule.

48 An aerolite is a body which lands in the surface of a planet and is thus a meteorite as opposed to a meteor which burns up in the atmosphere.

49 Waterson made an elementary error in his calculation since he used an escape velocity from the sun of 545 miles per second which is a factor $\sqrt{2}$ too large. Therefore his calculation concerning the amount of meteoric matter needed was half the amount required according to his hypothesis. He also assumed that the meteoric material had the specific heat of iron and the density of water which were common assumptions in this period.

50 At this rate it would take 80000 years for the sun to grow 1" in apparent diameter.

51 J. J. Waterson "On dynamical sequences in Kosmos" Athenaeum 1853: 1099.

52 P. S. Laplace had originally proposed this theory in 1796 in the final book of his "Exposition du Système du Monde" (Paris 1796) and although it went through several changes (see S. L. Jaki "The five forms of Laplace's Cosmogony" Am. J. Phys. 1976, 44: 4-11) it remained substantially the same. The final version in P. S. Laplace "Oeuvres de Laplace" (7 vols, Paris, 1843-7) VI: 447-60 became very well

known and received a good deal of attention in the nineteenth century being disseminated, in Britain at least, by J. P. Nichol in such books as "Views of the architecture of the heavens" (Edinburgh, 1837) and "The stellar universe: views of its arrangements, motions and evolutions" (Edinburgh, 1848).

53 Kelvin "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 64-5.

54 Athenaeum 1853: 1100.

55 ibid

56 Kelvin "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 64.

57 Kelvin "Universal tendency" Proc. Roy. Soc. Edinb. 1852, 3: 139-42.

58 Kelvin "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 64.

59 ibid 69

60 ibid 64

61 James Prescott Joule (1818-1889). Most of Joule's papers were collected in "The scientific papers of James Prescott Joule" (2 vols, London, 1884-1887). This will be cited as Papers.

62 J. P. Joule "On shooting stars" Phil. Mag. 1848, 32: 349-51; Papers I: 286-8. Kelvin cited this paper in "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 65.

63 ibid 66.

64 Kelvin to Stokes 2 March 1854 ULC MS add 7656, K64, Kelvin's emphasis. This also shows that Kelvin had already spotted Waterson's arithmetical error (see note 49) since 2000 pounds is just twice the amount Waterson required.

65 Kelvin "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 69-71.

66 Kelvin to Stokes 9 March 1854 ULC MS add 7656, K66.

Notes and references to Chapter 6 (cont.)

67 Stokes to Kelvin 28 March 1854 ULC MS add 7342, S369. It should be pointed out that Stokes's failure to produce an immediate response was because he had suffered a period of illness due to some public duties which he had carried out.

68 W. Herschel "On the nature and construction of the sun and fixed stars" Phil. Trans. 1795: 46-72 in J. L. E. Dreyer (ed) "The scientific papers of Sir William Herschel" (2 vols, London, 1912) I, 470-484.

69 Stokes to Kelvin 28 March 1854 ULC MS add 7342, S369. The source for the quotation has not been located. This is yet another example that J. D. Burchfield's assertion regarding the chemical theory of the sun is not true (see note 44).

70 See Chapter 5, note 77.

71 Kelvin to Stokes 2 and 9 March 1854 ULC MS add 7656 K64 and 66 respectively.

72 Stokes to Kelvin 28 March 1854, ULC MS add 7342, S369.

73 Kelvin to Stokes 21 March and 20 April 1854 ULC MS add 7656, K68, D. B. Wilson Correspondence 105. This presumably refers to J. F. W. Herschel "Outlines of Astronomy" art 897 where he discusses the zodiacal light.

74 ibid

75 Kelvin "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 63-80 was read to the Society on 17 April 1854.

76 ibid 67

77 Kelvin to Stokes 9 March 1854 ULC MS add 7656, K66

78 Kelvin "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 67.

79 ibid 67-8

80 ibid 67

81 Kelvin to Stokes 2 March 1854 ULC MS add 7656, K64.

Notes and references to Chapter 6 (cont.)

82 Kelvin "Note of the possible density of the luminiferous medium and on the mechanical value of a cubic mile of sunlight" Trans. Roy. Soc. Edinb. 1854, 21: 57-61.

83 Kelvin to Stokes 21 March and 20 April 1854, ULC MS add 7656, K68.

84 Kelvin "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 68.

85 ibid

86 ibid 80

87 ibid 76

88 Kelvin to Stokes 2 March 1854 ULC MS add 7656 K64

89 Stokes to Kelvin 24 February 1854 ULC MS add 7342, S366. D. Brewster "On the luminous lines" Rep. Brit. Ass. 1842, pt 2: 15. See Chapter 3, p74-5.

90 Stokes to Kelvin 24 February 1854 ULC MS add 7342, S366. D. Brewster "Observations sur le spectre solaire" Comptes Rendus 1850, 30: 578-81. See Chapter 3, p75.

91 Kelvin appendix no. 2 "Friction between vortices of meteoric vapour and the sun's atmosphere the immediate cause of solar heat" to "Mechanical energies" Trans. Roy. Soc. Edinb. 1854, 21: 75-77.

92 H. v. Helmholtz "Ueber die Wechselwirkung der Naturkräfte und die darauf bezüglichen neuesten Ermittelungen der Physik" (Königsberg 1854). This was translated into English as "On the interaction of natural forces" Phil. Mag. 1856, 11: 489-518.

93 ibid 503

94 Kelvin "Universal tendency" Proc. Roy. Soc. Edinb. 1852, 3: 139-42.

95 H. v. Helmholtz "Interaction" Phil. Mag. 1856, 11: 503.

Notes and references to Chapter 6 (cont.)

96 Helmholtz, being German, and lecturing at Königsberg, maintained that Kant had devised a nebular hypothesis similar to Laplace's which he had devised independently. Kant had made a much more speculative suggestion than Laplace in his "Allgemeine Naturgeschichte und Theorie des Himmels" (Königsberg 1755).

97 H. v. Helmholtz "Interaction" Phil. Mag. 1856, 11: 505.

98 ibid 507

99 ibid 506 and 516-8

100 ibid 506

101 ibid 517

102 Helmholtz here assumed that the sun emitted its energy uniformly over its whole mass and that its specific heat was the same as water (ibid 517). He seems to have used a solar radius of 717,600 kilometres.

103 ibid

104 ibid 514

105 ibid 507

106 ibid 506

107 Kelvin to David King 3 February 1862 in A. G. King "Kelvin the Man" (London 1925) 101-2.

108 Kelvin "On the mechanical antecedents of motion, heat, and light" Rep. Brit. Ass. 1854, pt 2: 59-63.

109 ibid 61-2

110 ibid 62. Quite who else Kelvin thought held the contraction hypothesis of solar heat at this time is not clear.

111 ibid

112 Apart from ULC MS add 7342, NB34, p204-5 where he attempted to examine on 6 and 15 August, and 27 October 1855, the effect on the excentricity of the planets due to the meteorites falling onto the sun. These considerations were not published.

Notes and references to Chapter 6 (cont.)

113 U. J. J. Leverrier "Sur la théorie de Mercure et sur le mouvement du périhélie de cette planète" Comptes Rendus 1859, 49: 379-83.

114 For a discussion of how Leverrier made this discovery see N. R Hanson "Leverrier: The zenith and nadir of Newtonian mechanics" ISIS 1962, 53: 359-78, especially section 2.

115 Kelvin "Mémoire sur l'énergie mécanique du système solaire" Comptes Rendus 1854, 39: 682-7.

116 Kelvin "Recent investigation of M. Leverrier on the motion of mercury" Proc. Glasg. Phil. Soc. 1859, 4: 263-66" Papers V: 134-7. Read 14 December 1859, p137.

117 ibid

118 ibid 134

119 Kelvin "On the variation of the periodic times of the earth and inferior planets, produced by matter falling into the sun" Proc. Glasg. Phil. Soc. 1860, 4: 272-4, Papers V: 138-40. Read 4 January 1860, p140.

120 ibid

121 Kelvin "Physical considerations regarding the possible age of the sun's heat" Rep. Brit. Ass. 1861, pt 2: 27-28, Papers V: 141-4 and "On the age of the sun's heat" Macm. Mag. 1862, 5: 388-93, Lectures I: 356-75. The latter is an expansion of the former and is more detailed. Since there are no new ideas in the latter, only a m re detailed exposition of those contained in the first paper, they will be treated together. The last paragraphs of each paper are identical.

122 This he did later in the century with the knowledge of J. H. Lane's work. Kelvin "On the equilibrium of a gas under its own gravitation only" Proc. Roy. Soc. Edinb. 1887, 14: 111-8; Papers V: 184-90.

123 Kelvin "Physical conditions" Papers V: 143.

124 A. M. Clerke "A popular history of astronomy during the nineteenth century" (3rd edition, London 1893) p378.

Notes and references to Chapter 6 (cont.)

125 See for example A. J. Meadows "Science and controversy: A biography of Sir Norman Lockyer" (London 1972) and "Early solar physics" (Oxford 1970).

126 See J. D. Burchfield "Lord Kelvin" for an account of this debate.

127 A point made quite explicitly by Kelvin in "On the mechanical action of radiant heat" Proc. Roy. Soc. Edinb. 1852, 3: 112-3.

NOTES AND REFERENCES TO CHAPTER SEVEN

Spectro-chemical analysis 1854-1861

1 See Chapter 5 p145

2 John Hall Gladstone (1827-1902). Studied chemistry under Liebig at the University of Giessen 1847-8. The remains of his scientific correspondence are now at the Royal Society, but have not yet been catalogued.

3 J. H. Gladstone "On the use of the prism in qualitative analysis" Quart. J. Chem. Soc. 1858, 10: 79-91, p79.

4 ibid 79-80

5 See W. Crookes "Examination of the spectrum produced by coloured flames" in E. E. F. D'Albe "The life of Sir William Crookes" (London, 1923) p26-7. This according to D'Albe (p27) is taken from an old notebook of Crookes dated April 1854.

6 W. Crookes "On the supposed new member of the calcium group of metals" Chem. News 1861, 3: 129-30, p129

7 J. H. Galdstone "On chromatic phenomena exhibited by transmitted light" in W. L. Bragg and G. Porter (eds) "The Royal Institution Library of Science: Physical Sciences" (10 vols and index, Barking, 1970) I, 219-26, p219.

8 W. Crookes "Photographic researches on the spectrum - The spectrum camera and some of its applications" J. Photogr. Soc. 1856, 2: 292-5.

9 William Swan (1818-1894). At this time he was teaching mathematics and natural philosophy at the Scottish Naval and Military Academy; later he became professor of natural philosophy at the University of St. Andrews. Most of his writings were on optical subjects.

10 W. Swan "On the prismatic spectra of the flames of compounds of carbon and hydrogen" Trans. Roy. Soc. Edinb. 1857, 21: 411-29.

11 ibid 413-4

Notes and references to Chapter 7 (cont.)

12 ibid 414

13 ibid 417 where Swan lists the hydrocarbons which he examined.

14 ibid 418

15 J. H. Gladstone "On the use of the prism" Quart. J. Chem. Soc. 1858, 10: 80.

16 ibid 81, Gladstone's emphasis.

17 ibid 90

18 ibid

19 ibid 91

20 Robert Wilhelm Bunsen (1811-1899). Bunsen had previously taught chemistry at Göttingen, Cassel, Marburg and Breslau.

21 Gustav Robert Kirchhoff (1824-1887). Bunsen and Kirchhoff met when they were both teaching at the Universtiy of Breslau. According to H. E. Roscoe "Bunsen Memorial Lecture" J. Chem. Soc. 1900, 77: 513-54, p530 Bunsen was able in 1854 to ensure that Kirchhoff was appointed to the post of professor of physics at Heidelberg when it became vacant.

22 See G. R. Kirchhoff "Untersuchungen über das Sonnenspectrum und die Spectren der Chemischen Elemente" Abh. Königl. Akad. Wiss. Berlin 1861: 63-95; 1862: 227-40. Translated into English (by H. E. Roscoe) as "Researches on the solar spectrum, and the spectra of the chemical elements" (2 vols, Cambridge, 1862-3) I, 6 where he says that Bunsen directed Cartmell.

23 Rowlandson Cartmell (d. 1888) was a student at the Royal College of Chemistry 1847-8. Later he became an analytical chemist to a brewery in Burton on Trent.

24 R. Cartmell "On a photochemical method of recognizing the non-volatile alkalies and alkaline earths" Phil. Mag. 1858, 16: 328-33. Dated September 1858.

25 ibid 328

Notes and references to Chapter 7 (cont.)

26 ibid

27 ibid

28 ibid 333

29 ibid

30 ibid

31 Aragonite is one of the mineral forms of calcium carbonate ($CaCO_3$)

32 G. R. Kirchhoff "Ueber den Winkel der optischen Axen des Aragonits für die verschiedenen Fraunhofer' schen Linien" Pogg. Ann. 1859, 108: 567-75. Dated September 1859.

33 ibid 568.

fallen die durch einen Spiegel in horizontaler Richtung reflectirten Lichtstrahlen durch ein Nicol'sches Prisma auf einen engen verticalen Spalt, der in dem Brennpunkte einer Linse sich befindet; nachdem sie diese Linse druchdrungen haben, treffen sie ein Flintglasprisma von etwa 45^{o} brechendem Winkel, dessen brechende Kante vertical ist, gehen dann durch ein astronomisches Fernrohr von ungefähr 12maliger Vergrösserung, gelangen, nachdem sie aus dem Ocular dieses ausgetreten sind, an die Aragonitplatte und durchlaufen dann noch ein zweites astronomisches Fernrohr von etwa $1\frac{1}{2}$ facher Vergrösserung und ein zweites Nicol'sches Prisma, bevor sie in das Auge Beobachters treten.

34 R. W. Bunsen and G. R. Kirchhoff "Chemishe Analyse durch Spectralbeobachtungen" Pogg. Ann. 1860, 110: 160-89; 1861, 113: 337-81. Translated into English as "Chemical analysis by spectrum-observations" Phil. Mag. 1860, 20: 89-109; 1861, 22: 329-49, 498-510, p90.

35 See Chapter 4, p117.

36 J. Plücker "Ueber die Constitution der elektrische Spectra" Pogg. Ann. 1859, 107: 479-539, art 175.
J. Babinet "Sur les coleurs des réseaux" Ann. Chim. 1829, 40: 166-77, p166.
M. Faraday Diary 29 June 1849, 4: 8695.
W. Swan "Prismatic Spectra" Trans. Roy. Soc. Edinb.

1857, 21: 414 and 24 and "Experiments on the ordinary refraction of Iceland Spar" ibid 1849, 16: 375-8. All describe the use of such devices.

37 R. W. Bunsen "Löthrohrversuche" Ann. Chim. Pharm. 1859, 111: 257-76. Translated into English as "Blowpipe Experiments" Phil. Mag. 1859, 18: 513-21.

38 ibid 517

39 ibid Bunsen's emphasis

40 I have been unable to discover any biographical information about Dr Folwarczny. The name is probably Hungarian.

41 Folwarczny "Untersuchung des Inhalts einer Nierencyste" Würzburg. med. Zeit. 1860, 1: 151-4.

42 ibid 153-4

43 Henry Enfield Roscoe (1833-1915) professor of Chemistry at Owen's College Manchester (now the University of Manchester). For an account of his life see H. E. Roscoe "The life and experiences of Sir Henry Enfield Roscoe" (London, 1906).

44 Bunsen to Roscoe 24 May 1859 DM HS 926. Vergeuden.

45 W. Ostwald "Klassiker der Exakten Wissenschaften Nr 72" (Leipzig, 1895) reprinted R. W. Bunsen and G. R. Kirchhoff "Chemische Analyse" Pogg. Ann. 1860, 110: 160-89; 1861, 113: 337-81. This also contains an account by Ostwald (p71-3) of a conversation between himself and Bunsen about the development of the latter's work on spectroscopy. In it this account of the origin of Bunsen and Kirchhoff's collaboration is given.

46 G. R. Kirchhoff "Ueber die Fraunhofer'schen Linien" Berlin Monatsber. 1859: 662-5. Translated into English by G. G. Stokes as "On Fraunhofer's lines" in "On the simultaneous emission and absorption of rays of the same definite refrangibility; being a translation of a portion of a paper by M. Léon Foucault, and of a paper by Professor Kirchhoff" Phil. Mag. 1860, 19: 193-7, p195-6. Dated 20 October 1859. On p196 he mentions Brewster's observation of the spectrum of saltpeter (see note 47). G. R. Kirchhoff "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 251-5, read on 28 October 1859. This mentions the same work of Brewster on p253 and 5.

Notes and references to Chapter 7 (cont.)

47 Both these observations are contained in D. Brewster "Optics" (4th edition, London, 1853) p98 and 93-4 respectively. The former observation also occurs in D. Brewster "Observations sur le spectre solaire" Comptes Rendus 1850, 30: 578-81. This was translated into German as "Beobachtungen über das Sonnenspectrum" Pogg. Ann. 1850, 81: 471-6.

48 Kirchhoff later wrote that at this time he did not know of the work of Talbot, Herschel or W. A. Miller. G. R. Kirchhoff "Zur Geschichte der Spectral-Analyse und der Analyse der Sonnenatmosphäre" Pogg. Ann. 1863, 118: 94-111. Translated into English as "Contributions towards the history of spectrum analysis and of the analysis of the solar atmosphere" Phil. Mag. 1863, 25: 250-62. p251-3.

49 Swan was the only one of his predecessors to whom Kirchhoff gave any credit in his "Contributions towards the history of spectrum analysis" Phil. Mag. 1863, 25: 255-6, but he stopped short of saying that Swan had any influence on their work. But he was cited by R. W. Bunsen and G. R. Kirchhoff in "Chemical Analysis" Phil. Mag. 1860, 20: 94, where they referred to his demonstration of the small quantities of salt required to produce the yellow lines.

50 G. R. Kirchhoff "On Fraunhofer's lines" Phil. Mag. 1860, 19: 195.

51 ibid 196

52 See Chapter 3, p75.

53 G. R. Kirchhoff "On Fraunhofer's lines" Phil. Mag. 1860, 19: 195

54 G. R. Kirchhoff "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 253. Das Sonnenlicht hatten wir gedämpft, damit trotz desselben das schwächere Licht der Kochsalzflamme wahrnehmbar wäre

55 ibid

56 Bunsen maintained that it was Kirchhoff alone who took this next step. See, for example, Bunsen to Roscoe 13 November 1859 DM HS 930. Translated into English by H. E, Roscoe "Life" p81-2 and partly in "Memorial Lecture" J. Chem. Soc. 1900, 77: 531 where it is also reproduced in facsimile between p536 and 7.

Notes and references to Chapter 7 (cont.)

57 G. R. Kirchhoff "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 253. Um die Gränze zu finden, bis zu welcher dasselbe die Natriumstreifen noch wahrzunehmen erlaube.

58 ibid

59 ibid

60 Thomas Drummond (1797-1840) invented, for the purpose of geodetic surveying, a lamp which burned a ball of lime in a jet of oxygen to produce a very intense beam of light with a continuous spectrum. This was subsequently named the Drummond lamp. See T. Drummond "On the means of facilitating the observation of distant stations in geodaetical operations" Phil. Trans. 1826: 324-37 and "Description of an apparatus for producing intense light, visible at great distances" Edinb. J. Sci. 1826, 5: 319-22.

61 G. R. Kirchhoff "On Fraunhofer's lines" Phil. Mag. 1860, 19: 195. He later artificially reversed the lithium spectrum (G. R. Kirchhoff "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 254) and together Bunsen and Kirchhoff later reversed the spectra of potassium, strontium, calcium and barium (R. W. Bunsen and G. R. Kirchhoff "Chemical Analysis" Phil. Mag. 1860, 20: 109).

62 ibid and G. R. Kirchhoff "On Fraunhofer's Lines" Phil. Mag. 1860: 19: 196. See Chapter 6 for details of contemporary solar theories.

63 According to H. E. Roscoe "Life" especially chapters 3 and 4, the members of the scientific community at Heidelberg were very well acquainted with each other; it should therefore not be found surprising that each scientist knew of the work of others in some detail.

64 D. Brewster and J. H. Gladstone "On the lines of the solar spectrum" Phil. Trans. 1860, 150: 149-60. p158-9 where they suggest that Fraunhofer's observations of stellar spectra might have been faulty. If this was the case then it followed that there was no certainty that stellar spectra differed from each other and from the solar spectrum, and therefore there was no need to argue that the lines originated in the stars, as had been done up to this point.

Notes and references to Chapter 7 (cont.)

65 Kirchhoff stated in "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 254 that this arrangement followed from his interpretation of his first experiment, but he does not explicitly pursue the analogy.

66 G. R. Kirchhoff "On Fraunhofer's lines" Phil. Mag. 1860, 19: 196

67 ibid

68 ibid

69 Helmholtz to Kelvin 15 November 1859 GUL Kelvin papers H16. die Linien E und die brechbarste der 3 Linien b vom Eisen.

70 G. R. Kirchhoff "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 255. dassEisen in derselben [der Sonnenatmosphäre] vorkommt.

71 See Chapter 6, p164-5 and p169.

72 G. R. Kirchhoff "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 251-5.

73 ibid 253-4. 1) dassdie Kochsalzflamme von den Strahlen, die durch sie hindurchgehen, gerade die Strahlen von der Farbe derer, die sie aussendet vorzugsweise schwächt, und 2) dass im Sonnenspektrum auch in den dunkeln Linien Licht ist, nur viel schwächeres, als in deren Nachbarschaft.

74 Bunsen to Roscoe 13 November 1859 DM HS 930. Helmholtz to Kelvin 15 November 1859 GUL Kelvin papers H16. John Ferguson, one of Kelvin's students in 1859, reported that Kelvin was satisfied that Kirchhoff had shown that "there must be an immense amount of iron in the sun's atmosphere" "Lord Kelvin" Glasg. Univ. Mag. 1908, 20: 279.

75 G. R. Kirchhoff "Ueber das Sonnenspektrum" Verhandl. Nat. Med. Ver. Heidelb. 1859: 254-5.

Notes and references to Chapter 7 (cont.)

76 G. R. Kirchhoff "Ueber das Zusammenhang zwischen Emission und Absorption von Licht und Wärme" Berlin. Monatsber. 1859: 783-7.

77 ibid 784. den allgemeinen Grundsätzen der mechanischen Wärmetheorie.

78 ibid für Strahlen derselben Wellenlänge bei derselben Temperatur das Verhältniss des Emissionsvermögens zum Absorptionsvermögen bei allen Körpern dasselbe ist.

79 ibid 786-7.
More formally if $e/a = f(\mu,t)$ (μ = wave-length, t = temperature) then when t is given, $e/a = g(\mu)$. Therefore absorption can only occur in the spectrum where emission occurs and vice versa, since otherwise the function would not have any meaning at that point.

80 In practice equilibrium occurs after a relatively short finite time.

81 For the mathematical details of this proof see appendix, p220-1.

82 G. R. Kirchhoff "Emission und Absorption" Berlin Monatsber. 1859: 785.

83 This analysis contradicts M. A. Sutton "Spectroscopy and the Structure of Matter" on p204 where he states, quite dogmatically, that Kirchhoff worked from Pierre Prevost's theory of exchanges. As we have seen, Kirchhoff analysed the phenomenon of reversal using thermodynamic arguments, whereas a contemporary of Kirchhoff's, Balfour Stewart (1828-1887) anticipated Kirchhoff's result so far as heat was concerned, but used Prevost's theory of exchange to achieve a less rigorous proof. B. Stewart "An account of some experiments on radiant heat, involving an extension of Prévost's theory of exchanges" Trans. Roy. Soc. Edinb. 1858, 22: 1-20, especially section 12. See D. M. Siegel "Balfour Stewart and Gustav Robert Kirchhoff: Two independent approaches to "Kirchhoff's radiation law"" ISIS 1976, 67: 567-600 especially sections 3 and 5 for an analysis of Stewart's work. Kirchhoff later stated that he had not been aware of Stewart's work before his own. G. R. Kirchhoff "Contributions towards the history of spectrum analysis" Phil. Mag. 1863, 25: 258-60.

Notes and references to Chapter 7 (cont.)

84 G. R. Kirchhoff "On Fraunhofer's lines" Phil. Mag. 1860, 19: 196.

85 ibid

86 G. R. Kirchhoff "Ueber das Verhältniss zwischen dem Emissionsvermögen und dem Absorptionsvermögen der Körper für Wärme und Licht" Pogg. Ann. 1860, 109: 275-301. Translated into English as "On the relation between the radiating and absorbing powers of different bodies for light and heat" Phil. Mag. 1860, 20: 1-21.

87 ibid 2. Schwarzer Körper.

88 It is not necessary here to examine Kirchhoff's second proof in detail since the results which he derived from both proofs are the same. For detailed treatments see J. Agassi "The Kirchhoff-Planck Radiation Law" Science 1967, 156: 30-7 and A. Cotton "The present status of Kirchhoff's law" Astrophysical J. 1899, 9: 237-68.

89 This may well imply that the two analyses were developed sequentially, since Kirchhoff's first proof could have employed a properly defined black body with very little modification.

90 G. R. Kirchhoff "Radiating and Absorbing Powers" Phil. Mag. 1860, 20: 12-13.

91 ibid 14

92 ibid 15-16 Kirchhoff's emphasis.

93 R. W. Bunsen and G. R. Kirchhoff "Chemical Analysis" Phil. Mag. 1860, 20: 99-106.

94 ibid 91-2, their emphasis.

95 G. R. Kirchhoff "Emission und Absorption" Berlin Monatsber. 1859: 787 man kann annehmen,dass diese Linien übereinstimmen mit denjenigen, die in dem Spectrum einer Flamme von sehr hoher Temperatur sich bilden würden, wenn man in diese dasselbe Metall in passender Form brächte.

96 R. W. Bunsen and G. R. Kirchhoff "Chemical Analysis" Phil. Mag. 1860, 20: 93.

Notes and references to Chapter 7 (cont.)

97 ibid 89-90

98 R. W. Bunsen "Ueber ein neues, dem Kalium nahestehendes Metall" J. Prak. Chem. 1860, 80: 477-80. Among the mineral waters which Bunsen examined were samples from Kreuznach, Durkheim and Baden-Baden (p479).

99 ibid 478-9

100 Bunsen to Roscoe 10 April 1860, DM HS 932. Translated into English in H. E. Roscoe "Memorial Lecture" J. Chem. Soc. 1900, 77: 531.

101 See below and V. Karpenko "The discovery of supposed new elements: two centuries of error" Ambix 1980, 27: 77-102 which includes details of numerous spurious elements though not all "discovered" by means of spectroscopic analysis.

102 R. W. Bunsen and G. R. Kirchhoff "Chemical Analysis" Phil. Mag. 1860, 20: 107.

103 ibid; Bunsen to Roscoe 10 April 1860 DM HS 932; R. W. Bunsen "Ueber Benutzung der Flammenspektrum bei der chemischen Analyse" Verhandl. Nat. Med. Ver. Heidelb. 1860: 31-2.

104 R. W. Bunsen "Ueber ein neues, dem Kalium nahestehendes Metall" J. Prak. Chem. 1860, 80: 479.

105 ibid Das Chlorid des neuen Alkalimetalls unterscheidet sich vom Kochsalz und Chlorlithium dadurch, dass es wie Chlorkalium mit Platinchlorid einen gelben Neiderschlag giebt. Vom Kalium ist es durch die Löslichkeit seines salpetersauren Salzes in Alkohol unterschieden.

106 Bunsen to Roscoe 6 November 1860 DM HS 936. Partly translated into English in H. E. Roscoe "Life" p532. R. W. Bunsen "Ueber ein fünftes der Alkaligruppe angehörendes Element" J. Prak. Chem. 1861, 83: 198-200. Translated into English as "On a fifth element belonging to the alkali group" Chem. News 1861, 3: 357.

107 Bunsen to Roscoe 6 November 1860 DM HS 936. R. W. Bunsen and G. R. Kirchhoff "Chemical Analysis" Phil. Mag. 1861, 22: 330. Since the characteristic line of the spectrum of this new element was in the blue Bunsen derived the name from "caesia" used in Aulus Gellius "Noctes Atticae" II, 26, to designate the blue of a clear sky.

108 Charles Hanson Greville Williams (1829-1910). At this time he was an industrial chemist in Glasgow. He later founded a firm of chemical dyestuff manufacturers in London. For a short account of his life see H. J. Stern "Greville Williams, discoverer of isoprene" Chem. Brit 1979, 80: 455-8. There are a small number of letters to Williams kept at Williams (Hounslow) Ltd, Hibernia Road, Hounslow. I am very grateful to Mr. V. Ward and Mrs. B. Bennett of the Personnel Department for providing me with every facility to study the Crookes-Williams correspondence. Since there are no manuscript numbers the letter dates only will be used.

109 Crookes to Williams 1 February 1861. Crookes's emphasis.

110 Crookes to Williams 2 March 1861. Crookes's emphasis.

111 On the first day of that year Bunsen wrote to Roscoe saying that he would send some samples of caesium salts to Roscoe to arrive later (Bunsen to Roscoe 1 January 1861 DM HS 937; an English translation by Roscoe is in the RSC MS collection). He must therefore have been in ignorance of any other new metal at that time. However on Monday 25 February 1861 (see Crookes to Williams 2 March 1861), Roscoe received a letter from Bunsen (which I have been unable to trace) saying that he had discovered a new chemical element and that the sample of caesium which he had sent in January contained traces of this new element. This letter Roscoe partly read to the Royal Institution on March 1 1861 in a lecture entitled "On Bunsen and Kirchhoff's spectral observations" Chem. News 1861, 3: 153-5, 170-2, p155.

112 R. W. Bunsen "On a fifth element" Chem. News 1861, 3: 357.

113 R. W. Bunsen and G. R. Kirchhoff "Chemical Analysis" Phil. Mag. 1861, 22: 330. Since the characteristic line of the spectrum of this new element was in the red, Bunsen derived the name from "rubidus" used in Aulus Gellius "Noctes Atticae" II, 26, to designate the darkest red colour.

114 Friedrich Wilhelm Dupré (before 1835-1908) and August Dupré (1835-1907). Both brothers worked under Liebig at Giessen and Bunsen at Heidelberg before coming to England in 1855 to work under W. Odling at Guy's Hospital Medical School.

Notes and references to Chapter 7 (cont.)

115 F. W. and A. Dupré "On the existence of a fourth member of the calcium group of metals" Phil. Mag. 1861, 21· 86-8; Chem. News 1861, 3: 116-7.

116 W. Crookes "On a supposed new member of the calcium group of metals" Chem. News 1861, 3: 129-30. This was acknowledged by F. W. and A. Dupré in "On the calcium spectrum" Phil. Mag. 1861, 21: 239.

117 W. Crookes "On a supposed new member of the calcium group" Chem. News 1861, 3: 129-30.

118 Crookes to Williams 1 February 1861

119 Crookes to Williams 11 February 1861, Crookes's emphasis.

120 ibid

121 Crookes to Williams 5 March 1861. Printed in E. E. F. D'Albe "William Crookes" 59-60. This was also recorded by Crookes in his laboratory notebook SM MS 408, p52 (entry for 7 March 1861).

122 Crookes to Williams 7 March 1861.

123 Crookes to Williams 8 March 1861. Partly printed in E. E. F. D'Albe "William Crookes" 60-1.

124 W. Crookes "Further remarks on the supposed new metalloid". Chem. News 1861, 3: 303. This came from θαλλός, a budding twig which was used to express the green tint of young vegetation since the characteristic line was in the green.

125 Crookes to Williams 8 March 1861.

126 Crookes to Williams 13 April 1861. W. Crookes "On the existence of a new element, probably of the sulphur group" Chem. News 1861, 3: 193-4.

127 Claude Auguste Lamy (1820-1878) Prof. of physics at Lille and (1865) Prof. of chemistry at the École Centrale des Arts et Manufactures in Paris.

128 A. Lamy 'De l'existence d'un nouveau métal, le thallium Comptes Rendus 1862, 54: 1255-8. Translated into English as "On the new metal thallium" Chem. News 1862, 6: 29-30; here he stated that it was in March 1862 that he observed the green line.

NOTES AND REFERENCES TO THE CONCLUSION

The early historiography of spectroscopy

1 G. R. Kirchhoff "Contributions towards the history of spectrum analysis" Phil. Mag. 1863, 25: 256.

2 [W. Crookes] "Early researches on the spectra of artificial light from different sources" Chem. News 1861, 3: 184-5, p184.

3 C. Wheatstone "On the prismatic decomposition of electrical light" Rep. Brit. Ass. 1835, pt 2: 11-12; Chem. News 1861, 3: 185.

4 C. Wheatstone "On the prismatic decomposition of the electric, voltaic, and electro-magnetic sparks" Chem. News 1861, 3: 198-201.

5 W. H. F. Talbot "Some experiments on coloured flames" Edinb. J. Sci. 1826, 5: 77-81; Chem. News 1861, 3: 261-2.

6 W. H. F. Talbot "On a method of obtaining homogeneous light of great intensity" Phil. Mag. 1833, 3: 35; Chem. News 1861, 3: 262. "On the flame of lithia" and "On the flame of cyanogen" in "Facts relating to optical science No. I" Phil. Mag. 1834, 4: 114; Chem. News 1861, 3: 262-3. "On prismatic spectra" and "Spectra of various galvanic flames" in "Facts relating to optical science No. III" Phil. Mag. 1836, 9: 3-4; Chem. News 1861, 3: 263.

7 W. A. Miller "Experiments and observations on some cases of lines in the prismatic spectrum produced by the passage of light through coloured vapours and gases, and from certain coloured flames" Phil. Mag. 1845, 27: 81-91; Chem. News 1861, 3: 304-7.

8 H. E. Roscoe "On the application of the induction coil to Steinheil's apparatus for spectrum analysis" Chem. News 1861, 4: 118-22, p119.

9 Roscoe to Gladstone 10 May 1861, RS MS Gladstone papers.

10 ibid Roscoe's emphasis.

11 W. A. Miller "The new method of spectrum analysis" Chem. News 1861, 4: 159-61, p160.

Notes and references to the conclusion (cont.)

12 W. A. Miller "On spectrum analysis", a lecture given to the Pharmaceutical Society Chem. News 1862, 5: 201-3, 214-8.

13 G. R. Kirchhoff "Contributions towards the history of spectrum analysis" Phil. Mag. 1863, 25: 250-62.

14 [W. Crookes] "Early researches on the spectra of artificial light" Chem. News 1861, 3: 303-4.

15 G. R. Kirchhoff "Contributions towards the history of spectrum analysis" Phil. Mag. 1863, 25: 255.

16 E. Frankland in the discussion of H. E, Roscoe's lecture "On the application of the induction coil" Chem. News 1861, 4: 118-22, ibid 131.

17 It is quite fascinating to observe that this pre-occupation with the history of spectro-chemical analysis has survived down to our own day. To take just the most recent example, M. A. Sutton in "Spectroscopy and the chemists: A neglected opportunity?" Ambix 1976, 23: 16-26 is entirely concerned with trying to explain why chemists did not use spectra before 1859, and not with what scientists were actually doing with spectra.

18 Stokes to Plücker 30 April 1860 RS MS Phl. 38 (Original at the National Research Council of Canada).

BIBLIOGRAPHY 1

Manuscripts

In the course of my research I consulted the manuscripts listed below and though I have not directly cited all of this material it has provided me with a useful insight into the workings of nineteenth century science.

Cambridge University Library

G. G. Stokes's papers (MS add 7656)
Lord Kelvin's papers (MS add 7342)

Royal Society Library

J. H. Gladstone's papers
John Herschel's papers
J. Larmor's papers
J. Lubbock's papers
Referees reports
Phil. Trans. manuscripts
Photostats of letters to Plücker

Imperial College

S. P. Thompson's papers

King's College London

C. Wheatstone's papers

University College London

Lord Brougham's papers

Royal Greenwich Observatory Hurstmonceux

G. B. Airy's papers

Royal Society of Chemistry

H. E. Roscoe's papers

Science Museum London

W. Crookes's notebooks

Bibliography 1 (cont.)

Lacock Abbey

W. H. F. Talbot's papers

Williams (Hounslow) Ltd.

Letters of W. Crookes to C. H. G. Williams

Glasgow University Library

Lord Kelvin's papers

Department of Natural Philosophy, University of Glasgow

Departmental records

St. Andrews' University

J. D. Forbes's papers

Edinburgh University Library

Letters of D. Brewster

National Library of Scotland

Letters of D. Brewster

University of Heidelberg

Letters of R. W. Bunsen, G. R. Kirchhoff, H. von Helmholtz

Deutsches Museum, Munich

Letters of R. W. Bunsen to H. E. Roscoe
Letters of J. von Fraunhofer, P. Guinand, J. von Utzschneider

BIBLIOGRAPHY 2

Printed Sources

This lists all papers, books etc. cited in the notes and references and additional material of which I have made use. I have not listed individual entries from the "Dictionary of Scientific Biography", "Dictionary of National Biography", "Nouvelle Biographie Général", "Poggendorff Biographisch-Literarisches Handwörterbuch", "Who was Who" or any other national biographical dictionary, although obituary notices where they have proved useful are cited.

Collected papers are cited under the author of the papers followed by the names of the editors (if known). The names of editors are cross-referenced to the author of the papers in the collected works; this is signified by the abbreviation (ed). Translators of papers or books are signified in the cross-references by (tr); contemporary reviews and discussions of a particular piece of work are indicated by the abbreviation (rev). Cross-references unless otherwise indicated refer to the authors of biographical studies of the person from which reference is made.

Papers or books of joint authorship are cited in full under each author. Where individual papers of an author for some reason occur in another work, this latter is cited in full under the name of the editor; the title of the individual paper is given under its author with a short title of the work in which it appears, but not full bibliographic information.

Adams, C. W.

William Allen Miller and William Hallowes Miller
(A note to the early history of spectroscopy)
ISIS 1943, 34: 337-9

Agassi, J.

Sir John Herschel's philosophy of success
Hist. Stud. Phys. Sci. 1969, 1: 1-36

The Kirchhoff-Planck Radiation Law
Science 1967, 156: 30-7

Airy, G. B.

Autobiography of Sir George Biddell Airy
edited by W. Airy
(Cambridge, 1896)

Remarks on Sir David Brewster's paper "On the absorption of specific rays &c"
Phil. Mag. 1833, 2: 419-24

Airy, W. see Airy, G. B. (ed)

Alter, D. see also Hamor, W. A.

On certain physical properties of the light of the electric spark, within certain gases as seen through a prism
Am. J. Sci. 1855, 19: 213-4

On certain physical properties of light, produced by the combustion of different metals in the electric spark, refracted by a prism
Am. J. Sci. 1854, 18: 55-7

Andrade, E. N. da C.

Doppler and the Doppler effect
Endeavour 1959, 18: 14-19

Ångström, A. J. see also Beckman, A.; Thalén, R.

Optiska Undersökningar
Kongl. Veten. Akad. Handl. 1854: 335-360
Translated into German as
Optische Untersuchungen
Pogg. Ann. 1855, 94: 141-65
Translated into English (by John Tyndall) as
Optical Researches
Phil. Mag. 1855, 9: 327-42

Arago, D. F. J

Oeuvres complètes de François Arago
edited by J. A. Barral
(17 vols, Paris, 1854-62)
cited as Oeuvres

Notice sur la polarisation de lumière
Oeuvres VII, 291-449
Translated by Thomas Young as
Refraction, double and Polarisation of light
in "Addenda et Corrigenda" to the "Supplement to the
fourth, fifth and sixth editions of the
Encyclopaedia Britannica" VI, 838-863

Rapport fait par M. Arago à l'Académie des Sciences,
au nom de la Commission qui avait été chargée
d'examiner les mémoires envoyés au concours pour
le prix de la diffraction
Ann. Chim. 1819, 11: 5-30
A. J. Fresnel: Oeuvres I: 229-37

Arago, D. F. J. and Fresnel, A. J.

Mémoire sur l'Action que les rayons de lumière
polarisée exercent les uns sur les autres
Ann. Chim. 1819, 10: 288-306
A. J. Fresnel Oeuvres I: 509-22

Arnold, H. J. P

William Henry Fox Talbot: pioneer of photography
and man of science
(London, 1977)

Aulus Gellius see under Gellius, A.

B., C. P. d. see R., E. (tr)

Babbage, C.

Reflections on the decline of science in England
(London, 1830)

Babinet, J.

Sur les Coleurs des réseaux
Ann. Chim. 1829, 40: 166-77

Badash, L.

The completeness of nineteenth-century science
ISIS 1972, 63: 48-58

Badcock, A. W.

Physical optics at the Royal Society 1660-1800
Brit. J. Hist. Sci. 1962, 1: 99-116

Baly, E. C. C.

Spectroscopy
(London, 1918)

Barr, E. S.

Men and milestones in optics 1. George Gabriel Stokes
App. Optics 1962, 1: 69-73

Barral, J. A. see Arago, D. F. J. (ed)

Beckman, A.

Anders Jonas Ångström
in S. Lindroth (ed) "Swedish men of science 1650-1950"
p193-203

Becquerel, A.-C.

Traité Expérimental de L'Électricité et du Magnétisme
et de leurs rapports avec les phénomènes naturels
(6 vols, Paris 1834-40)

Beer, A.

Einleitung in die Höhere Optik
(Braunschweig, 1853)

Berthelot, M. see Klooster, H. S. van

Biot, J.-B.

Sur le formation de l'eau par le seule compression,
et sur la nature de l'étincelle électrique
Ann. Chim. 1805, 53: 321-7
Translated into English as
Note on the formation of water by mere compression;
with reflections on the nature of the electric spark
J. Nat. Phil. 1805, 12: 212-5

Bodenstein, M see Bunsen, R. W. (ed)

Bowers, B. P.

The life and work of Sir Charles Wheatstone (1802-1875)
with particular reference to his contributions to
electrical science
(University of London (external) Ph.D. thesis 1975)

Sir Charles Wheatstone FRS 1802-1875
(London 1975)

Bradbury, S.

The evolution of the microscope
(Oxford, 1967)

Bragg, W. L. and Porter, G. (eds)

The Royal Institution Library of Science: Physical Sciences
(10 vols and index, Barking, 1970)

Brewster, D. see also Airy, G. B. (rev); Morse, E. W.

Account of a new monochromatic lamp depending on the combustion of Compressed Gas
Edinb. J. Sci. 1829, 1: 108

On certain peculiarities in the double refraction and absorption of light exhibited in the oxalate of chromium and potash
Phil. Trans. 1835: 91-3

On the colours of natural bodies
Trans. Roy. Soc. Edinb. 1834, 12: 538-45

On the decomposition and dispersion of light within solid and fluid bodies
Phil. Mag. 1848, 32: 401-12

Description of a monochromatic lamp for microscopical purposes, &c, with remarks on the absorption of the prismatic rays by coloured media
Trans. Roy. Soc. Edinb. 1822, 9: 433-44
reviewed in Edinb. J. Sci. 1825, 2: 344-8

Description of a monochromatic lamp, with observations on the composition of different flames as modified by reflexion, refraction and combustion
Edinb. Phil. J. 1822, 7: 163

On the laws of the polarisation of light by refraction
Phil. Trans. 1830: 69-84, 133-44

The life of Sir Isaac Newton
(London, 1831)

On the luminous bands in the spectra of various flames
Rep. Brit. Ass. 1842, pt 2: 15-16

On luminous lines in certain flames corresponding to the defective lines in the sun's light
Rep. Brit. Ass. 1842, pt 2: 15

More worlds than one
(London, 1858)

Brewster, D. (cont.)

On a new phenomenon of colour in certain specimens of fluor spar
Rep. Brit. Ass. 1838, pt 2: 10-12

Notes sur l'histoire de l'analyse spectrale
Comptes Rendus 1866, 62: 17-19

Observations on the absorption of specific rays, in reference to the undulatory theory of light
Phil. Mag. 1833, 2: 360-3

Observations on the lines of the solar spectrum, and on those produced by the Earth's atmosphere, and by the action of Nitrous Acid Gas
Proc. Roy. Soc. Edinb. 1833, 1: 21-4
Trans. Roy. Soc. Edinb. 1834, 12· 519-30

Observations sur le spectre solaire
Comptes Rendus 1850, 30: 578-81
Translated into German as
Beobachtungen über das Sonnenspectrum
Pogg. Ann. 1850, 81: 471-6

Observations on vision through coloured glasses, and on their application to telescopes, and to microscopes of great magnitude
Edinb. Phil. J. 1822, 6: 102-7

Report on the recent progress of optics
Rep. Brit. Ass. 1832: 308-22

A treatise on optics
(London, 1831; 2nd ed. 1838; 3rd ed. 1849; 4th rev. ed. 1853)
First edition translated into German (by F. Hartmann) as
Populäres, vollstandiges handbuch der Optik
(Leipzig, 1835)

Anon.

Memoir of the Life of M. le Chavalier Fraunhofer, the Celebrated Improver of the Achromatic Telescope, and Member of the Academy of Sciences at Munich
Edinb. J. Sci. 1827, 7: 1-11
reprinted in Am. J. Sci. 1829, 16: 304-13

Optics
Encyclopaedia Britannica 7th ed. XVI: 348-514

Review of W. Whewell "Astronomy and general physics considered with reference to Natural theology"
Edinb. Rev. 1834, 58: 422-57

Brewster, D. and Gladstone, J. H.

On the lines of the solar spectrum
Phil. Trans. 1860: 149-60

Broch, O. J.

Ueber die Fraunhofer'schen Linien im Sonnenspectrum; wie sie sich dem unbewaffneten Auge zeigen
Pogg. Ann. Engänz 1853, 3: 311-6

Brush, S. G.

The development of the kinetic theory of gases
II. Waterson
Ann. Sci. 1957, 13: 273-82

The wave theory of heat: a forgotten stage in the transition form the caloric theory to thermodynamics
Brit. J. Hist. Sci. 1970, 5: 145-67

Bunsen, R. W. see also Danzer, K.; Lockemann, G.; Roscoe, H. E.; Swan, W. (rev)

Gesammelte Abhandlungen
ed. by W. Ostwald and M. Bodenstein
(3 vols, Leipzig, 1904)

Ueber Benutzung der Flammenspektren bei der chemischen Analyse
Verhandl. Nat. Med. Ver. Heidelb. 1860: 31-2

Ueber Cäsium und Rubidium
Ann. Chim. Pharm. 1861, 119: 107-14

Ueber ein fünftes der Alkaligruppe angehörendes Element
J. Prak. Chim. 1861, 83: 198-200
Translated into English as
On a fifth element belonging to the alkali group
Chem. News 1861, 3: 357

Löthrohrversuche
Ann. Chim. Pharm. 1859, 111: 257-76
Translated into English as
Blowpipe Experiments
Phil. Mag. 1859, 18: 513-21

Ueber ein neues, dem Kalium nahestenendes Metall
J. Prak. Chem. 1860, 80: 447-80

Bunsen, R. W. and Kirchhoff, G. R.

Chemische Analyse durch Spectralbeobachtungen
Pogg. Ann. 1860, 110: 161-89; 1861, 113: 337-81
Reprinted in W. Ostwald (ed.) "Klassiker der Exakten Wissenschaften Nr. 72"
Translated into English as
Chemical analysis by spectrum-observations
Phil. Mag. 1860, 20: 89-109; 1861, 22· 329-49, 498-510

Kleiner Spectralapparat zum Gebrauch in Laboratorien
Zeit. Anal. Chim. 1862, 1: 139-40

Bunsen, R. W. and Kirchhoff, G. R. (cont.)

Die Spectren der Alkalien und alkalischen Erden
Zeit. Anal. Chim. 1862, 1: 1-2

Bunsen, R. W. and Roscoe, H. E.

Photo-chemical researches

Part 1	Phil. Trans.	1857: 355-80
Part 2	ibid	1857: 381-402
Part 3	ibid	1857: 601-620
Part 4	ibid	1859: 879-926
Part 5	ibid	1863: 139-160

Photo-chemical researches with reference to the laws of the chemical action of light
Rep. Brit. Ass. 1855, pt 2: 48-9

Burchfield, J. D.

Lord Kelvin and the age of the earth
(New York, 1975)

Buttmann, G.

The shadow of the telescope: a biography of John Herschel
(London, 1970)

Cannon, S. F.

Science in culture: The early Victorian period
(New York, 1978)

Cantor, G.

The changing role of Young's ether
Brit. J. Hist. Sci. 1970, 5: 44-62

The history of 'Georgian' optics
Hist. Sci. 1978, 16: 1-21

The reception of the wave theory of light in Britain: A case study illustrating the role of methodology in scientific debate
Hist. Stud. Phys. Sci. 1975, 6: 109-32

Cartmell, R.

On a photochemical method of recognizing the non-volatile alkalies and alkaline earths
Phil. Mag. 1858, 16: 328-33

Chaldecott, J. A.

The scientific works of Léon Foucault
(University of London (University College) M.Sc. thesis, 1949)

Chance, W. H. S

The optical glassworks at Benediktbeuern
Proc. Phys. Soc. 1937, 49: 433-43

Claggett, M. (ed.)

Critical problems in the history of science
(Madison, 1969)

Clerke, A. M.

Modern cosmogonies
(London, 1905)

A popular history of astronomy during the nineteenth century
(3rd ed., London, 1893)

Cooke, W. F. (ed) see also Hubbard, G.

The electric telegraph: was it invented by Professor Wheatstone?
(2 vols, London 1856-7)

Cotton, A.

The present status of Kirchhoff's law
Astrophysical J. 1899, 9: 237-68

Crookes, W. see also D'Albe, E. E. F.

On the existence of a new element, probably of the sulphur group
Chem. News 1861, 3: 193-4

Further remarks on the supposed new metalloid
Chem. News 1861, 3: 303

Photographic researches on the spectrum - The spectrum camera and some of its applications
J. Photogr. Soc. 1856, 2: 292-5

On the supposed new member of the calcium group of metals
Chem. News 1861 , 3: 129-30

Anon.
Early researches on the spectra of artificial light
Chem. News 1861, 3: 303-4

Farly researches on the spectra of artificial light from different sources
Chem News 1861, 3: 184-5

D'Albe, E. E. F.

The life of Sir William Crookes
(London, 1923)

Dalton, J.

A new system of chemical philosophy
(2 vols, London 1808-27)

Daniell, J. F.

An introduction to the study of chemical philosophy
(2nd ed., London, 1843)

Danzer, K.

Robert W. Bunsen und Gustav R. Kirchhoff
(Leipzig, 1972)

DeKosky, R.

George Gabriel Stokes, Arthur Smithells and the origin of spectra in flames
Ambix 1980, 27: 103-123

De la Rue, W. see Roscoe, H. E. (rev)

Devonshire Commission's Report see under Her Majesty's Government

DeVorkin, D. H.

An astronomical symbiosis: stellar evolution and spectral classification (1860-1910)
(Leicester University Ph.D. thesis, 1978)

Dingle, H.

A hundred years of spectroscopy
(Oxford, 1951)
reprinted in Brit. J. Hist. Sci. 1963, 1: 199-216

Doppler, C. see also Andrade, E. N. da C.

Ueber das farbige Licht der Doppelsterne und einiger anderer Gestirne des Himmels
Abh. Königl. Böhm. Ges. Wiss. 1843, 2: 465-82

Draper, J. W.

On certain spectral appearances, and on the discovery of latent light
Phil. Mag. 1842, 21: 348-50

Description of the tithonometer, an instrument for measuring the chemical force of the indigo-tithonic rays
Phil. Mag. 1843, 23: 401-15

On the interference spectrum, and the absorption of tithonic rays
Phil. Mag. 1845, 26: 465-78

Draper, J. W. (cont.)

On a new system of inactive tithnographic spaces in the solar spectrum analogous to the fixed lines of Fraunhofer
Phil. Mag. 1843, 22: 360-8

On the production of light by chemical action
Phil. Mag. 1848, 32: 100-14

Dreyer, J. L. E. see Herschel, W. (ed.)

Drummond, T.

Description of an apparatus for producing intense light, visible at great distances
Edinb. J. Sci. 1826, 5: 319-22

On the means of facilitating the observation of distant stations in geodaetical operations
Phil. Trans. 1826: 324-37

Dupré, F. W. and Dupré, A.

On the calcium spectrum
Phil. Mag. 1861, 21: 239

On the existence of a fourth member of the calcium group of metals
Phil. Mag. 1861, 21: 86-8; Chem. News 1861, 3: 116-7

Elkana, Y.

The discovery of the conservation of energy
(London, 1974)

Encyclopaedia Britannica

Supplement to the fourth, fifth and sixth editions
(6 vols, Edinburgh, 1824)

Seventh edition
(21 vols, Edinburgh, 1842)

Eleventh edition
(29 vols, Cambridge, 1910-11)

Euler, L.

Leonhardi Euleri Opera Omnia
(3 series, Berlin, Göttingen, Leipzig, Heidelberg, Zürich, 1911-)
cited as Opera Omnia

Lettres a une Princesse d'Allemagne
(2 vols, St. Petersburg, 1758)

Opera Omnia 3rd series, vols 11 and 12 (edited by A. Speiser) (Zürich, 1960)
Translated into English (by H. Hunter) as
Letters of Euler to a German Princess
(2 vols, London, 1795)

Nova Theoria Lucis et Colorum
Opuscula varii argumenti 1746, 1: 169-244
Opera Omnia 3rd series, vol. 5 "Commentationes Opticae" vol. 1, (ed. by D. Speiser) (Zürich, 1962) p1-45.

Faraday, M. see also Jeffreys, A. E. (ed); Roscoe, H. E. (rev); Williams, L. P.

Experimental Researches in Electricity
(3 vols, London 1839-55)

Faraday's Diary
(7 vols and index, London 1932-6)

The selected correspondence of Michael Faraday
ed. by L. P. Williams
(2 vols, Cambridge 1971)

Ferguson, J.

Lord Kelvin: A recollection and an impression
Glasg. Univ. Mag. 1908, 20: 276-82

Fizeau, A.-H.-L.

Acoustique et optique
L'Institut 1849-50, 17: 11

Fizeau, A.-H.-L. and Foucault, J. B. L.

Recherches sur l'intensité de la lumière émise par le charbon dans l'expérience de Davy
Comptes Rendus 1844, 18: 746-54

Addition à une précédente Note concernant l'application des procédés daguerriens à la photographie
ibid 860-2

translated into English as

Researches on the intensity of light emitted by the charcoal in Davy's experiment
Elec. Mag. 1845, 1: 325-32

and Addition to a preceding note concerning the application of the Daguerrien process to photometry
ibid 333-5

Folwarczny, ?

Untersuchung des Inhalts einer Nierencyste
Würzburg. med. Zeit. 1860, 1: 151-4

Forbes, J. D.

An index to the correspondence and papers of James David Forbes (1809-1868)
(St. Andrews, 1968)

Note relative to the supposed origin of the deficient rays in the solar spectrum; being an account of an experiment made at Edinburgh during the annular eclipse of 15th May 1836
Phil. Trans. 1836: 453-5

Fox, R.

The rise and fall of Laplacian physics
Hist. Stud. Phys. Sci. 1974, 4: 89-136

Foucault, J. B. L. see also Chaldecott, J. A.

Recueil des travaux scientifiques de Léon Foucault
(2 vols, Paris, 1878)

Physique. Lumière électrique
L'Institut 1849-50, 17: 44-6
Partly reprinted as "Note sur la lumière de l'Arc Voltaique"
Ann. Chim. 1860, 58: 476-8
Partly translated into English (by G. G. Stokes) as "On the simultaneous emission and absorption of rays of the same definite refrangibility"
Phil. Mag. 1860, 19: 194

Foucault, J. B. L. and Fizeau, A.-H.-L.

Recherches sur l'intensité de la lumière émise par le charbon dans l'expérience de Davy
Comptes Rendus 1844, 18: 746-54

Addition à une précédente Note concernant l'application des procédés daguerriens à la photographie
ibid 860-2

translated into English as

Researches on the intensity of light emitted by the charcoal in Davy's experiment
Elec. Mag. 1845, 1: 325-32

and Addition to a proceding note concerning the application of the Daguerrien processes to photometry
ibid 333-5

Francis, W. see Wrede, F. J. von (tr)

Frankel, E.

Corpuscular optics and the wave theory of light: The science and politics of a revolution in physics
Social Stud. Sci. 1976, 6: 141-84

Frankland, E. see Roscoe, H. E. (rev)

Fraunhofer, J. von see also Brewster, D.; Leitner, A.; Rohr, M. v.; Roth, G. D.

Bestimmung des Brechungs- und Farbenzerstreuungs-Vermögens verschieder Glasarten, in Bezug auf die Vervollkommnung achromatischer Fernröhre
Denksch. König. Akad. Wiss. München 1814-15 [pub 1817] 5: 193-226
Translated into English as
On the refractive and dispersive power of different species of glass, in reference to the improvement of achromatic telescopes, with an account of the lines or streaks which cross the spectrum
Edinb. Phil. J. 1823, 9: 288-99; 1824, 10: 26-40
This paper is briefly reported as "Frauenhofer's [sic] experiments on the prismatic spectrum"
Edinb. Phil. J. 1822, 7: 178-9
and "Frauenhofer's [sic] experiments on the illuminating power of the prismatic rays"
ibid 179

Ueber die Construction des so eben vollendeten grossen Refractors
Astr. Nachr. 1824, 4: 17-24, 35-8
Translated into English as
On the construction of the large refracting telescope just completed
Phil. Mag. 1825, 66: 41-7

Kurzer Bericht von den Resultaten neuerer Versuche über die Gesetze des Lichtes, und die Theorie derselben
Gilbert Ann. 1823, 74: 337-78
Translated into English as
A short account of the results of recent experiments upon the laws of light, and its theory
Edinb. J. Sci. 1827, 7: 101-13, 251-62; 1828, 8: 7-10

Neue Modification des Lichtes durch gegenseitge Einwirkung und Beugung der Strahlen, und Gesetzte desselben
Denksch. König. Akad. Wiss. München 1821-2, 8: 1-76
(each paper in this volume is individually paginated)
This is briefly reported in "Frauenhofer's [sic] experiments on the inflexion of light"
Edinb. Phil. J. 1822, 7: 179-80

Fresnel, A. J. see also Silliman, R. H.

Fresnel, A. J. (cont.)

Oeuvres Complètes d'Augustin Fresnel
edited by H. de Senarmont, E. Verdet, and L. Fresnel
(3 vols, Paris, 1866-1870; New York, 1965)
cited as: Oeuvres

De la Lumière
in supplement to T. Thomson "Système de Chimie"
(Paris, 1822)
Oeuvres II: 3-146
Translated into English (by T. Young) as
Elementary view of the undulatory theory of light
Quart. J. Sci. 1827, 23: 127-41, 441-54; 24: 113-35,
431-48; 1828, 25: 198-215; 26: 168-91, 389-407;
1829, 27: 159-65

Mémoire sur la Diffraction de la Lumière
Mém. Acad Sci. 1821-2 [published 1826] , 5: 339-475
Oeuvres I: 247-382

Second Mémoire sur la Double Réfraction (written 1822)
Mem. Acad. Sci. 1827, 7: 45-176
Oeuvres II: 479-596
Translated into English (by A. W. Hobson) as
Memoir on double refraction
Taylor's Sci. Mem. 1852, 5: 238-333

Fresnel, A. J. and Arago, D. F. J.

Mémoire sur l'Action que les rayons de lumière
polarisée exercent les uns sur les autres
Ann. Chim. 1819, 10: 288-306
A. J. Fresnel Oeuvres I: 509-22

Fresnel, L. see Fresnel, A, J. (ed)

Friday, J. R. and MacLeod, R. M.

Archives of British men of science
(London, 1972)

The quest for archives of British men of science
Hist. Sci. 1973, 11: 8-20

Fuchs, H.-U.

Frühe Spektralanalyse von Fraunhofer bis Kirchhoff
Orion 1974, 32: 98-102

Fusinieri, A.

Sopra il trasporto di materia ponderabile nelle
folgori
Gior. Fis. Chim. 1827, 10: 353-369
Translated into English as
On the transport of ponderable matter which occurs during
electrical discharges
Elec. Mag. 1844, 1: 235-47

Gassiot, J. P.

On the stratifications and dark bands in electrical discharges as observed in Torricellian vacua
Proc. Roy. Soc. 1858, 9: 146-50; Phil. Trans. 1858: 1-16

Gellius, A.

Noctes Atticae
English translation by J. C. Rolfe
(3 vols, London, 1954)

Gillispie, C. C.

The edge of objectivity
(Princeton, 1960)

Gizycki, R von

Centre and periphery in the international scientific community: Germany, France and Great Britain in the 19th century
Minerva 1973, 11: 474-94

Gladstone, J. H. see also Roscoe, H. E. (rev)

On chromatic phenomena exhibited by transmitted light in W. L. Bragg and G. Porter "The Royal Institution Library of Science: Physical Sciences" I, 219-26

On an optical test for didymium
Quart. J. Chem. Soc. 1858, 10: 219-21

On the use of the prism in qualitative analysis
Quart. J. Chem. Soc. 1858, 10: 79-91

Gladstone, J. H. and Brewster, D.

On the lines of the solar spectrum
Phil. Trans. 1860: 149-60

Glazebrook, R. T.

Sir George Gabriel Stokes, FRS
Good Words 1901: 312-6

Graves, R. P.

Life of Sir William Rowan Hamilton
(3 vols, Dublin, 1882-9)

Gray, A.

Lord Kelvin: An account of his Scientific Life and Work
(London, 1908; New York, 1973)

Grove, W. R.

On the electro-chemical polarity of gases, including the striae in electrical discharges
Phil. Trans. 1852: 87-102

On the striae seen in the electrical discharge in vacuo
Phil. Mag. 1858, 16: 18-22

Guinand, P. see R., E.

Guthrie, F. see Plücker, J. (tr)

Haldane, J. S. see Waterson, J. J. (ed.)

Hamilton, W. R. see Graves, R. P.; Sarton, G.

Hamor, W. A.

David Alter and the discovery of spectrochemical analysis
ISIS 1935, 22: 507-10

Hanson, N. R.

Leverrier: The zenith and nadir of Newtonian Mechanics
ISIS 1962, 53: 359-78

Helmholtz, H. von see also Koenigsberger, L.

Ueber die Erhaltung der Kraft: Eine physikalische Abhandlung (Berlin, 1847)
Translated into English as
On the conservation of force; a physical memoir
Taylor's Sci. Mem. 1853: 114-62

Selected writings of Hermann von Helmholtz
edited by R. Kahl
(Middletown, Conn., 1971)

Ueber die Wechselwirkung der Naturkräfte und die darauf bezüglichen neusten Ermittelungen der Physik
(Königsberg, 1854)
Translated into English as
On the interaction of natural forces
Phil. Mag. 1856, 11: 489- 518

Her Majesty's Government

Report of the Royal Commission on scientific instruction and the advancement of science
(3 vols, London, 1872-5)

Herschel, A. see Roscoe, H. E. (rev)

Herschel, F. W. for all entries see under Herschel, W.

Herschel, J. F. W. see also Agassi, J.; Buttmann, G.; Sutton, M. A.

On the absorption of light by coloured media, and on the colours of the prismatic spectrum exhibited by certain flames; with an account of a ready mode of determining the absolute dispersive power of any medium by direct experiment
Trans. Roy. Soc. Edinb. 1822, 9: 445-60
reviewed in Edinb. J. Sci. 1825, 2: 344-8

On the absorption of light by coloured media, viewed in connexion with the undulatory theory
Abstract: Rep. Brit. Ass. 1833: 373-4
Full: Phil. Mag. 1833, 3: 401-12

On the action of crystallized bodies on homogeneous light, and on the causes of the deviation from NEWTON'S scale in the tints which many of them develope on exposure to a polarized ray
Phil. Trans. 1820: 45-100

'Αμόρφωτα No. I. On a case of superficial colour presented by a homogeneous liquid internally colourless
Phil. Trans. 1845: 143-5

'Αμόρφωτα No. II. On the epipolic dispersion of light, being a supplement to a paper entitled "on a case of superficial colour presented by a homogeneous liquid internally colourless"
Phil. Trans. 1845: 147-53

Light
Encyclopaedia Metropolitana 1828, 2: 341-586
reprinted in Volume 4, 1845
Translated into French (by P. F. Verhulst and A. Quetelet) as
Traité de la Lumière
(2 vols, Paris, 1829-33) with a supplement by Quetelet 2: 533-620
Translated into German (by J. C. E. Schmidt) as
Vom Licht (Stuttgart, 1831)

Preliminary discourse on the study of natural philosophy (London, 1831)

Results of astronomical observations, made during the years 1834, 5, 6, 7, 8 at the Cape of Good Hope, being a completion of a telescopic survey of the whole surface of the visible heavens, commenced in 1825 (London, 1847)

Sound
Encyclopaedia Metropolitana 1830, 2: 747-825
reprinted in Volume 4, 1845

Herschel, J. F. W. (cont.)

A treatise on astronomy
(London, 1834)
revised second edition
"Outlines of astronomy" (London, 1849)

Herschel, W.

The scientific papers of Sir William Herschel
ed. by J. L. E. Dreyer
(2 vols, London, 1912)
cited as Papers

On the nature and construction of the sun and fixed stars
Phil. Trans. 1795: 46-72
Papers I: 470-484

Hobson, A. W. see Fresnel, A. J. (tr)

Hopkins, W. see Waterson, J. J. (rev)

Hubbard, G.

Cooke and Wheatstone and the invention of the electric telegraph
(London, 1965)

Hunter, H. see Euler, L. (tr)

Jaki, S. L.

The five forms of Laplace's Cosmogony
Am. J. Phys. 1976, 44: 4-11

The Milky Way
(Newton Abbott, 1973)

Planets and planetarians
(Edinburgh, 1978)

Jeffreys, A. E.

Michael Faraday: A list of his lectures and published writings
(London, 1960)

Jevons, W. S.

Spectrum analysis
Chem. News 1862, 5: 251-52
discusses the work of T. Melvill

Joule, J. P.

The scientific papers of James Prescott Joule
(2 vols, London, 1884-1887)
cited as Papers

Joule, J. P. (cont.)

Sur l'équivalent mécanique du calorique
Comptes Rendus 1849, 28: 132-5

On the mechanical equivalent of heat, as determined by the heat evolved by the friction of fluids
Phil. Mag. 1847, 31: 173-6
Papers I: 277-81

On shooting stars
Phil. Mag. 1848, 32: 349-51
Papers I, 286-8

Kahl, R. see Helmholtz, H. v. (ed)

Kane, R. J.

Case of interference of sound
Rep. Brit. Ass. 1835, pt 2: 13-14

Kant, I. see also Whitrow, G. J.

Allgemeine Naturgeschichte und Theorie des Himmels
(Königsberg, 1755)

Karpenko, V.

The discovery of supposed new elements: two centuries of error
Ambix 1980, 27: 77-102

Kelvin see also Burchfield, J. D.; Ferguson, J.; Gray, A.; King, A. G.; Larmor, J.; Murray, D.; Picard, E.; Sharlin, H. I.; Smith, C. W.; Thompson, S. P.; Wilson, D. B. (& ed)

Mathematical and Physical Papers
vols 1-3 edited by Kelvin
vols 4-6 edited by J. Larmor
(6 vols, Cambridge, 1882-1911)
cited as Papers

Popular lectures and addresses
(3 vols, London, 1889-94)
cited as Lectures

On the age of the sun's heat
Macm. Mag. 1862, 5: 388-93
Lectures I, 356-75

On the dynamical theory of heat with numerical results deduced from Mr. Joule's equivalence of a thermal unit, and M. Regnault's observations on steam
Trans. Roy. Soc. Edinb. 1851, 20: 261-98, 475-82; 1854, 21: 123-71
Papers I: 174-291

Kelvin (cont.)

On the equilibrium of a gas under its own gravitation only
Proc. Roy. Soc. Edinb. 1887, 14: 111-8
Papers V: 184-90

Index to the manuscript collection of William Thomson, Baron Kelvin in Glasgow University Library (ULP, 6) (Glasgow, 1977)

On the mechanical action of radiant heat or light: on the power of animated creatures over matter: on the sources available to man for the production of mechanical effect
Proc. Roy. Soc. Edinb. 1852, 3: 108-113
Papers I, 505-10

On the mechanical antecedents of motion, heat, and light
Rep. Brit. Ass. 1854, pt 2: 59-63
Papers II: 34-40

On the mechanical energies of the solar system
Abstract: Proc. Roy. Soc. Edinb. 1854, 2: 241-4
Full: Trans. Roy. Soc. Edinb. 1854, 21: 63-80
Papers II: 1-25
Translated into French as
Mémoire sur l'énergie mécanique du système solaire
Comptes Rendus 1854, 39: 682-7

On the mechanical value of a cubic mile of sunlight, and on the possible density of the luminiferous medium
Proc. Roy. Soc. Edinb. 1854, 2: 253-5

Note on the possible density of the luminiferous medium and on the mechanical value of a cubic mile of sunlight
Trans. Roy. Soc. Edinb. 1854, 21: 57-61
Papers II: 28-33

Physical considerations regarding the possible age of the sun's heat
Rep. Brit. Ass. 1861, pt 2: 27-28
Papers V: 141-4

The problem of a spherical gaseous nebula
Phil. Mag. 1908, 15: 687-711; 16: 1-23
Papers V: 254-283

Recent investigation of M. Leverrier on the motion of Mercury
Proc. Glasg. Phil. Soc. 1859, 4: 263-66
Papers V: 134-7

Kelvin (cont.)

The scientific work of Sir George Stokes
Nature 1903, 67: 337-8

On a universal tendency in nature to the dissipation of mechanical energy
Proc. Roy. Soc. Edinb. 1852, 3: 139-42
Papers I: 511-4

On the variation of the periodic times of the earth and inferior planets, produced by matter falling into the sun
Proc. Glasg. Phil. Soc. 1860, 4: 272-4
Papers V: 138-40

Kelvin and Stokes, G. G.

The correspondence between Sir George Gabriel Stokes and Sir William Thomson, Baron Kelvin of Largs
edited by D. B. Wilson
(Cambridge, forthcoming)

Kelvin and Tait, P. G.

Treatise on natural philosophy
(2 vols, Cambridge, 1883-6)

King, A. G.

Kelvin the Man
(London, 1925)

King, H. C.

The history of the telescope
(London, 1955)

Kirchhoff, G. R. see also Agassi, J.; Cotton, A.; Danzer, K.; Roscoe, H. E.; Siegel, D. M.; Swan, W. (rev)

Gesammelte Abhandlungen
(Leipzig, 1882)

Ueber die Fraunhofer'schen Linien
Berlin Monatsber 1859: 662-5;
Pogg. Ann. 1860, 109: 148-50
Translated into English (by G, G. Stokes) as On Fraunhofer's Lines in G. G. Stokes "On the simultaneous emission and absorption of rays of the same definite refrangibility"
Phil. Mag. 1860, 19: 195-6

Kirchhoff, G. R. (cont.)

Ueber die Fraunhofer'schen Linien
J. Prak. Chim. 1860, 80: 483-6
Translated into English (by H. E. Roscoe) as
Letter from Prof. Kirchhoff on the chemical analysis of the solar atmosphere
Phil. Mag. 1861, 21: 185-8. Partially reported as
"On the chemical analysis of the solar atmosphere"
Chem. News 1861, 3: 115-6

Zur Geschichte der Spectral-Analyse und der Analyse der Sonnenatmosphäre
Pogg. Ann. 1863, 118: 94-111
Translated into English as
Contributions towards the history of spectrum analysis and of the analysis of the solar atmosphere
Phil. Mag. 1863, 25: 250-62

Ueber einen neuen Satz der Wärmelehre
Verhandl. Nat. Med. Ver. Heidelb. 1860: 16-23
Translated into English as
On a new proposition in the theory of heat
Phil. Mag. 1861, 21: 241-7

Ueber das Sonnenspektrum
Verhandl. Nat. Med. Ver. Heidelb. 1859: 251-5

Untersuchungen über das Sonnenspectrum und die Spectren der chemischen Elemente
Abh. Königl. Akad. Wiss. Berlin 1861: 63-95; 1862: 227-40
Translated into English (by H. E. Roscoe) as
Researches on the solar spectrum, and the spectra of the chemical elements
(2 vols, Cambridge, 1862-3)
Volume 1 reviewed (anonymously) in Phil. Mag. 1862, 24: 52-7 and Westminster Rev. 1862, 78: 248-54

Ueber das Verhältniss zwischen dem Emissionsvermögen und dem Absorptionsvermögen der Körper für Wärme und Licht
Pogg. Ann. 1860, 109: 275-301
Translated into English as
On the relation between the radiating and absorbing powers of different bodies for light and heat
Phil. Mag. 1860, 20: 1-21

Ueber den Winkel der optischen Axen des Aragonits für die verschiedenen Fraunhofer'schen Linien
Pogg. Ann. 1859, 108: 567-75

Ueber das Zusammenhang zwischen Emission und Absorption von Licht und Wärme
Berlin Monatsber. 1859: 783-7

Kirchhoff, G. R. and Bunsen, R. W.

Chemische Analyse durch Spectralbeobachtungen
Pogg. Ann. 1860, 110: 161-89; 1861, 113: 337-81
Reprinted in W. Ostwald (ed.) "Klassiker der Exakten Wissenschaften Nr. 72"
Translated into English as
Chemical analysis by spectrum-observations
Phil. Mag. 1860, 20: 89-109; 1861, 22: 329-49, 498-510

Kleiner Spectralapparat zum Gebrauch in Laboratorien
Zeit. Anal. Chim. 1862, 1: 139-40

Die Spectren der Alkalien und alkalischen Erden
Zeit. Anal. Chim. 1862, 1: 1-2

Klooster, H. S. van

Bunsen, Berthelot, and Perkin
J. Chem. Ed. 1951, 28: 359-63

Koenigsberger, L

Hermann von Helmholtz
(3 vols, Braunschweig, 1902-3)
Abridged translation into English (by F. A. Welby)
(Oxford, 1906)

Koyré, A.

Mélanges Alexandre Koyré
(2 vols, Paris, 1964)

Kubrin, D.

Newton and the cyclical cosmos: providence and the mechanical philosophy
J. Hist. Ideas 1967, 28: 325-46

Kuhn, T.

Energy conservation as an example of simultaneous discovery
in M. Claggett (ed) "Critical problems in the history of science" p321-56

Lamy, A.

De l'existence d'un nouveau métal, le thallium
Comptes Rendus 1862, 54: 1255-8
Translated into English as
On the new metal thallium
Chem. News 1862, 6: 29-30

Lane, J. H.

On the theoretical temperature of the sun; under the hypothesis of a gaseous mass maintaining its volume by its internal heat, and depending on the laws of gases as known to terrestrial experiment
Am. J. Sci. 1870, 50: 57-74

Laplace, P. S. see also Jaki, S. L.; Whitrow, G. J.

Oeuvres de Laplace
(7 vols, Paris, 1843-7)
cited as Oeuvres

Exposition du Système du Monde
(2 vols, 1st ed Paris, 1796)
(5th ed Paris, 1824, Oeuvres VI)

Larmor, J. see also Kelvin (ed); Stokes, G. G. (ed)

William Thomson, Baron Kelvin of Largs 1824-1907
Proc. Roy. Soc. 1908, 81: iii-lxxvi

Latchford, K. A.

Thomas Young and the evolution of the interference principle
(University of London (Imperial College) Ph.D. thesis, 1974)

Leitch, J. see Young, T. (ed)

Leitner, A.

The life and work of Joseph Fraunhofer (1787-1826)
Am. J. Phys. 1975, 43: 59-68

Leverrier, U. J. J. see also Hanson, N. R.; Kelvin (rev)

Sur le théorie de Mercure et sur le mouvement du périhélie de cette planète
Comptes Rendus 1859, 49: 379-83

Lindroth, S. (ed)

Swedish men of science 1650-1950
(Stockholm, 1952)

Lindsay, R. B.

Julius Robert Mayer: Prophet of Energy
(Oxford, 1973)

Lloyd, H. see also Sarton, G.

On the phenomena presented by light in its passage along the axes of biaxal crystals
Phil. Mag. 1833, 2: 112-120, 207-10

Lloyd, H. (cont.)

Report on the progress and present state of physical optics
Rep. Brit. Ass. 1834: 295-413

Lockemann, G.

Robert Wilhelm Bunsen
(Grosse Naturforscher 6)
(Stuttgart, 1949)

Lockyer, N. see Meadows, A. J.

Lubbock, J. W.

Note on shooting stars
Phil. Mag. 1848, 32: 170-2

On shooting stars
Phil. Mag. 1848, 32: 81-8

McGucken, W.

Nineteenth century spectroscopy: Development of the understanding of spectra 1802-1897
(Baltimore, 1969)

MacLeod, R. M. and Friday, J. R.

The quest for archives of British men of science
Hist. Sci. 1973, 11: 8-20

Archives of British men of science
(London, 1972)

McRae, R. J.

The origin of the conception of the continuous spectrum of heat and light
(University of Wisconsin Ph.D. thesis, 1969)

Mach, E.

The principles of Physical Optics: An historical and philosophical treatment
(London, 1926)

Masson, A.-P.

Études de photométrie électrique
Ann. Chim. 1845, 14: 129-95; 1850, 30: 5-55; 1851, 31: 295-326; 1855, 45: 385-454

Mayer, J. R. see also Lindsay, R. B. (& tr)

Mayer, J. R. (cont.)

Beiträge zur Dynamik des Himmels, in populärer Darstallung (Heilbronn, 1848)
Translated into English as
On celestial mechanics
Phil. Mag. 1863, 25: 241-8, 387-409, 417-28

Die organische Bewegung in ihiem Zusammenhang mit dem Stoffwechsel. Ein Beitrag zur Naturkunde (Heilbronn, 1845)
Translated into English (by R. B. Lindsay) as
The motions of organisms and their relation to metabolism. An essay in natural science. in
R. B. Lindsay "Mayer" 75-145

Sur la transformation de la force vive en chaleur, et réciproquement
Comptes Rendus 1848, 27: 385-7

Meadows, A. J.

Early Solar Physics
(Oxford, 1970)

Science and controversy: a biography of Sir Norman Lockyer
(London, 1972)

Mellor, J. W.

Modern inorganic chemistry
(London, 1939)

Melvill, T. see also Jevons, W. S.; Wilson, P.

Observations on light and colours
Essays and Observations, Physical and Literary 1756, 2: 12-90

Merz, J. T.

A history of European thought in the nineteenth century
(4 vols, Edinburgh, 1904-1912)

Miller, W. A. see also Adams, C. W.; Roscoe, H. E. (rev); Trusell, C. W.

On the action of gases on the prismatic spectrum
Rep. Brit. Ass. 1845, pt 2: 28-9

Elements of chemistry
(3 vols, London, 1855-7)

Miller, W. A. (cont.)

Experiments and observations on some cases of lines in the prismatic spectrum produced by the passage of light through coloured vapours and gases, and from certain coloured flames
Phil. Mag. 1845, 27: 81-91
Chem. News 1861, 3: 304-7

The new method of spectrum analysis
Chem. News 1861, 4: 159-61

On spectrum analysis
Chem. News 1862, 5: 201-3, 214-8

Miller, W. H. see also Adams, C. W.

On the effect of light on the spectrum passed through coloured gases
Phil. Mag. 1833, 2: 381-2

Moigno, F. (ed)

Répertoire d'Optique Moderne
(4 vols, Paris, 1847-50)

Mommsen, W. A.

Die Nächlasse in den deutschen Archiven
(Boppard, 1971)

Morgan, G.

Observations and experiments on the light of bodies in a state of combustion
Phil. Trans. 1785: 190-211

Morse, E. W.

Natural philosophy, hypotheses, and impiety: Sir David Brewster confronts the undulatory theory of light
(University of California (Berkeley) Ph.D. thesis, 1972)

Motte, A. see Newton, I. (tr)

Murray, D.

Lord Kelvin as professor in the Old College of Glasgow
(Glasgow, 1924)

Newton, I. see also Brewster, D.; Kubrin, D.

The Mathematical Principles of Natural Philosophy
(translated from the Latin by A. Motte)
(3 vols, London, 1803)

Newton, I. (cont.)

Opticks
(4th ed, London, 1730)

Nichol, J. P.

The stellar universe: Views of its arrangements, motions and evolutions
(Edinburgh, 1848)

Thoughts on some important points relating to the system of the world
(Edinburgh, 1848)

Views of the architecture of the heavens
(Edinburgh, 1837)

Olson, R.

Scottish philosophy and British physics 1750-1880
(Princeton, 1975)

Ostwald, W. see also Bunsen, R. W. (ed); Kirchhoff, G. R. (ed)

Klassiker der Exakten Wissenschaften Nr 72
(Leipzig, 1895)

Partington, J. R.

A history of chemistry
(vol 4, London, 1964)

Peacock, G, see also Young, T. (ed)

Life of Thomas Young
(London, 1855)

Perkin, W. H. see Klooster, H. S. van

Picard, É.

Notice historique sur la vie et l'oeuvre de Lord Kelvin
(Paris, 1920)

Pingree, J.

List of the papers and correspondence of Silvanus Phillips Thompson FRS preserved in the Imperial College Archives
(London, 1967)

Planck, M. see Agassi, J.

Plücker, J.

Abstract of a series of papers and notes concerning the electric discharge through rarefied gases and vapours
Proc. Roy. Soc. 1860, 10: 256-69

Plücker, J. (cont.)

Ueber die Constitution der elektrischen Spectra der verschiedenen Gase und Dämpfe
Pogg. Ann. 1859, 107: 497-539

Ueber die Einwirkung des Magneten auf die elektrischen Entladung in verdünnten Gasen
Pogg. Ann. 1858, 103: 88-106, 151-7
Translated into English (by F. Guthrie) as
On the action of the magnet upon the electrical discharge in rarefied gases
Phil. Mag. 1858, 16: 119-135

Fortgesetzte Beobachtungen über die elektrische Entladung
Pogg. Ann. 1858, 105: 67-84
Translated into English (by F. Guthrie) as
Observations on the electric discharge
Phil. Mag. 1859, 18: 7-20

Fortgesetzte Beobachtungen über die elektrische Entladung durch gasverdünnte Räume
Pogg. Ann. 1858, 104: 113-28
Translated into English (by F. Guthrie) as
Observations on the electrical discharge through rarefied gases
Phil. Mag. 1858, 16: 408-18

Fortgesetzte Beobachtungen über die elektrische Entladung in gasverdünnten Räumen
Pogg. Ann. 1859, 107: 77-113

Nachtrag zu der Abhandlung über die Constitution der elektrischen Spectra der verschiedenen Gase und Dämpfe
Pogg. Ann. 1859, 107: 638-43

Ueber einen neuen Gesichtspunkt, die Einwirkung des Magneten auf den elektrischen Strom betreffend
Pogg. Ann. 1858, 104: 622-30
Translated into English (by F. Guthrie) as
Observations on the electric discharge
Phil. Mag. 1859, 18: 1-7

Porter, G. and Bragg, W. L. (eds)

The Royal Institution Library of Science: Physical Sciences
(10 vols and index, Barking, 1970)

Pouillet, C.-S.-M.

Mémoire sur le chaleur solaire, sur les pouvoirs rayonnants et absorbants de l'air atmosphérique, et sur la température de l'espace
Comptes Rendus 1838, 7: 24-65
Translated into English as
Memoir on the solar heat, on the radiating and absorbing powers of atmospheric air, and on the temperature of space
Taylor's Sci. Mem. 1846, 4: 44-90

Quet, J. A.

Sur quelques faits relatifs au courant et à la lumière électrique
Comptes Rendus 1852, 35: 949-52

Quetelet, A. see Herschel, J. F. W. (tr)

R., E.

Notice sur feu Mr. Guinand
Bib. Univ. Gen. 1824, 25: 142-58, 227-36
Translated into English (by C. P. d. B.) as
Some account of the late M. Guinand and of the important discovery made by him in the manufacture of flint glass for large telescopes
(London, 1825)
Reviewed in Edinb. J. Sci. 1825, 2: 348-54

Rayleigh

Sir George Gabriel Stokes, Bart. 1819-1903
Proc. Roy. Soc. 1905, 75: 199-216

Riffault, J. see Thomson, T. (tr)

Rive, A. de la

Traité D'Électricité théorique et appliquée
(3 vols, Paris, 1854-58)
Translated into English as
A treatise on electricity in theory and practice
(3 vols, London, 1853-8)

Rohr, M. von

Fraunhofer's work and its present day significance
Trans. Opt. Soc. 1925-6, 27: 277-94

Rolfe, J. C. see Gellius, A. (tr)

Ronchi, V.

The nature of light
(London, 1970; first published in Italian in 1939)

Roscoe, H. E. see also Kirchhoff, G. R. (tr); Thorpe, E.

On the application of the induction coil to Steinheil's apparatus for spectrum analysis
Chem. News 1861, 4· 118-22
Discussed by W. de la Rue, W. A. Miller, E. Frankland, A. Herschel, M. Faraday, J. H. Gladstone
ibid 130-3

On Bunsen and Kirchhoff's spectral observations
Chem. News 1861, 3: 153-5, 170-2

Roscoe, H. E. (cont.)

Bunsen Memorial Lecture
J. Chem. Soc. 1900, 77: 513-54
summarised in Chem. News 1900, 81: 200

A course of three lectures on spectrum analysis
Chem. News 1862, 5: 218-22, 261-5, 287-93

The life and experiences of Sir Henry Enfield Roscoe
(London, 1906)

Scientific Worthies XVII - Robert Wilhelm Bunsen
Nature 1881, 23: 597-600

Spectrum analysis
(London, 1869)

On the solar spectrum, and the spectra of the chemical elements
Phil. Mag. 1862, 23: 63-4

Roscoe, H. E. and Bunsen, R. W.

Photo-chemical researches
Part 1 Phil. Trans. 1857: 355-80
Part 2 ibid 1857: 381-402
Part 3 ibid 1857: 601-620
Part 4 ibid 1859: 879-926
Part 5 ibid 1863: 139-160

Photochemical researches with reference to the laws of the chemical action of light
Rep. Brit. Ass. 1855, pt 2: 48-9

Roth, G. D.

Joseph von Fraunhofer (Grosse Naturforscher 39)
(Stuttgart, 1976)

Joseph von Fraunhofer und die angewandte Forschung
Tech. Ges. 1976, 43: 177-91

Royal Society

Catalogue of scientific papers
(12 vols, London, 1867-1902)

Minutes of council of the Royal Society 1846-1858
(London, 1858)

Sarton, G.

Discovery of conical refraction by William Rowan Hamilton and Humphrey Lloyd (1833)
ISIS 1932, 17: 154-71

Schaffner, K. F.

Nineteenth-century aether theories
(Oxford, 1972)

Schmidt, J. C. E. see Herschel, J. F. W. (tr)

Scott, W. L.

The conflict between atomism and conservation theory
1644-1860
(London, 1970)

Senarmont, H. de see Fresnel, A. J. (ed)

Sharlin, H I.

Lord Kelvin, the dynamic Victorian
(University Park, Penn., 1979)

Sherman, P. D.

Problems in the theory and perception of colour:
1800-1860
(University of London (Imperial College) Ph.D. thesis, 1971)

Siegel, D. M.

Balfour Stewart and Gustav Robert Kirchhoff: Two
independent approaches to 'Kirchhoff's radiation law"
ISIS 1976, 67: 567-600

Silliman, R. H.

Fresnel and the emergence of physics as a discipline
Hist. Stud. Phys. Sci. 1974, 4: 137-62

Somerville, M.

On the connexion of the physical sciences
(6th ed, London, 1842)

Spencer, H.

Recent astronomy, and the nebular hypothesis
Westminster Rev. 1858, 70: 185-225

Smith, C. W.

Natural philosophy and thermodynamics: William
Thomson [Kelvin] and the 'Dynamical theory of heat'
Brit. J. Hist. Sci. 1976, 9: 293-319

Smithells, A. see DeKosky, R.

Speiser, A. see Euler, L. (ed)

Speiser, D. see Euler, L. (ed)

Stern, H. J.

Greville Williams, discoverer of isoprene
Chem. Brit. 1979, 80: 455-8

Stewart, B. see also Siegel, D. M.

An account of some experiments on radiant heat, involving an extension of Prévost's theory of exchanges
Trans. Roy. Soc. Edinb. 1858, 22: 1-20

Reply to some remarks by G. Kirchhoff in his paper "On the history of spectrum analysis"
Phil. Mag. 1863, 25: 354-60

Stokes, G. G. see also Barr, E. S.; DeKosky, R.; Foucault, J. B. L. (tr); Glazebrook, R. T.; Kelvin; Kirchhoff, G. R. (tr); Rayleigh; Tait, P. G.; Wilson, D. B. (& ed)

Mathematical and Physical papers
vols 1-3 edited by G. G. Stokes
vols 4-5 edited by J. Larmor
(5 vols, Cambridge, 1880-1905)
Cited as Papers

Address on presenting the Copley medal to M. Foucault delivered by Lord Wrottesley
Proc. Roy. Soc. 1855,7: 571-4

On the change of refrangibility of light
Phil. Trans. 1852: 463-562;
Papers III, 267-409

On the dynamical theory of diffraction
Trans. Camb. Phil. Soc. 1849, 9: 1-62
Papers II: 243-328

Fluorescence
in G. G. Stokes "Science lectures at South Kensington"
p22-43

On light
(London, 1892)

On light as a means of investigation
(London, 1885)

Memoir and scientific correspondence of the late Sir George Gabriel Stokes
ed. by J. Larmor
(2 vols, Cambridge, 1907)

Stokes, G. G. (cont.)

Science lectures at South Kensington
(London, 1876)

On the simultaneous emission and absorption of rays of the same definite refrangibility; being a translation of a portion of a paper by M. Léon Foucault, and of a paper by Professor Kirchhoff
Phil. Mag. 1860, 19: 193-7
Papers IV: 127-30

On the theories of the internal friction of fluids in motion, and of the equilibrium and motion of elastic solids
Trans. Camb. Phil. Soc. 1845, 8: 287-319
Papers I: 79-129

Stokes, G. G. and Kelvin

The correspondence between Sir George Gabriel Stokes and Sir William Thomson, Baron Kelvin of Largs
edited by D. B. Wilson
(Cambridge, forthcoming)

Sutton, M. A.

Sir John Herschel and the development of spectroscopy in Britain
Brit. J. Hist. Sci. 1974, 7: 42-60

Spectroscopy and the chemists: A neglected opportunity?
Ambix 1976, 23: 16-26

Spectroscopy and the structure of matter: A study in the development of physical chemistry
(University of Oxford D.Phil. thesis, 1972)

Swan, W.

Experiments on the ordinary refraction of Iceland Spar
Trans. Roy. Soc. Edinb. 1849, 16: 375-8

Note on Professors Kirchhoff and Bunsen's paper "On chemical analysis by spectrum-observations"
Phil. Mag. 1860, 20: 173-5

On the prismatic spectra of the flames of compounds of carbon and hydrogen
Trans. Roy. Soc. Edinb. 1857, 21: 411-29
Translated into German as
Ueber die prismatischen Spectra der Flammen von Kohlenwasserstoffverbindungen
Pogg. Ann. 1857, 100: 306-335

Swenson, L. S.

The ethereal aether
(Austin, 1972)

Szabadváry, F.

History of analytical chemistry
(Oxford, 1966)

Tait, P. G.

Lectures on some recent advances in physical science
(2nd ed, London, 1876)

Scientific worthies V: George Gabriel Stokes
Nature 1875, 12: 201-3

Tait, P. G. and Kelvin

Treatise on natural philosophy
(2 vols, Cambridge, 1883-6)

Talbot, W. H. F. see also Arnold, H. J. P.

Facts relating to optical science. No. I.
Phil. Mag. 1834, 4: 112-4

1. Microscopic cleavages in talc or mica
   ibid 112
2. Optical properties of chromium
   ibid 112-3
3. Purple crystals from a green liquid
   ibid 113
4. A body in rapid motion, yet apparently at rest
   ibid 113-4
5. On the flame of lithia
   ibid 114
   Chem. News 1861, 3: 262
6. On the flame of cyanogen
   Phil. Mag. 1834, 4: 114
   Chem. News 1861, 3: 263

Facts relating to optical science. No. III.
Phil. Mag. 1836, 9: 1-4
Optical properties of the iodide of mercury
ibid 1-3
On prismatic spectra
ibid 3
Chem. News 1861, 3: 263
Spectra of various galvanic flames
Phil. Mag. 1836, 9: 3-4
Chem. News 1861, 3: 263

On a method of obtaining homogeneous light of great intensity
Phil. Mag. 1833, 3: 35
Chem. News 1861, 3. 262

On the nature of light
Phil. Mag. 1835, 7: 113-8

Talbot, W. H. F. (cont.)

Note on the early history of spectrum analysis
Proc. Roy. Soc. Edinb. 1870-1, 7: 461-6

Some experiments on coloured flames
Edinb. J. Sci. 1826, 5: 77-81;
reprinted in Chem. News 1861, 3: 261-2

Thalén, R.

Anders Jonas Ångström
Lefnadsteckningar öfver Svenska vetenskapsakademiens ledamöter 1878-85, 2: 103-130

Spektralanalysens Historik
Upsala Universitets årsskrift 1866: 1-54

Thompson, J. S. and Thompson, H. G.

Silvanus Phillips Thompson, his life and letters
(London, 1920)

Thompson, S. P. see also Pingree, J. (ed); Thompson, J. S. and H. G.

The life of William Thomson, Baron Kelvin of Largs
(2 vols, London, 1910)

Thomson, T.

A system of chemistry
(5th ed, 4 vols, London, 1817)
Translated into French, with a supplement (by J. Riffault)
as
Système de Chimie
(5 vols, Paris, 1818-22)

Thomson, William for all entries see Kelvin

Thorpe, E.

The Right Honourable Sir Henry Enfield Roscoe. A biographical sketch
(London, 1916)

Todhunter, I.

William Whewell
(2 vols, London, 1876)

Trusell , F.

William Allen Miller· Pioneer Stellar Spectroscopist
J. Chem. Ed. 1963, 40: 612-3

Tuckerman, A.

Index to the literature of the spectroscope
(Smithsonian Miscellaneous Collections, 658)
(Washington, 1888)

Turner, E.

On the means of detecting lithia in minerals by the blowpipe
Edinb. J. Sci. 1826, 4: 113-7

Tyndall, J. see also Ångström, A. J. (tr)

Six lectures on light
(fifth edition, London, 1895)

Verdet, E. see Fresnel, A. J. (ed)

Verhulst, P. F. see Herschel, J. F. W. (tr)

Waterson, J. J. see also Brush, S. G.

The collected scientific papers of John James Waterson
edited by J. S. Haldane
(Edinburgh, 1928)

On certain inductions with respect to the heat engendered by the possible fall of a meteor into the sun; and on a mode of deducing the absolute temperature of the solar surface from thermometric observation
Phil. Mag. 1860, 19: 338-43

On dynamical sequences in Kosmos
Athenaeum 1853: 1099-1100
discussed by W. Hopkins ibid 1100

On a law of mutual dependence between temperature and mechanical force
Rep. Brit. Ass. 1853, pt 2: 11-12

Welby, F. A. see Koenigsberger, L. (tr)

Wheatstone, C. see also Bowers, B. P.; Hubbard, G.

The scientific papers of Sir Charles Wheatstone
(London, 1879)
cited as Papers

An account of some experiments to measure the velocity of electricity and the duration of electric light
Phil. Trans. 1834: 583-91
Papers 84-96

The case of Professor Charles Wheatstone in the arbitration between himself and Mr. William Fothergill Cooke
in W. F. Cooke (ed.) "The electric telegraph: was it invented by Professor Wheatstone?" II: 81-114

On the prismatic decomposition of the electric, voltaic and electro-magnetic sparks
Chem. News 1861, 3: 198-201

Wheatstone, C. (cont.)

On the prismatic decomposition of electrical light
Rep. Brit. Ass. 1835, pt 2: 11-12
Phil. Mag. 1835, 7: 299
Papers 223-4
Chem. News 1861, 3: 185
Translated into German as
Ueber die prismatische Zerlegung des elektrischen Lichts
Pogg. Ann. 1835, 36: 148-50
Translated into French in A.-C. Becquerel
"Traité Expérimental de L'Électricité" IV: 34-5

On the resonances, or reciprocated vibrations of columns of air
Quart. J. Sci. 1828, 1: 175-83, Papers 36-46

On the velocity and nature of electricity
Lit. Gaz. March 9, 1833, p152
Read by Michael Faraday

Whewell, W. see also Todhunter, I.

Address to the 1833 British Association
Rep. Brit. Ass. 1833: xi-xxvi

Astronomy and general physics considered with reference to natural theology (3rd Bridgewater treatise)
(London 1833)

History of the inductive sciences
(2nd ed, 3 vols, London, 1847)

Suggestions respecting Sir John Herschel's remarks on the theory of the absorption of light by coloured media
Rep. Brit. Ass. 1834: 550-2

Whitrow, G. J.

The nebular hypotheses of Kant and Laplace
Actes XIIe Cong. Inst. Hist. Sci. 1968, IIIB: 175-80

Whitrow, M. (ed)

ISIS Cumulative Bibliography
(5 vols, London, 1971-)

Whittaker, E.

A history of theories of aether and electricity
(Edinburgh, 1962)

Williams, C. H. G. see Stern, H. J.

Williams, L. P. see also Faraday, M. (ed.)

Michael Faraday
(London, 1965)

Willigen, V. S. M. van der

Ovet Het Electrische Spectrum
Versl. Meded. Akad. Weten. 1858, 7: 209-32, 267-73, 274-80, 362-7; 8: 32-51, 189-208, 308-15; 9:300-6
The first paper was translated into German as
Ueber das elektrische Spectrum
Pogg. Ann. 1859, 106: 610-32

Wilson, A. see Wilson, P.

Wilson, D. B. see also Kelvin (ed); Stokes, G. G. (ed)

Catalogue of the manuscript collections of Sir George Gabriel Stokes and Sir William Thomson, Baron Kelvin of Largs in Cambridge University Library
(Cambridge, 1976)

George Gabriel Stokes on stellar aberration and the luminiferous aether
Brit. J. Hist. Sci. 1972, 6: 57-72

Kelvin's scientific realism: The theological context
Phil. J. 1974, 11: 41-60

Wilson, P.

Biographical Account of Alexander Wilson, M.D., late Professor of practical astronomy in Glasgow
Edinb. J. Sci. 1829, 10: 1-17
Also contains details of the life of Thomas Melvill p5-8

Wollaston, W. H.

A method of examining refractive and dispersive powers by prismatic reflexion
Phil. Trans. 1802: 365-80
Translated into German as
Neue Methode die brechenden und zerstreuenden Kräfte der Körper vermittelst prismatischer Reflexion zu erforschen
Gilbert Ann. 1809, 31: 235-51, 398-416

Woolf, H.

The beginnings of astronomical spectroscopy
in A. Koyré "Mélanges" I: 619-34

Wrede, F. J. von

Försök att härleda Ljusets absorbtion från Undulations-Teorien
Kongl. Veten. Acad. Handl. 1834: 318-53

Translated into German as
Versuch, die Absorption des Lichts nach der Undulationstheorie zu erklären
Pogg. Ann. 1834, 33: 353-89
Translated into English (by W. Francis) as
Attempt to explain the absorption of light according to the undulatory theory"
Taylor's Sci. Mem. 1836, 1: 477-502

Wrottesley see under Stokes, G. G.

Young, T. see also Arago, D. F. J. (tr); Cantor, G.; Fresnel, A. J. (tr); Latchford, K. A.; Peacock, G.

Miscellaneous works of the late Thomas Young
edited by G. Peacock and J. Leitch
(3 vols, London, 1855)
cited as Works

An account of some cases of the production of colours, not hitherto described
Phil. Trans. 1802: 387-97
Works I: 170-8

Chromatics
in "Supplement to the fourth, fifth and sixth editions of the Encyclopaedia Britannica" III: 141-63
Works I: 279-342

Dr. Young's reply to the animadversions of the Edinburgh reviewers, on some papers published in the Philosophical Transactions
(London, 1804)
Works I: 192-215

Experiments and calculations relative to physical optics
Phil. Trans. 1804: 1-16
Works I: 179-91

On the mechanism of the eye
Phil. Trans. 1801: 23-88
Works I: 12-63

Outlines of experiments and enquiries respecting sound and light
Phil. Trans. 1800: 106-50
Works I: 64-98

Théorie des couleurs observées dans les expériences de Fraunhofer
Ann. Chim. 1829, 40: 178-83
Translated into English as
Theory of the colours observed in the experiments of Fraunhofer
Edinb. J. Sci. 1829, 1: 112-6

Young, T. (cont.)

Theoretical investigations intended to illustrate the phenomena of polarisation
in "Addenda et Corrigenda" to the "Supplement to the fourth, fifth and sixth editions of the Encyclopaedia Britannica" VI, 860-3
Works I: 412-17

On the theory of light and colours
Phil. Trans. 1802: 12-48
Works I: 140-69