

THE C-AXIS THERMAL EXPANSION OF GRAPHITE
AND ITS CRYSTAL COMPOUNDS.

A Thesis
submitted for the Degree of
Doctor of Philosophy

by

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ABSTRACT

The principal object of this research has been to measure the thermal expansion of the crystal compounds of graphite. In order to achieve this object it has been necessary to study in detail the preparation of these compounds from pyrolytic graphite. This material, prepared by thermal cracking of methane, has not previously been used for the preparation of these compounds and hence new techniques have had to be developed.

The acid compounds have been prepared by anodic oxidation of graphite in strong acids. This method has been applied successfully to bisulphate, perchlorate, selenate and chloro-sulphonate compounds. The nitrate compounds have been prepared by direct immersion in nitric acid. Alkali metal compounds and those with metallic chlorides have been prepared by simple modifications to published methods for powdered graphites. In general there is little difference between compounds prepared from pyrolytic graphite and those reported previously. It is possible however to draw more detailed conclusions from the X-ray diffraction photographs of compounds based on pyrolytic graphite. A different structure has been found for the caesium graphite compounds and for the ferric chloride compound. With reference to the nitrate compounds two modifications have been found one stable above approximately -25°C and the other stable below this temperature the latter has not been reported previously. There is a difference in lattice spacing of approximately $0.05 \text{ \AA}$ in these two forms.

The thermal expansion of compounds has been measured by the shift in X-ray diffraction lines using a diffractometer and proportional detector. The temperature range studied has been 30°C to -60°C . The thermal expansion of the acid compounds is considerably larger than graphite; a two to three fold increase is reported for the first sequence compounds. The thermal expansion decreases as the amount of intercalate decreases and measurements have been extended as far as the third sequence

compound.

The expansion of the alkali metal compounds is rather smaller than the acid compounds and the caesium graphite compound has an expansion very close to that of graphite.

A clearly defined anomaly in the thermal expansion of the nitrate compounds occurs at the transition temperature noted above. There is also evidence of a similar transition in the third sequence bisulphate compound.

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CHAPTER 1: THERMAL EXPANSION

1.1 Introduction

1.1.1. The nature of thermal expansion

The change of ~~dimensions~~ associated with an increase or decrease in the temperature of the material is the phenomena of thermal expansion. It is most conveniently considered as the change in volume with temperature at constant pressure and can be expressed as the partial differential $\left(\frac{\partial V}{\partial T}\right)_P$. The most common method of reporting thermal expansion data is by means of the thermal expansion coefficient $\alpha = 1/V \left(\frac{\partial V}{\partial T}\right)_P$.

As the volume is a function of the free energy i.e. $V = \left(\frac{\partial G}{\partial P}\right)_T$, the thermal expansion is a second order derivative of the free energy $\frac{\partial^2 G}{\partial P \partial T}$, if $\frac{\partial G}{\partial T}$ is replaced by $-S$, the entropy, then the thermodynamic relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ results.

In a classical solid consisting of harmonic oscillators thermal expansion has no meaning. The thermal expansion in effect measures the change in position of the mean position of an atom with temperature. In the harmonic case this does not change, the amplitude of oscillation merely becomes larger. Thus in considering thermal expansion

the potential energy of the vibration is generally assumed to have the form:

$$V(x) = cx^2 - gx^3 - fx^4 \dots$$

where x is the displacement from the equilibrium position at 0°K .

1.1.2. The relation between thermal expansion and other properties

The equation $C_V - C_P = \frac{T \alpha^2 V}{K}$ relates the thermal expansion coefficient α to the isothermal compressibility $K = \left(\frac{\partial V}{\partial P} \right)_T$ and to the specific heats at constant volume $C_V = \left(\frac{\partial H}{\partial T} \right)_V$ and constant pressure $C_P = \left(\frac{\partial H}{\partial T} \right)_P$. Thus if these parameters are known, the thermal expansion can be evaluated; however, these parameters are in general not easy to determine and the principal application of this formula is to calculate them knowing the thermal expansion and the compressibility. The thermal expansion is also related to the temperature change on adiabatic compression $\left(\frac{\partial T}{\partial P} \right)_H$ by the equation $\left(\frac{\partial T}{\partial P} \right)_H = \frac{T \alpha V}{C_P}$. This similarly is also mainly used to calculate the other parameters when the thermal expansion is known.

1.2. Vibrational Thermal Expansion

1.2.1. Introduction

The theoretical approach to thermal expansion has been largely directed to the evaluation of the contribution due to lattice vibration or the vibrational entropy term in the equation:

$$S_{\text{total}} = S_{\text{vibration}} + S_{\text{electronic}} + S_{\text{transition}} \dots$$

A discussion of the vibrational contribution can initially be based on the force fields ^{rat}existing in a solid. The forces acting between two atoms at an equilibrium separation are both attractive and repulsive. If the energy of the attractive and repulsive forces varied in the same manner with interatomic separation then as noted earlier no expansion would take place because the oscillations would be harmonic. However, the repulsive forces increase more rapidly than the attractive forces and a typical potential energy versus interatomic separation curve is shown in Fig.1.1. The potential energy curve can be represented by a curve of the general type $V(r) = -\frac{a}{r^x} + \frac{b}{r^y}$ where $y > x$ and the attractive forces are conventionally given a negative sign. Thus it follows that a displacement from the equilibrium position produces two distinct forces, one due to the attractive forces and one due to the repulsive forces. In

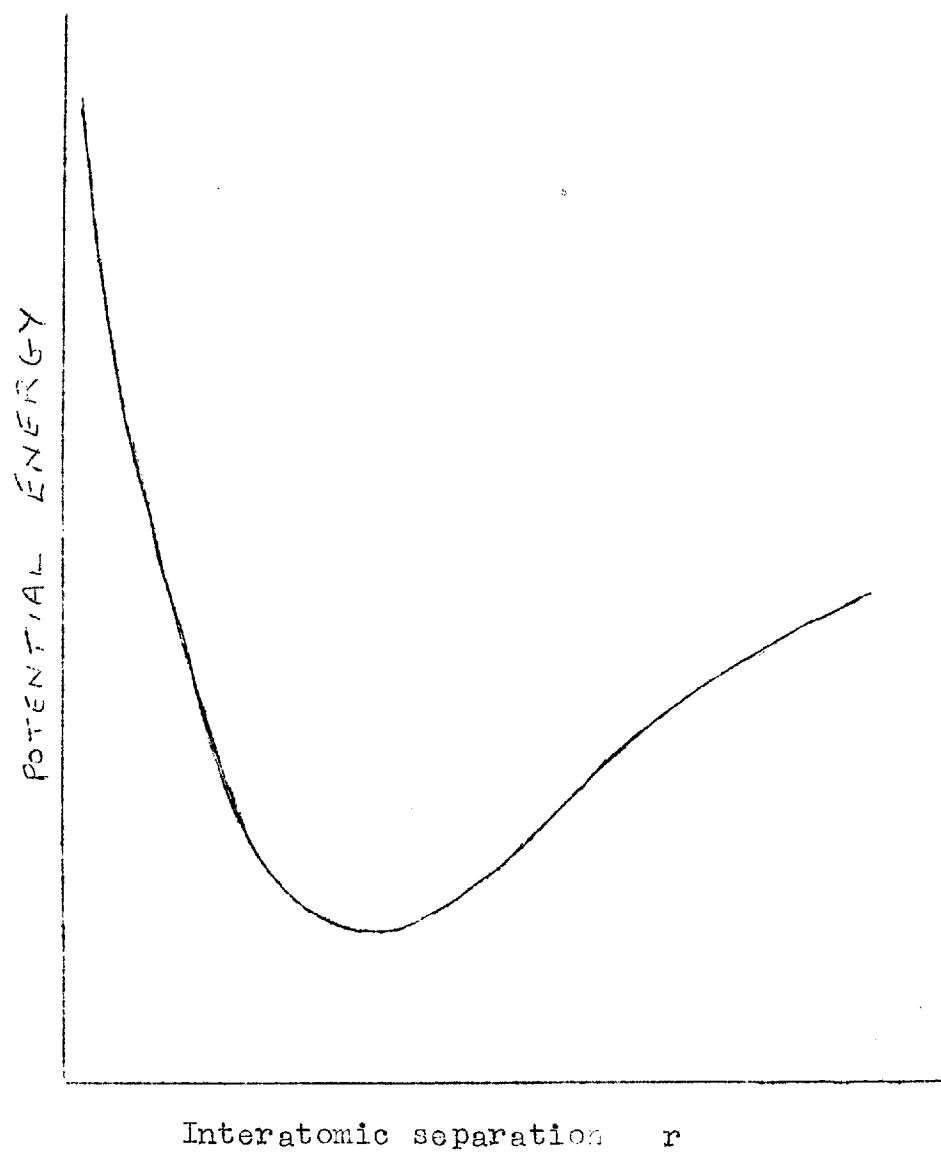


Figure 1.1. Typical potential energy well for
a pair of atoms distance apart r

general the change in potential energy for a small displacement x is given by $V(x) = cx^2 - gx^3 - fx^4 \dots$ where the x^3 term represents the asymmetry of the mutual repulsion of the atoms and the x^4 term the general softening of the vibrations at large amplitudes. If the average displacement $\bar{x}$ of any atom is now considered, from the Boltzmann distribution function:

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x e^{-\frac{V(x)}{KT}} dx}{\int_{-\infty}^{\infty} e^{-\frac{V(x)}{KT}} dx}$$

then neglecting terms in x^5 for small displacements, i.e. low anharmonic energy $\bar{x} = \frac{3KTg}{4c^2}$. From this expression, it follows that the thermal expansion is a linear function of temperature and that it falls to zero at 0°K . Thus any more refined theory of thermal expansion must conform to these restrictions.

1.2.2. Grüneisen Theory

The theory of thermal expansion developed by Grüneisen (1912) is based on the equation of state for solids. This equation can be derived from rather different view points. Two ~~de~~^{dev}iations will be outlined, the first based on classical solid state theory and the second based on force fields. The classical equations for the energy of a solid body are:

$$E = \frac{3 h \nu_E}{e^{\frac{h \nu_E}{KT}} - 1} \quad (\text{Einstein Theory})$$

$$E = \int_0^{\nu_D} a \nu^2 \frac{h \nu}{e^{\frac{h \nu}{KT}} - 1} d\nu \quad (\text{Debye Theory})$$

Thus the energy can be expressed in the form $E = E(T, V)$ if the volume of the solid is assumed to be the controlling factor of ν_E or ν_D , the Einstein or Debye frequency respectively. By following simple thermodynamical arguments, it is possible to derive the equation of the solid state

$$pV + V \frac{d\bar{F}}{dV} = - \frac{d \ln \nu}{d \ln V} \{ F.(T, V) \}$$

(see Roberts, 1928). The reference state is a volume V_0 at 0°K and $\bar{F}$ is the free energy required to compress the solid from a volume V to a volume V_0 .

The second derivation based on force field assumes the Virial Law of Clausius (Clausius, 1870) and that the potential energy between two atoms is given by an equation

$$V(r) = - \frac{a}{r^x} + \frac{b}{r^y}$$

It can be shown (see Roberts, 1928) that:

$$pV + G(V) = - \frac{d \ln \gamma}{d \ln V} E$$

where $G(V) = V \frac{d}{dV} W(V)$ and $W(V) = - \frac{A}{V^{1/3}} + \frac{B}{V^{1/3}}$

i.e. the potential energy per gm. atom when the atoms are at rest. If the Grüneisen constant $\gamma = - \frac{d \ln \gamma}{d \ln V}$ is now introduced, the two derivations give similar equations of the form $pV + F(V) = \gamma E$

Grüneisen (1912) used this equation as a basis for his theory of thermal expansion. In the derivation of this equation it is assumed that $F(V)$ is not a function of temperature, this should be a valid approximation if electronic effects are small. A second assumption needs now to be made and this is that $\frac{d\gamma}{dT} = 0$; the significance of this will be discussed later. However, with this assumption it can be shown (see Roberts 1928) that $\alpha = \frac{K \gamma C_V}{V} \quad (1)$

where K is the compressibility. Further if it is assumed in the Equation of the Solid State that $p = 0$, this is approximately true for atmospheric pressure, then it can be shown (see Roberts, 1928) that $\frac{\Delta}{V_0} = \frac{E/Q_0}{1-m E/Q_0} \quad (2)$ where $Q_0 = V_0/\gamma K$, Δ is the change in volume and m is a function of the law of force between the atoms. At

high temperatures

$$E = \frac{3 R T}{1 + \frac{h\nu}{2KT}}$$

(Einstein Theory) and $E = 3RT \left[D\left(\frac{\Theta}{T}\right) \right]$ where $D\left(\frac{\Theta}{T}\right)$ is the Debye specific heat function (Debye Theory); thus E is a linear function of T . Hence equation (2) reduces to

$$\frac{\Delta}{V_0} = \frac{A T}{1-x AT} \quad (3) \text{ and the thermal expansion will increase}$$

faster than linearly with temperature, a point which is sometimes overlooked in criticism of Grüneisen's Theory.

1.2.3. Application of the Grüneisen Theory to Real Solids

If a potential law of the form $V(r) = -\frac{a}{r^x} + \frac{b}{r^y}$ is assumed then $m = \frac{x+y+3}{6}$ and this can be substituted in equation (2). By suitable choice of the value of m and A good agreement can be obtained for the ionic salts and simple metals. Fig. 1.2 shows theoretical and experimental results for copper and palladium (Nix and Macnair, 1941, 1942).

1.2.4. The nature of the Grüneisen Constant

A critical point in the derivation of equation (1) is the assumption that $\left(\frac{\partial \gamma}{\partial T}\right)_V = 0$. It is true at high temperatures that γ tends to a constant value γ_∞ due to the fact that all the modes of vibration are excited and a limiting value of γ is approached. Also at low temperatures γ tends to a second constant value γ_0 , this is because Debye's rule is obeyed with an equivalent temperature Θ_0 and $\gamma_0 = -\frac{d \ln \Theta_0}{d \ln V}$. But in general γ_∞ is not equal to γ_0 . Thus Grüneisen's

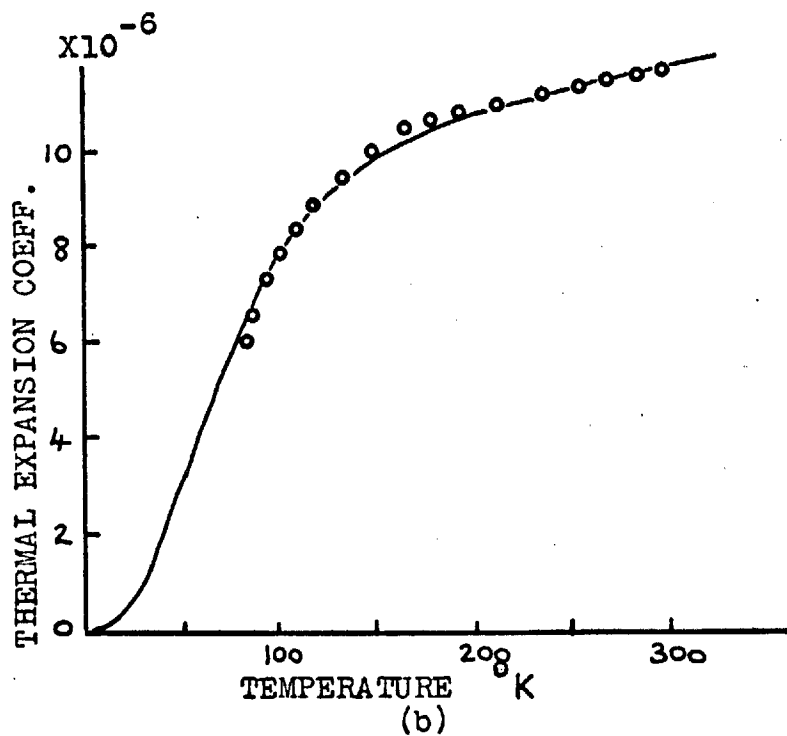
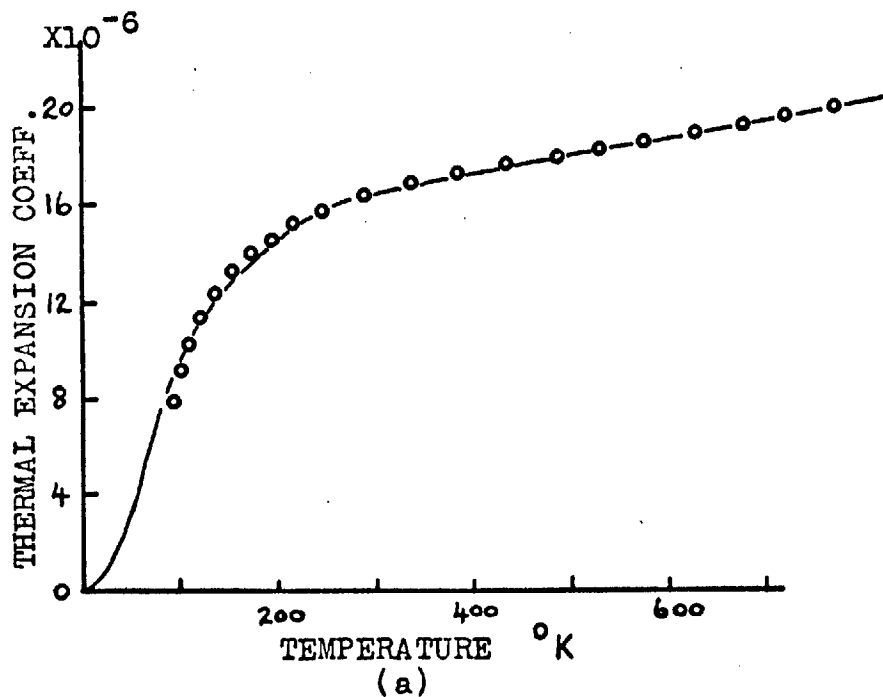


FIG 1.2. COMPARISON OF EXPERIMENTAL AND THEORETICAL DATA FOR SIMPLE METALS
(a) COPPER (b) PALLADIUM

approximation is acceptable at low and high temperatures but breaks down between these extremes. For a potential of the form $-ar^{-6} + br^{-12}$ it is found that $\gamma_0 = 3$ and $\gamma_0 - \gamma_0 = 0.15$ so that Grüneisen's rule should be obeyed fairly closely at all temperatures not too near the melting point (Barron, 1955). The reason γ is not constant lies in the assumption that one value of γ can be taken to cover the whole frequency spectrum (this is not valid; each frequency has its own γ and these may not all be the same). In addition however there is a deviation due to variation of the individual γ values of the frequencies with temperature at constant volume, i.e. $\gamma_j = - \frac{d \ln \nu_j}{d \ln V}$ is not strictly constant.

The Grüneisen assumption that all γ_j were equal is rather more rigorous than necessary and it has been proposed (Blackman, 1957, 1959) that the assumption of a constant value for γ can be valid if

$$\frac{\int \gamma_j P(\nu) E \frac{h\nu}{KT} d\nu}{\int P(\nu) E \frac{h\nu}{KT} d\nu} = \gamma$$

where $P(\nu)$ is the distribution function for the frequencies between ν and $\nu + d\nu$ with average $\gamma_j = \bar{\gamma}_j$. This is a less stringent requirement than the original one of

Grüneisen and probably explains the good experimental agreement of the theory. Some success has been achieved at fitting theoretical deviations from a constant value of γ with experimental values (Barron, 1955).

1.3 Thermal Expansion of a Non-Vibrational Origin

1.3.1 Introduction

The theoretical approach to thermal expansion has been largely directed to the vibrational entropy terms. Entropy contributions from other sources have not yet been rigorously calculated and only estimates of their relative importance in various types of solid can be made. However, the principal sources other than vibration will be briefly surveyed in the following sections.

1.3.2 Electronic contributions

In the case of a metal a contribution to the energy would be expected from the conduction electrons. This contribution is proportional to the square of the absolute temperature $E = aT^2$ (cf vibrational energy is proportional to T^4) however, the proportionality constant is of the order 10^{-4} cal per mole per degree. Thus the contribution to the energy is only 3×10^{-2} cal/mole at room temperature, compared with 6 cal/mole for vibrational energy. The influence on the thermal expansion of the

electronic energy although finite is necessarily very small and no consideration is generally given to this source.

1.3.3 Defect Contributions

Borelius (1959) has attempted to assess the role of various defects on the thermal expansion of a simple metal. The defects were divided into two types with the temperature functions $E_1 = A_1 \exp^{-H_1/RT}$ and $E_{11} = A_{11} \exp^{-H_{11}/RT}$ where A_1 , A_{11} , H_1 , H_{11} are empirical constants. The expansion was then expressed in the form

$$\frac{V - V_0}{V_0} = a E_{\text{vib}} + b E_I + \frac{1}{E_{II}} E_{II}$$

and the results are shown in Table 1.1 for gold. At lower temperatures defects are contributing a negligible amount but at high temperatures about 10% of the expansion can be shown to be due to defects in the solid.

1.3.4 Contributions from Transitions

The preceding types of energy contributions are in general functions of temperature and result in a gradual change in thermal expansion. However, a large anomalous change in volume may often arise at a clear transition temperature or possibly in a small temperature region. This type of anomaly will be associated with discontinuity or rapid change in entropy and can occur in many types of transition.

TABLE 1.1.

THERMAL EXPANSION OF SOLID GOLD

$^{\circ}\text{K}$	Experimental $\frac{V-V_0}{V_0} \times 10^{-5}$			$.702E_{\text{vib}}$	$1.65E_1$	$\frac{10^5}{H_{11}} E_{11}$
100	221					
150	401					
200	596					
250	801					
273	900	900	900	896	2	
323	1113	1112	1113	1105	3	
373	1324	1328	1330	1314	8	
423	1535	1547	1550	1523	18	
473	1761	1769	1773	1733	33	
523	1984	1996	2000	1942	53	
623	2465	2461	2465	2360	106	
723	2954	2947	2950	2779	175	
823	3455	3454	3454	3197	256	4
923	3976	3983	3980	3615	347	17
1023		4542	4532	4034	411	57
1123		5127	5110	4453	538	157
1223		5749	5717	4871	634	361
	N. & M.	A.	E. E.			

N. & M. Nix & Macnair Phys. Rev. 60 597 1941

A. Austin Physics 3 240 1932

E. E. Esser & Easterbrook Arch. Eisenhüttenw
14 341 1941

In the case of a first-order transition, e.g., the phase changes of iron Fig. 1.3, there will necessarily be a discontinuity in the thermal expansion due to the step volume change at the transition temperature. It is not necessary for such a radical change in the structure to take place however, the expansion coefficient of Teflon (Fig. 1.4) shows a sharp peak at 20°C which is probably caused by onset of rotation in the long chain molecules (Kirby, 1956). Similar anomalies are reported for the transition between oscillation and rotation of the nitrate ions in sodium nitrate (Austin and Pierce, 1933).

Similar anomalies in thermal expansion are associated with transitions between antiferromagnetic and ferromagnetic states, and the normal paramagnetic state. Similarly, for ferroelectric and antiferroelectric and the normal state. Thus around the Curie and Neel points anomalously high values of thermal expansion are often found (Nix and Macnair, 1941, 1942). In many cases the transition is not sharp but is "smeared" over a temperature interval of up to 50°C as in the case of nickel, fig. 1.5. Similar anomalies are observed at the onset of superconductivity in solids but no theory has been developed to cover any of these anomalous changes in the thermal expansion coefficient

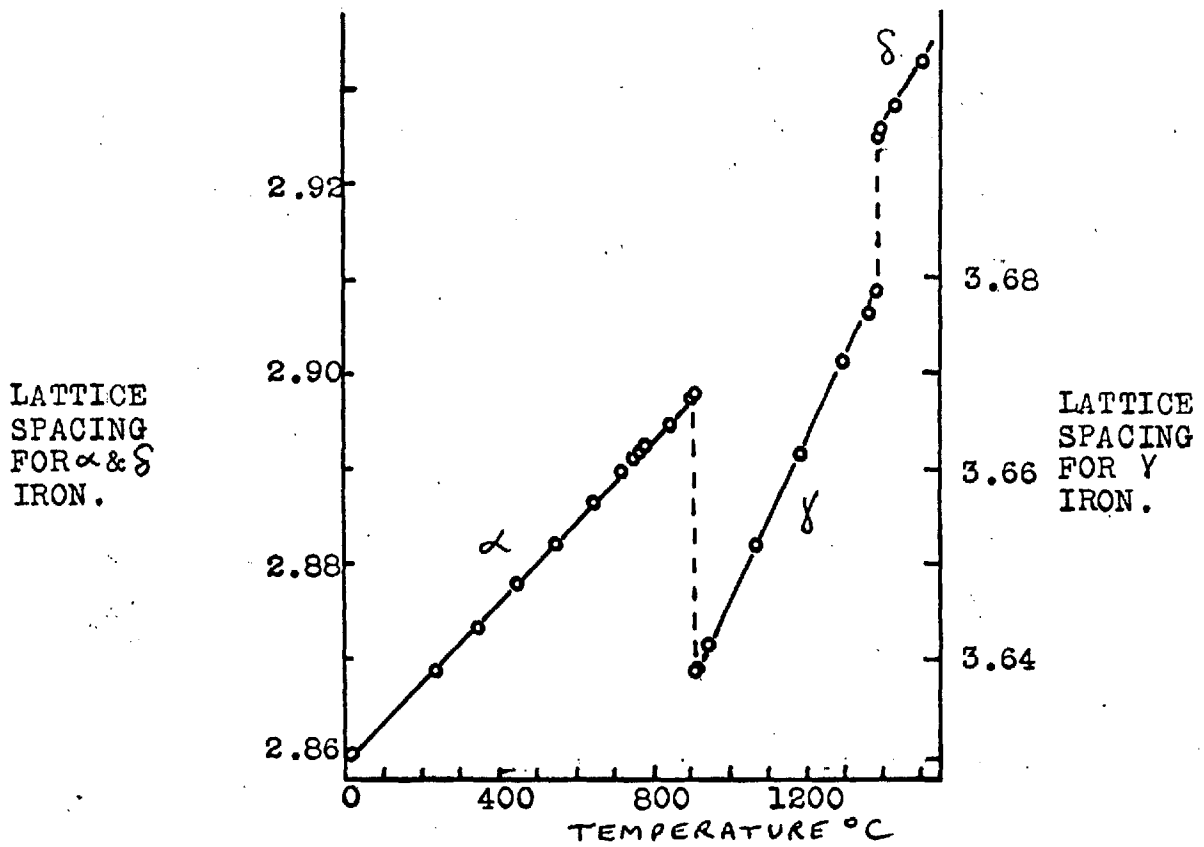


FIG.1.3. VARIATION OF LATTICE PARAMETER OF IRON WITH TEMPERATURE.

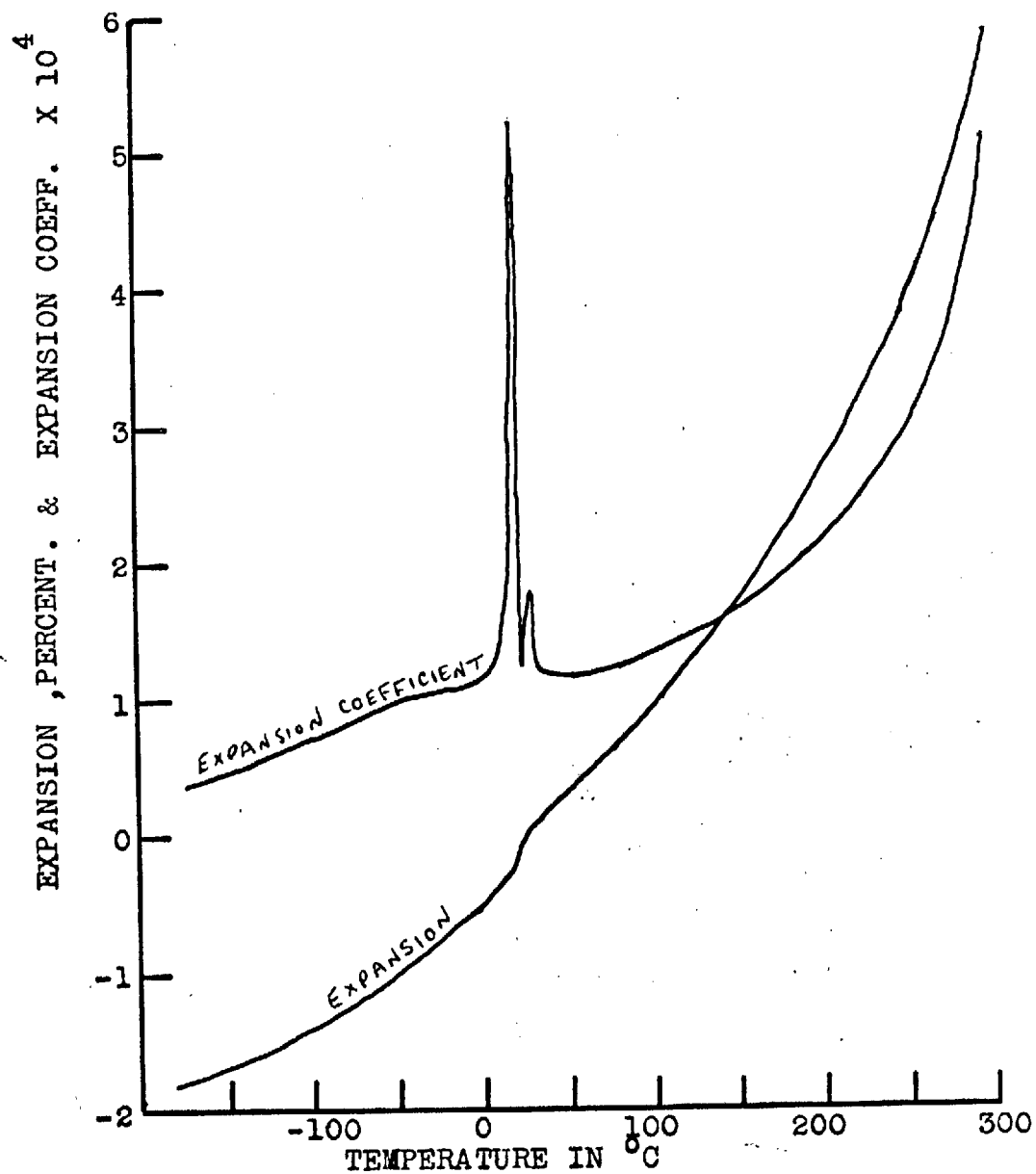


FIG.1.4. THERMAL EXPANSION OF P.T.F.E.

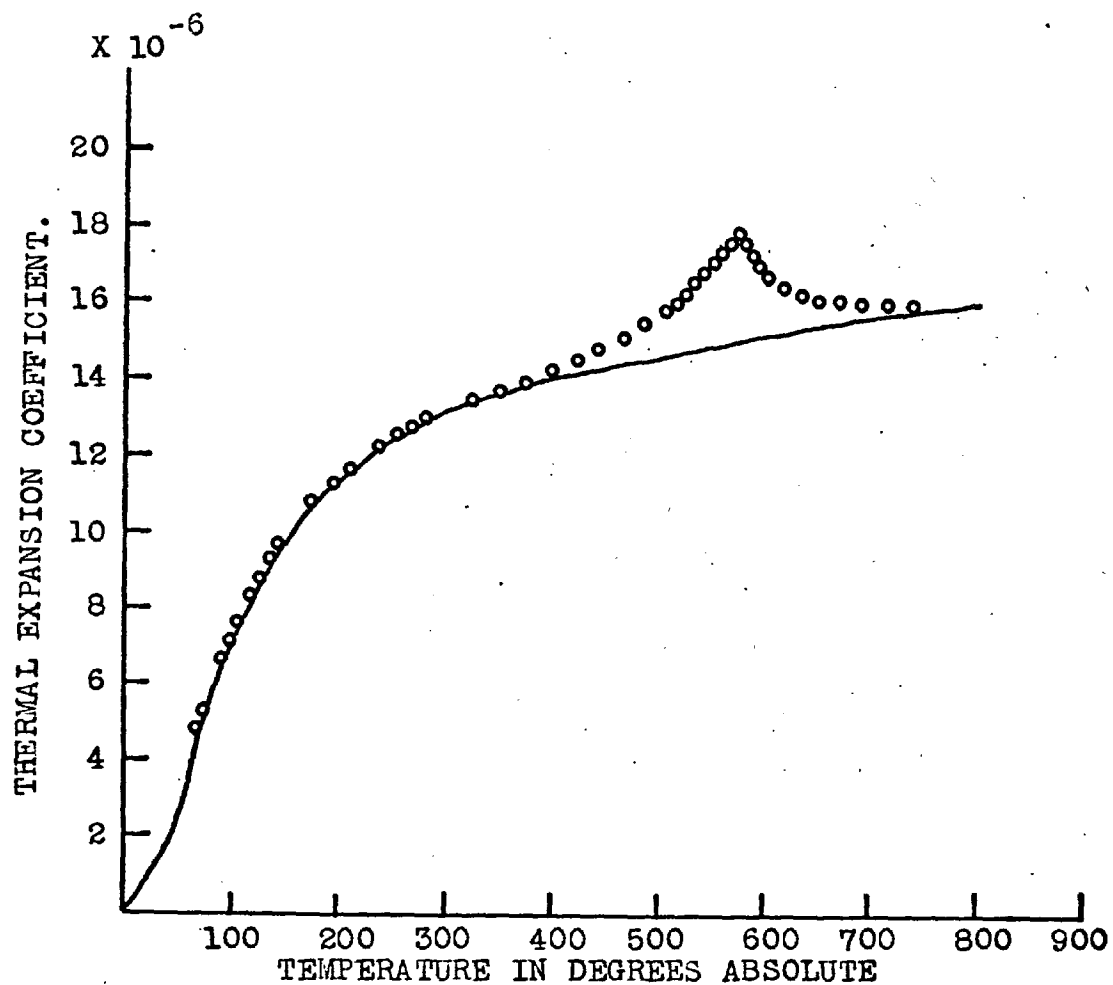


FIG.1.5. EXPERIMENTAL AND THEORETICAL VALUES FOR THE THERMAL EXPANSION OF NICKEL SHOWING ANOMALY DUE TO FERROMAGNETIC TRANSITION.

1.4 The Thermal Expansion of Anisotropic Solids

For anisotropic solids the general position is very similar to the isotropic case. However, in anisotropic solids the dependence of the potential energy curve and consequently of the linear compressibility on direction has two important results. The first is that at low temperatures lattice vibrations will be excited preferentially in the direction of greatest compressibility because of the lower vibrational frequencies in this direction. Thus the expansion in this direction will be greater than that at right angles to it. The second result is that an expansion in one direction is accompanied by elastic contractions in the perpendicular directions (The Poisson Effect). This contraction may be sufficient in magnitude to exceed the intrinsically small expansion in these directions at low temperatures and hence produce a nett contraction in lattice dimensions.

1.4.1 The Hexagonal System

For the hexagonal system the expansion in the three mutually perpendicular directions, $\alpha_x \alpha_y \alpha_z$, can be replaced by the two principal coefficients of expansion, one perpendicular to the principal hexagonal or c-axis $\alpha_{\perp}$ and the other parallel to this axis $\alpha_{\parallel}$. By symmetry, if a, b, and c are the new axes, $\alpha_a = \alpha_b = \alpha_{\perp}$ and $\alpha_c = \alpha_{\parallel}$;

and the coefficient of cubical expansion is given by

$2\alpha_{\perp} + \alpha_{\parallel}$.. Knowing the thermal expansion coefficients

$\alpha_{\perp}$ and $\alpha_{\parallel}$ for the hexagonal system it is possible to evaluate the expansion in any direction α_{θ} from :-

$\alpha_{\theta} = \alpha_{\parallel} \cos^2 \theta + \alpha_{\perp} \sin^2 \theta$, where θ is the angle between the direction and the principal axis. Similarly by measurements of α_{θ_1} and α_{θ_2} , $\alpha_{\parallel}$ and $\alpha_{\perp}$ can be calculated. If the anisotropy of the hexagonal crystal is high (cf. c/a ratio for zinc and cadmium are 1.09 and 1.11 respectively and that for graphite is 2.36), then the relatively weak interlayer bonding results in an elastic deformability parallel to the principal axis much greater than perpendicular to this axis. This is reflected in the elastic moduli $S_{33} \gg S_{11}$ (For graphite $S_{33} = 58.5 \times 10^{-13}$ cm²/dyne $S_{11} = 1 \times 10^{-13}$ cm²/dyne.) Due to this large difference in deformability the lattice is essentially only stretched in one direction on heating at relatively low temperatures. Thus a Poisson contraction proportional to S_{13} will result perpendicular to the principal axis which in these solids exceeds the low intrinsic expansion. Thus over a certain temperature range these layer structures exhibit negative expansions in the a-axis direction (Fig. 1.7).

1.4.2 Theory of Anisotropic Thermal Expansion

A theoretical approach to the thermal expansion

of anisotropic substances can be made if the separation between the two directions is considered to be well defined. In this case a Debye temperature can be ascribed to the separate directions in the lattice, i.e. $\Theta_{\perp}$ and $\Theta_{\parallel}$ and the frequency spectrum assumed is shown in fig. 1.6.

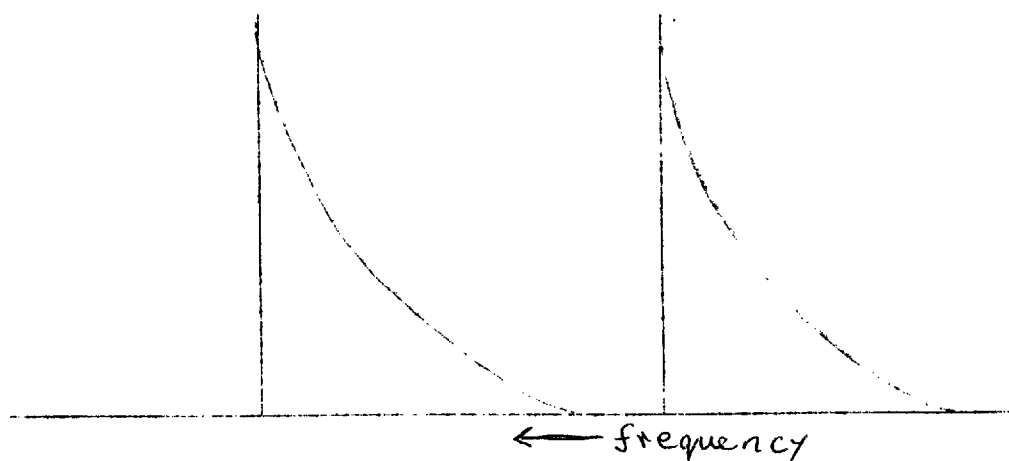


Figure 1.6. Frequency spectrum assumed in separating the vibrations into two directions.

This method of approach has been applied to zinc and cadmium (Grüneisen and Goens, 1924) and also to graphite (Riley, 1945).

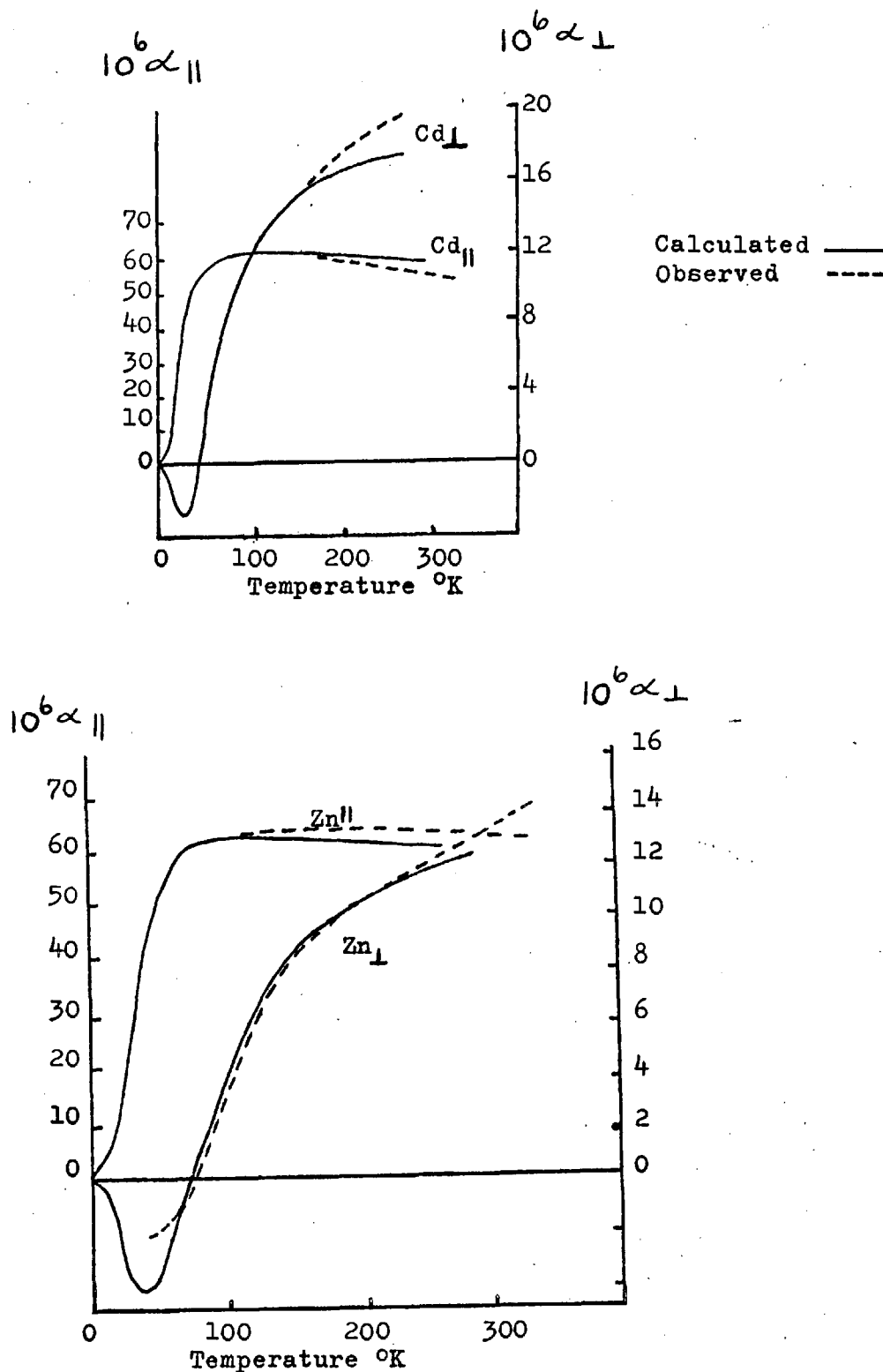


FIG.1.7. The thermal expansion of zinc and cadmium perpendicular and parallel to the principal axis showing region of negative expansion.

The treatment for graphite required the specific heat to be split into two components one parallel to the principal axis C_{V_3} and one perpendicular to this axis C_{V_x} . Equations were derived for the thermal expansion parallel $\alpha_{||}$ and perpendicular $\alpha_{\perp}$ to the principal axis

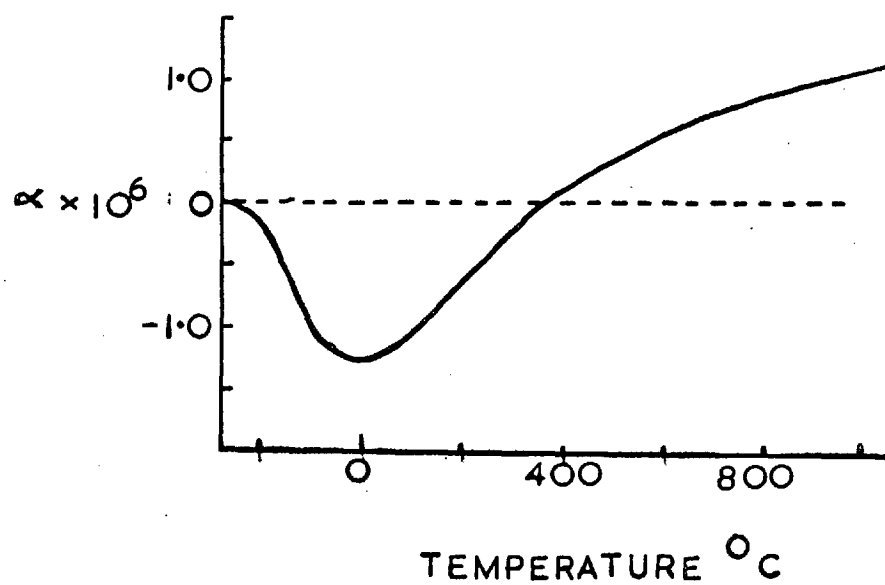
$$\alpha_{||} = L C_{V_x} + M C_{V_3} + NT$$

$$\alpha_{\perp} = A C_{V_x} + B C_{V_3} + CT$$

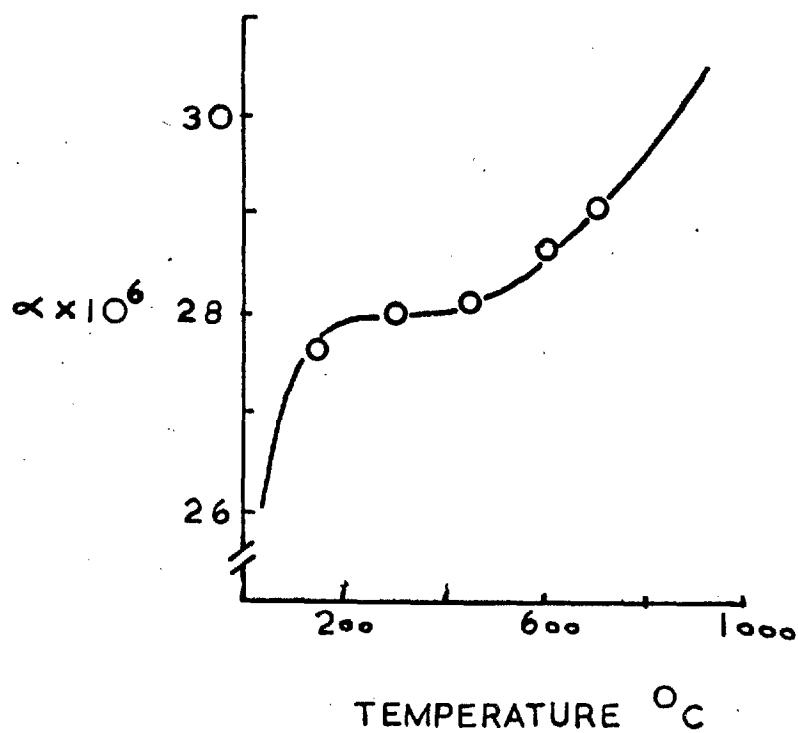
where A, B, C, L, M, N are constants expressed in terms of the Grüneisen constants in directions x and 3 and of the elastic moduli for the lattice.

The theoretical and experimental curves for graphite in the a-axis and c-axis directions are shown in Fig. 1.8 (Riley, 1945). Reasonable agreement between theory and experiment is found. The curve for the c-axis expansion of graphite shows that the thermal expansion coefficient is constant approximately over the region 200-500°C but begins to fall at an approximate rate of 10% per 100°C.

Selected values of the thermal expansion coefficient for other anisotropic elements are shown in table 1.2.



A.



B.

FIG.1.8. THEORETICAL THERMAL EXPANSION
COEFFICIENTS OF GRAPHITE
A. A-AXIS
B. C-AXIS

TABLE 1.2: Selected Comparisons with other anisotropic elements at 20°C

	$\alpha_{11} \times 10^6$	$\alpha_{11} \times 10^6$	α_{11}/α_{11}
Graphite	28	-1	-
Zinc	64	13	5
Cadmium	100	11	9
Thallium	72	9	8
Indium (tetra)	11.7	45	$\frac{1}{4}$
Tellurium	-1.7	27	-
Selenium	-18	74	-

All these are hexagonal except for Indium which is tetragonal. Tellurium and Selenium have strong covalent binding along the chains and weak molecular forces holding the chains together and are among the most anisotropic substances known.

1.5 Measurement of Thermal Expansion

Methods of measuring thermal expansion can be divided into two clearly distinct categories, firstly, those methods which measure the macroscopic expansion and secondly those which measure the lattice expansions, usually by x-ray diffraction methods. The results given by the two methods need not agree with one another. For a crystal with a well ordered lattice the results do in general agree but in cases where the structure contains large numbers of defects or if the material has macroscopic pores then the two methods of measurement will not yield the same results.

1.5.1 Macroscopic Methods

- (a) Pycnometer and dilatometer methods - the volume expansion coefficient is measured by the volume of gas or liquid it displaces on expansion. The main limitation of this method is that it gives only the volume/^{expansion} and can give no indication of any anisotropy that may exist in the sample.
- (b) Comparator methods - the change in length of a specimen is measured with the aid of a comparator or similar apparatus. This method suffers from the serious drawback that in order to produce accurate results a long bar of the sample must

be available to produce easily measurable expansions.

- (c) Mirror and optical lever methods - the extension of the specimen is no longer measured directly but it is optically amplified and is a logical extension of the previous method leading to much higher accuracy and hence feasible use of much smaller specimens, but it may require special preparation of surfaces.
- (d) Heterodyne Beat methods - the expansion of the specimen causes a change in the capacity of a condenser in an oscillatory circuit. The change of frequency of the oscillator can be detected by the heterodyne beat method and can be compensated for by the alteration of a standard condenser in the circuit. The method is capable of high accuracy and compares favourably with the interference methods below.
- (e) Interference methods - the expansion of the specimen causes an alteration in the optical path length of one of two interfering light beams. This produces a shift in the interference pattern and the number of fringes can be counted either visually

or by electronic means. This method can use very small pyramids of crystals and can be used to measure anisotropy if the crystals are cut in the correct orientation. Also the method is fairly easy to adapt to high or low temperature measurements as the whole apparatus can be enclosed and thermostatically controlled.

1.5.2 X-ray Methods

The x-ray methods can be subdivided into reflection and transmission methods. The transmission method will be considered first: the sample is usually prepared as a powder and formed into a cylindrically shaped specimen and the photographic method of detection of the diffracted x-rays is normally employed because the lines produced are generally too weak for the counter methods of detection used in the diffractometer. If the sample is a single crystal however, either method of detection is feasible although even so the photographic method is the more common.

When a photographic method of detection is used, care has to be taken that the shrinkage of the film after processing does not influence the results. This is normally achieved by use of a camera with accurately calibrated knife edges which place reference marks on the film; an alternative

method is to mix a standard sample with the one under investigation so that a series of standard diffraction lines appear on the photograph which allows accurate interpretation of θ for the specimen being investigated.

The accuracy of measurement of accurate lattice parameters by the transmission method has been studied in some detail (see International Crystallographic Tables) and the principal sources of error have been evaluated. These are due to absorption of the specimen, horizontal and vertical divergence of the x-ray beam and in the photographic method radius errors and film shrinkage. It has been found that practically all the errors in the transmission method extrapolate to zero at $\theta = 90^\circ$. Thus the lattice parameter from the various lines must be plotted against some function of the angle θ for accurate results to be obtained. However, the high angle lines must be weighted in some way, because of their higher accuracy, and it has been found that the extrapolation function which gives the best linear plot is:

$$F(\theta) = \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$$

Theoretical justification for this formula can be fairly easily derived by consideration of errors due to absorption which can often be considered to be the principal error in

this method. For the reflection method it is possible to use photographic methods of detection but it is more usual to use counter methods of detection. Ideally a sample with continuously variable curvature is required but this is difficult to arrange and the usual sample geometry is a flat plate. Flat powder samples or single crystals having a flat face in the direction perpendicular to the direction in which the thermal expansion is required are used. Samples can be ground to have flat faces in the required direction if they do not possess suitable faces already. Errors of the film technique and transmission method, i.e. shrinkage and absorption are absent in this method but the actual errors are not so well evaluated. The measurement of accurate lattice parameters has been discussed in detail (Klug and Alexander, 1960) but although the measurement of thermal expansion is dependent on the lattice parameter there are considerable differences in the general technique of measurement which will be discussed in Chapter 5.

1.5.3 Summary

The thin c-axis dimensions of the graphite compounds available made the use of macroscopic methods much inferior to the x-ray methods. This is especially so in the acid salts where the spongy graphite compound would be completely unsuitable for macroscopic methods except for the dilatometer

method. In this case, the choice of displacement fluid would be limited to liquids for which thermal expansion data is not known to sufficient degree of accuracy. The x-ray method has a further big advantage in that some knowledge of the oxidation state and structure can be obtained from the diffraction pattern.

Chapter 2: GRAPHITE AND ITS CRYSTAL COMPOUNDS

2.1 The Nature of Graphite

Unlike diamond which defines a specific carbon structure, the term graphite embraces a range of carbon structure modifications. These all have in common a layer structure consisting of parallel sheets of carbon atoms arranged on a hexagonal net. The modifications arise in two ways: firstly the orientation of the sheets of carbon atoms varies and secondly, the orientation of the crystallites making up the bulk material also varies. These modifications will be discussed in order of decreasing perfection but first of all the structure of the carbon layers is considered. The planar carbon layers consist of a hexagonal net of carbon atoms with a C-C bond distance of $1.415 \text{ \AA}$. This distance, which is intermediate between a C-C single bond $1.54 \text{ \AA}$ and a C-C double bond $1.32 \text{ \AA}$ (cf Benzene $1.39 \text{ \AA}$), suggests $sp^{2.11}$ hybridisation of the atoms and the layers in the graphite structure can be considered as the ultimate aromatic macromolecule with strong bonding in the layer. The bonding between these layers is relatively weak and is due to Van der Waals forces. The direction perpendicular to the layers is referred to as the c-axis and that in the layer, parallel

to the hexagon edges, the a-axis.

The most highly ordered form of graphite is that in which the layers are completely ordered with respect to each other. This form of graphite, which occurs in natural single crystals, is termed hexagonal graphite (Fig.2.1). This structure was one of the first to be examined by x-ray diffraction (Ewald, 1914) and this and later work (Bernal, 1924; Ott, 1928) showed that the carbon layers stacked with the hexagon centre of one layer over a carbon atom in the layer below. The third layer then occupies the same a-axis orientation as the first layer. This form of stacking is referred to as ...ABAB... Hexagonal graphite has a unit cell extending over two carbon layers with four atoms per unit cell; the space group is $P6_3/mmc$. The c-axis repeat distance is approximately $6.7 \text{ \AA}$ and this gives an interlayer spacing of $3.354 \text{ \AA}$; the theoretical density is 2.267 g/cm^3 .

A second modification of graphite has been known to exist for some time and is referred to as rhombohedral graphite (Lipson and Stokes, 1942). Unlike hexagonal graphite the third layer does not occupy the same orientation as the first layer but takes up the alternative position with the hexagon centres above carbon atoms. This leads to a stacking sequence ...ABC ABC ... with a c-axis repeat distance

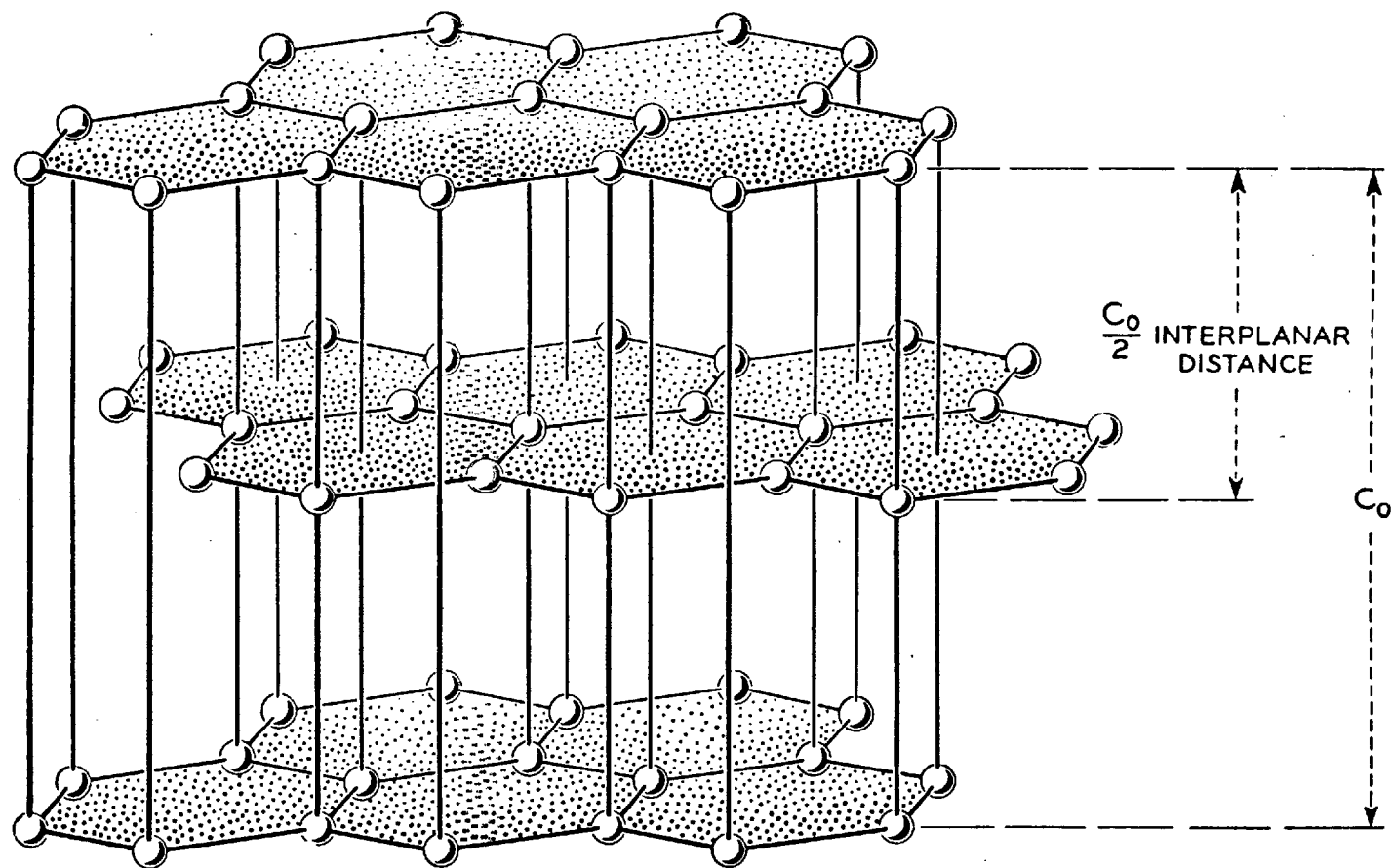


FIG.2.1. THE STRUCTURE OF THE HEXAGONAL FORM OF GRAPHITE $C_0 = 6.7$ ANGSTROMS

of $10.05 \text{ \AA}$. Rhombohedral graphite is found in small quantities in natural graphites and is detected by additional lines in the diffraction photographs. The percentage of rhombohedral graphite is small, 5-10%, but can be increased by cold-working to about 30%. On annealing at high temperatures it reverts to hexagonal graphite. Recent work (Freise and Kelly, 1963) has shown that rhombohedral graphite does not exist as a separate structure but is formed by dislocations in the hexagonal form. Thus small regions of rhombohedral graphite exist as a result of dislocations which cause the stacking sequence to change from ...ABAB... to ...ABC ABC... In addition to these two forms of graphite, as mentioned earlier, there are many forms less well defined crystallographically. If the carbon layers are not stacked in the regular ...ABAB... arrangement then the perfection is lowered. In the extreme case where the layers are randomly oriented to one another the structure is termed "Turbostratic" graphite. As the order between the layers decreases then the interplanar spacing increases, in Turbostratic graphite it has risen to $3.44 \text{ \AA}$. There is a gradual change in this spacing and the value can be expressed in terms of a p factor; p is defined as the fraction of misoriented layers and varies from 1 for turbostratic graphite to 0 for hexagonal graphite, Fig.2

The interplanar spacing for any degree of disorder C_p is

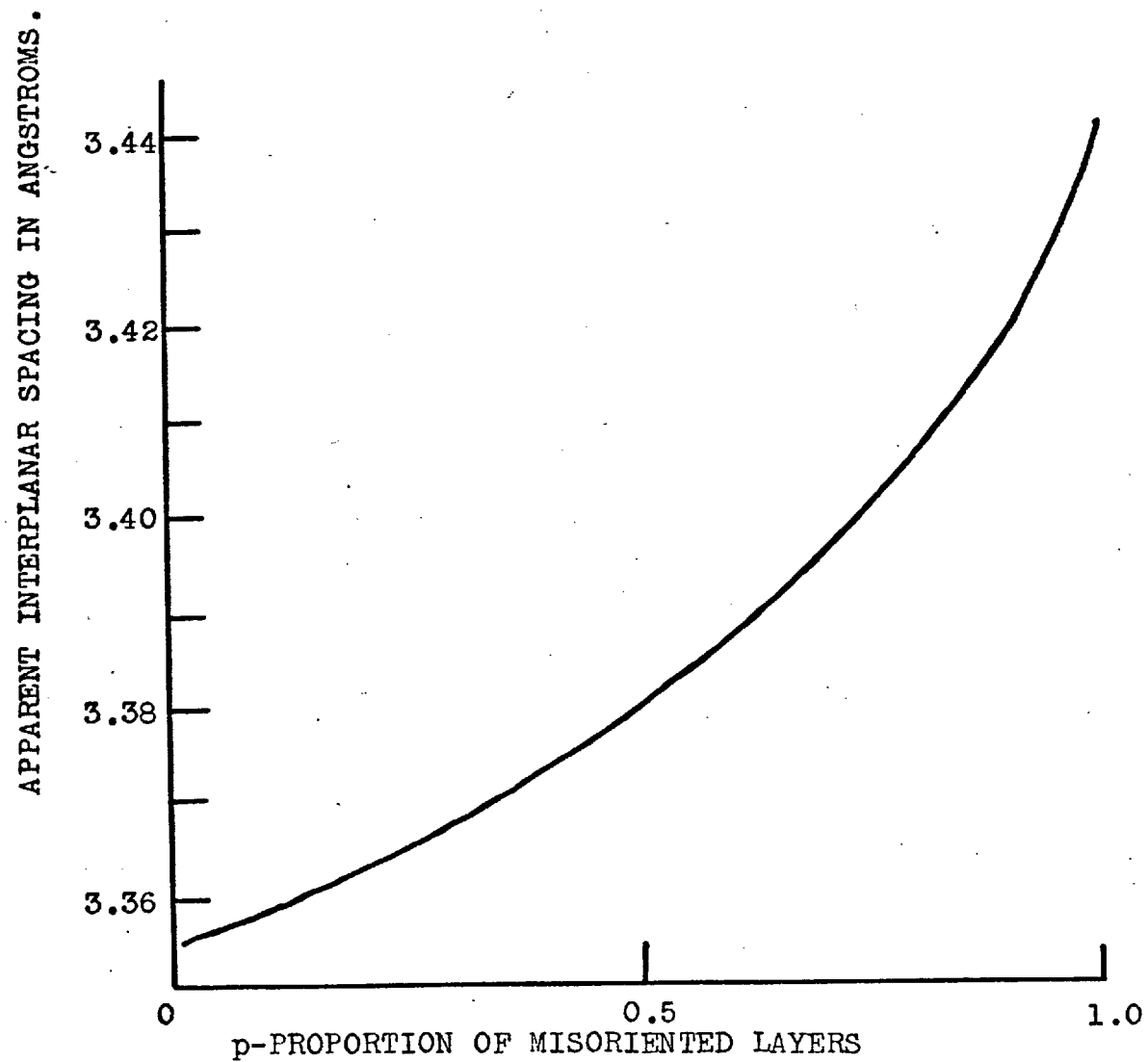


FIG. 2.2. VARIATION OF INTERPLANAR SPACING OF GRAPHITE WITH MISORIENTATION.

given by $C_p = 3.440 - 0.086 (1-p) - .064 p(1-p)$ (Bacon, 1951).

In addition to the increase in c-axis spacing as the order between the layers decreases there is also a broadening of the $hk0$ reflexions as they change from three dimensional to two dimensional diffraction peaks (Franklin, 1951). Further modifications of the graphite structure can arise where the bulk specimen is made up of a large number of small crystallites. This occurs in both polycrystalline and pyrolytic graphites. The structure of the crystallites themselves may be hexagonal graphite or they may be disordered to a greater or lesser extent. In pyrolytic graphite (2.3) the crystallites are generally hexagonal graphite and their c-axes are closely aligned to a common axis, there is however complete randomness of the a-axes. In the best pyrolytic graphite the c-axis spread is only about 1° of arc but this increases to up to $10-15^\circ$ in the poorer specimens. In polycrystalline graphite neither the a-axis nor the c-axis have any preferred orientation and in addition macroscopic defects in the structure reduce the density to $1.5-1.9 \text{ g/cm}^3$. Thus the term graphite includes a wide range from the ideal single crystal, hexagonal graphite to polycrystalline graphites in which the crystallites are themselves turbostratic in nature.

2.2 Forms of Graphite

Graphite occurs naturally in small quantities, the principal locations being Ceylon, Madagascar and the USA. Single crystals are most often found in calcite which is dissolved away to leave the graphite. Small traces of metallic impurities are removed by treatment with hydrochloric acid followed by hydrofluoric acid this results in a graphite of low ash content (0.04%) (Wirtz, 1956). Large single crystals are rarely found, about 0.5 mm in the a-axis direction is typical.

Kisk graphite is a second type of well oriented graphite which is readily available. This occurs as small flakes that separate either in the melt or in the solid in the manufacture of cast iron. The flakes are obtained by dissolving away the iron and the ash content is usually about 2% after purification (Walker and Imperial, 1957).

Apart from these natural graphite sources a large amount of synthetic graphite is now manufactured. This will be considered starting with the less well defined graphites and progressing to those of greater perfection. The basis of the majority of the preparative techniques for artificial graphite is that carboniferous matter, formed by decomposition of organic materials, forms itself into graphite material at high temperatures. This process, known as graphitisation,

begins at about 1600°C and proceeds rapidly at above 2000°C.

Industrially, anthracite or coke particles are bonded with pitch, extruded into bars and then heated in the absence of air at temperatures up to 3000°C. This results in a graphite consisting of small crystallites which have very little preferred orientation to one another. This is referred to as polycrystalline graphite; it is of low density (ca 1.55 g/cc.) and is essentially isotropic in both thermal and electrical properties. The density of this type of graphite is often increased by heating the pitch bonded aggregate to only 1000°C initially and then outgassing under vacuum and impregnating this material with hot pitch at 100 psi. Final heating of this material to 3000°C results in a polycrystalline graphite of density 1.7 - 1.9 g/cc. Although synthetic graphites have been prepared by decomposition of aluminium carbide (Foster, Long and Stumpf, 1958) ~~the~~ the main source other than polycrystalline graphite is pyrolytic graphite which is discussed in the next section.

2.3 Pyrolytic graphite

This includes the products of a number of methods of preparing graphite by the deposition of the thermal decomposition products of hydrocarbons (methane, propane, benzene etc.) on a hot substrate (Brown, Hall and Watt, 1953;

Brown and Watt, 1958). This graphite, which is now manufactured on an industrial scale in the U.S.A. (High Temperature Materials Co.) is often prepared by cracking methane on to a polycrystalline substrate at temperatures between 1800° - 2400°C . There is a preferred orientation of the crystallites, the most probable c-axis direction being at right angles to the deposition surface but no ordering of the crystallites in the a-axis takes place. Graphite prepared by this method at the optimum temperature of 2150°C has a spread of crystallite c-axes of about 10° - 15° as deduced from the half width of the CO_2 reflexion. The alignment of the c-axes can be improved by annealing this material at 3100°C in a resistance furnace (Blackman, Saunders and Ubbelohde, 1961), but better results are obtained by continuing the deposition of graphite until a very thick deposit has been formed (Moore, 1963). This results in shearing stresses at a temperature of up to 3600°C in the neighbourhood of the substrate and produces very good alignment of the c-axes (1° spread) (Moore, 1963).

The graphite with the smallest c-axis spread has however been produced by a rather different method. Graphite prepared at 2100 - 2200°C was heated to 2900°C under a c-axis pressure of up to 500 Kg/cm^2 (Moore, 1963). The graphite prepared by this method has a c-axis spread of only $\frac{1}{2}^{\circ}$; it

shows very high optical reflectivity and has the theoretical bulk density of 2.267 g/cm^3 .

This graphite, although it has very good alignment of the c-axes, still shows very little ordering in the perpendicular direction and is therefore far removed from single crystal graphite. Prolonged heating at 3500°C of this 'hot pressed' material does result in the growth of the crystallites in the a-axis (Moore, 1963). Evidence for this growth is apparent from the 'spotiness' of the hkl diffraction rings.

2.4 Classification and Nomenclature of Graphite Compounds

Graphite reacts with many inorganic compounds to form stoichiometric compounds in which the inorganic species are generally contained in an expanded graphite matrix the carbon layer planes being up to $10 \text{ \AA}$ apart. The intercalate does not necessarily occupy all the possible positions in the graphite matrix and thus a series of compounds can be formed from each inorganic species. In the following discussion of the compounds of graphite it is useful to define the terms which are generally used. The basis of nomenclature is the fact that the intercalate layers do not enter the graphite matrix in a random manner. Regular sequences of x carbon layer planes and one intercalate layer always exist, the number of carbon layers between each intercalate layer decreasing as

the compound forms. The numerical ratio of carbon layers to intercalate layers is used to define the sequence of a compound. Thus in a fourth sequence compound the intercalate layers are separated by four carbon layers. As a result of the preparation of the salt like compounds of graphite by electrochemical oxidation it is usual to refer to those compounds with a large number of the graphite layers expanded by intercalate as compounds of higher oxidation state.

In the compounds when two layers of carbon atoms are adjacent they take up the AB orientation to one another with a separation of $3.35 \overset{0}{\text{Å}}$. This can be referred to as a 'graphite layer pair'. Each intercalate layer is also adjacent to two carbon layers and this 'sandwich' is termed a 'filled or expanded layer pair'. As noted above, the carbon layers in a graphite layer pair usually stack AB however in an expanded layer pair they generally stack AA although AB stacking has been reported in a few compounds (Rüdorff, 1939). Thus in a second sequence compound a typical orientation of the carbon layer planes would be ... ABIB AIA BIB AIA ... and in a third sequence compound ... AB AIA B AIA B AIA ... In addition to this ordering of the carbon layer pairs there is in some compounds, ordering of the intercalate layers both with respect to each other and to the graphite matrix. This differs

from one compound to another and is discussed later for individual compounds.

Graphite compounds can be broadly divided into four groups. The first group contains the compounds in which the planar configuration of the carbon layers has been destroyed. In this class of compounds which includes graphite oxide, fluoride and graphitic acid the intercalate atoms are covalently bonded to the carbon network, the $sp^2\pi$ hybridisation is destroyed. In some cases, e.g. graphite oxide and fluoride a buckled carbon network still remains but these compounds differ from those in the other three groups in that they are not interlamellar compounds in the narrow sense. The second and third groups of compounds are those in which the planar carbon layers are retained and function as macroanions or cations. These compounds are generally well characterised and in some cases, e.g. graphite potassium, the detailed structure and space group are known (2.6). The compounds with a carbon macro-cation include those formed with strong mineral acids which are often referred to as the graphite salts. Graphite bisulphate is typical of this type of salt and can be formed by reaction of sulphuric acid and graphite in the presence of strong oxidising agents (Rüderff and Hofmann 1938). The carbon macro-anion occurs in the compounds of graphite with the alkali metals and also in compounds containing these

metals and ammonia or amines, e.g. graphite lithium ethylamine $C_{28}Li(CH_3CH_2NH_2)$ (Rüdorff, Schulze and Rubisch, 1955). The fourth group of compounds is a much broader group which essentially includes all the compounds not assigned to the previous three groups. This group is termed the molecular compounds, however there is considerable evidence of charge transfer in some of the compounds of this group, e.g. graphite bromine and gallium chloride compounds. Many compounds in this group are not well characterised and little is known about their detailed structures. Typical compounds in this group are those formed with the halogens, metal halides and metal oxides (2.7).

2.5 The acid salts of graphite

Although acid salts have been known for over one hundred years (Schafhautl, 1841), very little was known as to their controlled preparation or structure until the work of Rüdorff (Rüdorff, 1939; Rüdorff and Hofmann, 1938). Detailed studies of both the structure and methods of preparation by chemical oxidation were reported. The salt which formed the basis of the work was graphite bisulphate which was prepared by chemical oxidation of various types of flake and powder graphite in concentrated sulphuric acid. A large range of oxidising agents gave successful results, the more usual being CrO_3 , Mn^{+++} and HIO_4 . The oxidation proceeded in a

quantitative manner and by controlling the amount of oxidising agent present a full range of compound from first to fifth sequence could be prepared. The first sequence compound was blue, all the other compounds were black. Analysis of the first sequence compound gave an empirical formula $C_8H_2SO_4$; however from the amount of oxidising agent necessary to produce this compound it was possible to calculate the oxidation state of the first sequence compound. This gave a value of roughly C_{24}^+ showing that if the empirical formula was $C_8H_2SO_4$, then a considerable number of sulphuric acid molecules were present in excess of those concerned in the charge transfer process. Therefore the formula proposed for this compound was: $C_{24}^+HSO_4^-2H_2SO_4$; the two molecules of sulphuric acid can be likened to 'water of crystallisation' (see Ubbelohde and Lewis, 1960). Other acid compounds were studied and it was found possible by similar methods to prepare first sequence graphite nitrate, perchlorate and selenate; in addition lower oxidation state compounds of weaker acids, e.g., phosphoric, arsenic and periodic acids could also be prepared. Second sequence graphite nitrate formed spontaneously in fuming nitric acid (s.g. 1.52) presumably due to the oxidising nature of the acid, and the first sequence compound could be prepared using this acid and nitrogen pentoxide in a 1:1 mixture by weight.

It was also possible to prepare compounds by washing

the graphite salt of one acid with an excess of another acid. A replacement reaction took place to give the new acid salt. In addition to the chemical methods of oxidation, graphite bisulphate was prepared by electrochemical oxidation of a graphite anode in concentrated sulphuric acid. Single crystal graphite had to be used for this method as polycrystalline or compressed aggregates quickly break up as the electrode expands.

As a result of x-ray diffraction photographs taken of graphite bisulphate first sequence compound, the c-axis lattice repeat distance was found to be $7.98 \overset{\circ}{\text{\AA}}$. Further analysis of the diffraction data showed that in the intercalate layer the sulphuric acid molecules and ions were packed on a triangular net of side $4.92 \overset{\circ}{\text{\AA}}$ (Fig. 2.3). The intensities of the 001 reflexions also showed that the tetrahedral sulphuric acid molecules were not free to rotate about an axis perpendicular to the c-axis but were held as in Fig. 2.4a, with two oxygen atoms equidistant from one carbon layer and the other two the same distance from the other carbon layer.

In addition to the ordered c-axis stacking, all the bisulphate compounds showed ordering of the carbon planes with respect to each other. The planes were generally AA either side of an intercalate layer but first sequence bisulphate also showed AB stacking which causes a doubling of the c-axis repeat distance. The sulphuric acid layers were also found to be

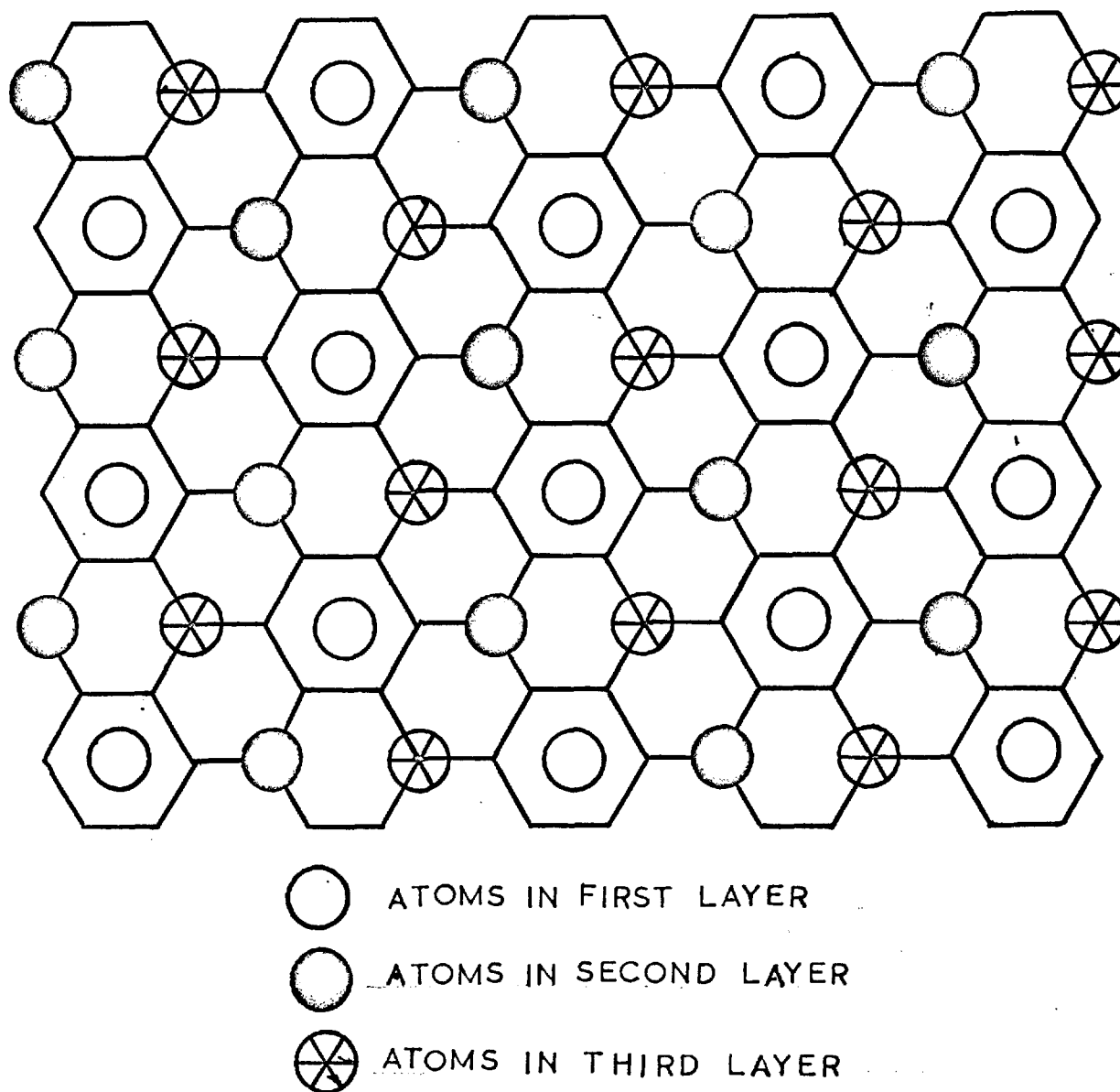
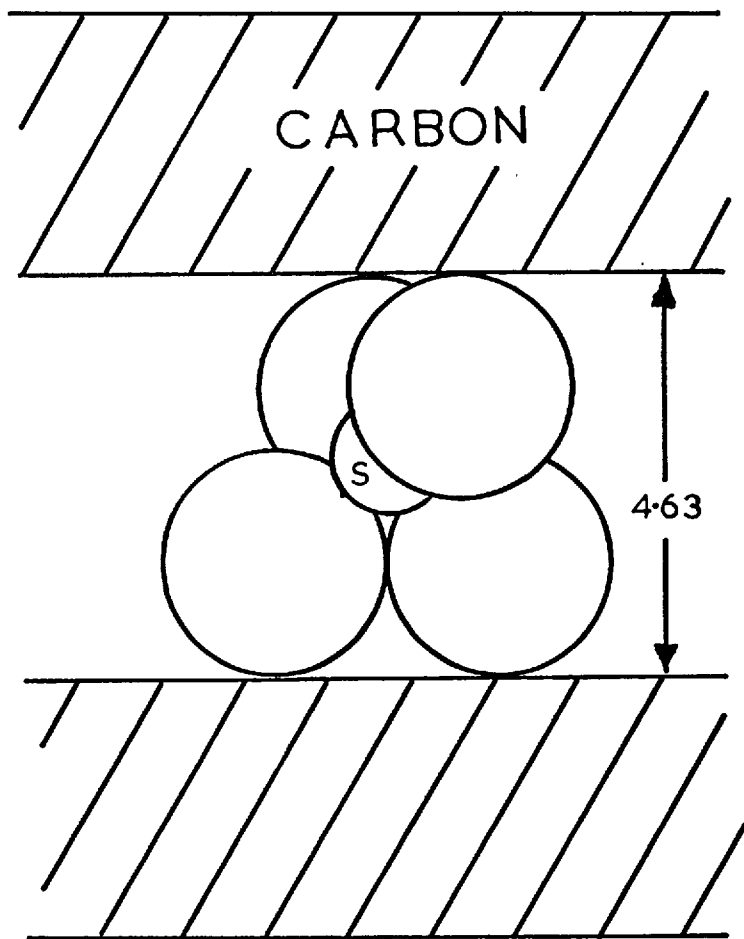
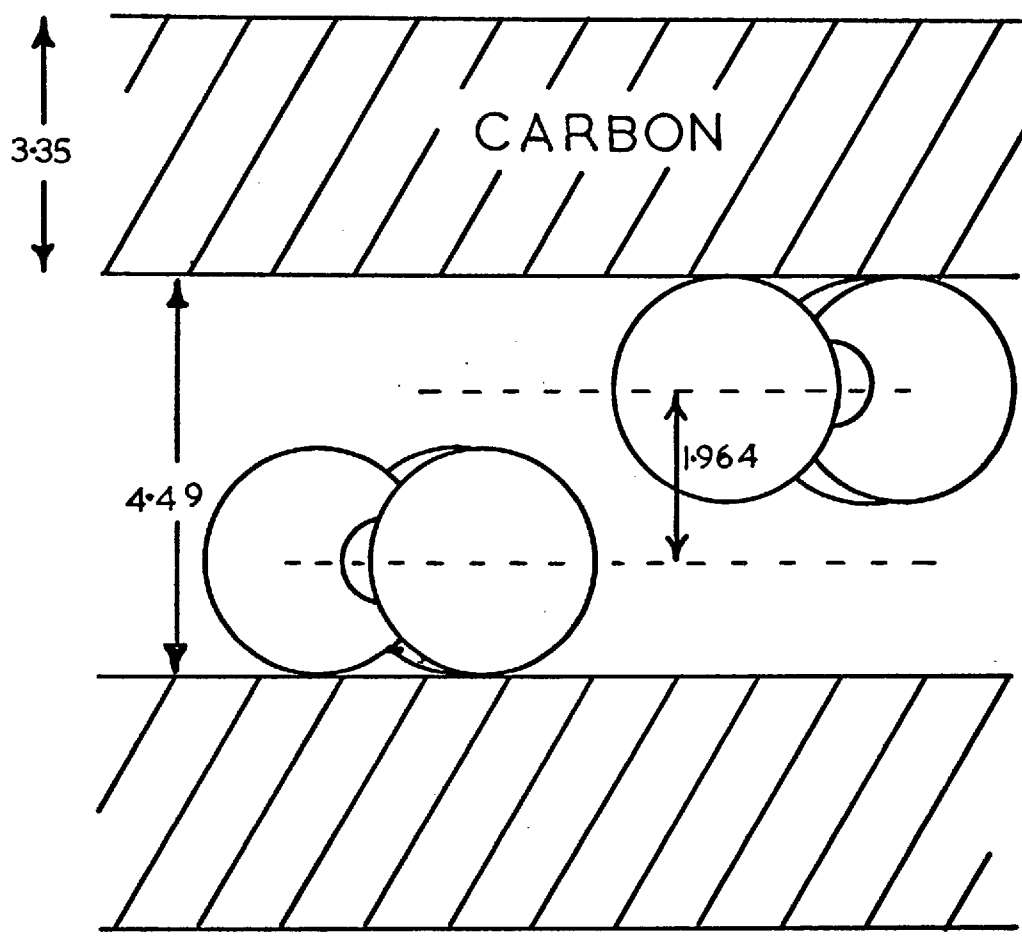


FIG.2.3.

THE ARRANGEMENT OF SULPHURIC ACID SPECIES
IN GRAPHITE BISULPHATE I



(a)



(b)

FIG. 2.4.

THE SPACIAL ORIENTATION OF INTERCALATE
MOLECULES IN GRAPHITE COMPOUNDS

(a) GRAPHITE BISULPHATE

(b) GRAPHITE NITRATE

ordered with respect to each other and to the expanded graphite matrix in the first sequence compound. This ordering only occurred for AB stacking of the carbon layers and the pattern repeated every three layers thus giving an overall c-axis repeat distance of $48 \overset{\circ}{\text{\AA}}$ (Fig. 2.3). The orientation of the perchlorate and selenate ions in the respective compounds was shown from 001 intensities to be the same as in graphite bisulphate but the arrangement in the intercalate layer was not examined and no ordering between the intercalate layers was apparent. In the nitrate where the intercalate molecules are flat, the acid species were arranged either side of the layer centre (Fig. 24b); again the arrangement in the intercalate layer was not examined. The formula of the perchlorate selenate and nitrate has not been studied in detail but a similar formula to the bisulphate has been suggested. The conversion of one graphite salt to a different salt by washing with excess acid confirmed the oxidation state of these compounds to be similar; there may however still be considerable difference in the number of molecules of acid associated with each ion. Thus the problem of whether free acid molecules are present in the acid compounds has not been investigated apart from the case of the bisulphate. Similarly, large gaps exist in the present knowledge of the structure of the acid compounds where in most cases only the c-axis repeat distance is known

(Table 2.1). Very little work has been carried out on these compounds from the preparation or structural aspect since the detailed work of Rüdorff. Apart from a recent attempt to prepare acid salts by washing the chromic^m oxide compound of graphite with the respective acid (Hlatzer and Prouvost^m, 1962), no new method of preparation has been investigated. There is a dearth of information concerning the preparation of acid compounds from pyrolytic graphite, in addition there is no information available as to whether the same products are formed as with powder and flake graphites.

2.6 Alkali metal compounds of graphite

In 1926 Fredenhagen and Cadenbach showed that molten potassium, rubidium and caesium reacted rapidly with graphite to give a bronze coloured solid. Schleede and Wellmann (1932) studied this compound by x-ray diffraction and found it to have a lamella structure. They also showed that a whole series of these compounds could be formed, the first sequence being bronze, the second sequence blue, and the lower oxidation states black. The first sequence compound was shown by chemical analysis to have the empirical formula C_8K and they deduced the second sequence would be $C_{16}K$. Rüdorff and Schulze (1954) carried out further work on these compounds and by chemical analysis were able to prove that the second

TABLE 2.1: The lattice spacings in Angstroms of graphite compounds

HNO_3	1	7.84	InCl	2	12.80
	2	11.14		3	16.20
	3	14.49	CrO_2Cl_2	2	14.6
	4	17.84		1	5.40
	5	21.19	K	2	8.75
H_2SO_4	1	7.98		3	12.10
	2	11.33		1	5.65
	3	14.72	Rb	2	9.02
	4	18.09		3	12.34
	5	21.46		1	5.94
HClO_4	1	7.94	$\text{Li}(\text{NH}_3)_2$	1	6.6
	2	11.12		2	9.9
	3	14.30	CF_3COOH	1	8.2
	4	17.65		$\text{BF}_3(\text{CH}_3\text{CO}_2\text{H})_2$	8.08
	5	21.00			
H_3PO_4	2	11.3		2	11.30
$\text{H}_4\text{P}_2\text{O}_7$	2	11.5			
Br_2	2	10.4			
ICl	1	10.58			
FeCl_3	1	9.37			
	3	16.21			
AlCl_3	1	9.62			
	2	12.80			
	4	19.65			

sequence was in fact $C_{24}K$ and that the lower oxidation states in this series were $C_{36}K$, $C_{48}K$ and $C_{60}K$. They also noticed that at nominal composition $C_{16}K$ the diffraction pattern was a mixture of C_8K and $C_{24}K$. All the compounds of the alkali metals can be prepared by heating the metal with graphite at 200°C and above. The lower sequence compounds can be prepared either by keeping the graphite much hotter than the metal or by decomposing first sequence compounds at above 350°C . Herold (1955) investigated the effect of varying the temperature difference between the graphite and alkali metal and his results are shown in Fig. 2.5. Plateaus are apparent at C_8K and $C_{24}K$ confirming the results of Rüdorff for the formula of the second sequence compound. Detailed analysis of powder diffraction photographs (Rüdorff and Schulze, 1954) enabled the arrangement of the atoms in the a-axis to be elucidated. In the first sequence compound the atoms are arranged on a triangular net (Fig. 2.6b), in the lower oxidation state compounds the loss of one in every three atoms leads to an open hexagonal net (Fig. 2.6a). Although the carbon layers were first thought to be stacked AB (Schleede and Wellmann, 1932), it has now been confirmed that the true stacking sequence is AA (Rüdorff and Schulze, 1954). The intercalated layers in the first sequence are also ordered with respect to each other and the intercalate pattern

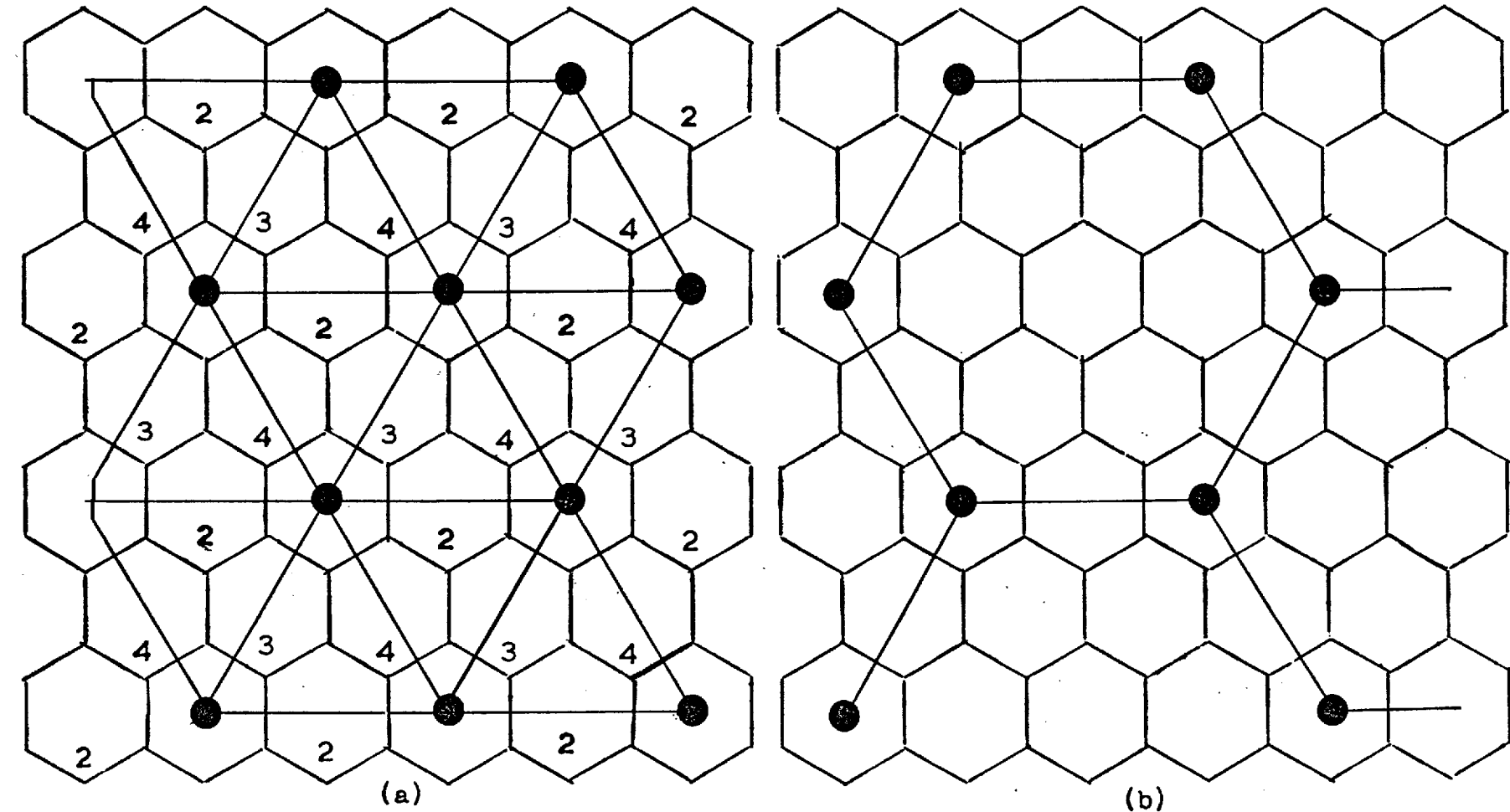


FIG.2.6. THE SPACIAL ARRANGEMENT OF INTERCALATE ATOMS IN THE ALKALI METAL COMPOUNDS (a) FIRST SEQUENCES (b) OTHER SEQUENCES.

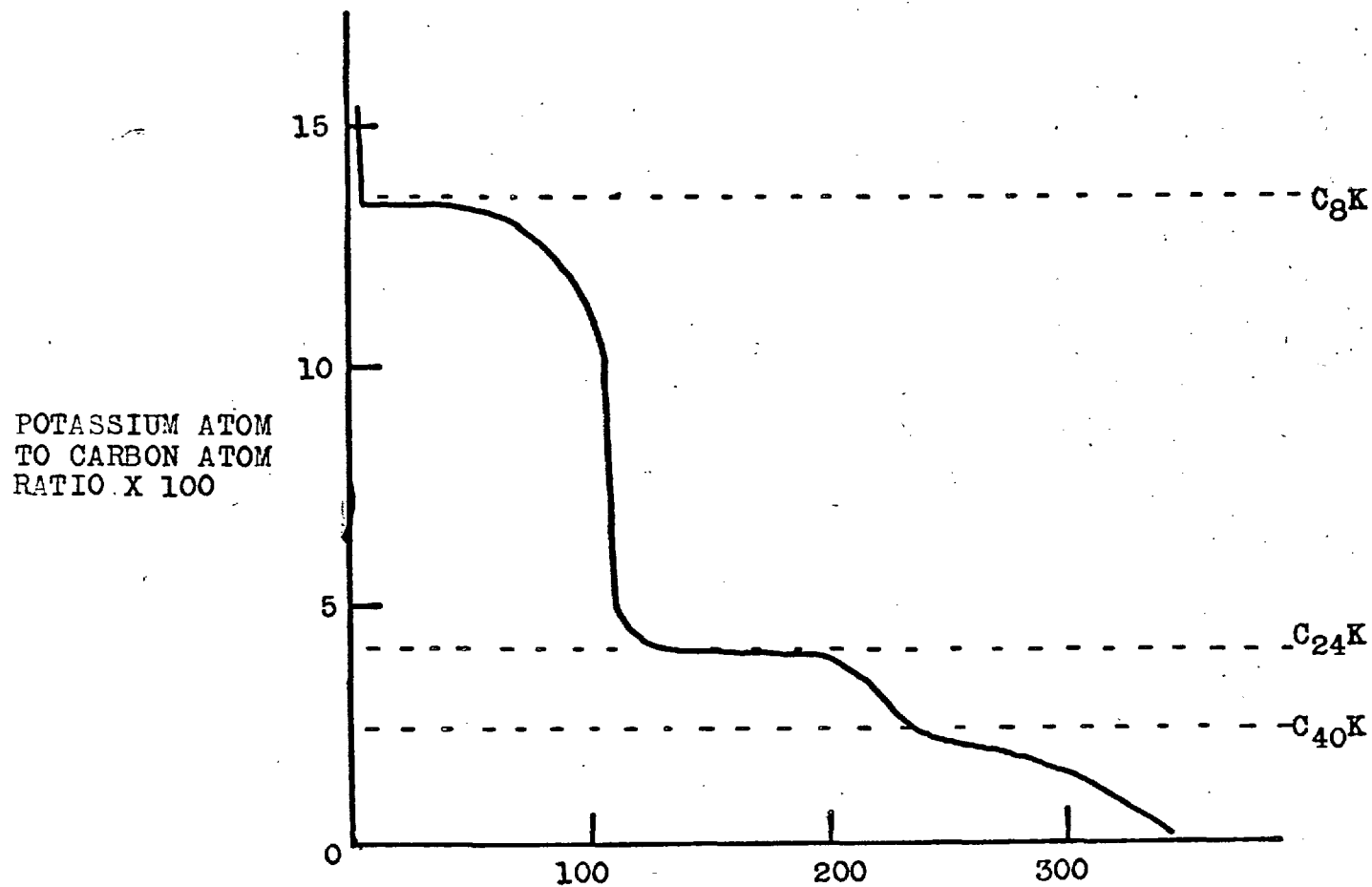
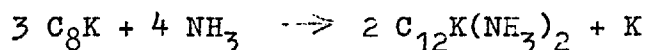


FIG. 2.5. TEMPERATURE DIFFERENCE BETWEEN THE GRAPHITE AND
THE POTASSIUM IN DEGREES CENTIGRADE.

ABSOPTION CURVE FOR POTASSIUM BY GRAPHITE

repeats every four intercalate layers as can be inferred from the numbers in Fig. 2.6a. The full structure of potassium graphite (C_8K) is shown in Fig. 2.7; this has been ascribed the space group C_{222} ; and the atomic positions evaluated (Wolten, 1960). The layer spacings for the alkali metals are shown in Table 3.1. Only the eighth sequence sodium compound has yet been prepared (Asher and Wilson, 1958; Asher, 1959), and this has the formula $C_{64}Na$ with the layer structure as in Fig. 2.6b. The rubidium and caesium compounds are reported (Rüdorff and Schulze, 1954) to have the same structure as the potassium compounds apart from the difference in c-spacing.

All the alkali metal compounds are sensitive to air and moisture. They react to give oxide or hydroxide and graphite. They also react with chlorine to give the alkali halide and graphite, no compound formation has been reported however (Diebold and Herold, 1961). Compounds are however formed with ammonia and amines, some of the metal is lost and the lattice further expands to give complex compounds, i.e. $C_{12}K(CH_3CH_2)_2$ and $C_{12}K(NH_3)_2$ which are blue (Rüdorff, Schulze and Rubisch, 1955):



It is also possible to form similar compounds of sodium and

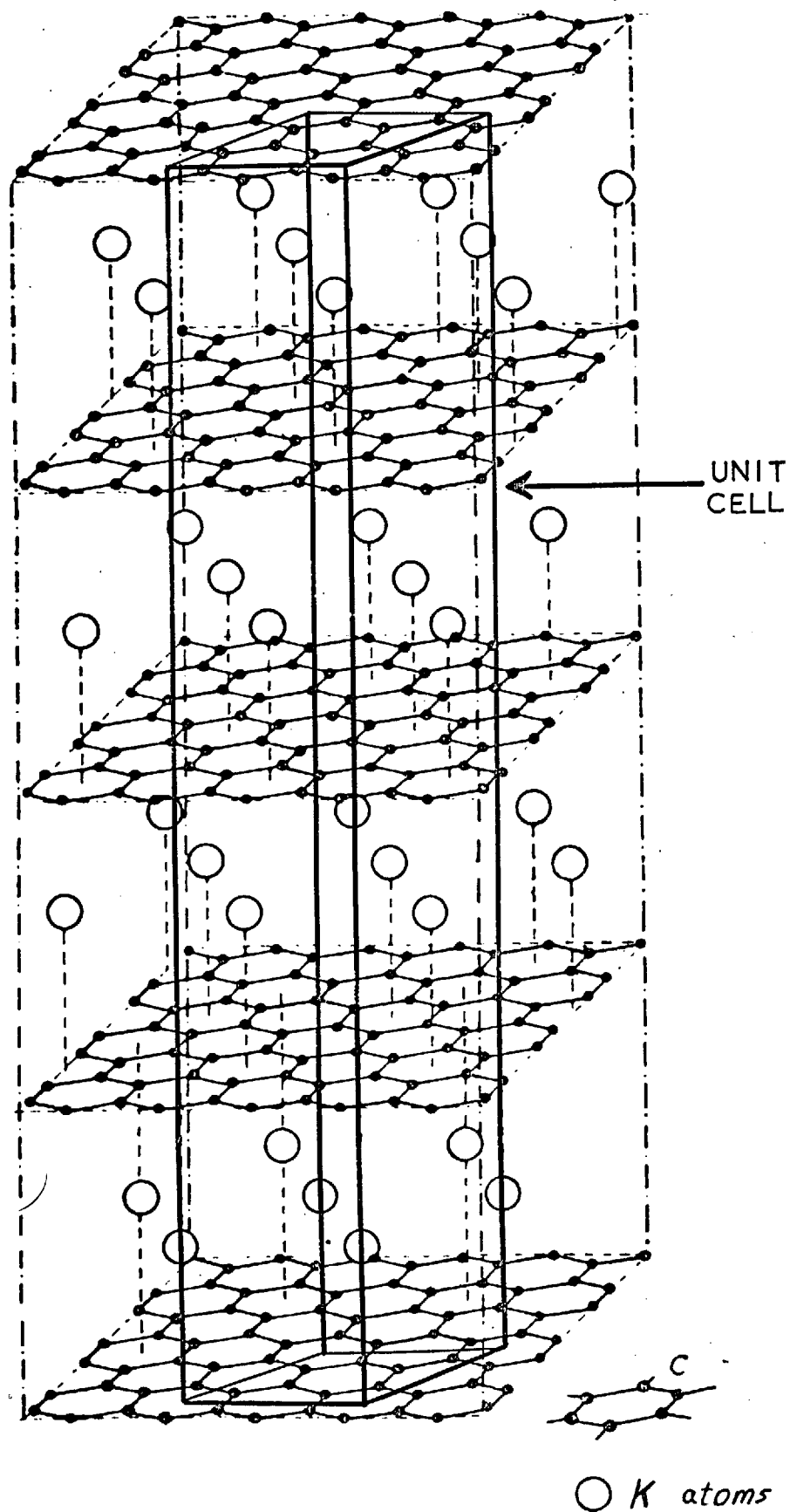


FIG.2.7. STRUCTURE OF POTASSIUM GRAPHITE

lithium by electrolysis of solutions of the metal in the amine. The c-axis spacing is larger than for the normal alkali metal compounds, i.e. $C_{12}Li(CH_3NH_2)_2$ 6.9 Å and $C_{28}Li(CH_3CH_2NH_2)_2$ 8.5 Å.

2.7 Compounds of graphite with chlorides, oxides, sulphides and the halogens

It was noticed (Thiele, 1932) that in addition to the previous classes of compounds graphite would also absorb $FeCl_3$ if the two were heated together. The study of the intercalation of metallic halides has been greatly extended (Croft, 1952, 1953 and 1956) and a summary of the results is given in Table 2.2

TABLE 2.2: Summary of Intercalation Test Results

<u>Substances intercalated in graphite</u>			<u>Substances not intercalated in graphite</u>			
CuCl ₂	TaCl ₅	RhCl ₃	CuCl	SiCl ₄	AsCl ₃	PdCl ₂
CuBr ₂	FeCl ₃	PdCl ₄	BeCl ₂	GeCl ₄	SbCl ₃	PtCl ₂
AuCl ₃	CrCl ₃	PtCl ₄	MgCl ₂	TiCl ₄	BiCl ₃	LaCl ₃
BCl ₃	CrO ₂ Cl ₂	ICl	CaCl ₂	SnCl ₂	VCl ₄	CeCl ₃
AlCl ₃	CrO ₂ F ₂	ICl ₃	BaCl ₂	SnCl ₄	SO ₂ Cl ₂	PrCl ₃
AlBr ₃	MoCl ₅	YCl ₃	ZnCl ₂	PbCl ₂	SOCl ₂	NdCl ₃
GaCl ₃	WCl ₆	SmCl ₃	CdCl ₂	PbCl ₄	SeOCl ₂	ErCl ₃
InCl ₃	UCl ₄	GdCl ₃	CdI ₂	ThCl ₄	TeCl ₄	SeCl ₃
TiCl ₃	UO ₂ Cl ₂	YbCl ₃	Hg ₂ Cl ₂	ThI ₄	MnCl ₂	
ZrCl ₄	ReCl ₄	DyCl ₃	HgCl ₂	PCl ₃	CoCl ₂	
HfCl ₄	CoCl ₃	EuCl ₃	CCl ₄	PCl ₅	NiCl ₂	
SbCl ₅	RuCl ₃					

Only a few of these compounds have been investigated in detail but it has been found for AlCl_3 (Dzurus and Hennig, 1957) and GaCl_3 (Rüdorff and Landel, 1958) that no intercalation occurs unless free chlorine is present. FeCl_3 does intercalate without chlorine but a detailed study by x-ray and electron diffraction (Cowley and Ibers, 1956) showed a lack of homogeneity, the structure apparently consisted of ferric chloride layers and carbon layers with the chlorine atoms in preferred positions with respect to the carbon layers but not forming a three dimensional compound. Croft also found that compounds were formed between graphite and oxides and sulphides under similar conditions to the halides but in general the amount intercalated is small (see Table 2.3) In the case of the sulphides an excess of sulphur was added.

The halogens also react with graphite; bromine is the only one to react at room temperature (Rüdorff, 1941) and most types of graphite absorb in both liquid and vapour to give a limiting composition C_8Br . This is a second sequence compound and no first sequence compound has been reported. The c-axis repeat distance is $7.05 \overset{\circ}{\text{Å}}$, but the a-axis arrangement appears to be complex (Leles, 1963). A three to one ratio of molecules to ions has been deduced from the electrical properties (Hennig, 1952), giving a tentative formula, $\text{C}_{56}^+ \text{Br}^- \cdot 3\text{Br}_2$. The corresponding chlorine compound is

Composition of Reaction mixture	Composition of products by %		
	Metal	S	C
Graphite+S	-	-	99.87
Graphite+Sb ₂ S ₅	5.80	3.60	90.60
Graphite+S+Ti ₂ S	20.60	6.45	72.95
Graphite+S+Cu	9.75	6.45	83.80
Graphite+S+Fe	5.70	6.54	87.76
Graphite+S+Cr ₂ S ₃	1.93	2.08	95.99
Graphite+V ₂ S ₃	1.77	1.95	96.28
Graphite+S+MoS ₂	0.32	0.23	99.45
Graphite+WS ₂	10.02	4.09	85.89
Graphite+PdS	5.30	3.50	91.20
Graphite+Sb ₂ O ₄	1.08	0.28	98.64
Graphite+CrO ₃	28.60	26.4	45.00
Graphite+MoO ₃	7.18	3.57	89.25

TABLE 2.3. The intercalation of oxides and sulphides in graphite.
(from Austr.j.Chem. 9, 184 1956)

known (Juza, Jönck and Schmeckenbecher, 1957; Juza, Schmidt, Schmeckenbecher and Jönck, 1955) and can be prepared by absorption of chlorine at -70°C : the reaction accelerates up to -16°C but above 0°C no compound is formed. Iodine does not react with pure graphite but will react if small traces of bromine are already present. Iodine monochloride and chromyl chloride are both absorbed rapidly in large amounts the former to give roughly C_4ICl .

This general group of compounds has not been studied in as much detail as the other groups and neither the detailed structure of the metal halides (other than FeCl_3) nor of the halogen compounds has been attempted. There is no definite information in many cases of the state of the intercalated species, i.e. Br^- or Br_2 ; GaCl_3 or GaCl_4^- and the principal data available about these compounds is the extent of the expansion of the graphite lattice necessary to incorporate the intercalate.

2.8 Residue Compounds

When graphite compounds are decomposed by heating or by reversal of the electrolytic process in the case of graphite salts, not all the intercalate is removed (Hennig, 1951, Hennig, 1952).

Graphite bromine compounds will retain some bromine even after heating at 300°C under vacuum for some hours. These

compounds which tenaciously hold the intercalate are termed 'residue' compounds. The ratio of ions to molecules differs in these compounds and the intercalate is assumed to be trapped at defects or at edge sites and not to be present as a true lamella compound (Kacser and Ubbelohde, 1949). Recent work suggests that the residual bromine is definitely confined to small areas in the compound and not uniformly distributed (Heerschop and Delavignette, 1963). The chemical properties of these compounds are similar to graphite apart from a slight increase in reactivity.

Chapter 3: PREPARATION AND STRUCTURE OF GRAPHITE COMPOUNDS

3.1 Introduction

In order to prepare suitable compounds for thermal expansion measurements it was found necessary to investigate the controlled preparation of some of the compounds of graphite. The preparation of compounds from pyrolytic graphite had not been studied in detail before and thus although the products of many of the preparations could be predicted beforehand from work on powdered graphites the kinetics of the preparation were unknown. It was not possible to carry out routine quantitative analysis of these compounds because the techniques required for the accurate analysis necessary to differentiate between compounds as close in composition as $C_{40}K$ and $C_{48}K$ would involve a separate research topic. The principal method of analysis of these compounds has therefore been based on the observation of 001 reflexions: studied on the diffractometer (chapter 5) or x-ray diffraction photographs taken using a conventional forward reflexion flat-plate camera. From these photographs new features of the structure have become apparent in some cases. The flat plate photographs of compounds prepared from pyrolytic graphite were taken with the x-ray beam perpendicular to the c-axis. Because of the lack of a-axis ordering between crystallites in

pyrolytic graphite; these photographs of graphite compounds are comparable to those of a single crystal rotated about its c-axis. This point must be borne in mind in any discussion of the structure of graphite compounds which is based on these photographs.

In all the photographs included in this thesis the c-axis direction is horizontal and the a-axis direction vertical. A Bernal chart can be superimposed on these patterns; the layer lines running from top to bottom of the photograph. Rather prominent in these photographs are lines of reflexions running across the photographs. These can be considered as pseudo-layer lines and the reflexions in these lines have the same h and k indices but the l index varies. In typical diffraction photographs of graphite in this orientation, these pseudo-layer lines are particularly noticeable (Plate 3.1a). The innermost of these pseudo-layer lines is that containing the 10l reflexions. The 100 reflexion corresponding to a lattice spacing of $2.13 \overset{\circ}{\text{A}}$. This is the largest a-axis spacing which occurs in graphite.

In the compounds however larger a-axis spacings occur; these are apparent in the diffraction photographs as reflexions or diffuse bands inside the typical graphite pseudo-layer line. These diffraction effects arise from the intercalate layers and are referred to subsequently as "super-lattice"

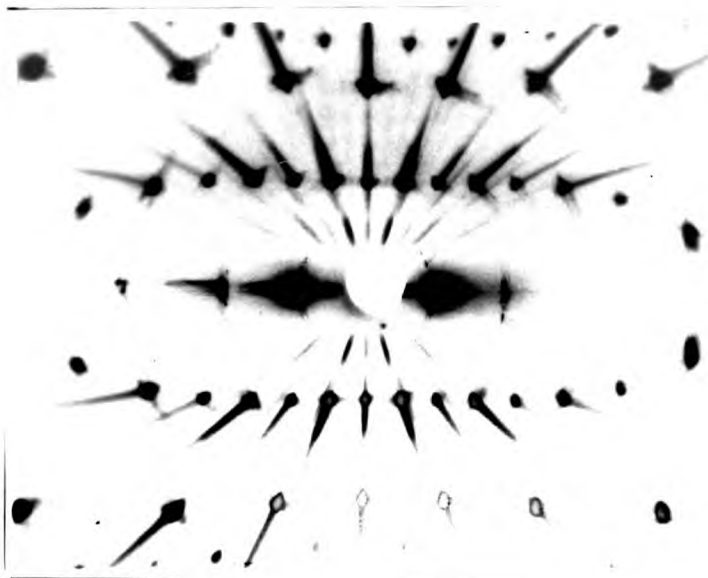


Plate 4 cm Flat plate diffraction photograph of
3.1a hot pressed graphite

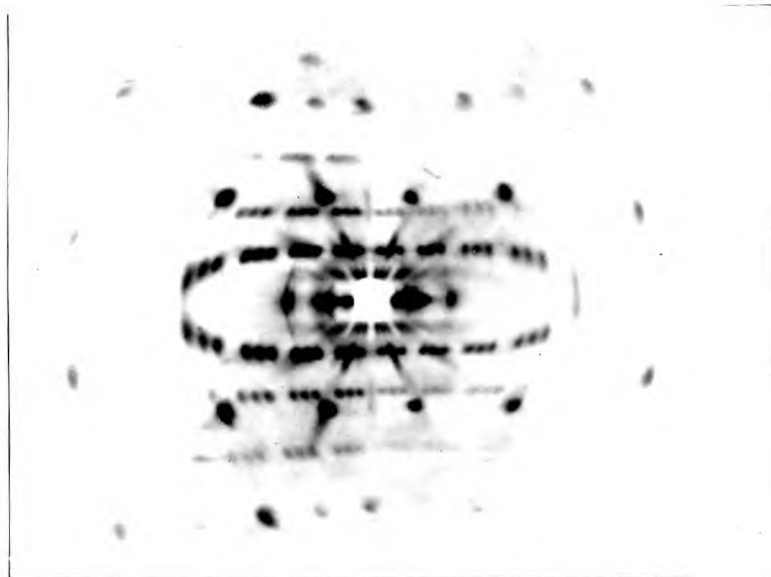


Plate 4 cm Flat plate diffraction photograph of first
3.1b sequence potassium graphite showing super lattice
reflexions parallel to c-axis.

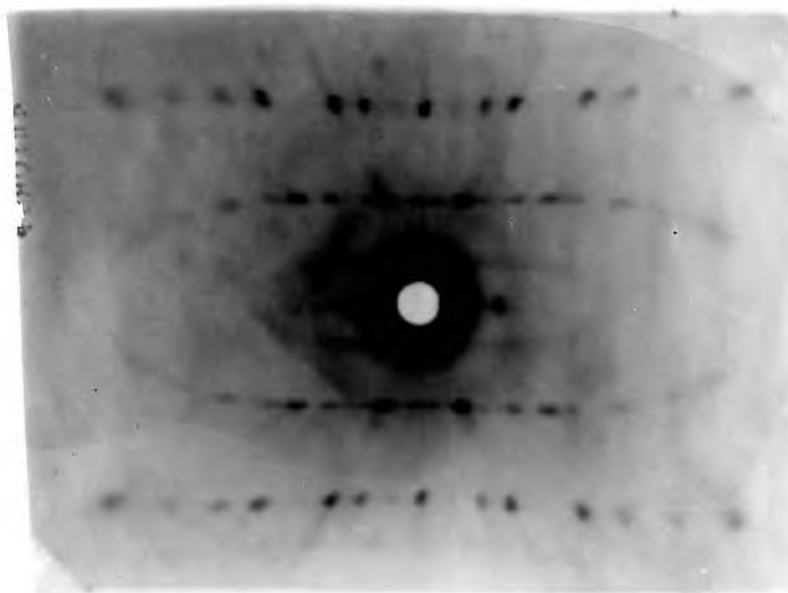


Plate 4 cm Flat plate diffraction photograph of second
3.1c sequence potassium graphite showing diffuse scatter
parallel to c-axis.

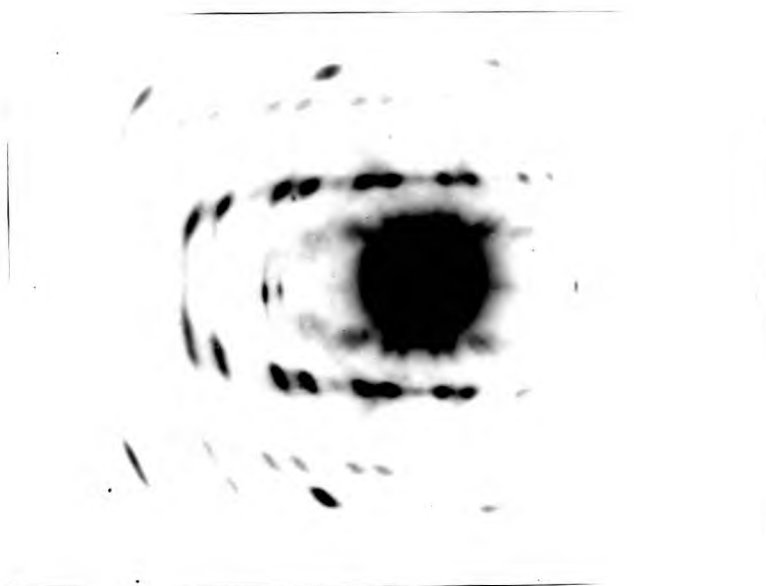
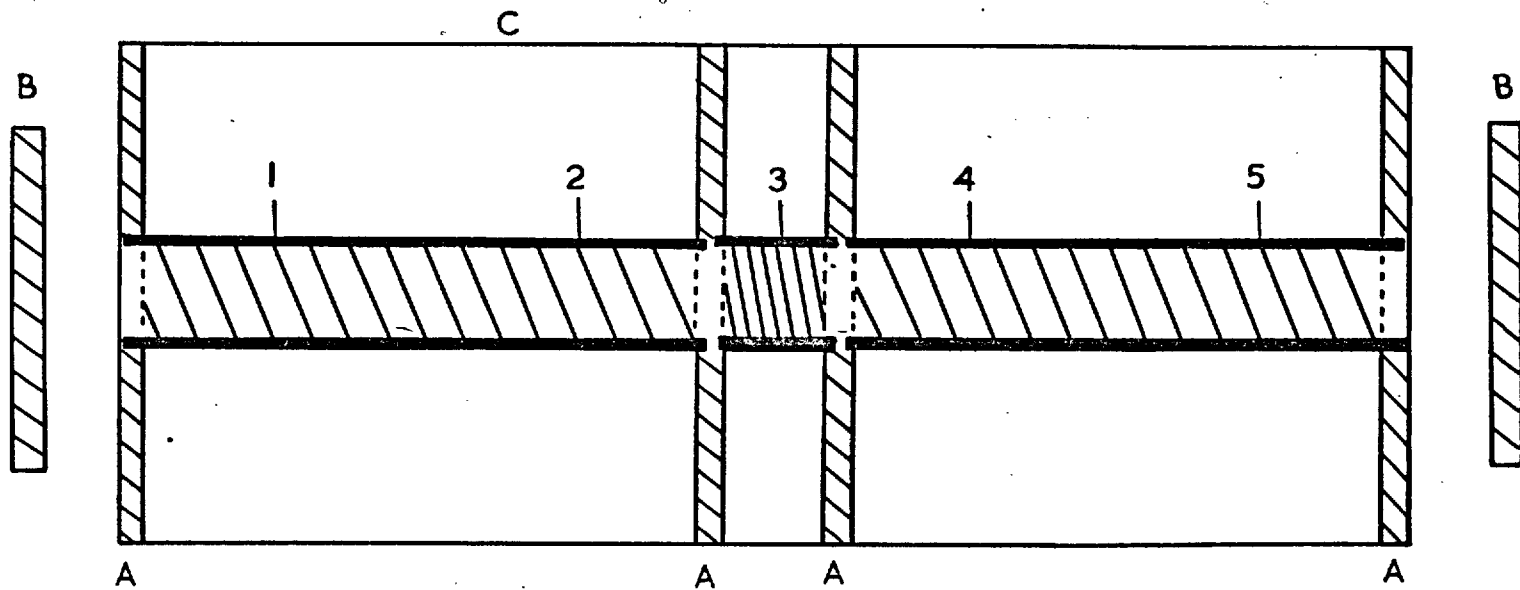


Plate 6 cm Flat plate diffraction photograph of first
3.1d sequence caesium graphite showing super lattice
reflexions parallel to c-axis.

reflexions or bands.

3.1.1 The furnace used for the preparation of compounds

For the preparation of alkali metal and metal chloride compounds it was desirable to follow the general procedure of previous workers (see Mathews, 1960). This involves a furnace with two regions which can be varied in temperature relative to each other and which have a very even temperature within the separate sections. The furnace in Fig. 3.1 is designed to meet these requirements and in addition has a central hot zone to prevent condensation of the reactant in this region of the tube. The basis of the furnace is a 1" internal diameter steel tube of $\frac{1}{4}$ " wall thickness which gives very good heat conduction and hence an even temperature. The two main sections, each 16" long, are separated by a 2" long centre section. These furnace sections are all supported at each end on Pyrophyllite plates (a) which are screwed to an aluminium box 6" square (c) filled with Vermiculite for thermal insulation. The furnace sections are heated by nichrome tape wound on to mica wrapped round the furnace tubes. The centre section is wound in series with one end section but has closer winding of the tape to ensure a higher temperature. No attempt was made in winding the furnace to correct for heat losses through the ends as this was expected to vary



1~5 THERMOCOUPLE POSITIONS

A INERT SUPPORTS

B END HEATERS

C ALUMINIUM BOX

FIG. 3.1. THREE ZONE FURNACE

from one temperature to another. The evennessⁿ of temperature in the two main sections is arranged by the end plates (b) which contain small nichrome heaters. The current to these heaters is controlled by Variacs which are in series with the main furnace sections. The electrical circuit is shown in Fig. 3.2. The furnace section wound in series with the centre section has two sets of $3/8$ " holes drilled into the top and side: these enable the specimens in the tube to be illuminated from above and viewed from the side. Thus a check can be made on the appearance of the sample whilst the furnace is hot. The temperature was measured by Chromel-Alumel thermocouples mounted in small holes in the furnace tubes and the output of the thermocouples was measured on a potentiometer. In this furnace the sections could be run at temperatures up to 600°C . The temperature gradient in each of the main sections was less than 5°C over the whole length at this temperature. At 300°C control to $\pm 1^{\circ}\text{C}$ was achieved over the length between the thermocouples (8"). This furnace was perfectly adequate for the preparations carried out but samples larger than about $\frac{1}{2}$ " square would require a bigger furnace for which the design could easily be sealed up.

3.2 The Alkali Metal Compounds

The preparation of potassium, rubidium and caesium compounds has been carried out using pyrolytic graphite as

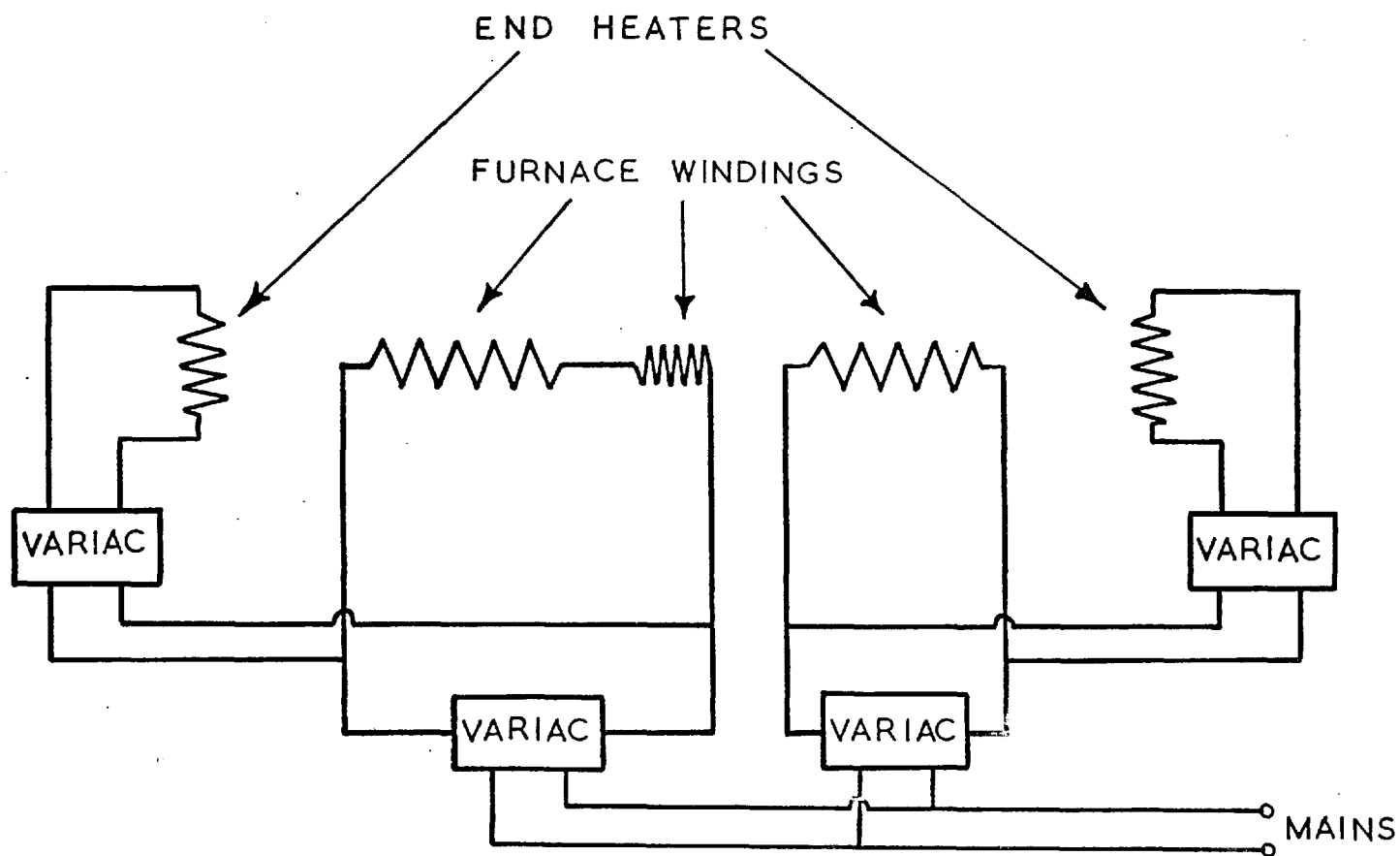


FIG.3.2.CIRCUIT DIAGRAM OF FURNACE

starting material. These compounds were all prepared from hot-pressed material (see 2.3 and Moore, 1963). A flat plate diffraction photograph of this material is shown in Plate 3.1a.

3.2.1. Techniques of preparation

Samples were prepared in two ways. At first conditions were very carefully controlled; all traces of air, water and oxide contaminant on the metal were removed. This method has been reported previously (Mathews, 1960). Later experiments were carried out with no attempt to remove all the oxide and rather less care was exercised in the removal of residual gases. There was no detectable difference in the x-ray diffraction photographs of samples prepared by the two methods so for routine experiments the latter method appears to be satisfactory. The two methods used were, in detail:

(a) A tube similar to Fig. 3.3a was used. The graphite sample was placed in the section G before the constriction H was made; the tube was then connected to a vacuum system at H. Reagent grade potassium, packed under naphtha was cut free of the heavy oxide crust and washed with 80°-100 b.p. petroleum ether. About 5g was then placed in A and a current of dry nitrogen was passed through the tube whilst the potassium was melted and run into section C leaving most of the remaining oxide coating in section A. The constriction B was then sealed and the tube evacuated using a silicon oil

Diagram approximately one third scale

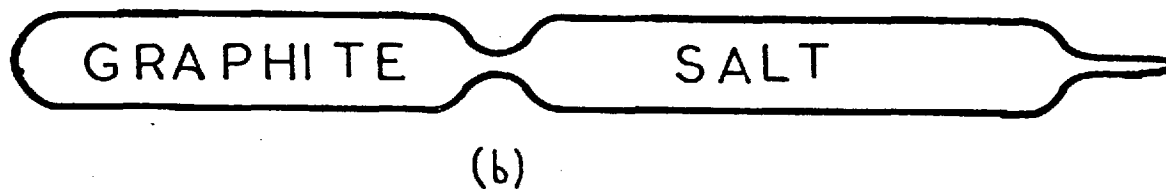
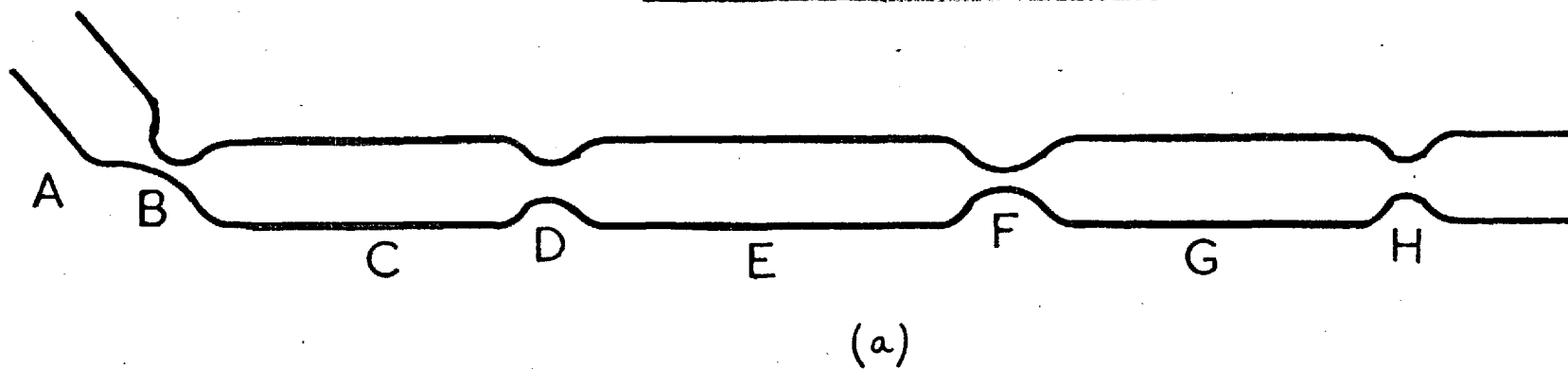


FIG.3.3. GLASS REACTION TUBES USED TO PREPARE
GRAPHITE COMPOUNDS

diffusion pump backed by a rotary pump. About 2g. of potassium was then distilled under vacuum from C to E and then the constrictions D and H were sealed off.

(b) The graphite was placed in a simpler tube (Fig. 3.3b) and a piece of potassium from which the bulk of the oxide coating had been cut was washed free of naphtha and placed in the reagent section; the tube was then evacuated using a rotary pump alone. The tube was sealed off, thus some oxide was left on the surface of the potassium.

For the preparation of rubidium and caesium compounds high purity metals (Rubidium 99.9% and Caesium 99.9%, Lights and Co., Slough) were used. These were available in 1g. sealed glass ampoules and as it was essential to exclude moisture and oxygen from these highly reactive metals the following procedure was adopted. The ampoules were scratched at the neck with a glass knife and a platinum wire was wound around the scratch to form a closed loop which could be coupled to an induction heater. The ampoules were then placed in the reagent section of the tubes (Fig. 3.3b) which were then evacuated using a diffusion pump backed by a rotary pump. After sealing off, the tubes were held with the loop of platinum in the output coil of an induction heater. The platinum became white hot and on cooling caused the ampoules to fracture at the scratch. Thus caesium and rubidium metals could be introduced into the

reaction tubes without coming in contact with the atmosphere.

Although it was possible to use Pyrex glass for all these preparations severe discolouration occurs on prolonged heating in contact with alkali metals. This makes it difficult to see the colour of the sample and in some preparations this was important in estimating the sequence of the compound formed. In order to overcome this difficulty two types of resistant glass were tried. The first was a soft glass (G.E.C. NaIO) which had a thin resistant coating on the tube walls. This glass was subject to rapid deterioration in the atmosphere and also was rather difficult to work with as it required very careful annealing which was difficult to arrange when sealing off tubes. A second resistant glass (G.E.C. H26 X) was found to be more suitable; this glass has a softening point about 100°C above Pyrex and was comparatively easy to work with as it could be joined directly to Pyrex without a graded glass seal. This glass was used in the majority of experiments on the alkali metals and proved very satisfactory; only a pale yellow colour was present after 24 hours with caesium at 350°C .

The sample tubes were heated in the furnace described in 3.1.1, or alternatively, for some of the more routine experiments, in a simple muffle furnace at 350°C .

In order to prevent the samples being attacked by oxygen and water vapour it was necessary to protect them from the

atmosphere whilst they were transferred from the preparation tubes to the thermal expansion cells. It was originally intended to use a dry-box for this operation but considerable difficulty was experienced in producing an inert atmosphere good enough to preserve the surface colour of the samples. Even with complex drying chains and careful flushing of the box no success was achieved. Unfortunately monitoring of moisture content in the parts per million range is not easy to arrange and the dry box was finally abandoned in favour of the "Vaseline" method discussed below. (The dry-box was used for the transferring of samples to weighing bottles before weighing in order to determine the composition of the caesium and rubidium compounds).

A method of opening the preparation tubes and transferring the samples which proved very successful was to immerse the end of a preparation tube in a bath of liquid "Vaseline" (60-70°C): when the end was snipped off with pliers the tube immediately filled with liquid Vaseline. On cooling the tube now containing solid Vaseline could be broken open. Thus the samples were obtained encased in solid "Vaseline". Samples treated in this way could be obtained with the surface still gold in colour. Samples required for the thermal expansion measurements were immediately mounted in cells (5,2,3), whilst those which were to be studied by photographic methods were normally placed into

small polythene bags which were then sealed up. (Polythene bags about 1cm x $\frac{1}{2}$ cm are easily made using a soldering iron and a piece of "P.T.F.E." sheet to stop the polythene sticking to the hot iron.)

3.2.2. Results

(i) The compounds C_8K , C_8Rb , and C_8Cs can be prepared from pyrolytic graphite under the same conditions as previously described for powdered graphites (Herold, 1955; Rüdorff and Schulze, 1954). The reaction temperature is not very critical and temperatures between 250-400°C gave similar results forming the first sequence compound in less than 24 hours. There was no detectable difference in diffraction pattern between samples prepared in the refined method using a high vacuum and those prepared using a low vacuum without removing all the oxide crust from the metal. All the alkali metal first sequence compounds were gold or bronze in colour.

(ii) X-ray diffraction photographs were taken of the first sequence compounds and those shown in Plate 3.1.b and 3.1.d are typical of the potassium and caesium compounds respectively. (The rubidium photograph is not shown because of the heavy fluorescence of rubidium in molybdenum radiation. The photograph was however almost identical to that of the caesium compound.)

The diffraction photographs of the potassium compound are in very good agreement with the structure proposed by

Rüdorff and Schulze, 1954). The reflexions associated with the graphite matrix, the rather heavy reflexions in Plate 3.1.b are by no means the only ones apparent. Inside these reflexions are two "super lattice" pseudo-layer lines arising from the intercalate layers. These reflexions show that a high degree of ordering exists between the intercalate layers which are themselves highly ordered. Thus the potassium graphite compound can be represented by a unit cell (see Fig. 2.7) with the potassium atoms at definite positions. The diffraction photograph of potassium graphite has been indexed in Fig. 3.4 on the basis of this unit cell.

The structure of the caesium and rubidium compounds has up till now been assumed to be the same as the potassium compound but the diffraction photograph (Plate 3.1.d) shows a different pattern of "super lattice" reflexions. No detailed analysis of the photographs has been attempted but the arrangement of caesium atoms in the intercalate layers appears to be similar; the difference in structure appears to arise from the stacking arrangement of the intercalate layers leading to a different unit cell in the c-axis.

In view of the difference in structure between the caesium and potassium first sequence compounds an approximate analysis of the caesium and rubidium compounds was undertaken to confirm that the compounds were C_8M (Rüdorff and Schulze,

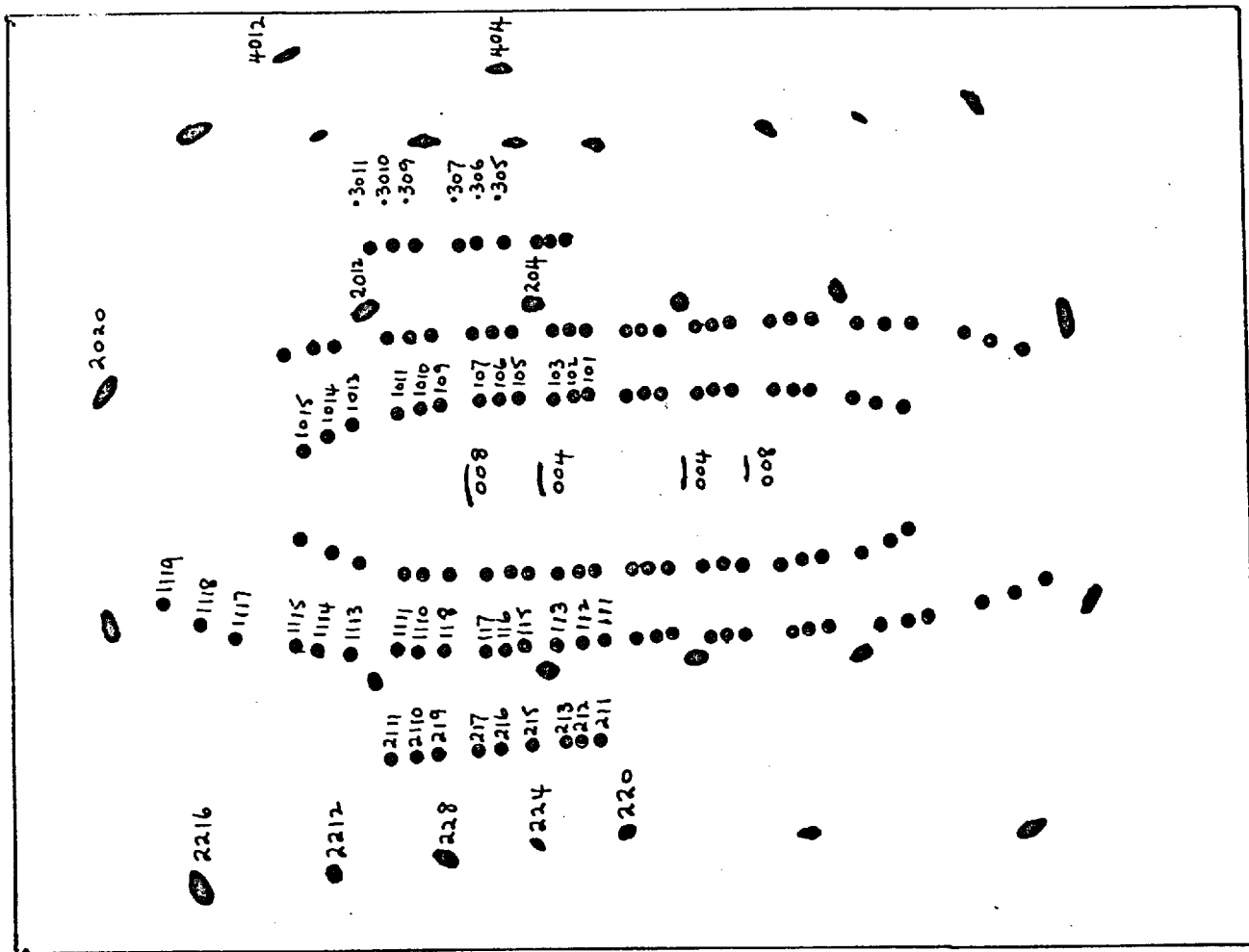


FIG.3.4. Diagram showing indexing of the Graphite Potassium photograph in Plate 3.1.b. using a hexagonal unit cell with $a = 4.92\text{\AA}$ and $c = 21.36\text{\AA}$

1954, have confirmed the formula C_8K). Weighed samples of graphite were converted to compounds in the zone furnace as described earlier and the preparation tubes were opened in the dry box and the samples transferred to weighing bottles. From the weight uptake of alkali metal the approximate formula could be calculated. Samples heated at 370°C with the caesium at 350°C after 5 hours gave empirical formulae $C_{8.4}\text{Cs}$ and $C_{10.2}\text{Cs}$. Samples heated at 360°C with the rubidium at 340°C after 24 hours gave empirical formulae $C_{7.9}\text{Rb}$ and $C_{8.0}\text{Rb}$. Thus although the caesium compounds had probably not fully reacted in 5 hours there seems little doubt that the approximate formula of both the caesium and rubidium compounds is C_8M . Having established that the formula of all three compounds was the same an attempt was made to convert one structure to the other by thermal treatment. Samples of the first sequence compound were prepared as described and opened under "Vaseline". As the samples were to be heated and cooled, polythene bags could not be used, so the samples were sealed into thin walled (0.01 mm) Lindemann glass capillaries. These tubes were very suitable as they had a very low absorption and could be very easily heated or cooled by conventional techniques. (These tubes could be used in place of polythene bags throughout, but it was found rather difficult to handle them when the samples were coated in Vaseline.)

Samples of potassium and caesium graphite were heated

to 150°C in a small furnace and diffraction photographs were taken at this temperature. A similar procedure was adopted whilst cooling the samples in a nitrogen drip. Thus photographs were obtained at 150°C, 20°C and -180°C; no difference between the photographs taken at high and low temperatures was detected. It was not therefore possible to produce a change in structure in either the potassium and caesium compounds within this temperature range. Both structures appear to be stable for the respective compounds.

(iii) The second sequence potassium compound was prepared by two methods; firstly, direct from graphite and secondly, by decomposition of first sequence compound. The diffraction patterns of compounds prepared by these two methods were identical. Preparation direct from graphite was carried out in the zone furnace with the graphite at 350-400°C and the potassium at 250°C. Decomposition of the first sequence compound occurred at 350-400°C and the excess potassium distilled into the cooler parts of the reaction tube. The second sequence compound prepared by both methods was dark blue and reported evidence (Herold, 1955) indicates a formula $C_{24}K_{\text{second}}$.

The diffraction photograph of the /second sequence compound (Plate 3.1.C) shows discrete reflexions from the graphite matrix but the superlattice reflexions present in the first sequence compound have merged into a diffuse band. Thus in the second

sequence compound the ordering of the potassium atoms in the intercalate layer still remains but there is no ordering between these intercalate layers. The second sequence compound seems to consist of an ordered graphite matrix with layers of potassium intercalate which are well ordered in the layer but with no order between intercalate layers. As this compound can be prepared from the first sequence compound where the intercalate layers are ordered with respect to each other it seems reasonable to assume that the second sequence compound is never ordered at room temperature. If this is the case then the forces causing the ordering of the intercalate layers with respect to each other would appear to be short range forces incapable of operating over an empty graphite layer pair. (The presence of long range forces in graphite compounds is discussed in detail later.)

In addition to the diffraction photographs the lattice repeat distances of the alkali metal compound were measured on the diffractometer (see Chapter 5). The values calculated from high angle 001 reflexions are shown in Table 3.1, where they are compared with those of previous workers on powder and flake graphites.

TABLE 3.1: Lattice Spacings in Angstroms

	Present Work	Rudorff 1954	Herold 1955	Schleede and Wellmann, 1932.
Potassium I	5.34	5.40	5.34	5.34
II	8.73	8.75	-	8.74
Rubidium I	5.63	5.65	-	5.68
Caesium I	5.94	5.94	-	5.94

The agreement with the parameters obtained from other graphites is good.

Although a consistent lattice spacing of 5.34 $\overset{\circ}{\text{A}}$ was obtained for potassium graphite for numerous samples, one sample gave a spacing of 5.40 $\overset{\circ}{\text{A}}$. This could not be reproduced and the significance of this anomalous value is discussed later in conjunction with other spacing anomalies (see Chapter 6).

3.2.3. Summary

The preparation and properties of alkali metal compounds from pyrolytic graphite are very similar to other graphites. This graphite does however enable high quality x-ray diffraction photographs to be produced. These photographs have shown ordering between the intercalate layers in the first sequence compounds but no such ordering is present in the second sequence compound. In addition a difference in structure has been found between the potassium compound and the caesium

and rubidium compounds.

In view of this difference in structure, the original evidence for the unit cell dimensions of the caesium and rubidium compounds was examined (Schleede and Wellmann, 1932). Although there was evidence from single crystal photographs for the unit cell dimension in potassium graphite $21.34 \overset{\circ}{\text{\AA}}$, the unit cell dimensions of the caesium and rubidium compounds were assumed to be analogous. Taking a lattice spacing of $22.73 \overset{\circ}{\text{\AA}}$ for the rubidium compound the agreement between the calculated and observed reflexions was examined and the values are presented in Table 3.2. Also included are values calculated on a unit cell of three times the basic spacing ($5.68 \times 3 = 17.04 \overset{\circ}{\text{\AA}}$).

The correlation between the two sets of calculated values and the observed values is very similar, the present unit cell gives perhaps marginally better agreement. Thus it seems likely that the compound prepared by Schleede and Wellmann did not have a different structure to those prepared from pyrolytic graphite.

The evidence for the caesium and rubidium graphite compounds having the same structure as potassium graphite is limited to that quoted above and thus in the light of the photographs obtained of the caesium and rubidium graphites a different structure for these two compounds is very

TABLE 3.2.

Intensity	Observed $\sin^2$	Schleede & Wellman Calculate $\sin^2$ unit cell 22.73 Å		Present Structure Calculate $\sin^2$ unit cell 17.04 Å	
			index		index
v.w.	.0272		101 β		101 β
m - st.	.0343	.0335	103 β 101	.0343	101
v.w.	.0406	.0419	103	.0399	102
v.v.w.	.0477		105 β	.0492	103
m - st.	.0546	.0587	008 β 105	.0545	006 β
st.	.0671	.0672	008	.0672	006
v.v.w.	.0805	.0665	107 β	.0803	111 β
w.	.0981	.0839	107	.0988	111
v.w.	.1048	.1014	112	.1050 .1045	200 β 112
w.	.1181		204 β	.1184	203 β
v.w.	.1292	.1296	200	.1296	200
m - st.	.1456	.1464	204	.1464	203
w.	.2270	.2269 .2353	211 213	.2286	211
v.w.	.2681	.2521	215	.2566	214
		.2773	217	.2734	215
v.w.	.2798	.2927 .3013	301 303	.2743	209
w.	.3858	.3886	220	.3886	220
v.v.w.	.4209	.4253 .4054	312 224	.4221	311
v.v.w.	.4538	.4589 .4558	316 228		

v.v.w. very very weak v.w. very weak w. weak

m. medium st. strong.

likely even for the powder and flake graphites.

3.3 The compounds of graphite with the metallic chlorides

The details of the study of the compounds with the metallic chlorides are contained in Appendix 1. The compounds do not give sufficiently well defined 001 reflexions to enable the thermal expansion to be measured.

The only metallic chloride compound which was studied in detail, the ferric chloride compound, gave rise to interesting results which were not in agreement with previous workers (Cowley and Ibers, 1956). The compound which forms when graphite and ferric chloride are heated at 300°C contains approximately 55% FeCl_3 . Previous work has shown this compound to be a mixture of first sequence compound and graphite. The present work indicates that a second sequence compound is present with a c-axis spacing of 12.7 Å. This compound has an expanded graphite matrix in which the expanded layers are filled with ferric chloride. No ordering between these intercalate layers was detectable from the diffraction photographs but the expanded graphite matrix is ordered. The existence of ordering between the graphite layers has not been reported previously but this is in agreement with all the other compounds of graphite which have so far been investigated in detail.

The molecular compounds undergo the largest expansion

of the graphite layers in their formation ($9-10 \text{ \AA}$) and the strain imposed by this may seriously influence the definition of the 001 reflexions. These compounds appear to be the ultimate in weakly banded graphite compounds; each of the layers has its own structure but there is very little interaction between the two and no ordering of the intercalate with respect to the graphite matrix appears to exist.

3.4 Bromine Graphite

Bromine graphite has been investigated in considerable detail; the kinetics of its formation from pyrolytic graphite and also details of the x-ray diffraction traces obtained are contained in Appendix 2.

Similar difficulties were encountered as with the metallic halide compounds in that the resolution of K_{α_1} and K_{α_2} in the high angle diffraction peaks was not generally good enough for thermal expansion measurements to be made. However it was possible to measure an approximate value of the expansion coefficient and this is discussed in Chapter 5.

The uptake of bromine by pyrolytic graphite has been discussed in detail previously (Saunders, Ubbelohde and Young, 1963) and the general findings of this research are in agreement with the suggested kinetics. A rapid uptake of bromine was found in liquid bromine but on removal most of this was lost very rapidly. The rate of uptake was controlled by the edge

to surface ratio of the graphite. The rate of uptake increased with temperature up to a maximum at approximately 80°C; the compounds formed at higher temperatures also appear to be more stable.

The x-ray diffraction evidence showed the existence of second, third and fourth sequence compounds; the third sequence compound was only present on debromination.

Very little information was obtained about the arrangement of the bromine species in the intercalate layer but a spacing in the layer of $8.5\overset{\circ}{\text{Å}}$ was observed. This is in agreement with recent work (Eeles, 1963) which suggests a complex arrangement in the layer with a spacing of $17\overset{\circ}{\text{Å}}$.

Chapter 4: THE PREPARATION AND STRUCTURE OF THE ACID SALTS OF GRAPHITE

4.1 Introduction

The work on graphite bromine (Appendix 2) had indicated that the rate of reaction of large pieces of graphite was rather slower than for the flake and powdered graphites used by Rüdorff for his preparative work. In order to avoid the preparation of these compounds by chemical methods, it was decided to investigate the conditions for the electrochemical preparation of large samples of the acid salts. The method had the added advantage that very careful control of the oxidation state of the compound formed was possible. The size of sample required for thermal expansion measurements was 1cm square and $\frac{1}{4}$ to $\frac{1}{2}$ mm. thick; the only graphite of this size available at the time and of suitable c-axis alignment was the inner layers of thick deposits (2.3). A typical diffraction photograph of this material is shown in Plate 4.1a. The preliminary experiments to determine the conditions suitable for the preparation of the expansion specimens were carried out on small pieces of graphite of this quality. As a result of these experiments, the most satisfactory conditions of preparation were selected and used for the thermal expansion samples. These recommended methods of preparation for the acid compounds are listed in Appendix 3 for convenient reference.

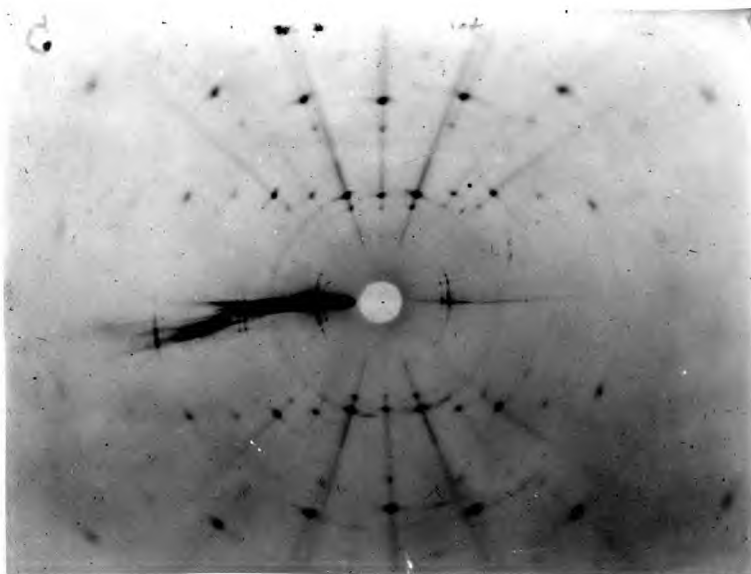


Plate 4.1.a. X-ray diffraction photograph of the inner layer material of a thick deposit of pyrolytic graphite.

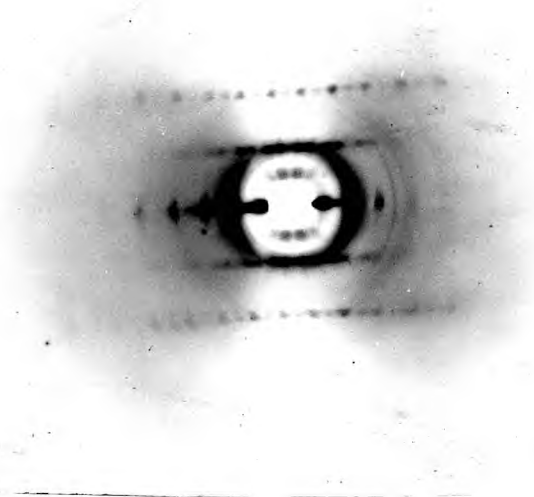


Plate 4.1.b. X-ray diffraction photograph of first sequence graphite bisulphate prepared by anodic oxidation.



Plate 4.1.c. X-ray diffraction photograph of graphite chlorosulphonate prepared by anodic oxidation.

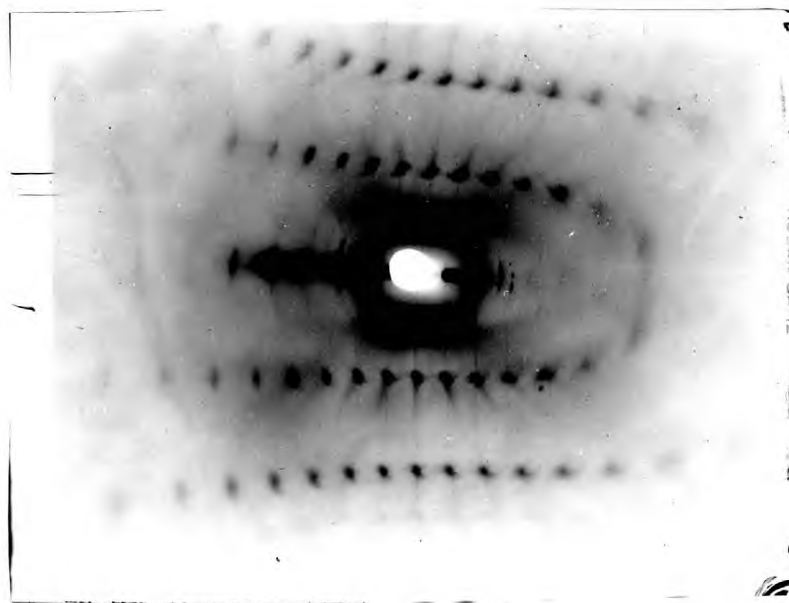


Plate 4.1.d. X-ray diffraction photograph of graphite perchlorate prepared by anodic oxidation.

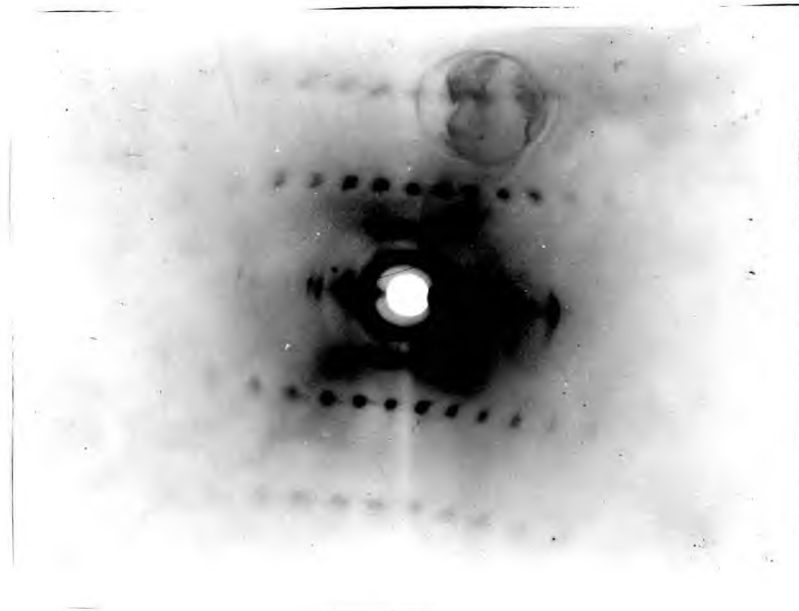
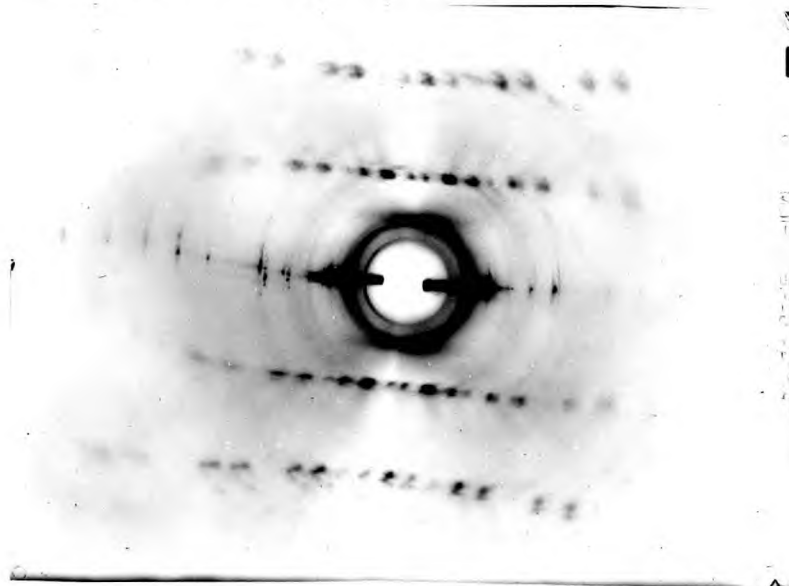


Plate 4.1.e. X-ray diffraction photograph of graphite nitrate first sequence compound prepared by immersion in fuming nitric acid/nitrogen pentoxide.



(g)

Plate 4.1.f. X-ray diffraction photograph of graphite nitrate second sequence compound prepared by double decomposition from first sequence graphite bisulphate.



(f)

Plate 4.1.g. X-ray diffraction photograph of graphite nitrate second sequence compound prepared by immersion in fuming nitric acid.

4.1.1 The Apparatus used for the study of the Electrochemical Preparations

The apparatus used for the preparations of the acid salts consisted of a glass vessel divided into two compartments by a sintered glass disc (Porosity No. 1). The larger, anode compartment (Fig. 4.1) contained two platinum electrodes B and C. The samples of graphite approximately 1 cm x 0.5cm and weighing 0.02-0.05 g. were placed in sliding contact with the electrode B and a larger piece of graphite placed in sliding contact with C. This was usually a piece of pyrolytic graphite of lesser quality (i.e. outer layer material) and was used as a reference electrode during the electrolysis. The voltage (V_C) between this electrode and the sample was recorded. The cathode, which was attached to the electrode A, was a piece of bright platinum foil 1cm x 0.5cm. A voltage (V_A) of 24 or 36 volts was applied to the cell through a 60,000 ohm resistance to give a current of about 400 μ a. By using this large resistance it was possible to maintain the current constant to 2% throughout a preparation. In some preparations V_A was lowered to 1.5 or 3 volts and a proportionately smaller resistance was used; this did not give a constant current but in some cases reduced the amount of side reaction which occurred (4.3). The voltage (V_C) between the reference electrode and the sample and also the current flowing through the cell (I) were continuously recorded and thus the integrated current Q

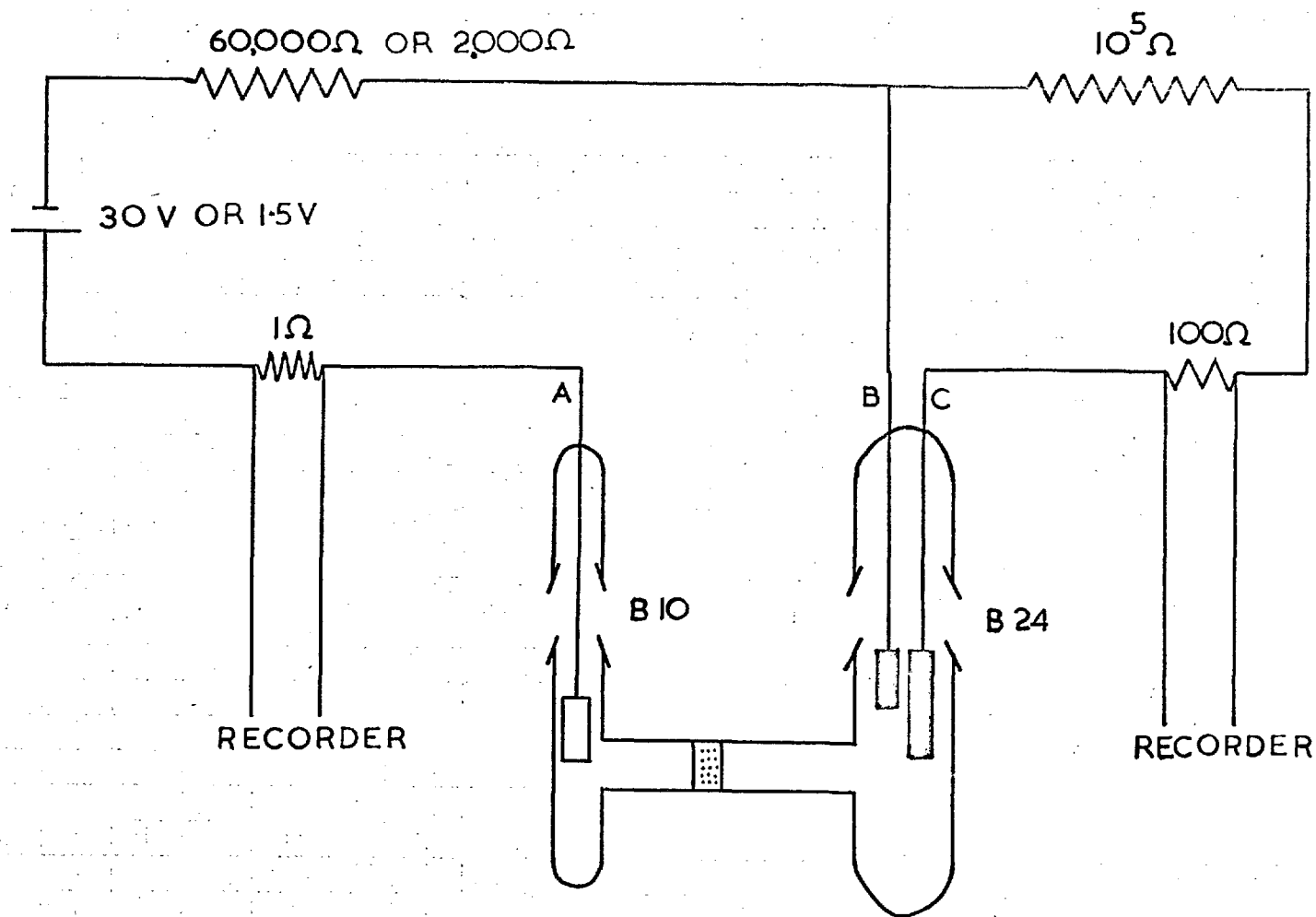


FIG. 4.1. EXTERNAL CIRCUIT AND CELL FOR ELECTROLYSIS

could be calculated $Q = \int_0^T I_t dt$.

Because of the difficulties of chemical analysis (3.1) samples were characterised by x-ray diffraction photographs. The samples were heat sealed into small polythene bags and diffraction photographs taken using molybdenum radiation.

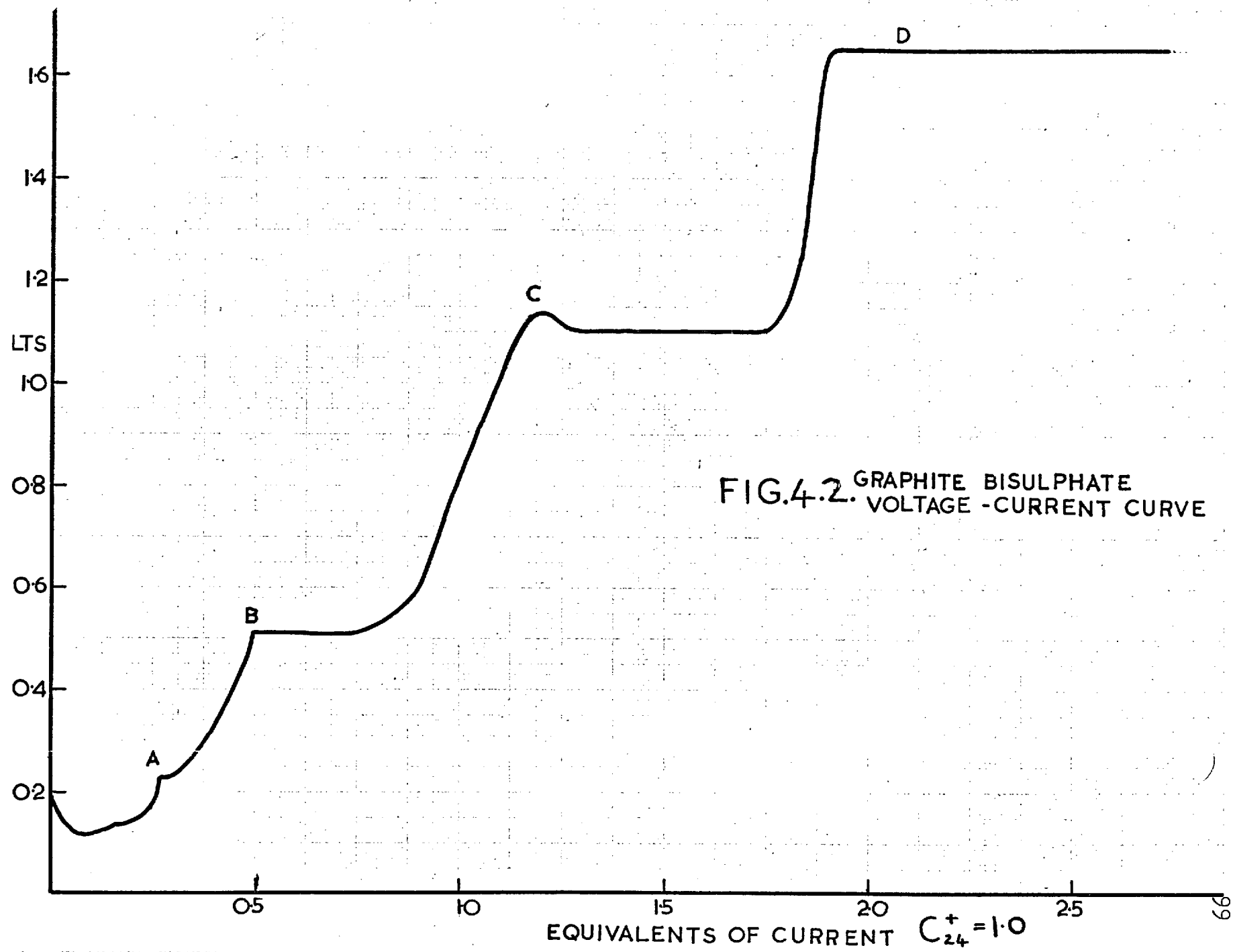
4.2 Results

The variation of V_C with the total current passed (Q) was measured for many of the compounds and these are plotted in Figs. 4.2, 4.3, 4.4, and 4.5. The value of Q theoretically required to produce the oxidation state C_{24}^{+} was taken as unity. The effect of varying the current density was studied for the compounds but no difference in the general shape of the $V_C - Q$ plot was observed for $500 \mu\text{a}/\text{cm}^2$ and $50 \mu\text{a}/\text{cm}^2$. However the lower current density gave slightly better definition of the plateaus, especially for the lower oxidation states.

The c-axis repeat distances were measured for many of the compounds; the results are recorded in Table 4.1, and are compared with those due to Rüdorff.

4.2.1 Graphite Bisulphate

The preparation of graphite bisulphate compounds was carried out using both large and small values of V_A ; the electrolyte used initially was concentrated sulphuric acid



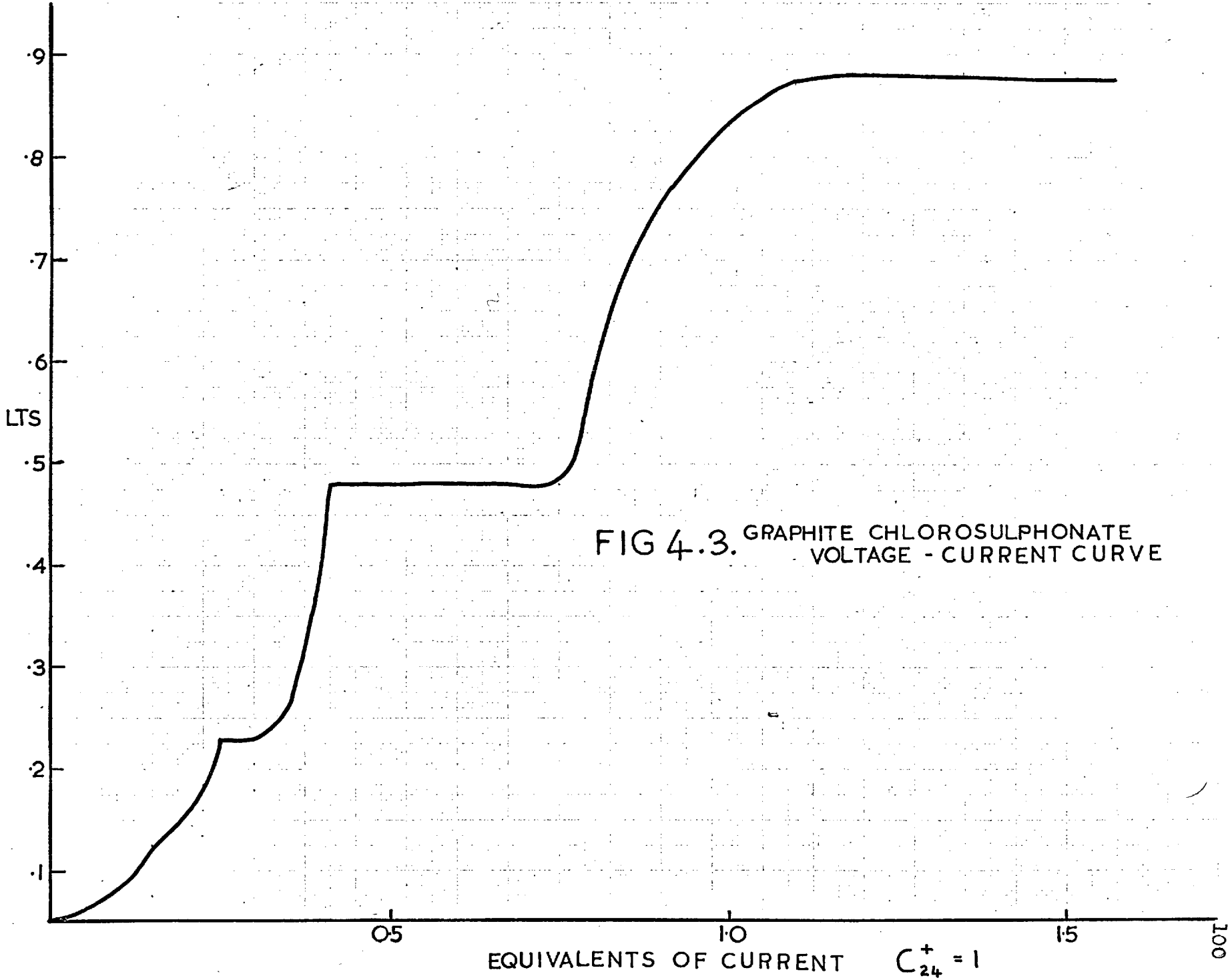
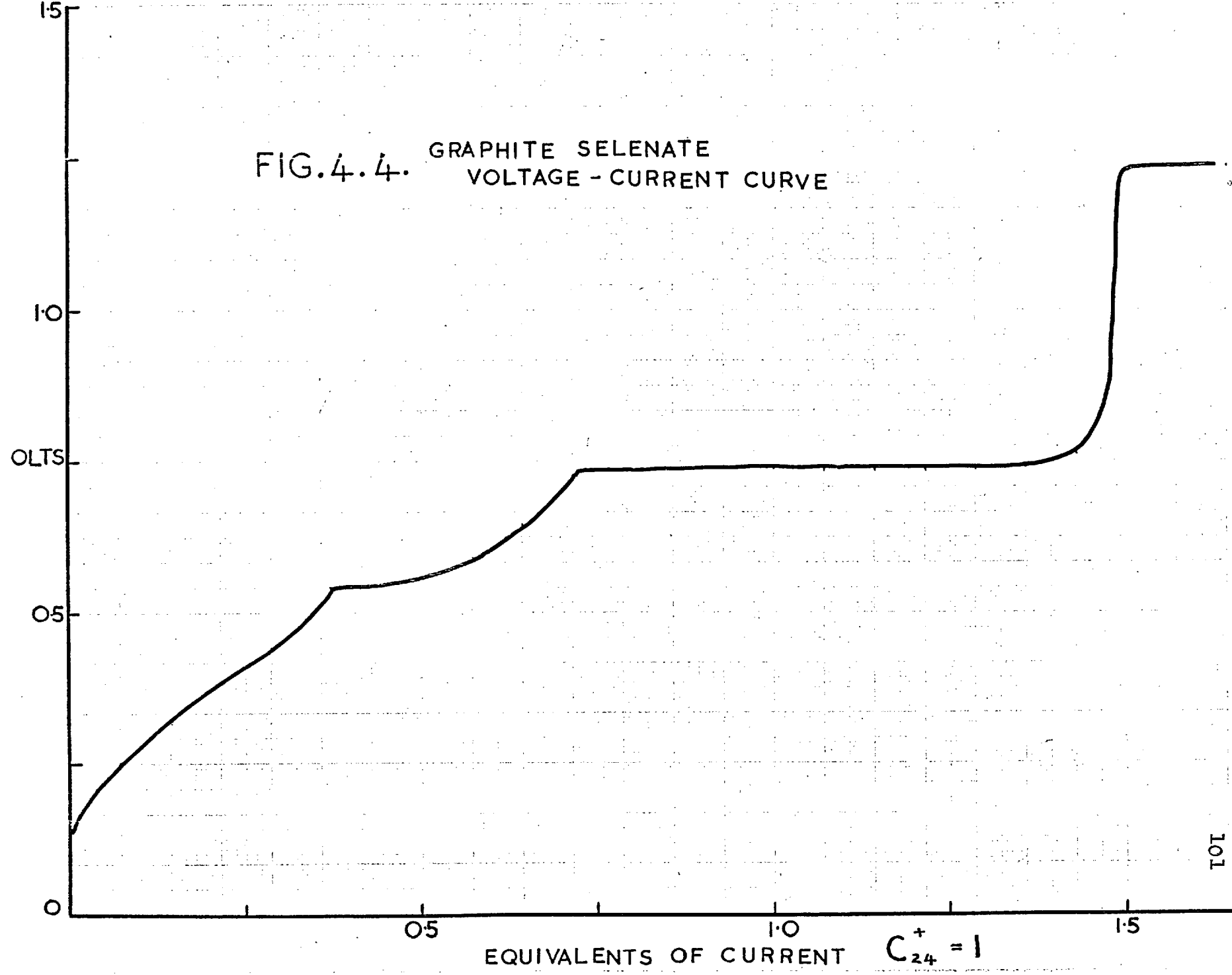


FIG.4.4. GRAPHITE SELENATE
VOLTAGE - CURRENT CURVE



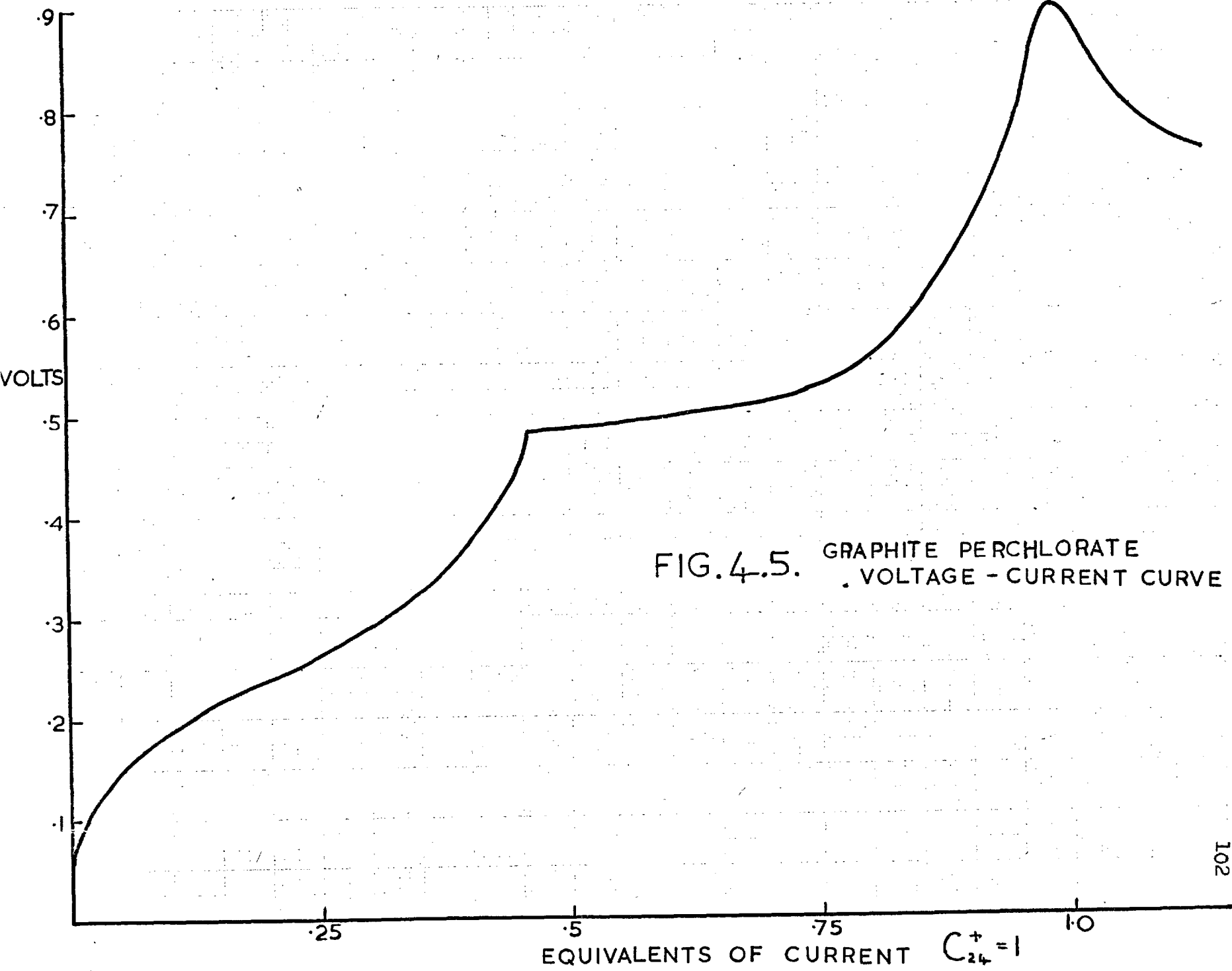


TABLE 4.1

Compound	Lattice Spacing		Reduced Lattice Spacing	
	Present work	Rüdorff 1939	Present work	Rüdorff 1939
Bisulphate 1	8.02	7.98	8.02	7.98
Bisulphate 2	11.33	11.33	7.98	7.98
Bisulphate 3	14.72	14.72	8.02	7.98 ‡
Nitrate 1	7.84	7.82	7.82	7.84
Nitrate 2	11.14	11.14	7.79	7.79
Nitrate 3	14.49	14.49	7.79	7.79
Perchlorate 1	7.73*	7.94	7.73	7.94
Perchlorate 2	11.06	11.12	7.71	7.75
Perchlorate 3	14.43	14.30	7.73	7.60
Graphite	3.354	-	-	-

All values are mean values in Å

‡ Rüdorff used a value of 3.37 Å to reduce this spacing.

* One value of 7.94 Å was obtained which is not included in this mean.

(Analar 98% W/W acid), but later experiments utilised 100% sulphuric acid (Griffin and George Ltd.) and this acid led to a slight increase in the overall efficiency of the reaction. A representative V_C versus Q curve for a current density of approximately 500 A/cm^2 is shown in Fig. 4.2. The plateaux were always observed at approximately the same voltages; a spread of about 0.1 V was found on the six runs followed in detail (Table 4.2). The table also shows the efficiency of each run; the efficiency being the theoretical value of Q expressed as a percentage of the experimental value of Q . The reference datum for the figures in table 4.2 was the point C where the formula is assumed to be $\text{C}_{24}^+ \text{HSO}_4^- 2\text{H}_2\text{SO}_4$. The samples of graphite being oxidised remained black until point B but then very rapidly became blue just at the point where the plateau starts.

TABLE 4.2

Sample	Voltages of Plateaux				Efficiency
	A	B	C	D	
1	.22	.51	1.11	1.65	83
2	.22	.49	1.22	1.82	87
3	.18	.45	1.00	"	88
4	.22	.46	1.03	1.59	83
5	.22	.49	1.03	"	83
6	.30	.51	"	"	96

X-ray diffraction photographs were taken at various stages of the electrolysis. The photographs taken at C and D were identical in all respects and confirmed the formation of the first sequence compound; a typical example is shown in Plate 4.1b. The photographs at B showed the diffraction pattern of second sequence bisulphate (cf Rüdorff and Hofmann, 1938). The compounds at A when examined on the diffractometer showed a pattern of 001 reflexions corresponding to a third sequence compound but no diffraction photographs were taken. The 001 reflexions for the higher oxidation states were also examined on the counter diffractometer (5.2.1) and typical traces for the 001 reflexions at points B, C are shown in Fig. 4.6a; a third trace is also shown intermediate between B and C.

4.2.2. Graphite Chlorosulphonate

Preparations were carried out using 100% chlorosulphonic acid (B.D.H. Assay 99.5% 95% chlorine). The efficiency of this preparation was rather low particularly at low values of V_A , but it was possible to produce consistent V_C versus Q curves. The final plateau is not approached suddenly as in the bisulphate, but instead the value of V_C gradually levels off at about 0.87 V (fig. 4.3). The lower oxidation states show up particularly well as plateaux and the existence of three compounds can be inferred. Although the efficiency of the preparation is low (~ 70%), the experimental value of Q is consistent with the

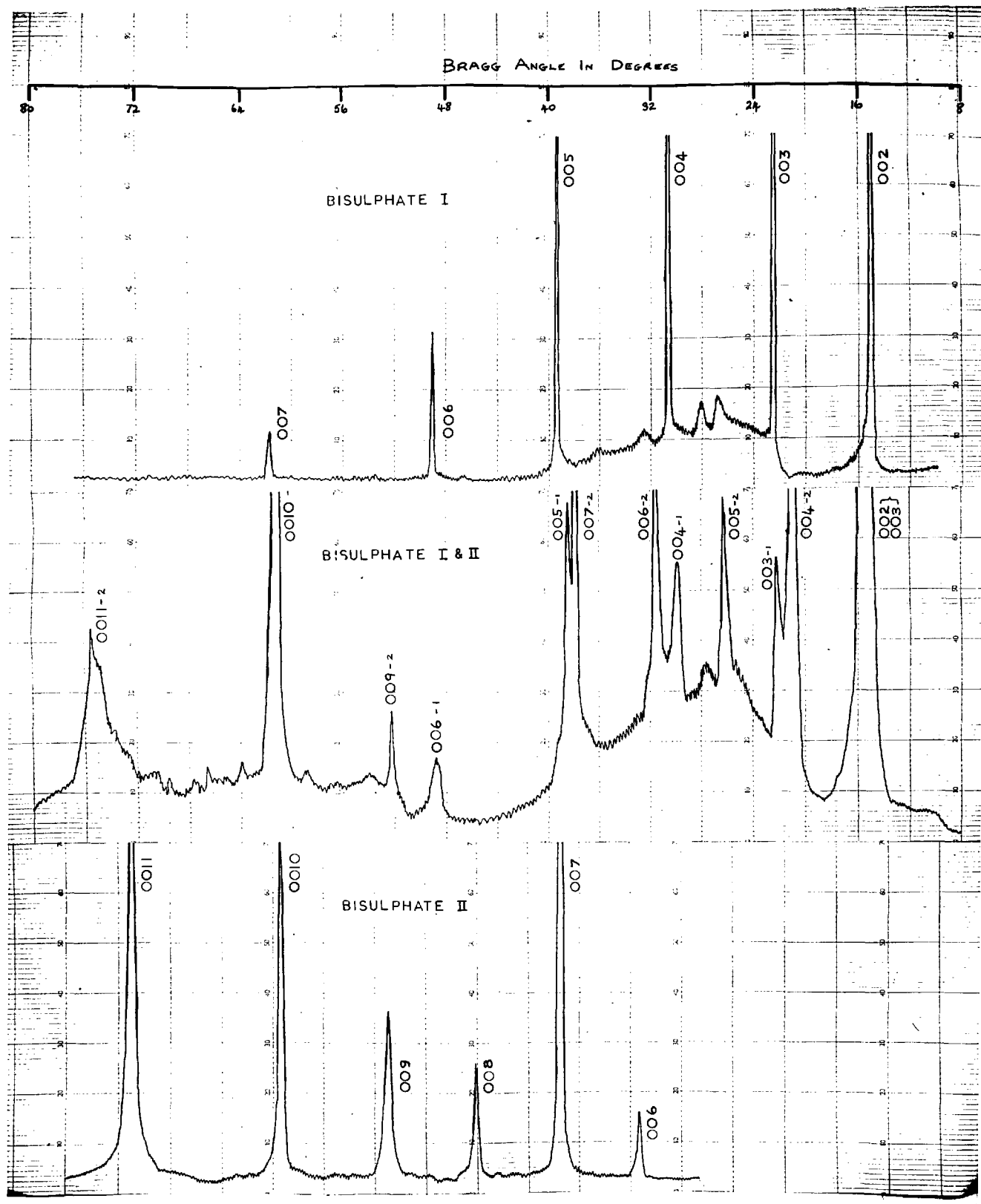


Figure 4.6a. Diffractometer traces of graphite bisulphate compounds, the scanning rate is 2 degrees per minute.

inefficient formation of C_{24}^+ and C_{48}^+ oxidation states. An x-ray diffraction photograph taken of the compound after full oxidation (Plate 4.1c) showed reasonable 001 reflexions. There is however considerably greater arcing of these reflexions suggesting a rather larger c-axis misorientation of the crystallites than in the bisulphate compound.

4.2.3 Graphite Selenate

Preparation of graphite selenate by electrochemical oxidation required careful selection of the electrolyte. At ordinary temperatures commercially available 100% selenic acid crystallised out in the cell; nucleation occurred at the sintered disc and rapidly spread throughout the cell. Raising the temperature kept the electrolyte molten but above 30°C no first sequence compound could be formed. The alternative to warming the acid was to dilute until the acid remained liquid. This lowered the efficiency of the process but a workable compromise was to add just sufficient distilled water to keep the electrolyte liquid at 25°C . The electrolysis was then carried out at this temperature with V_A equal to 1.5V to reduce side reactions. A typical V_C versus Q curve under these conditions (fig. 4.4) showed three plateaus and from this and other curves an efficiency of about 80% was estimated. The sharp rise at 1.5 equivalents of current was sometimes much more gradual; it is probably associated with an oxygen overvoltage.

With the selenate it is important to stop the electrolysis at the completion of the formation of the first sequence; any overcharging rapidly leads to exfoliation of the sample and evolution of oxygen from the surface. The sample turned blue after about 0.35 equivalents of current had passed which suggests the second sequence graphite selenate is blue as well as the first sequence compound.

4.2.4 Graphite Fluorosulphonate

Graphite fluorosulphonate was prepared using anhydrous fluorosulphonic acid (kindly provided by Imperial Smelting Corporation), as the electrolyte. A high value of V_A was used and from the V_C versus Q curve (not shown), only one compound appeared to be formed. No x-ray diffraction photographs could be obtained, principally because of difficulties in handling the samples which evolved hydrogen fluoride in large amounts unless they were kept absolutely dry.

4.2.5 Graphite Perchlorate

Anodic oxidation of graphite in 70% analar perchloric acid (the strongest acid available commercially) using both high and low values of V_A resulted in very similar V_C versus Q curves (fig. 4.5). The loss of efficiency due to side reactions was usually small and amounted to between 5 and 10%. The oxidation "end point" was marked by a maximum in V_C rather than the onset of a constant V_C . X-ray diffraction photographs

(Plate 4.1d) of samples which had roughly reached the top of the peak showed very well defined hkl reflexions and confirmed the compound formed to be first sequence. Interesting results were found in further x-ray studies of the perchlorate compound on the diffractometer. One sample, which had been electrolysed for the theoretical time required to give first sequence compound showed predominantly 001 reflexions for the first sequence compound but with a weak pattern of the second sequence superimposed. Farther electrolysis decreased the intensity of the second sequence lines relative to the main pattern. However on still further electrolysis, the first sequence pattern disappeared and was replaced by a mixed pattern of lines corresponding to the second and third sequence compounds. This result was confirmed on two other samples and in the low angle region lines were also observed in some cases with spacings appropriate to the fourth and fifth sequence compounds. From the 001 reflexions observed on the diffractometer the c-axis lattice parameter could be calculated. All except one sample of the first sequence perchlorate compounds showed a lattice spacing of $7.73 \pm 2^{\circ} \text{ \AA}$. The anomalous sample had a lattice spacing of $7.94^{\circ} \text{ \AA}$, which agrees with that of Rüdorff (this is discussed later).

The results on the perchloric acid compound suggested that the acid concentration was very near the lower limit of

stability for first sequence compound. Because of this, attempts were made to "strengthen" the acid by adding anhydrous magnesium perchlorate; however this did not overcome the rapid degradation which took place on overcharging.

4.2.6 Graphite Nitrate

The oxidising nature of nitric acid results in considerable reaction taking place between the acid and graphite before any current is passed (Rüdorff and Hofmann, 1938). In fact second sequence graphite nitrate was easily prepared by immersing pieces of pyrolytic graphite in fuming nitric acid. The first sequence compound was reported as forming in a 50/50 mixture by weight of fuming nitric acid and nitrogen pentoxide and samples for the thermal expansion measurements described later (5.3.4) were prepared in this way. The nitrogen pentoxide was distilled from a mixture of fuming nitric acid and phosphorous pentoxide.

Experiments on the electrochemical preparation of nitrate compounds are limited by the spontaneous formation of second sequence compound in fuming nitric acid. However, if a current was passed through the cell after the samples had reacted to this stage then ^ablue compound was formed. X-ray diffraction photographs (Plate 4.1e) showed this to be first sequence compound. The blue colour disappeared on standing in fuming nitric acid but could be regenerated by passing further current. The plots of V_C against Q did show a plateau presumably associated

with first sequence compound, but the efficiency of the electrochemical preparation was poor possibly because of the continuous decomposition of the first sequence nitrate. The preparation of nitrate compounds by washing graphite bisulphate with excess fuming nitric acid was investigated and it was found that first sequence bisulphate gave second sequence nitrate. The x-ray diffraction pattern of second sequence nitrate compound prepared by this method is shown in Plate 4.1f, for comparison with that of graphite nitrate prepared directly (Plate 4.1g).

Little is known about the structure of the intercalate layer in graphite nitrates but the formation of the nitrate from the bisulphate suggests a similar structure. With a view to estimating the number of carbon atoms associated with each nitric acid or nitrate species in the unit cell, experiments were carried out to measure the density of the second sequence graphite nitrate. Weighed samples of graphite were placed on a glass stirrup attached to a quartz spiral spring and the sample and stirrup immersed in fuming nitric acid (fig. 4.6). When the sample had reached a constant weight it was dislodged from the stirrup and the change in length of the spring recorded (Δl). From the weight of the graphite in air W_G and the known density of graphite ρ_G the volume of the graphite (V) could be calculated $V = \frac{W_G}{\rho_G}$. A theoretical increase in spacing in the second sequence compound from $6.7 \text{ \AA}$ to $11.14 \text{ \AA}$

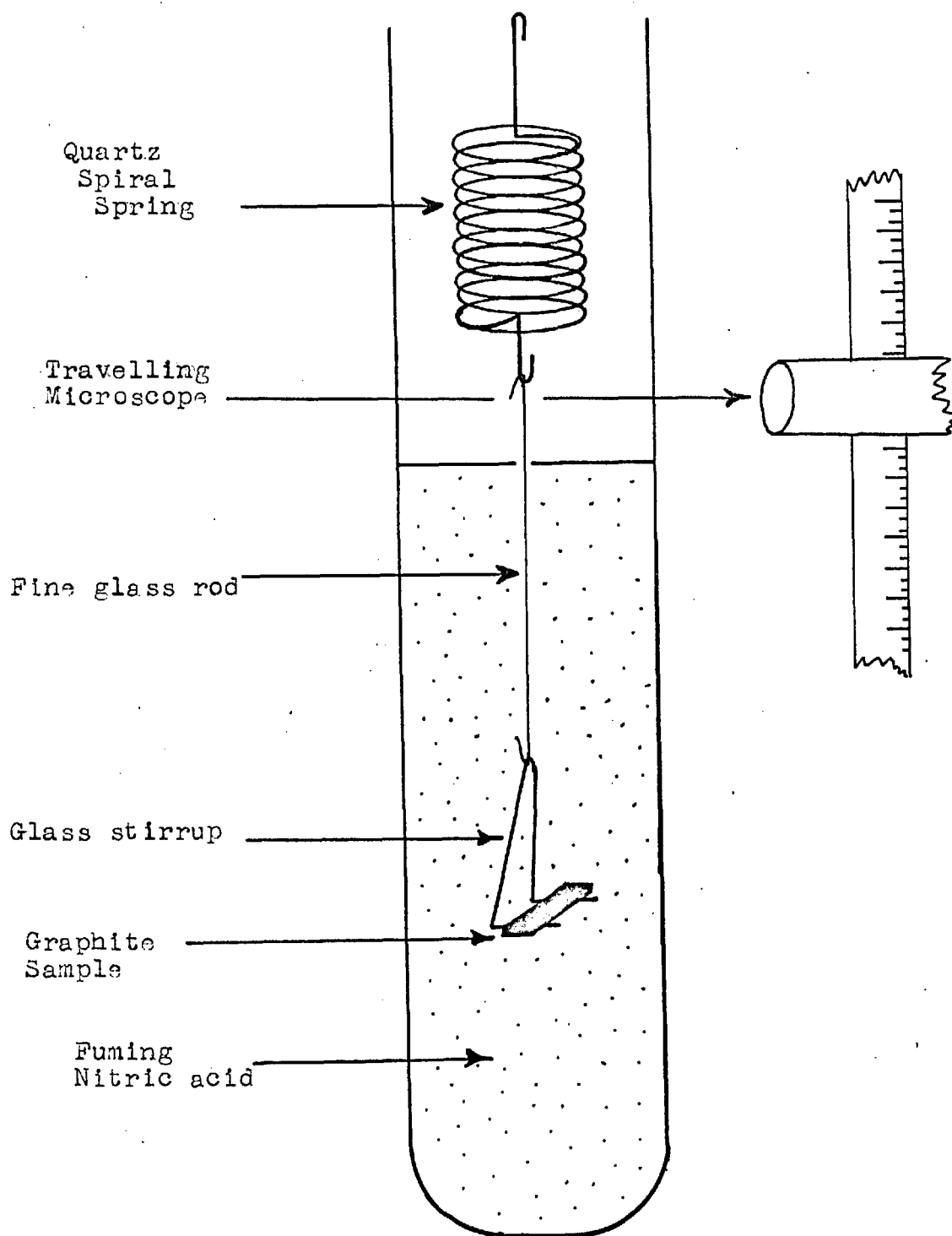


FIG.4.6. APPARATUS USED TO MEASURE THE DENSITY OF SECOND SEQUENCE GRAPHITE NITRATE COMPOUNDS

was assumed and thus the volume of the nitrate compound was given by $\frac{11.14}{6.7}$ V. The volume of the graphite nitrate was thus known, and from the change in length of the spring (Δl) which had an extension of x cm/g, the weight in nitric acid was given by $\frac{\Delta l}{x}$ g. Thus the relative density of the graphite nitrate $\rho_R = \frac{\Delta l}{x} \cdot \frac{\rho_G}{W_G} = \frac{3.35}{7.79}$. The actual density of the compound was obtained by adding the density of the nitric acid, previously measured in a specific gravity bottle. The densities of the four samples measured in this way were: 2.00, 1.97, 1.96, 1.99 g cm⁻³. The significance of this density is discussed later.

4.2.7 Compounds formed between graphite and other acids

Some further acids were investigated and the results are briefly summarised below.

- (a) Boron trifluoride diacetic acid - A 40% solution of BF_3 in acetic acid was used as the electrolyte. A blue compound formed and from the current equivalent required for the oxidation to this stage, the compound formula was approximately $\text{C}_{32}^+ x$. No x-ray diffraction study was attempted because of the hydrogen fluoride which is evolved unless the sample is kept absolutely dry.
- (b) Trifluoro-acetic acid - With this acid as the electrolyte the resistance of the cell was too high (~ 1 megohm) and

a negligible current passed through the cell (V_A was increased to 50-60 V with very little effect).

- (c) Chlorinated acetic acids - Preparation of compounds using trichloro- and dichloro-acetic acids as electrolytes was not successful. There was no evidence of swelling of the sample and the diffraction photographs of the product were identical to that of graphite. It was inferred that no reaction had occurred.
- (d) Phosphoric, arsenic and periodic acids - Phosphoric acid, as syrupy phosphoric acid, arsenic acid as 40% aqueous solution and periodic acid as a saturated aqueous solution were all used as electrolytes. In all cases there was evidence of compound formation from the swelling of the sample. Although the diffraction pattern of all three showed that the graphite pattern had been destroyed, no clearly defined 001 or hkl reflexions were observed.

None of the above acids, except for the boron complex, gave blue compounds. Those compounds which were formed are possibly lower sequence compounds; the results obtained by Rüdorff on the formation of similar compounds by chemical methods suggest that first sequence compounds cannot be formed with these acids.

4.3 Side Reactions in the Preparation of Acid Compounds

In order to investigate the loss of efficiency due to side reactions, the conductivity of the bulk acids used in the preparations was measured approximately. The products formed at high current densities using both platinum and graphite anodes were also examined. The passage of current between two platinum electrodes was first studied. The voltage V_A across the cell was varied and the current flowing was plotted against V_A (Fig. 4.7). It is apparent that when V_A is low (1.5 V) for all acids very little current flows except for chlorosulphonic acid where a current of approximately $150 \mu a$ was recorded. As V_A increases the current increases rapidly and a considerable loss of integrated current would be expected for V_A equal to 12 volts. This will be especially important towards the end of the preparation when the apparent resistance of the cell rises and produces a voltage of some 8-10 volts across the electrodes. At low currents, e.g. 1 m.a., insufficient biproducts are formed to be easily detectable, so experiments were carried out using graphite anodes and a current of $\frac{1}{2}$ -1 amp. The initial reaction in all cases was the formation of first sequence compound but subsequently biproducts appeared at the anode (Table 4.3). Thus prolonging the passage of current once the first sequence compound has formed produces a violent oxidation reaction. The general products at the anode are consistent with this. The

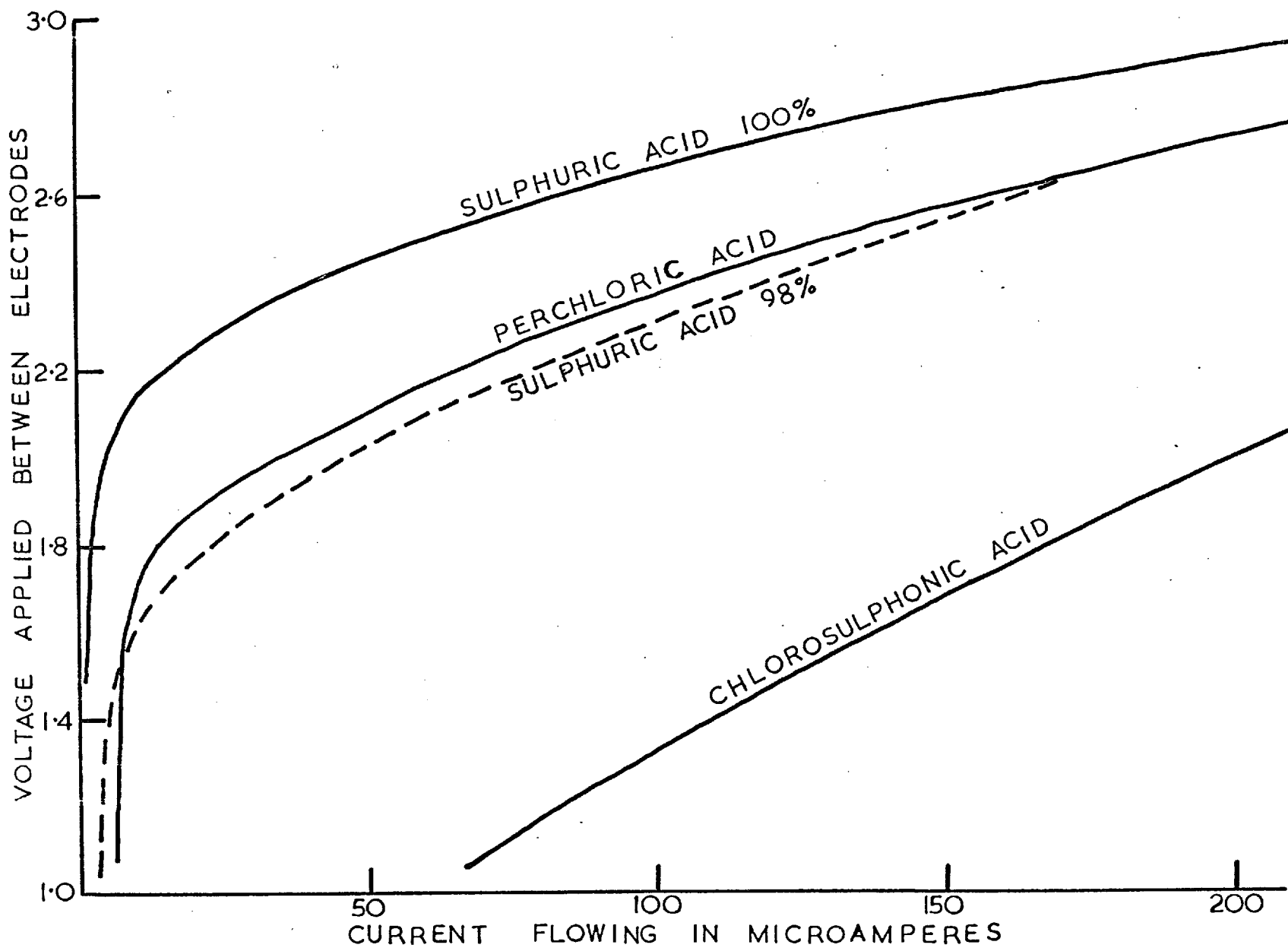
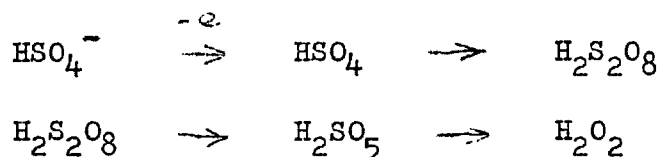


FIG. 4.7.

TABIE 4.3: **Bi-products formed at the anode when high currents were passed through a graphite sample**

Acid	Bi-product at Anode	Effect on Sample
Sulphuric	Oxygen	Gradually exfoliated
Chlorosulphonic	Yellowish colour (smell similar to thionyl chloride)	Gradually exfoliated
Nitric	Oxygen	Amorphous brown deposit formed first on edges then on surface of the sample
Perchloric	Oxygen ? and chlorine oxides	Rapidly exfoliated
Selenic	Oxygen	Rapidly exfoliated

reaction with sulphuric and selenic acid is probably first to give oxy-acids which decompose to give hydrogen peroxide, ozone and oxygen:



It is likely that the final product of the oxidation of graphite in nitric acid is graphitic oxide and the amorphous brown powder covering the graphite surface is very similar to the reported appearance of the oxide (see Ubbelohde and Lewis, 1960). With chlorosulphonic acid, the product formed at the anode was not analysed but was probably a sulphur-chlorine compound.

4.4. Discussion

The voltage V_C versus Q plots show that the formation of graphite compounds takes place in stages. Detailed study in the case of the bisulphate showed that at point B in Fig. 4.2, the x-ray diffraction evidence indicated the existence of a single phase: graphite bisulphate second sequence. Thus the formation of first sequence bisulphate from graphite passes through the intermediate second sequence compound. The sample however changes to blue at point B, and it has been shown that only the first sequence compound is blue (Rüdorff and Hofmann, 1938). Thus at B the first formation of first sequence compound takes place on the surface of the sample and this

does not occur until the graphite has almost all been converted to second sequence compound. This evidence and the further evidence provided by the coexistence of the first and second sequence diffraction patterns between B and C confirms the presence of two separate phases in this region. Thus the formation of graphite compounds does not take place gradually by a progressive change of intercalation sequence from second sequence to first sequence. Instead, it appears that regions of the sample are completely converted to first sequence compound while other regions remain as second sequence compound. Because of this step wise formation the preparation of lower sequence compounds is easily accomplished by stopping the electrolysis when the theoretical quantity of current has passed or when the required plateau has been reached. The high value of Q found experimentally as compared with the theoretical value is explicable in terms of the small flow of current between the platinum supports. If this small current is integrated over the time of preparation and subtracted from the experimental value of Q , then the agreement between the corrected value and the theoretical value is good. For the bisulphate which has been considered in greater detail the agreement is within 5%. This agreement with the theoretical value is very good and similar agreement is possible with the other salts but the larger the conductivity of the acid the greater the error involved.

The agreement between the experimental measured lattice parameters and those reported by Rüdorff is good in all the graphite salts. The spacing of the lower sequence compounds is also ⁱⁿvery good agreement with the value expected by adding the first sequence compound spacing to the relevant number of graphite spacings.

4.4.1 Graphite Bisulphate

The results showed that the preparation of graphite bisulphate using 100% sulphuric acid as electrolyte was highly successful. The general shape of the V_C versus Q curve was normal except for the rise in V_C to the plateau D. The diffraction pattern at this point was similar to C and it is likely that this rise was due to an oxygen overvoltage effect. This was consistent with the experimental fact that it occurred independently of the quantity of excess current that passed.

The diffraction photographs of the first sequence bisulphate (Plate 4.1b) showed a superlattice pseudo layer line corresponding to a spacing in the a-axis larger than that present in graphite. Similar reflexions were observed by Rüdorff in graphite bisulphate prepared from single crystals and indicate ordering of the intercalated sulphuric acid layers with respect to one another. The second sequence compound (photograph not reproduced) did not show any such ordering. The presence of ordering between the intercalate layers has

only been observed in a few first sequence compounds (potassium, rubidium and caesium graphites), and never in any second sequence compounds. It seems probable that the forces which cause this ordering are weak and cannot operate over an empty carbon layer phase. The x-ray diffraction evidence for the first sequence compound is consistent with the structure proposed by Rüdorff (1939).

4.4.2 Graphite Chlorosulphonate

The formation of this compound is clearly possible by electrochemical oxidation. The low efficiency of the preparation is associated with the high conductivity of the acid (Fig. 4.7) which allows a comparatively large current to flow for a small applied voltage V_A . More successful preparations are possible using a higher value of V_A , the losses being smaller due to the short time of preparation. There appear to be three well defined compounds and the first sequence compound corresponds to an oxidation state C_{24}^+ so that its formula is tentatively $C_{24}SO_3Cl \cdot n(HSO_3Cl)$. The 001 reflexions of the x-ray diffraction photograph give a lattice spacing of approximately $8 \overset{o}{\text{\AA}}$ consistent with a first sequence compound, but it was not possible to measure the lattice spacing accurately as no samples were studied on the diffractometer.

4.4.3 Graphite Selenate

Although the preparation of graphite selenate by

electrochemical oxidation is possible, it is not always easy to determine the "end point" of the reaction; in the V_C versus Q plot there is not always a sharp rise on to a plateau, as for the bisulphate, nor is there a clear peak, as for the perchlorate. This may be because the small difference between the formation potential of the first sequence compound and the overpotential is not sufficient to produce a well defined break. This view was supported by some samples which showed only a slight inflexion at the expected voltage of the first sequence plateau. The breakdown of the selenate compound on overcharging may be due to the formation of per-acid radicals, i.e. $\text{SeO}_3(\text{OOH}^\bullet)$ which are unstable and decompose to give oxygen which causes exfoliation of the sample.

The failure to form the first sequence compound on raising the temperature of the electrolyte suggests that this compound is unstable above about 30°C and is in agreement with the behaviour of graphite bisulphate where no formation of first sequence compound has been observed above $30-35^\circ\text{C}$.

The x-ray diffraction photographs of the selenate compound showed very few reflexions; only the lower order 001 reflexions were observed and no hkl reflexions were apparent. This may partly be due to the heavy background scatter caused by fluorescence of the selenium atoms, but the calculated intensities of the 001 reflexions are much weaker than the bisulphate (Table 4.4)

TABLE 4.4

	Bisulphate observed	001 intensities calculated	Biselenate observed	001 intensities calculated
001	-	3170	weak	2420
002	very very strong	46500	strong	21700
003	very strong	6330	medium	616
004	strong	1570	medium	1350
005	strong	665	weak	32
006	medium	1110	medium	862
007	very weak	71	-	0.1

Because of the general weakness of the reflexions and the absence of any high angle reflexions, no x-ray diffractometer measurements of the lattice spacing or of the thermal expansion were possible. The preparation of graphite selenate by washing the bisulphate has been suggested previously (Rüdorff and Hofmann, 1938) but it is difficult to decide when all the sulphate has been replaced by selenate. The detection of small amounts of sulphate in concentrated selenic acid is a difficult analytical problem. The best route available for the preparation of graphite selenate would appear to be the treatment of the graphite chromic acid compound with excess selenic acid (Hennig, 1962), but there is always the possibility with replacement methods

that some of the original intercalate will be retained in a similar manner to "residue compounds".

4.4.4 Graphite Fluorosulphonate

There is evidence of a compound formed between graphite and fluorosulphonic acid but more detailed study of the system is necessary. The compound was not used for thermal expansion measurements because of the difficult handling problems.

4.4.5 Graphite Perchlorate

The preparation of graphite perchlorate is simplified by the clearly defined "end point" marked by a peak in the V_C versus Q curve. It is however very important to stop the current at this point. The breakdown of first sequence compound on further electrolysis is almost certainly a result of the decomposition of the intercalated perchloric acid. By analogy with the bisulphate compound where the first sequence compound can only be formed in acid stronger than 80% W/W, it is reasonable to suppose that perchloric acid (70% W/W) is close to the critical concentration necessary for the stability of the first sequence perchlorate. Thus any decomposition of the acid between the layers to give oxygen and water as biproducts would rapidly dilute the remaining acid and result in catastrophic degradation of the sample to lower sequence compounds. To test this hypothesis it would be desirable to increase the concentration of the perchloric acid but for safety reasons the

introduction of carbon compounds into acid stronger than 70% was not practicable.

The c-axis lattice spacings observed for the perchlorate compounds are in general agreement with those of Rüdorff (Table 4.1) except for the first sequence compound. It is completely outside experimental error limits for the two values 7.73 (present) and $7.94 \text{ \AA}^{\circ}$ (Rüdorff) to represent the same parameter. The perchlorate compounds prepared by Rüdorff are unusual in that the lattice spacing of the second sequence compound is not given by the usual rule of addition of the lattice spacing of the first sequence compound and that of graphite; the third sequence compound also differs. The agreement of the present values is better but not as good as most of the other graphite compounds (the additivity of lattice spacings is discussed further in Chapter 6).

Perchlorate compounds can also be prepared by washing the sulphuric acid compounds with excess perchloric acid but this method is only suitable for the lower sequence compounds as more concentrated perchloric acid than that available would be desirable for the preparation of first sequence compound by this method.

4.4.6 Graphite Nitrate

The first sequence graphite nitrate compound can be prepared by electrochemical oxidation of graphite in fuming nitric

acid but the compound does not appear to be stable in this acid. The diffraction photograph of the first sequence graphite nitrate is in agreement with the structure proposed by Rüdorff and shows the existence of good order between the graphite layers. No ordering between the intercalate layers can be detected. The diffraction photograph of the second sequence compound is not in agreement with the proposed structure. The first set of reflexions associated with the graphite layers, i.e. the 10l reflexions, do not agree with the unit cell proposed by Rüdorff. A larger unit cell is necessary to explain the extra reflexions observed.

The diffuse streak (Plate 4.1g) inside the reflexions associated with the graphite layer indicates that the intercalate layer contains at least local ordering in each layer. However the lack of intensity modulation in this streak suggests that there is no detectable ordering between the intercalate layers.

The first sequence nitrate does not result when the bisulphate first sequence is washed with excess fuming nitric acid; only the second sequence is formed; this again confirms the instability of the first sequence nitrate. The samples of second sequence nitrate prepared in this way show a greater arcing of the 00l reflexions and this indicates a greater misalignment of the crystallites in the c-axis direction. This may be due to the severe strain which is imposed on the sample

but it is difficult to see why this should be greater than that involved in the process of expanding the layers by direct immersion in nitric acid.

There has been no reported evidence in the case of the nitrate compounds as to the number of carbon atoms associated with each nitrate species. The formation of a second sequence nitrate compound direct from first sequence bisulphate suggests a rather similar oxidation state; possible formulae would be $C_{48}NO_3^- \cdot xHNO_3$ or $C_{48}^{2-}NO_3^- \cdot yHNO_3$. The theoretical densities for the series $C_{48}NO_3^- \cdot xHNO_3$ are listed in Table 4.5, for $x = 0$ to 3.

TABLE 4.5

x	<i>P</i>
0	1.510
1	1.659
2	1.808
3	1.957

The comparison of the experimental density of 1.97 g cm^{-3} with these figures confirms that free acid must also be present in the nitrate compounds. Tentatively a formula $C_{48}NO_3 \cdot 3HNO_3$ is suggested for the second sequence compound, but there is a

possibility that it may be $C_{48}2NO_3^2HNO_3$. Unfortunately, analysis of these compounds to the accuracy required to distinguish between these two formulae is not possible at present. Careful analysis should make possible the confirmation of the ratio 'Carbon' to 'nitrate' but the amount present as ions and free nitric acid molecules will not be easy to determine.

Summary

The electrochemical method for preparing the acid salts is successful in forming well ordered compounds from pyrolytic graphite. It has the advantage of very accurate control of the extent of oxidation and in addition it does not require the addition of any oxidising agent which may contaminate the compound being prepared. Control of the oxidation state of the samples can be arranged conveniently by comparison of the potential of sample with a reference electrode. It is however possible that the more direct method of calculating the theoretical current required from the weight of sample may have a wider application. In the present work the use of stout electrodes which also serve as sample supports resulted in a loss of efficiency and this has limited the application of the direct method. If however the electrical connection were made very fine (40-50 gauge platinum wire) and an independent non - conducting support were provided then very good agreement with theoretical calculations could be expected. The electrochemical

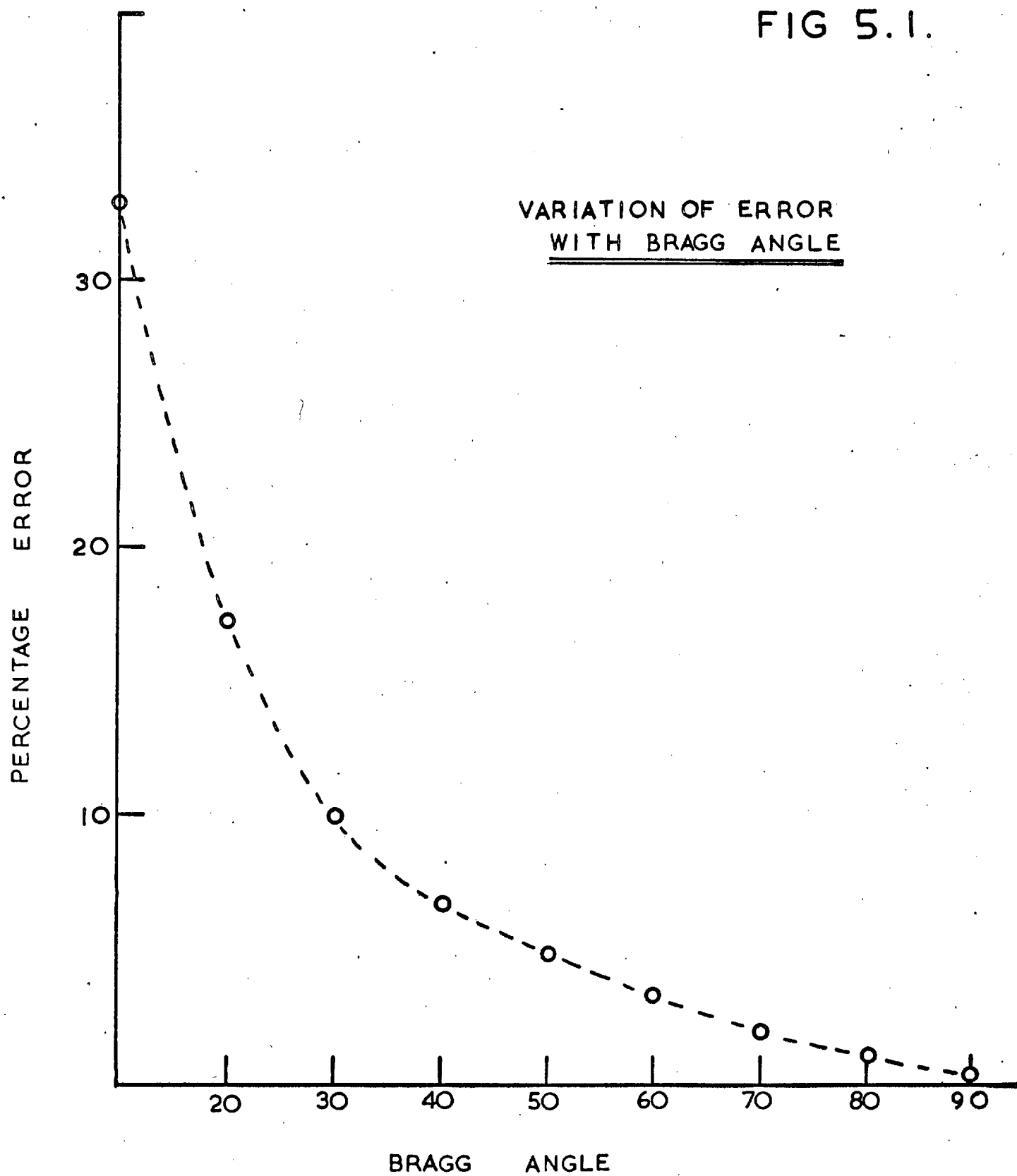
method is particularly suited to the preparation of the lower sequence compounds where the very careful control necessary for the chemical preparation can be eliminated; here of course the side effects can be lessened by using a lower driving voltage V_A .

CHAPTER 5: The Thermal Expansion of Graphite and its Compounds

5.1

The availability of pyrolytic graphite in the form of flat specimens makes it highly convenient for measurement of the c-axis thermal expansion. The geometry of the sample is particularly suitable for the measurement of x-ray diffraction line shifts using a diffractometer. Although, as noted in the introduction, the systematic errors of this method do not lend themselves to extrapolation techniques, this does not seriously limit the accuracy of the thermal expansion results. For thermal expansion it is not necessary to have a very accurate value of the lattice parameter as can be ^{seen by} substituting the Bragg equation $n\lambda = 2d \sin \theta$ into the expansion coefficient equation $\alpha = \frac{1}{d} \frac{d(d)}{dt}$. This gives $\alpha = \sin \theta \frac{d \operatorname{cosec} \theta}{dt}$. It is relatively easy to measure $\sin \theta$ to 1% i.e. an accuracy of 1° of arc. The real problem lies in the term $\frac{d \operatorname{cosec} \theta}{dt}$ which is very small even at high angles. If a probable error of $1'$ is assumed on the change in Bragg angle $\Delta \theta$, then for a typical thermal expansion coefficient for these compounds of $50 \times 10^{-6}/^\circ\text{C}$ it is possible to calculate a probable percentage error for a chosen temperature interval. The probable percentage error for a 100 Centigrade degree interval is plotted against Bragg angle in Fig. 5.1. Thus

FIG 5.1.



even with a small error in $\Delta \theta$ (1 min of arc) there is only a restricted range of angle where the probable error is 2% or less. The scale of the diffractometer cannot be read to better than 1' of arc, producing a probable ^{error} of $\sqrt{2}$ ' on $\Delta \theta$. Thus the limitation of the instrument will produce an error of the order of 1% on the thermal expansion even at the maximum working angle of 80° in θ .

With the above error in mind it was possible to compromise on the accuracy with which the temperature of the sample was measured. Thus $\pm \frac{1}{4}^\circ\text{C}$ over 100°C will give an error of $\frac{1}{4}\%$ which can be neglected when compared with the error on $\frac{d \cos \theta}{dt}$.

It is apparent that accurate results can be expected only from measurements at high Bragg angles. It is important therefore always to utilize the highest angle peak that can be made available. The room temperature lattice parameter is necessarily fixed thus any optimisation of the peak position must be made by varying the value of λ . Thus a radiation is selected which will move the peak under observation to a suitable high angle. The variation of Bragg angle with commonly available radiations is shown in Fig. 5.2.

Because small errors in the absolute Bragg angle of the diffraction peak, caused by inaccuracies of sample mounting and errors in the scale zero of the diffractometer,

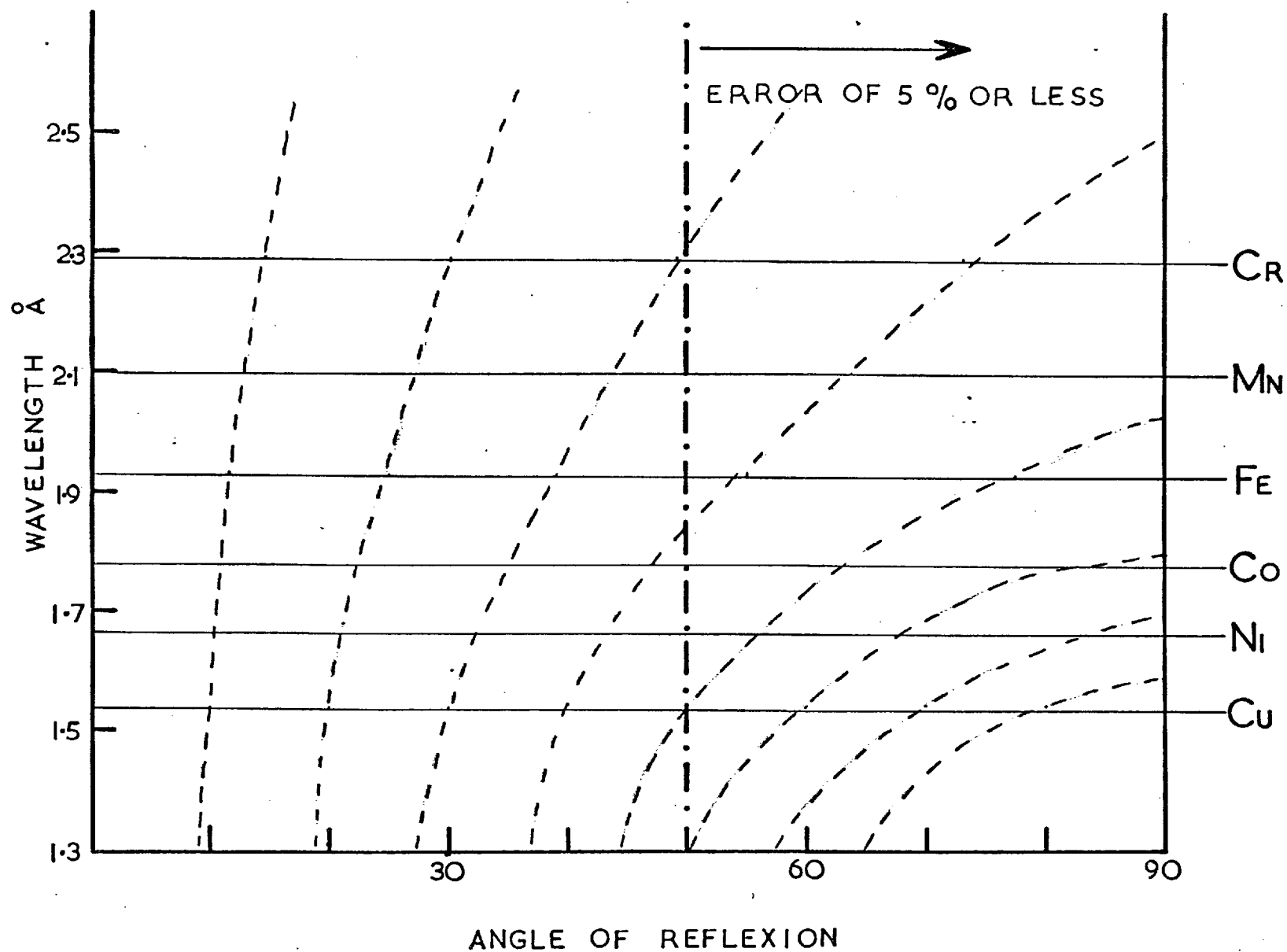


FIG 5.2.

are essentially self compensating; they will be of less importance than for the precision determination of lattice parameters.

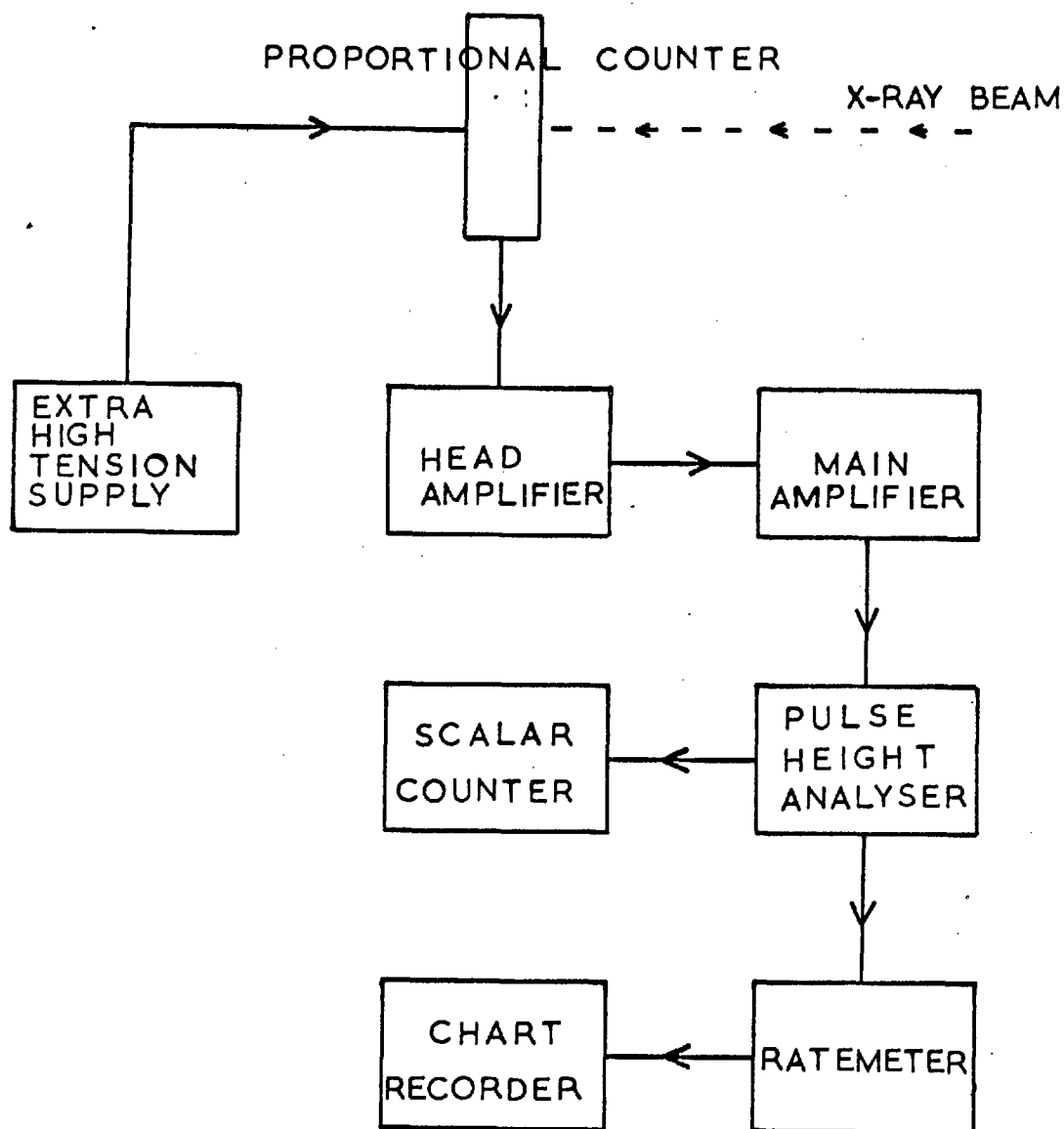
Thus scale zero error which is important in precision lattice parameter determination is negligible in thermal expansion calculations as it has no contribution to $\Delta\theta$ and only occurs in the $\sin\theta$ term. It has already been shown that the error on $\Delta\theta$ is at least 1%, thus errors in $\sin\theta$ can be neglected. A detailed discussion of the errors influencing the $\sin\theta$ term is available (see Parrish and Wilson, 1959), but these can be neglected in thermal expansion determinations of this accuracy (approx. 5% as shown later).

5.2 Experimental

5.2.1. The Diffractometer and Associated Equipment

The x-ray generator used has been described previously (McKoe, 1954). A stabilised high voltage generator (Max. power 300 Watts, Max. current 15 m.a. Max. Voltage 30 KV) supplies a Philips x-ray tube (Type 2529/-) mounted in a horizontal position. The diffracted x-ray beam was detected by a Xenon (Methane) filled proportional counter (PX 28 F/Xe 20th Century Electronics Ltd.) whose output was amplified and fed to a conventional pulse height analyser, ratemeter, scalar counter and chart recorder (Fig. 5.3). The Berthold diffractometer

BLOCK DIAGRAM OF X-RAY DETECTION CIRCUIT



(Solus-Schall, London) had a θ scale whose vernier could be read to 1' of θ . It was modified by removing the central sample mount assembly and attaching a cooling block to the worm wheel of the diffractometer (Plate 5.1).

5.2.2. The Cooling System for the Sample Holders

Due to the large size of the samples used for thermal expansion and the need for complete encapsulation, a cooling system using a circulating liquid was preferred. The more conventional gas cooling techniques would not hold the temperature of such large masses constant to a satisfactory extent.

The cells containing the samples (see 5.2.3.) were held in a split brass block (Fig. 5.4.ii). This block had 1/16" channels cut longitudinally, through which cooled petroleum ether was forced using a Plessey rotary vane pump (Type FP3). This is designed for pumping petrol and operates at pressures up to 60p.s.i. It replaced an earlier centrifugal water pump which developed only 10p.s.i. This was not capable of producing a large enough flow of coolant through the narrow channels. The petroleum ether was cooled by using a standard low temperature tank (Townson and Mercer -70° Bath). This had two separate compartments linked by a heat exchanger (Fig. 5.4.iii). Compartment "B" was filled with "Cardice" - petroleum ether mixture at -78°C, while the second compartment



Plate General view of thermal expansion assembly and
5.1a diffractometer mounted on x-ray tube.

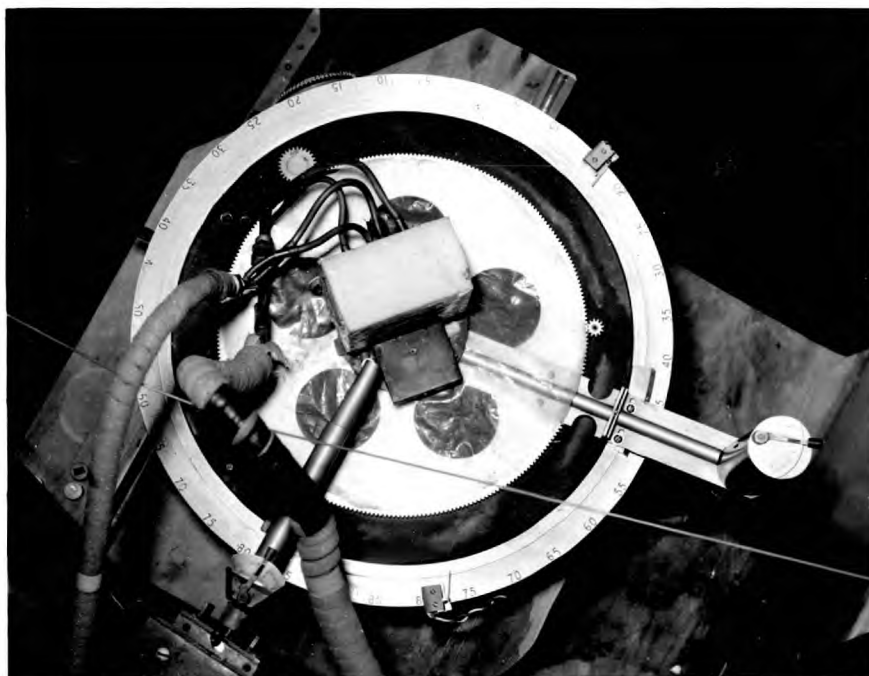


Plate Plan view of diffractometer showing collimator
5.1b and counter tube geometry.



Plate Cooling block on diffractometer. The polystyrene
5.1c insulation has been removed.

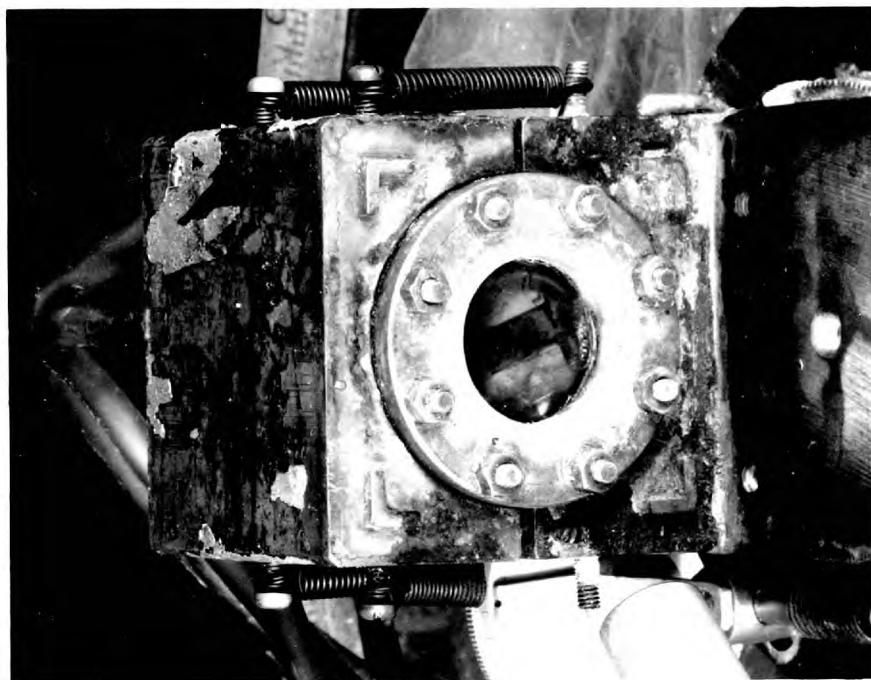


Plate Close-up of cooling block showing thermal expansion
5.1d cell completely enclosed by the block.

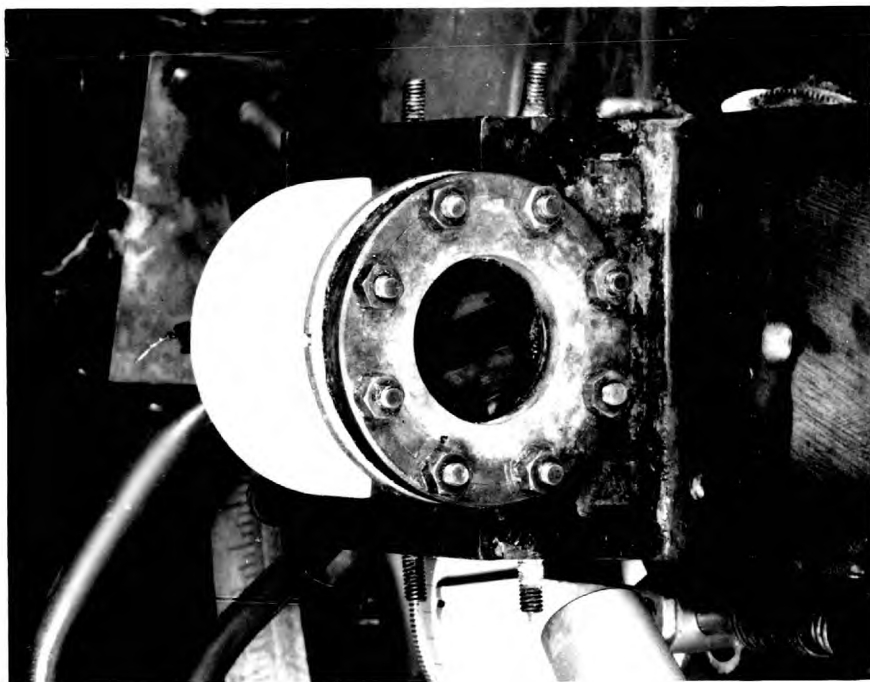


Plate 5.1e Upper section of cooling block removed to show seating of the cell in the block.

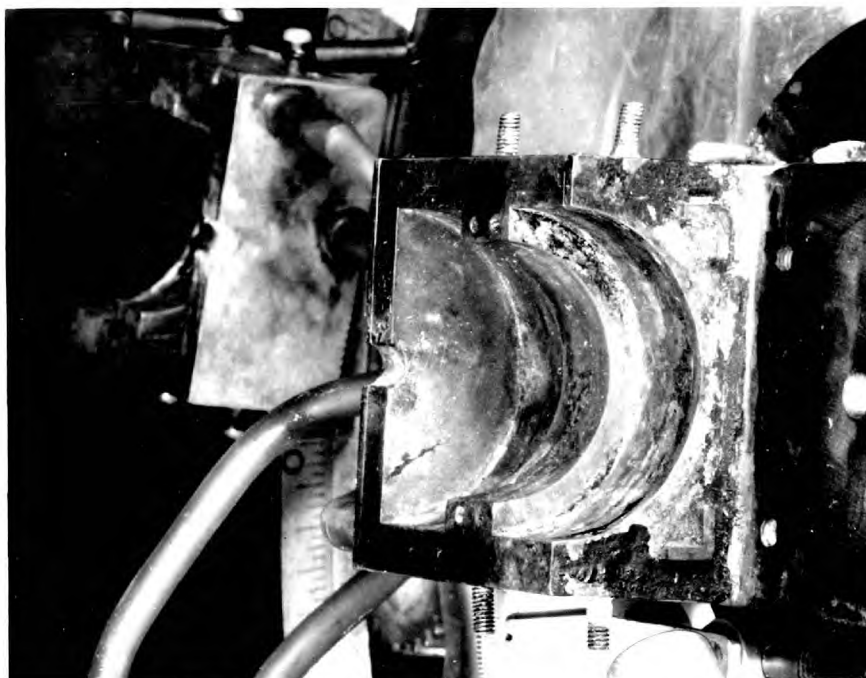
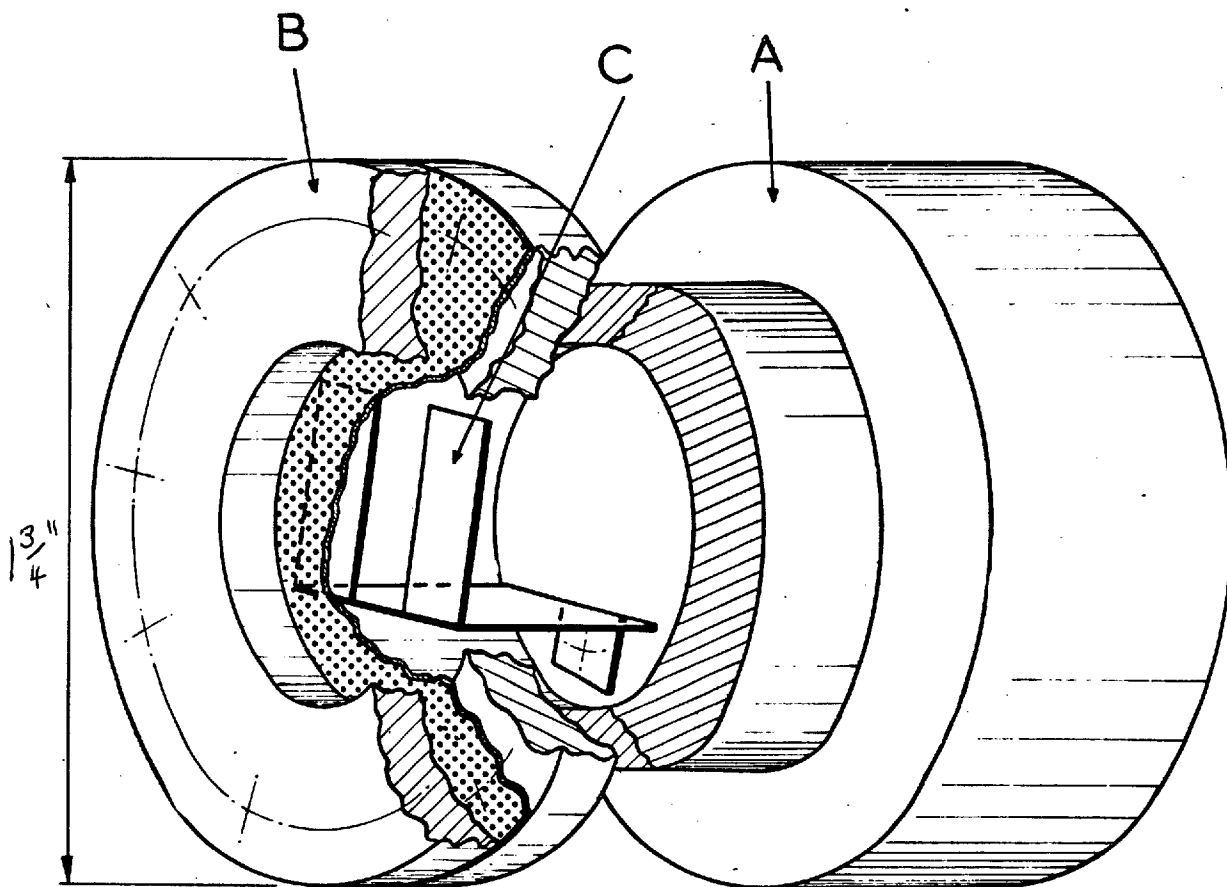
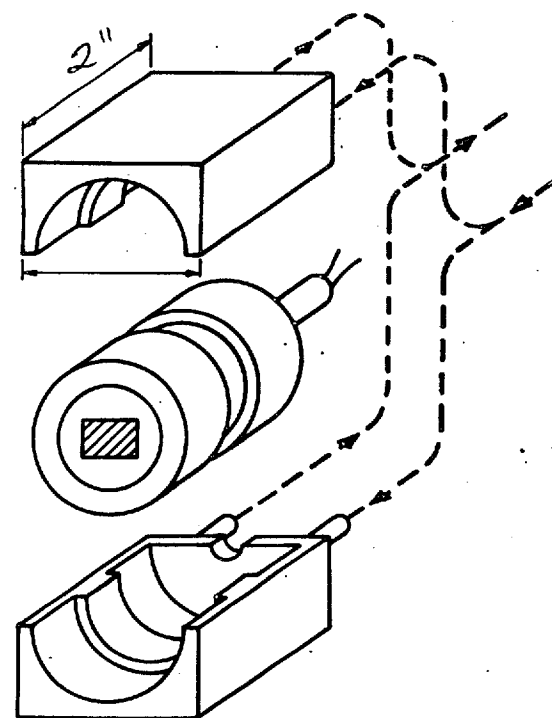


Plate 5.1f Cell removed from the cooling block showing small hemispheric gap to allow a thermistor to pass through the cooling block.



(i)

DIAGRAM OF CELL AND COOLING
FIG. 5. 4.



(ii)

BLOCK

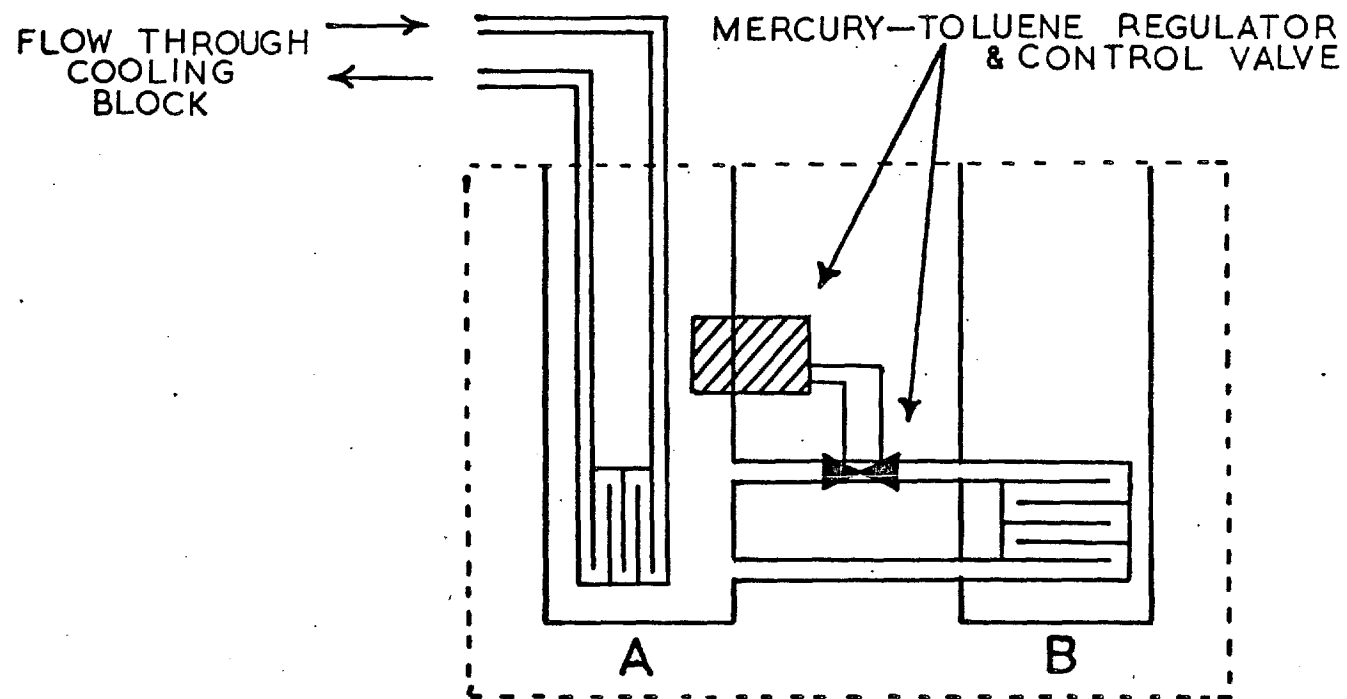


FIG. 5.4. (iii) DIAGRAM OF COOLANT TANK.

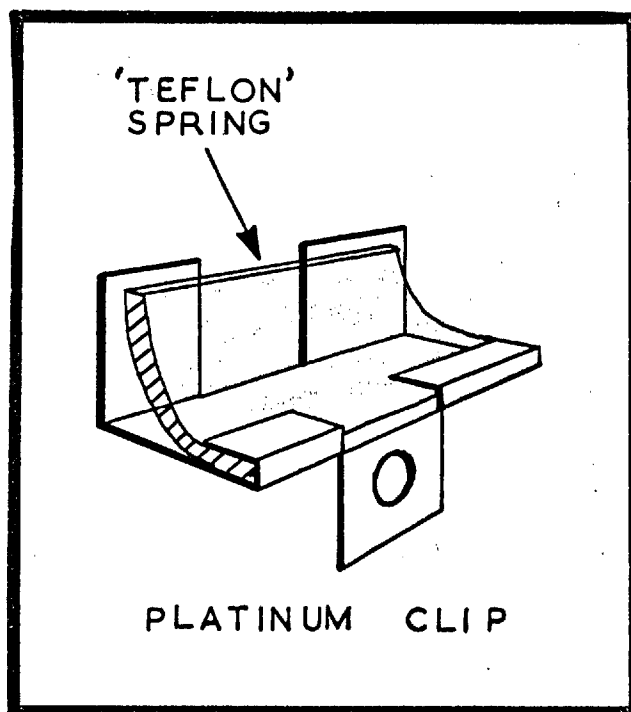
"A" filled with petroleum ether, was thermostatically controlled by a mercury-toluene regulator which varied the liquid flow through the heat exchanger contained in "B". Normal operation with a small heat leak from "A" enables the liquid in this compartment to be controlled to $\pm 0.1^{\circ}\text{C}$ down to -70°C .

However with the large heat leak caused by circulating the liquid from A through the cooling block, a minimum temperature of -55°C was maintained in "A". In the earlier experiments, this cooled liquid was circulated directly through the cooling block but the narrow channels were prone to blockage by small ice crystals which rapidly accumulated in the cold petroleum ether. In the final system the coolant was pumped through a copper heat exchanger in the thermostatically controlled compartment "A". This system had the added advantage that "Cardice" could be added to compartment "A" instead of "B". This produced a temperature of -78°C in "A" and enabled one much lower stable temperature to be obtained in the cell as a result of the lower temperature produced in "A". The minimum temperature reached in the cell using this system was -60°C compared with about -40°C using the thermostat. The brass block was thermally insulated from the worm wheel of the diffractometer by a $\frac{1}{2}$ " slab of "Pyrophyllite" which considerably reduced the heat loss to the diffractometer whilst maintaining a rigid mount for the block. Insulation from the atmosphere

was achieved by use of $\frac{1}{2}$ " expanded polyurethane foam at the back, sides and top. ~~and~~ the front of the cell was protected by a single film of "Cellophane" which kept the front window clear of ice crystals. (No radiation loss was apparent using this cell, as discussed later.)

5.2.3. The Design of Cells for Thermal Expansion Measurements

The cells which had to resist the chemical action of strong acids and liquid bromine were made from P.T.F.E., the interior metal parts being platinum. The body of the cell A (Fig. 5.4.1) was turned to be a very close fit in the brass cooling block, thus assuring reproducibility of mounting of the cell, and hence of the sample, with respect to the diffractometer. The cell was made gas tight by the film of P.T.F.E. .003" thick held in place by the brass ring "B" and the eight brass bolts. A raised ridge machined in the front face of the cell functioned as an O-ring seal when the film was pressed against it by the brass ring. The samples were held in the cell by a platinum clip (C) (shown enlarged below). The sample was held against the front face of the clip by the P.T.F.E. sheet bent into a curve which produced a light forward pressure towards the front face. The other upright of the clip was screwed to the body of the cell by an iridium-plated screw. This arrangement assured that the sample was kept lightly pressed against the vertical surface formed by the



platinum clip. This surface was aligned so as to be coincident with the specimen axis of the diffractometer by replacing the sample by a similar sized piece of microscope cover slip. A beam of light was then passed through the collimator and the sample clip adjusted to bring the reflected beam into alignment with the receiving slit on the proportional counter. The samples used in this cell were about

1cm x 0.5cm x 0.01cm.

In another cell the support for the sample was as in Fig. 5.5; this required slits to be made in the sample and larger specimens (approx. 1.5cm x 1cm x 0.5cm) were needed. This cell was used for some of the earlier experiments and served as a useful check on the measurements made later. The principal disadvantage to this method of mounting was the difficulty of cutting the slits and sliding the sample on to the supports without damage. In both cells the metal support for the sample served as an electrical connection for the passage of current during the electrochemical preparations.

5.2.4. The Measurement of Sample Temperature

The measurement of temperature in a confined space is conveniently arranged by use of thermocouples. In the case of the thermal expansion cells the thermocouples have to resist severe chemical attack and would have to be made of platinum group metals. Unfortunately, the thermo-E.M.F. of these thermocouples is too low in the temperature range -50°C to 20°C and it was necessary therefore to use another method of temperature measurement. The use of small platinum resistance thermometers was tried but it was not possible to wind thermometers that were small enough to be placed in close contact with the sample. The method finally adopted was to use glass encapsulated thermistors. They had the

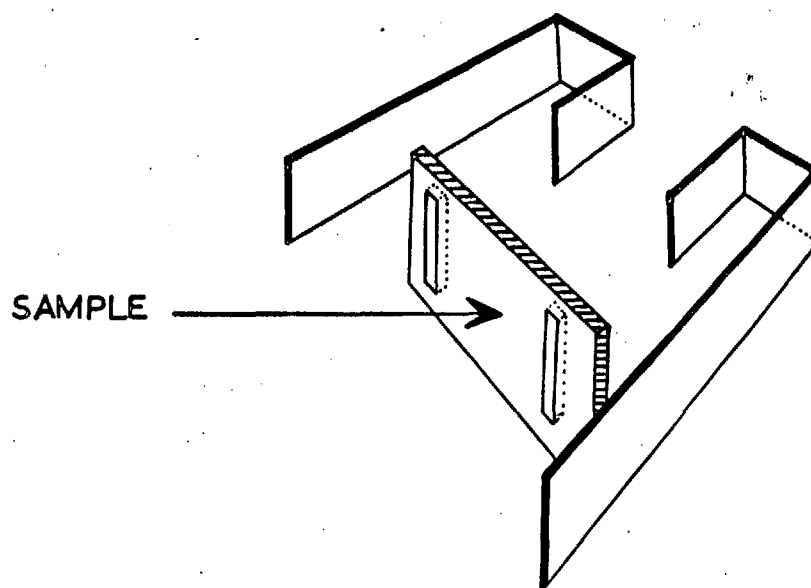


FIG. 5.5. SAMPLE MOUNT USED FOR
EARLY EXPERIMENTS

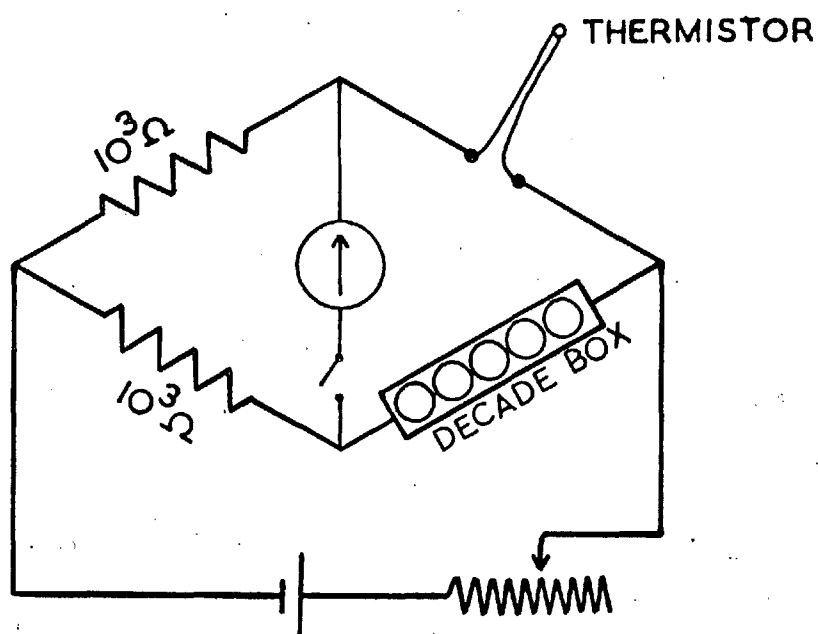


FIG. 5.6. CIRCUIT USED FOR RESISTANCE
MEASUREMENTS

advantage of a very small sensitive tip which could be placed just behind the sample. In addition the glass coating made them completely resistant to chemical attack. In the thermal expansion cells, the glass coated thermistors (Standard Telephone and Cables Type F22, nominally 200 ohms at 20°C, 4000 ohms at -60°C) passed through the back of the cell and the tip rested just behind the sample. The thermistor was used in a standard Wheatstone bridge circuit (Fig. 5.6) and temperature measurement was possible to $\pm 1^\circ\text{C}$.

5.2.5. Preparation and Characterisation of Samples

The acid compounds were obtained as described in Chapter 4 except that they were prepared in situ by placing the cell face downwards in the relevant acid and using a platinum wire dipping into the acid as the cathode. After the oxidation was complete, the cell was removed from the acid and the brass ring and window bolted into position; the cell was then mounted on the diffractometer. The alkali metal compounds were prepared as described in Chapter 3, and the alkali metal graphite samples sealed off from the remaining alkali metal. The tubes were then immersed in a bowl of "Vaseline" which was just liquid ($\sim 60^\circ\text{C}$) and broken open. The "Vaseline" was cooled and the samples which were now coated in a thick layer of "Vaseline" were removed and mounted in the spring clip in the expansion cell. In the process

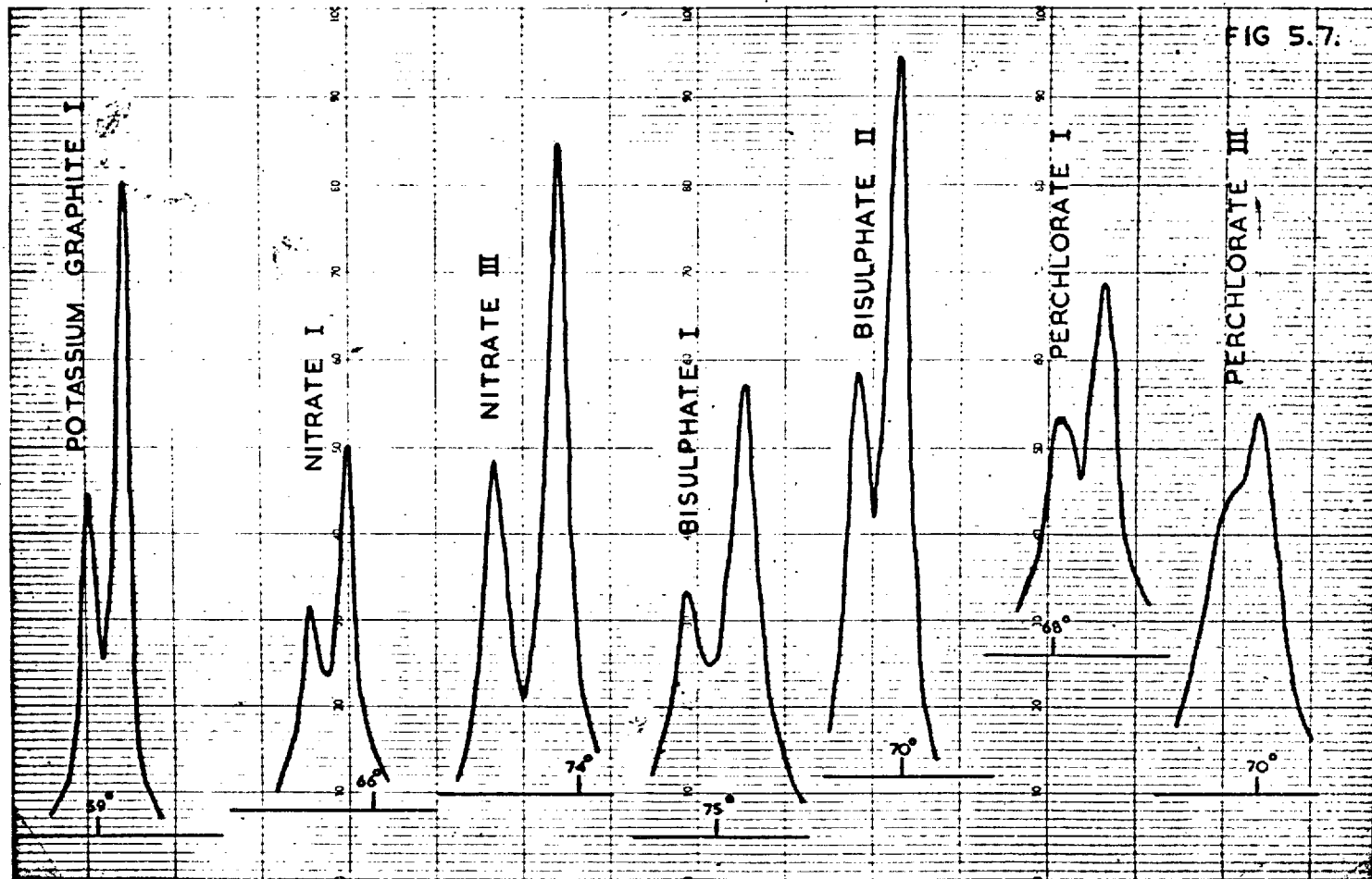
of mounting the excess "Vaseline" between the clip and the sample was squeezed out to leave a very thin film (approx. .01mm). Thus although the surface was still protected by a film .025mm thick where the sample was not in contact with the clip, no error in mounting was introduced by this protective layer. (At this point, the surface of the sample was still gold in colour showing very little surface attack had taken place.) The cell front was then bolted into place.

The cells containing the samples were then mounted in the cooling block on the diffractometer. The radiation which would give the highest 001 reflexion was then calculated and the relevant x-ray tube connected to the generator. A scan of the x-ray diffraction pattern with the sample rotating at $2^{\circ}/\text{min}$ was run over the full range ($10^{\circ} - 85^{\circ}$) and the resultant trace analysed and checked for lines due to compounds of higher or lower oxidation states. If the trace showed no such lines the compound was considered to be a homogeneous ^{not} compound and/contaminated with other oxidation states (5% of a different oxidation state would easily be detected by this criterion). The reflexion to be used for the thermal expansion measurements was then scanned at $\frac{1}{3}^{\circ}/\text{min}$ and the resolution of the $K\alpha_1$, and $K\alpha_2$ lines noted. The resolution of these two lines varied considerably from sample to sample but in most cases the broadening due to disorder in the compound was

small enough to have negligible effect on the peak separation. Thus the separation of the $K\alpha_1$ and $K\alpha_2$ peaks was in agreement with the separation calculated from their wavelengths. In some cases the first sample prepared had to be discarded and a second sample prepared before this standard was attained. With a few compounds, notably those with perchloric acid, this standard of resolution was never achieved and expansion measurements had to be carried out on less well defined peaks. Typical peaks showing resolution of $K\alpha_1$ and $K\alpha_2$ are shown in Fig. 5.7 for a range of compounds.

5.2.6. Measurement of Thermal Expansion

Because the plastic pipes which carried the coolant to and from the cell became rigid at low temperatures and imposed lateral strain on the cell, it was not possible to run complete peak profiles. Therefore the thermal expansion measurements were based on the movement of the peak maximum of the $K\alpha_1$ reflexion. This maximum was located by scalar counting at intervals of 1 min. of arc; the time of counting usually being 100 secs. This method can be very accurate; in the case of graphite, accurate location of the peak maximum was attempted using 1 min intervals of arc but longer counting times and the results are shown in Fig. 5.8. It is apparent that, providing the peak is sharply defined, an accuracy of up to 0.2 minute of arc would be possible. For the graphite



PEAK PROFILE OF HIGH ANGLE DIFFRACTION LINES

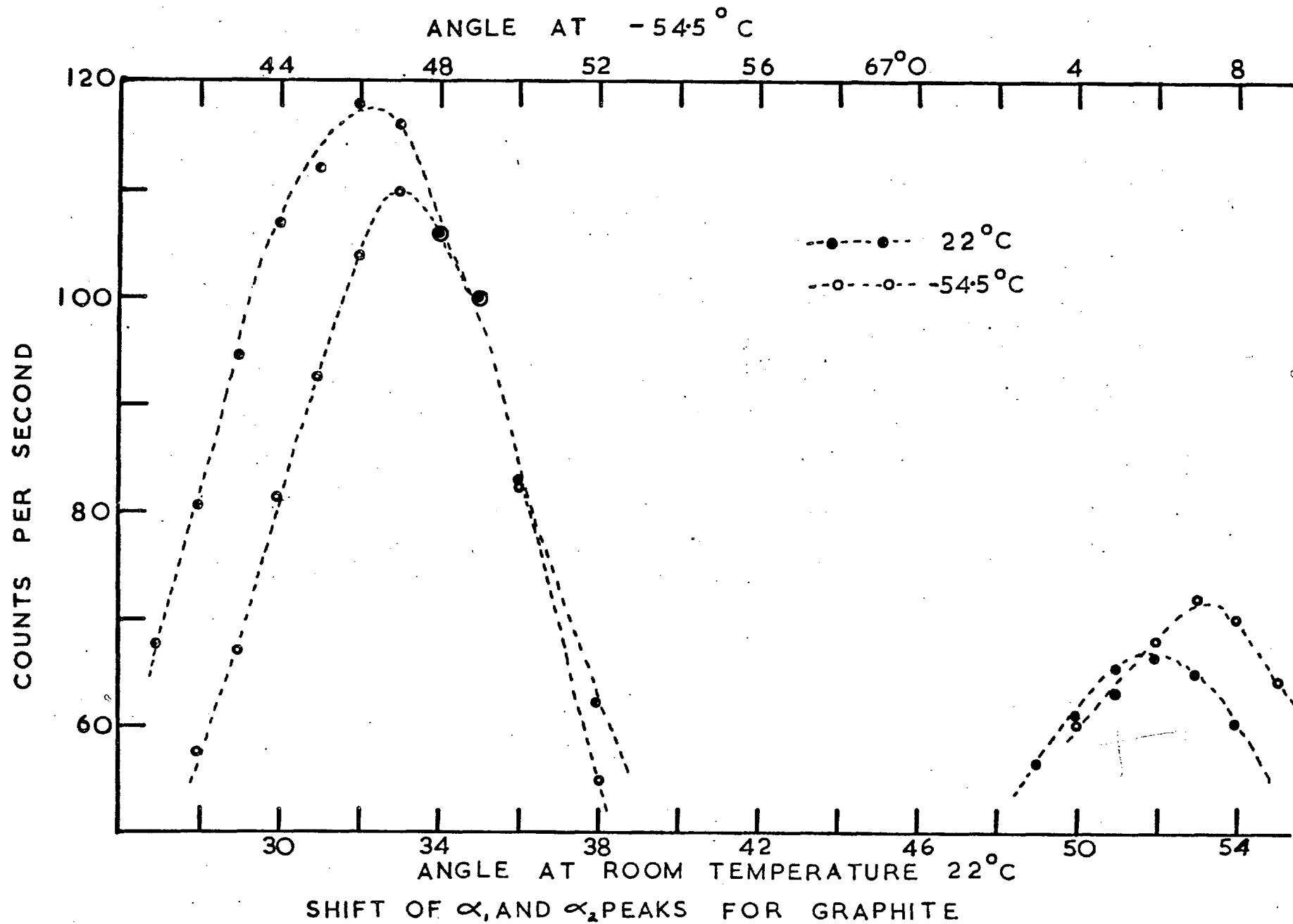


FIG. 5.8. 149

compounds the peaks are not always so well defined and typical scans over $K\alpha_1$ peaks are shown in Fig. 5.9.

After the peak had been accurately located at room temperature, the cell was cooled and when the temperature as measured by the thermistor became constant (usually after $\frac{1}{2}$ - 1 hour) the peak was relocated using scalar counting. This procedure was repeated both raising and lowering the temperature (to check reproducibility in both directions) over the full temperature range and values of θ (Bragg angle) and T (temperature) were recorded. Measurements on some samples extended over 5-10 days and during this time traces at $2^\circ/\text{min}$ were taken at frequent intervals with the sample at room temperature to check that the sample still showed the same diffraction pattern as when prepared. A final trace at $2^\circ/\text{min}$ was always taken before the sample was removed from the cell. In general no deterioration of the sample was detected in any run; if any such effect was noticed, the experiment was discontinued. Usually two samples of each compound were prepared and their thermal expansions measured. In such cases, the absolute angles for the two samples are not always the same due to slight errors in mounting; as discussed earlier this does not significantly affect the thermal expansion values.

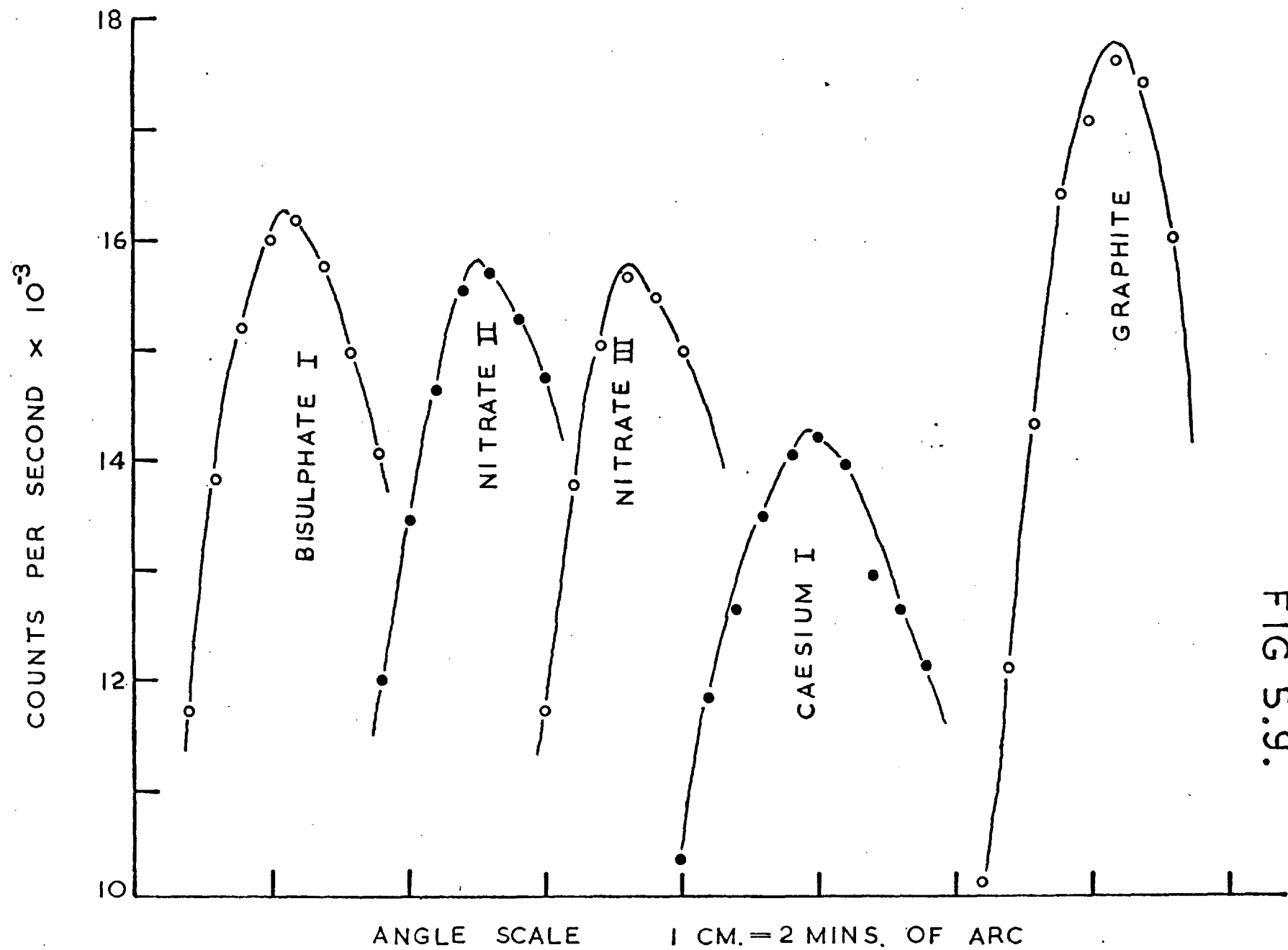


FIG 5.9.

5.3. Results

The data recorded for all the thermal expansion results is presented in Appendix 4. For each measurement the temperature, Bragg angle, and lattice spacing are recorded. The page number of the text reference to the results is also noted. A summary table, 5.1, shows the radiations and reflexions used for each compound and the room temperature Bragg angle which gives some indication of the relative accuracy of the expansion results. Table 5.2 lists the expansion coefficients of all the compounds studied with the limits of error. (The derivation of this table and the significance of the error limits are discussed in detail in the following sections.)

5.3.1 Mathematical Analysis of the Results

The lattice parameter C_t at any temperature t can be expressed in terms of the lattice parameter C_o at a reference temperature, t_o often 0°C , and the temperature difference between these two $(t-t_o)$. In the general case this relation is:

$$C_t = C_o + a(t-t_o) + b(t-t_o)^2 + c(t-t_o)^3 \dots$$

Thus from the definition of $\alpha = \frac{1}{C_o} \frac{dC}{dt}$ it follows that:

$$\alpha = \frac{1}{C_o} \left[a + b(t-t_o) + c(t-t_o)^2 \dots \right]$$

TABLE 5.1

Compound	Reflexion	Radiation	Angle	Shift in mins.	Approx. $\alpha \times 10^6$
Nitrate I	008	Co K α_1	66	90	85-95
II	0020 0022	Fe K α_1	60 73	90	62-72
III	0018	Cu K α_1	73	75	55-66
Bisulphate I	008	Fe K α_1	74.5	40	62
II	0022	Fe K α_1	70	40	43
III	0026	Fe K α_1	59	15	36
Perchlorate I	006	Cu K α_1	48	20	98
II	0020	Fe K α_1	61	20	55
III	0014	Fe K α_1	69.5	50	-
Potassium I	006	Fe K β	80.5	60	44
II	0011	Cu K α_1	76	25	36
Rubidium I	007	Cu K α_1	72	20	36
Caesium I	006	Fe K α_1	78	20	24
Graphite	008 006	Cu K α_1 Co K β	67 75	20	25
Bromine	0012	Cu K α_1	63	20	50

TABLE 5.2

	Stage	Sample	No. of point	$\alpha \times 10^{-6}$	90% confidence limits
Bisulphate	I	1	9	62	3
	I	2	13	63	3
	II	1	4	43.5	3.5
	II	2	8	44	4
	II	3	9	42	4
	above -5°C	III)	8	32	6.5
	below -5°C	III)	6	36	2.5
Nitrate	I	1	4	85	4.5
above -20°C	I	2	6	83.5	8
	II	1	25	61	6
at 20°C	III	-	-	55	-
Nitrate	I	1	-	94	3.5
below -30°C	II	1	3	72	6
	III	-	-	66	-
Perchlorate	I		40	106	12
	II		2	49	-
	II		4	55	20
	III		6	80	-
Potassium	I		2	44	-
	I		9	44	4
Rubidium			2	38.5	
			2	34.5	
Caesium			4	24	1
			2	26	
			2	28	
Graphite			6	25.2	1

It is assumed in all the following discussion that within the accuracy of these results α is not a function of $(t-t_0)$, thus the equation for the lattice parameter C_t reduces to: $C_t = C_0 + a(t-t_0)$ (eq. 5.i). That is a straight line of the general form $y = mx + c$.

Three types of data have to be considered. The first type is where only one room temperature and one low temperature value of the lattice parameter were recorded. In this case the thermal expansion coefficient was derived simply as:

$$\alpha = \frac{C_{t_1} - C_{t_2}}{(t_1 - t_2)} \frac{1}{\frac{1}{2}(C_{t_1} + C_{t_2})}$$

which follows directly from equation 5.i for temperatures t_1 and t_2 .

The second, more usual type of data involves numerous values of the lattice parameter as a function of temperature. These results were fitted to a straight line chosen by the standard method of minimising the squares of the deviations from this line. If x_i, y_i is a typical experimental point in a set of n points, then the gradient m of this line can be shown to be given by:

$$m = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2} \quad (\text{Eq. 5.ii})$$

(see Levy and Preidel, 1944). If $\sum x_i/n$ is designated $\bar{x}$, the mean of x_i , and similarly $\sum y_i/n = \bar{y}$, then equation 5.ii becomes:

$$m = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2}$$

This gives a value for the gradient of the line but it is important to know the reliability of this estimate of the gradient. In order to proceed further, it is necessary to make some assumptions about the nature of the distribution of the experimental data (see Acton, 1959). It is assumed that if a large number of values of y_i were collected for each x_i , then the mean of these values $\bar{y}$ would lie on the line $y = mx + c$. In addition, if this were to be repeated for each x_i then the distribution of error would be normal in each case and the standard deviation (σ_i) of the distribution would be the same for each point. These assumptions are valid in the case being considered as the error at any point x_i is random (principally arising from the scale error of the diffractometer) and uninfluenced by the value of x_i ; the points are also expected to lie on a straight line, $y = mx + c$. Thus it is possible to assign a reliability to the calculated gradient. The standard deviation of the gradient σ_m is given by:

$$\sigma_m^2 = \frac{\sigma_i^2}{\sum (x_i - \bar{x})^2}$$

where σ_i is the true standard deviation of the points from the line. Unfortunately, σ_i^2 is not available; only a calculated standard deviation of the points from the line

σ_n is known. This is given by $\frac{1}{n-2} \sum (y_i - Y_i)^2 = \sigma_n^2$ (eq. 5.iii) where $Y_i = mx_i + c$ and the $n-2$ factor arises

because of the loss of two degrees of freedom in calculating the line. Equation 5.iii can be expressed in terms of x_i, y_i only:

$$\sigma_n^2 = \frac{\sum (y_i - \bar{y})^2 - \left[\sum (x_i - \bar{x})(y_i - \bar{y}) \right]^2}{(n-2) \sum (x_i - \bar{x})^2}$$

Thus the reliability of the gradient is dependent on the distributions of σ_n and σ_i . If the distribution of the original points is normal then σ_n^2 has a χ^2 distribution of order n ; σ_i^2 has necessarily a χ^2 distribution of order ∞ . This results in a distribution of errors on the gradient which is a Student t distribution of order n ; for a very large number of points this becomes a normal distribution.

Thus the distribution of the error on the gradient will not in general be normal but will have a Student t distribution of order n , and the confidence limits of the calculated

gradient must be defined in terms of this distribution. Values of this distribution for 90% confidence limits in terms of the standard deviation are given in Table 5.3. (90% confidence limits are the limits such that if it is stated that the true value lies between these limits then there is a 90% probability of this statement being correct.)

TABLE 5.3

No. of points	Student t dist. t-2	No. of points	Student t dist. t-2
3	6.31	11	1.83
4	2.92	12	1.81
5	2.35	13	1.80
6	2.13	14	1.78
7	2.01	15	1.77
8	1.94	16	1.76
9	1.89	17	1.75
10	1.86	18	1.75
		∞	1.64

Thus the 90% confidence limits on m the gradient are given by:

$$m = \frac{1}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot \sqrt{\frac{(t-2)}{n-2} \left[\sum (y_i - \bar{y})^2 - \frac{\left[\sum (x_i - \bar{x})(y_i - \bar{y}) \right]^2}{\sum (x_i - \bar{x})^2} \right]}$$

The effect of this error function is that if the number of experimental points is very small then the reliability of the gradient is considerably reduced. The reliability becomes reasonably constant at about 15 points and only increases a further 8% if an infinite number of points is included.

The third type of data which had to be considered was that which could not be fitted to a single straight line. This situation arose either because of lattice parameter drift with time or because of a variation in lattice parameter between two samples. These results were analysed by assuming that the data could be described by one thermal expansion coefficient and a variable room temperature lattice parameter. The method (Ergun, 1956) minimises the root mean square deviations of all the points from a set of parallel lines and is a more general case of that discussed in detail above. The gradient of this line is given by:

$$m = \frac{\sum (\sum (x_i - \bar{x})(y_i - \bar{y}))}{\sum (\sum (x_i - \bar{x})^2)}$$

the summation being over the number of points and over the number of lines. The standard deviations of the gradient can be calculated and is given by:

$$\sigma_m^2 = \frac{\sum (\sum (x_i - \bar{x})^2)}{\sum (\sum (x_i - \bar{x})^2)^2} \sigma^2$$

where $\sigma^2 = \frac{\sum \sigma_p^2}{\sum (N-1)-1}$ where N is the number of points

per line and σ_p the deviation of each point from its respective line.

This method is theoretically subject to the same ~~restriction~~ of low reliability for a low number of points but in order for this treatment to be attempted in the first place a relatively large number of points is required and the deviation from normality is generally neglected as a result.

5.3.2. The Thermal Expansion of Graphite

The first measurement of the thermal expansion coefficient for graphite was carried out in the earlier cell where the supports passed through the sample. The only radiation then available was copper and the highest peak which it was possible to use was the 008 at 67° in θ . As the thermal expansion was known to be such that only a small peak shift would occur, the lattice spacing was measured at

the lowest temperature attainable and at room temperature. The results for four samples of pyrolytic graphite type AB which had been carefully selected from the inner layers of the deposit, gave the results 24.6×10^{-6} , 24.9×10^{-6} , 24.8×10^{-6} , $24.6 \times 10^{-6}/^{\circ}\text{C}$. Subsequently cobalt radiation became available and because of the higher accuracy which could be expected using the 008 Co $K\beta$ line at a Bragg angle of 75° , further experiments were carried out. The later design of cell was used for these results and the lattice parameter is plotted against temperature in Fig. 5.10. The thermal expansion coefficient calculated from the line of root mean square fit is $25.2 \times 10^{-6}/^{\circ}\text{C} \pm 1.0$.

5.3.3. Graphite Bisulphate Compounds

These compounds were all prepared by controlled electrolysis in 100% sulphuric acid.

5.3.3.1. Graphite Bisulphate I - Two samples of this compound were studied. The results for the first of these are shown in Fig. 5.11 where the order in which the points were taken is given by the numbers appended. These results were taken over a period of 2 days and no drift of the peak was observed during this time (cf second sample). The thermal expansion calculated from Eq. 5-ii was $62 \pm 3 \times 10^{-6}/^{\circ}\text{C}$.

The results for the second sample of Graphite Bisulphate I did not lie on a good straight line (Fig. 5.12).

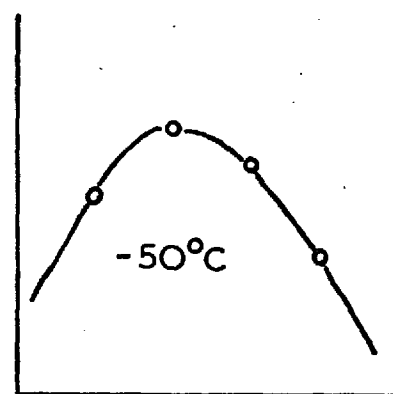
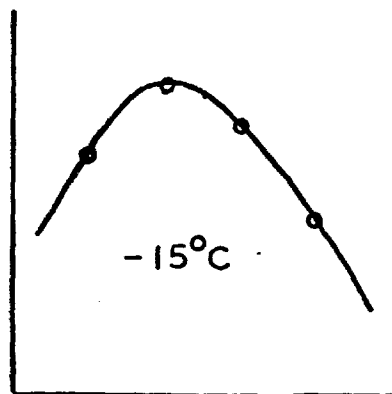
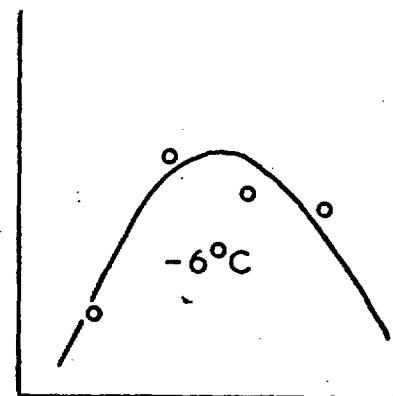
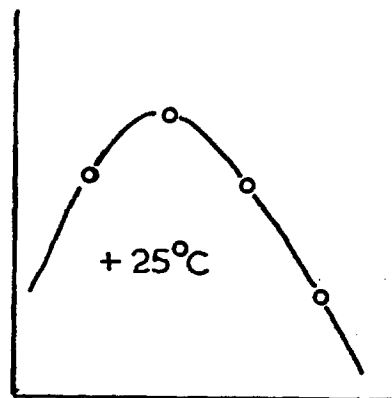
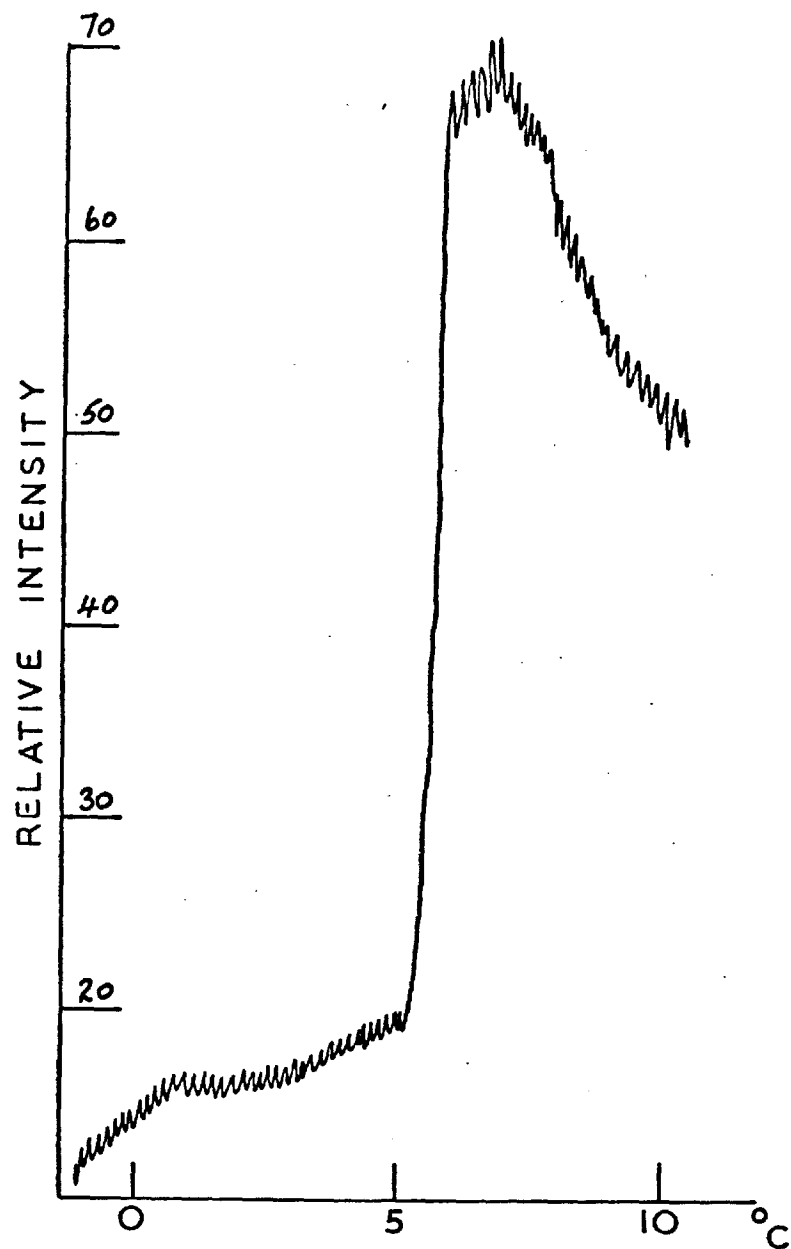
From the order in which the points were taken it was apparent that there was a change in dimensions with time. The lattice parameter at room temperature was plotted against time (Fig. 5.13) and it can be seen that there was a linear change of about $.00017 \text{ \AA}^{\circ}$ per hour in the lattice spacing. After this increase of dimension with time had been allowed for, the results in Fig. 5.12 were replotted (Fig. 5.14). The thermal expansion coefficient calculated from Eq. 5.ii and the corrected data was $63 \pm 3 \times 10^{-6} / ^{\circ}\text{C}$ in good agreement with the first sample and thus justifying the method of interpretation.

5.3.3.2. Graphite Bisulphate II - Three samples of this compound were studied. The first was prepared in the earlier cell and only limited data collected. The thermal expansion from Eq. 5.ii was $43.5 \pm 3.5 \times 10^{-6} / ^{\circ}\text{C}$. The other two samples were studied in greater detail over a number of days and were found to change in c-axis dimensions with time at room temperature (Figs. 5.15 and 5.16). The first sample showed an apparent contraction of $.0005 \text{ \AA}^{\circ} / \text{hr.}$, the second sample showed an expansion of $.001 \text{ \AA}^{\circ} / \text{hr.}$; the significance of the shifts is discussed later.

The reproducibility on any one day was within the limits of experimental error for lattice spacings at room temperature before and after a cooling run. It was assumed

in the treatment of these results that the rate of drift of the peak was a function of temperature, and that as the temperature was lowered the rate of drift rapidly decreased. Thus if any drift did occur on a series of results on any one day, the extent of this drift would be much smaller than the random errors resulting from location of the peak position and could therefore be neglected. Because of this drift the results were fitted to a set of parallel lines, each line corresponding to the measurements taken over one day. The thermal expansion coefficients calculated by this method for the two samples were $44 \pm 4 \times 10^{-6}/^{\circ}\text{C}$ and $42 \pm 4 \times 10^{-6}/^{\circ}\text{C}$. The agreement between the three sets of results is good and justifies the method used in their derivation.

5.3.3.3. Graphite Bisulphate III - Only one sample of this bisulphate compound was prepared and the results it gave are shown in Fig. 5.17. As a result of the sudden intensity change which occurred at -5°C (Fig. 5.17a) and strongly suggested an anomaly in the expansion, it was decided to analyse the results above and below this point separately. The sudden reduction in maximum intensity which occurred was not accompanied by any pronounced broadening of the peak (Fig. 5.17a) hence a reduction in integrated intensity was assumed to have occurred. From the lattice spacing versus temperature graph (Fig. 5.17), there is marginal evidence of a spacing anomaly



PEAK PROFILE AT DIFFERENT
TEMPERATURES FOR BISULPHATE III
~INTENSITIES SCALED TO GIVE
COMPARABLE MAXIMA~

FIG. 5. 17a.

at about -5°C . Certainly if one r.m.s. line is fitted to the results, the deviations about this line do not appear random. Nevertheless, the justification of splitting the data is principally the anomalous change in intensity. The sudden reduction in intensity is reversible on warming to above -5°C and no difference in room temperature lattice parameter was observed after samples had been cycled through this anomaly. The thermal expansion coefficients calculated from Eq. 5.11 were $32 \pm 6.5 \times 10^{-6}/^{\circ}\text{C}$ above -5°C and $36 \pm 2.5 \times 10^{-6}/^{\circ}\text{C}$ below -5°C .

5.3.4. Graphite Nitrates

The results for the nitrates did not suffer from the peak drifts present in the bisulphates and in general the resolution of the $K\alpha_1$ and $K\alpha_2$ peaks was extremely good (cf Fig. 5.7). The results for the three compounds studied, all prepared by immersion of the sample in the appropriate acid (Rüdorff, 1938) are shown in Figs. 5.18, 5.19, 5.20 for the first, second and third sequences respectively. The results for the nitrate I are for two separate samples but the data is restricted because of the instability of this compound. The second sequence compound (Fig. 5.19) shows considerable scatter; this is principally because after the sample had been cooled below the transition the peak did not always return to exactly the same position. In addition, however, the

curve does contain data for two samples over a period of five days and the slight irreproducibility is not unexpected in view of the solid state transition which obviously occurs (chapter 6). Two separate samples of the nitrate III gave good agreement with one another (Fig. 5.20). Analysis of the results by use of Eq. 5.11 for the nitrate I and by fitting a set of parallel lines for the nitrate II gave the values of thermal expansion coefficient in Table 5.2. Due to the curvature of the lattice parameter plot the thermal expansion of the nitrate III can only be estimated at room temperature and at -40°C , these values are quoted in Table 5.2. On passing through the transition at -25°C none of the nitrate peaks under observation at the time showed any large diminution in intensity. Intensity reductions of about 10% being typical below the transition, cf, bisulphate III.

5.3.5. Graphite Perchlorate

The preparation of graphite perchlorates does not lead to such well ordered compounds as for the other acid salts. The resolution of $K\alpha_1$ and $K\alpha_2$ is generally poor (Fig. 5.7). Measurements have been made on all three perchloric acid compounds and the results are plotted in Figs. 5.21, 5.22 and 5.23. The values of the thermal expansion coefficients calculated by least squares fit are quoted in Table 5.2. The high value of α' for the third sequence compound was suspect and an investigation of the variation of peak profile of the third sequence compound with temperature was made. The results are shown in Fig. 5.24 and it is obvious that considerable broadening is taking place on cooling

the sample. This may indicate approach to a solid-solid transformation.

5.3.6. Graphite Bromine compound

It was difficult with graphite bromine to obtain well defined high angle diffraction peaks for the C_8Br compound (see Appendix 2). The resolution of $K\alpha_1$ and $K\alpha_2$ was generally poor; only one sample which showed good resolution of the $K\alpha_1$ and $K\alpha_2$ peaks at high angles was in fact obtained. It was nevertheless possible to make some measurements on other peaks which were not so well defined. The results obtained are shown in Table 5.4, in each case the result was calculated from one low temperature and one room temperature value of the lattice spacing.

TABLE 5.4

$\alpha \times 10^{-6}$	Bragg Angle at 20°C
43.7	63°35'
44.2	63°50'
41.6	64° 6'
49.2	62°53'

Graphite bromine has an expanded layer spacing of 7.05 Å (Rüdorff, 1941) which is very similar to twice the graphite spacing 6.7 Å. Thus on bromination the 008 graphite peak at 67° shifts and becomes the 0012 graphite bromine peak

at $62^{\circ}30'$. If this shift is assumed to be continuous, then the absolute peak position will be related to bromine content. The thermal expansion coefficient is plotted against the peak position in Fig. 5.25. The points, including that for graphite, lie on a reasonable straight line and some estimate of the value of the expansion coefficient for C_8Br can be made by extrapolation. The value of α for C_8Br , a second sequence compound, is estimated to be $50 \pm 3 \times 10^{-6}/^{\circ}C$. Also indicated in Fig. 5.25 are the peak positions for the third sequence compound, nominally $C_{12}Br$ and for the fourth sequence compound, nominally $C_{16}Br$.

5.3.7. Graphite Alkali metal compounds

The thermal expansion of the first sequence alkali metal compounds has been measured for potassium, rubidium and caesium graphites. The expansion of the second sequence potassium compound has also been measured. The results are plotted in Fig. 5.26 and 5.27 for potassium and caesium graphites. The rubidium and second sequence potassium results were calculated from room temperature and low temperature values only and are therefore not plotted. The thermal expansion coefficients are listed in Table 5.2. The alkali metal compounds behaved in a simple manner giving linear lattice parameter against temperature plots. One anomaly

occurred; in the first sequence potassium graphite compound one sample showed a spacing of $5.40 \text{ \AA}$ (in agreement with Rudorff) on cooling this changed to a spacing of $5.36 \text{ \AA}$ and the change was not reversible on warming.

5.4 Critique of the Results

There are numerous points in the measurement of the thermal expansion which warrant careful examination. Some of the more important ones are noted below:

- (a) Does the thermistor measure the true sample temperature or is there radiation loss from the front face which results in inaccuracies which cannot be neglected?
- (b) Can the spacing drift which occurs in some bisulphate sequences be entirely ruled out in measurements on other compounds?
- (c) Do movements of the sample in the clip, or of the cell in the cooling block introduce significant systematic or random errors into the expansion results?
- (d) Is the broadening of the peak profile detected in the Perchlorate III likely to occur in any of the other compounds and influence the results in a similar way?

The first and third points can be answered from the very close agreement of the expansion results of graphite in two different cells utilising reflexions at considerably different Bragg angles. It is most unlikely that either the difference in temperature or the sample movement would be the same with two such different designs of cell. Further, calculations of the sample movement necessary to influence the expansion results by 1% show it to be considerably larger than that expected as a result of the differential expansion of the sample mount. The question of drift in other compounds has been obviated in all cases by taking readings both with increasing temperature and with decreasing temperature. Thus although measurements made over long periods of time showed no large drifts, if any small drifts had occurred they would be effectively eliminated by the process of fitting a r.m.s. line to the results. The fourth point (peak profile broadening) can only be examined by measurement of the separation of $K\alpha_1$ and $K\alpha_2$ peaks at different temperatures. This was generally not possible because of the strain imposed on the cell by the coolant pipes (discussed earlier), but in the case where this was studied, i.e. the nitrate compounds, no difference in separation of these peaks was observed. There was no detectable change in the shape of the $K\alpha_1$ peak in these compounds and as far as can be ascertained only

the perchlorate III behaved anomalously.

Apart from these specific points, there are numerous limitations in experimental procedure imposed by the very nature of the compounds being studied. The accuracy of the thermal expansion results increases with the magnitude of the actual expansions. This means that for the alkali metal series of compounds the overall accuracy is lower than for the acid salts. This is particularly important in the investigation of the lower sequence compounds of the alkali metals. For instance before it is possible to test the hypothesis that the nett expansion of the second sequence potassium compound can be taken as the sum of two parts, one due to the graphite and one to the potassium, it is apparent that greater accuracy in the values of the thermal expansion coefficients is required (Table 5.5). The position becomes even more difficult in the case of rubidium and caesium graphites which have smaller expansions. In fact the observed expansion of caesium I ($26 \times 10^{-6}/^{\circ}\text{C}$) is not distinguishable from that of graphite so that the solution of the problem here becomes impossible unless very accurate thermal expansion values can be measured.

TABLE 5.5

	<u>for Potassium II</u>	<u>Calculated</u>	<u>for Potassium I</u>
	33		37.9
	34		39.6
experimental	35		41.2
value 36 ± 1	36		42.8
	37		44.4
	38		46.0
	39		47.6
	40		49.2

The problem of measuring the thermal expansion of the alkali metal compounds is also made more difficult than the acid salts because of their smaller lattice spacing. This means that there is less likelihood of a diffraction line being at a suitable high angle as there are fewer lines in the pattern. The results on rubidium graphite are less accurate than the other metals. This is principally because of the low peak to background ratio of the weak 007 reflexion which had to be used for these measurements.

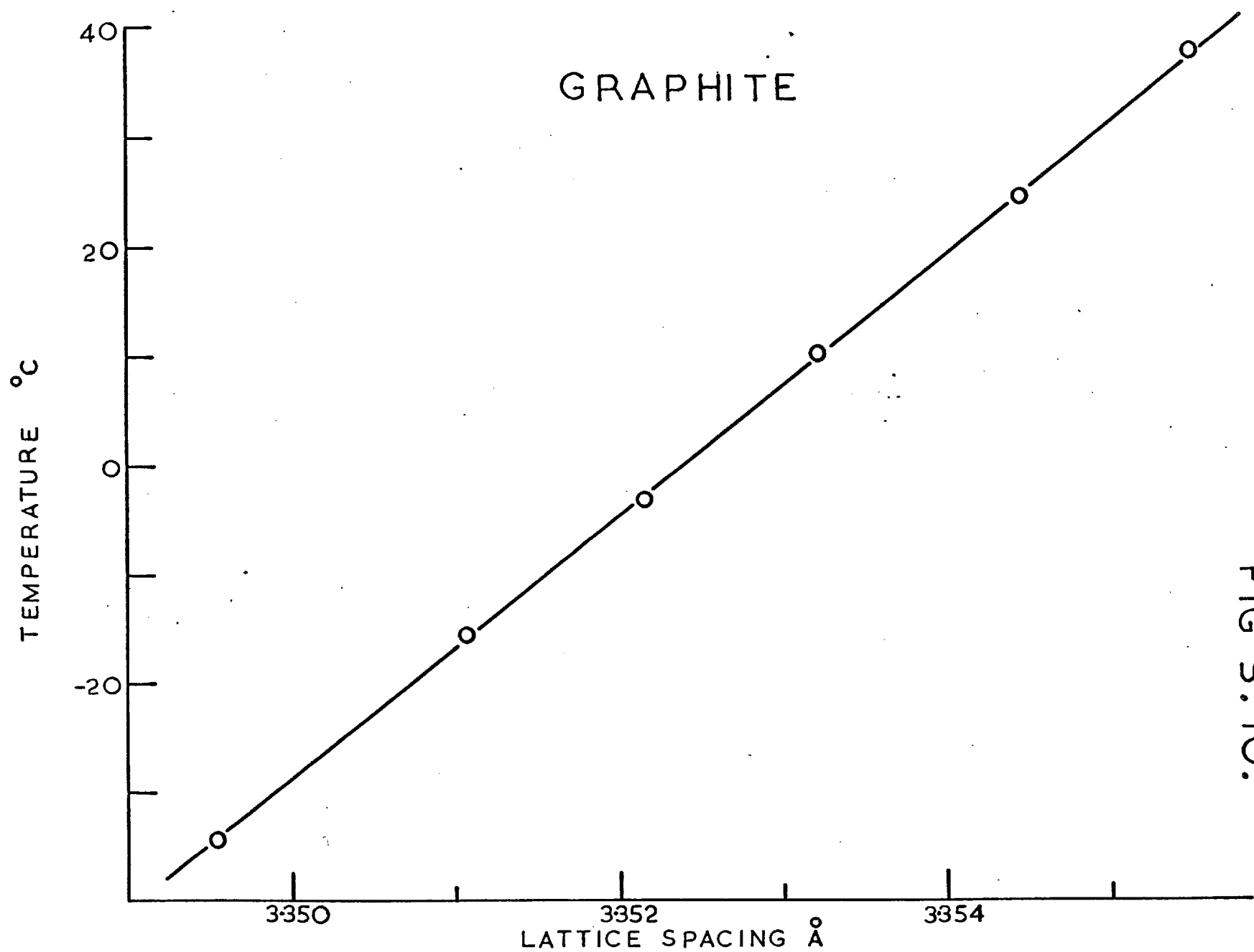
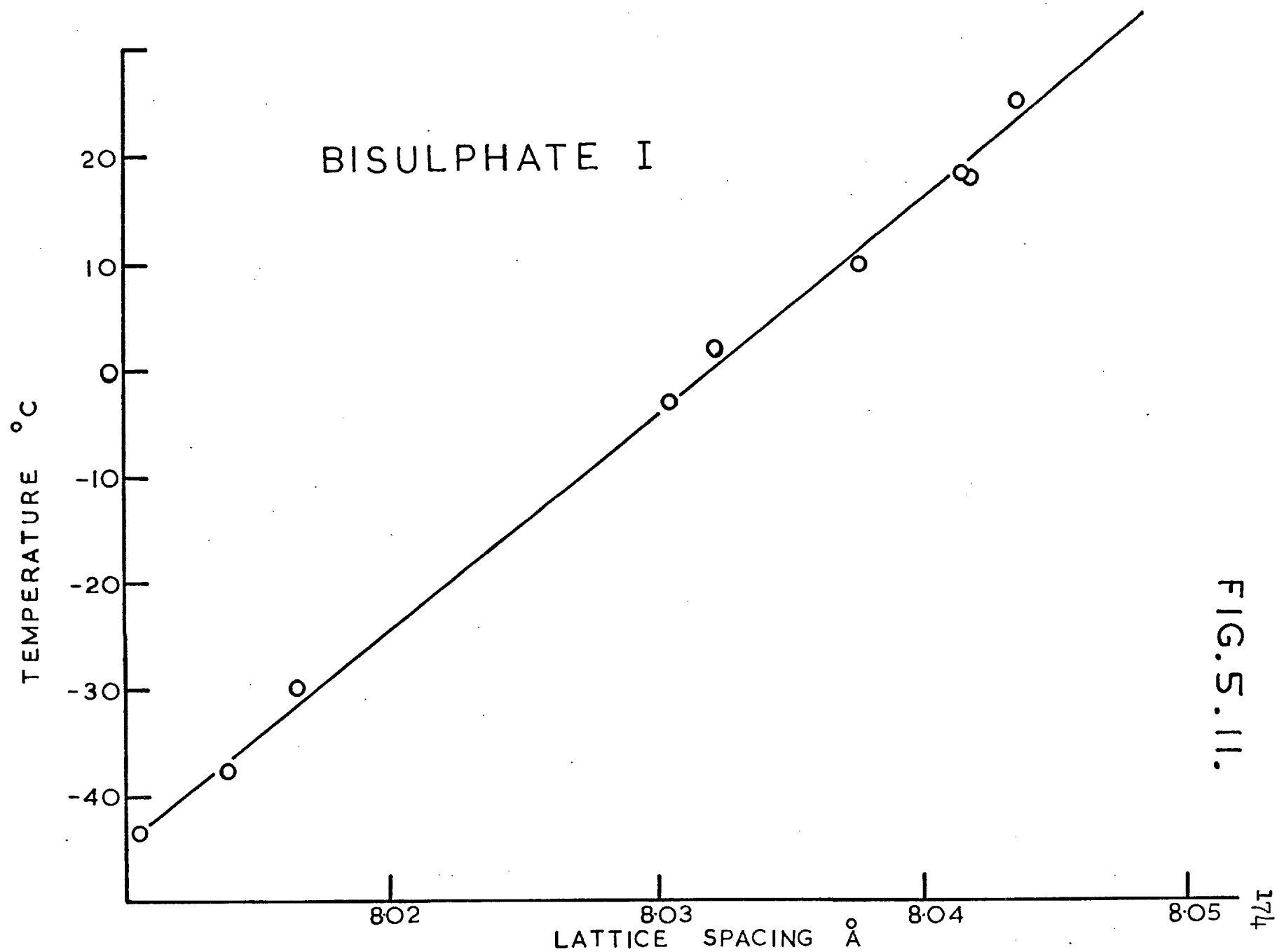


FIG 5.10.



BISULPHATE I

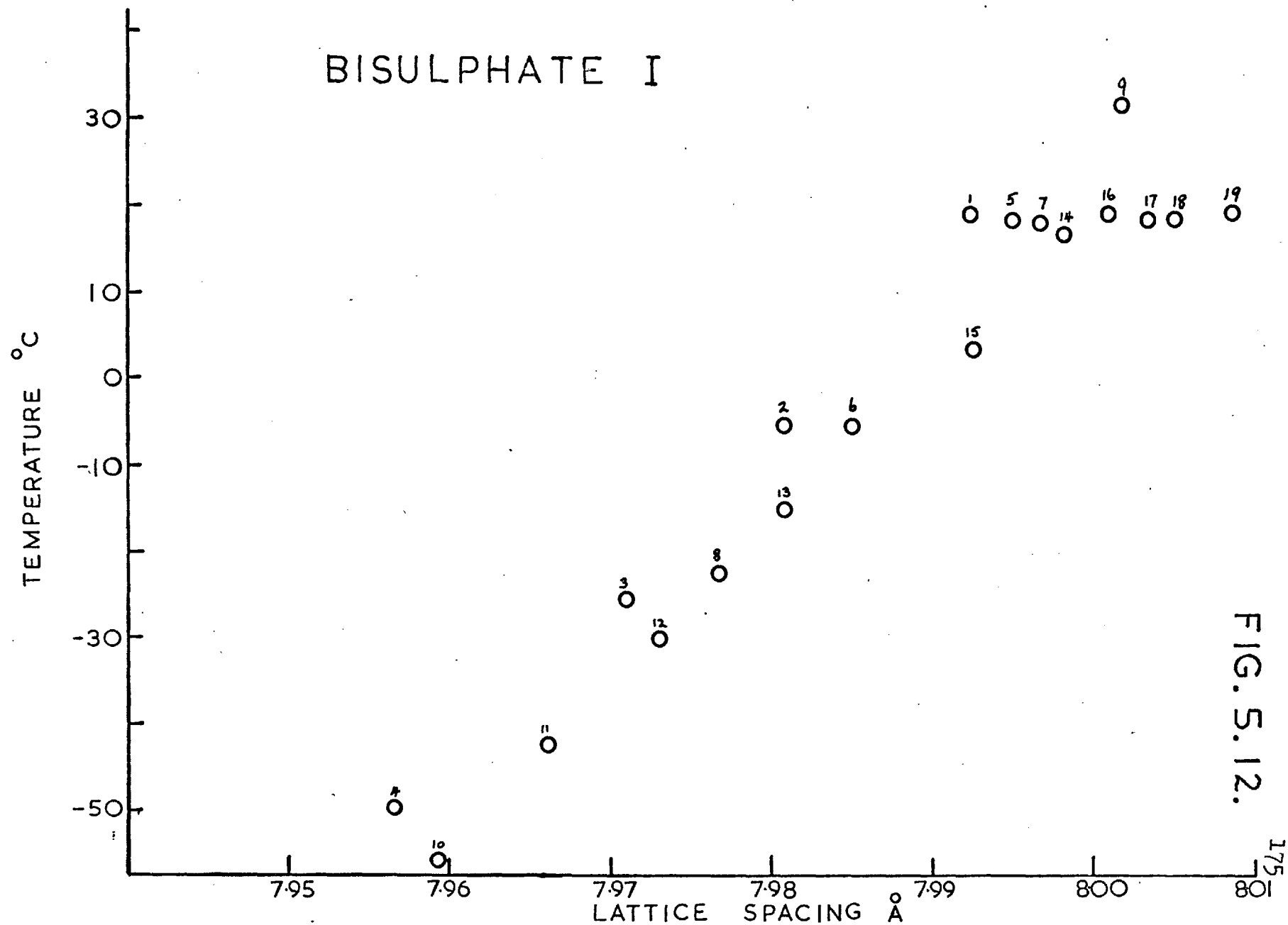


FIG. 5.12.

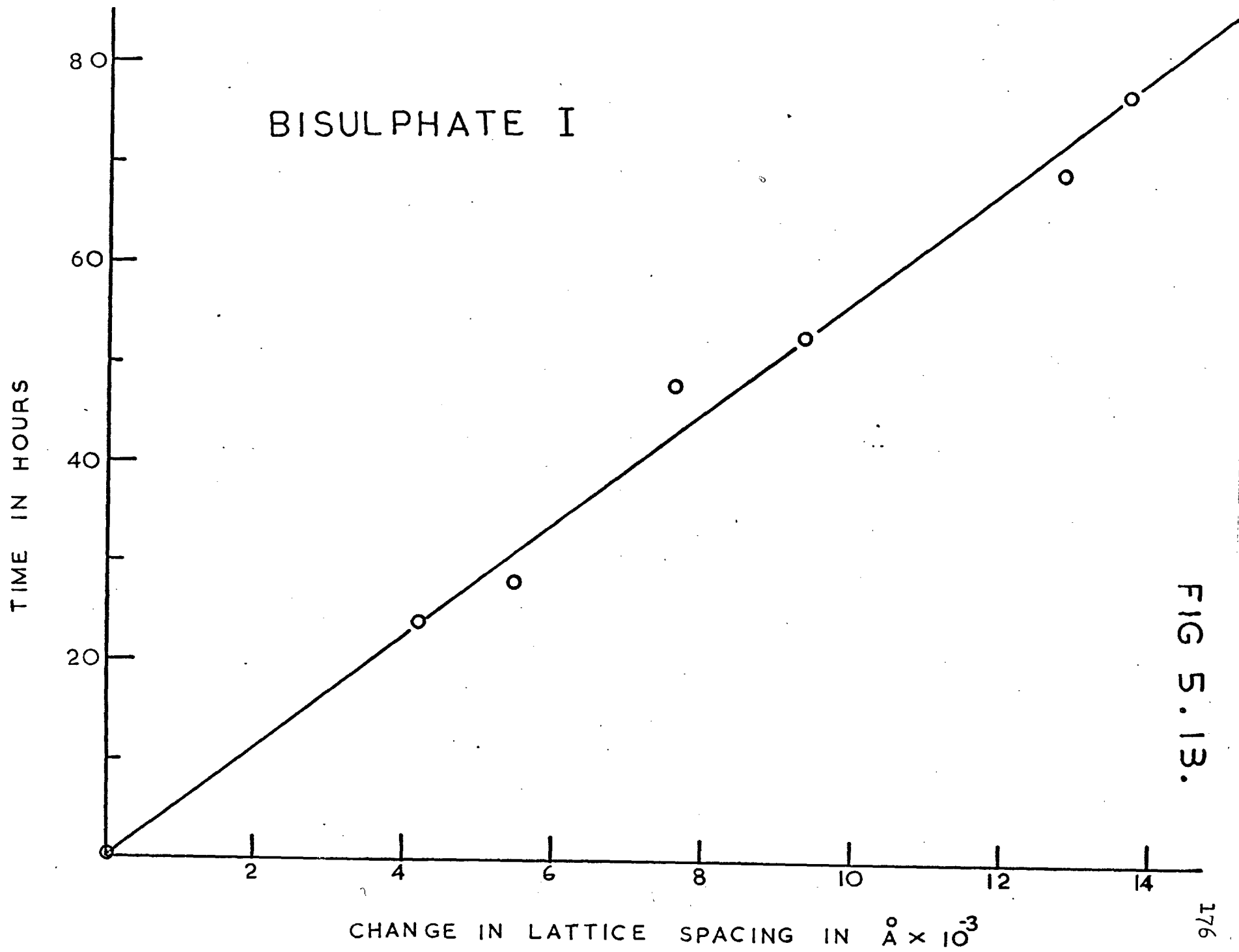


FIG 5.13.

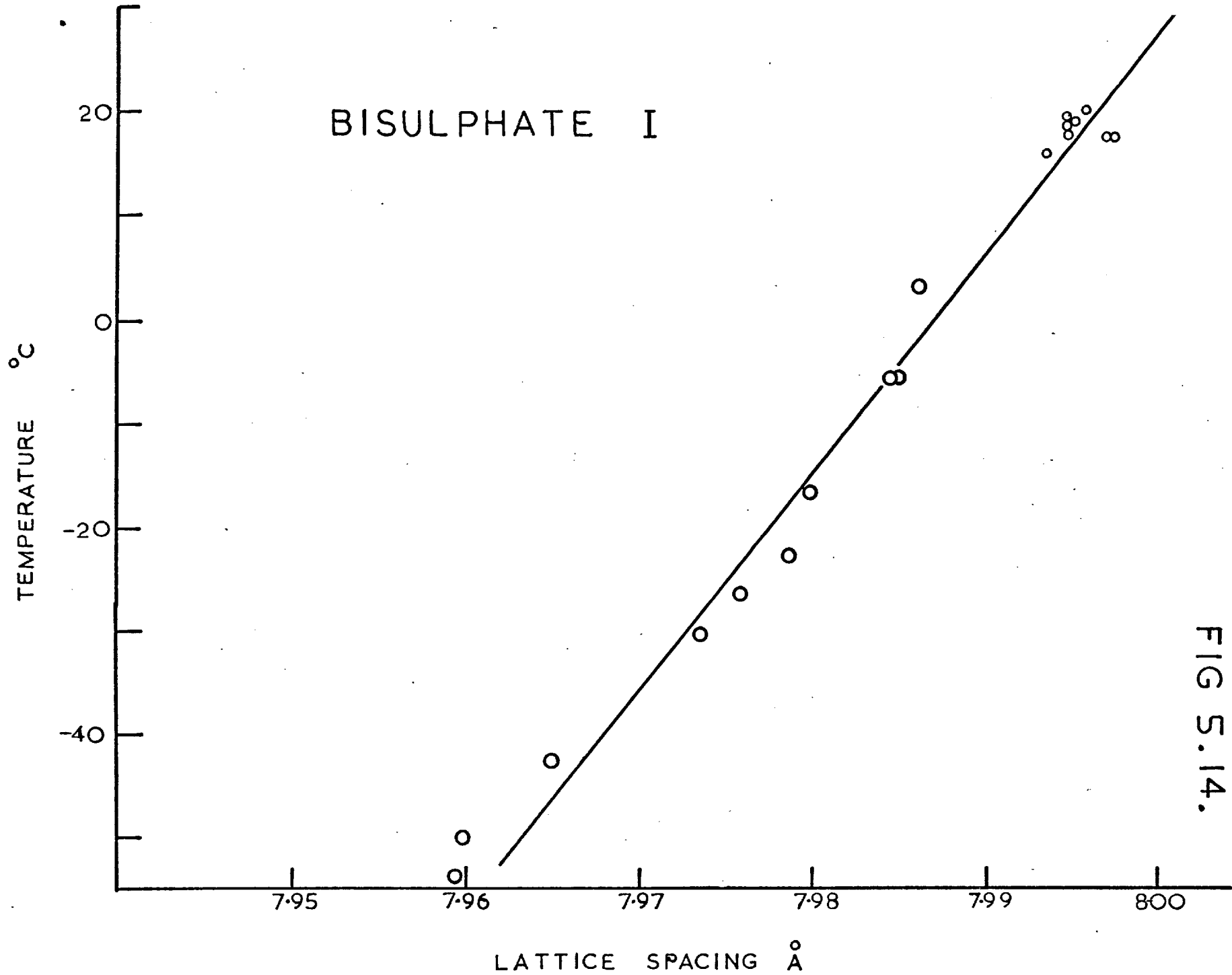


FIG 5.14.

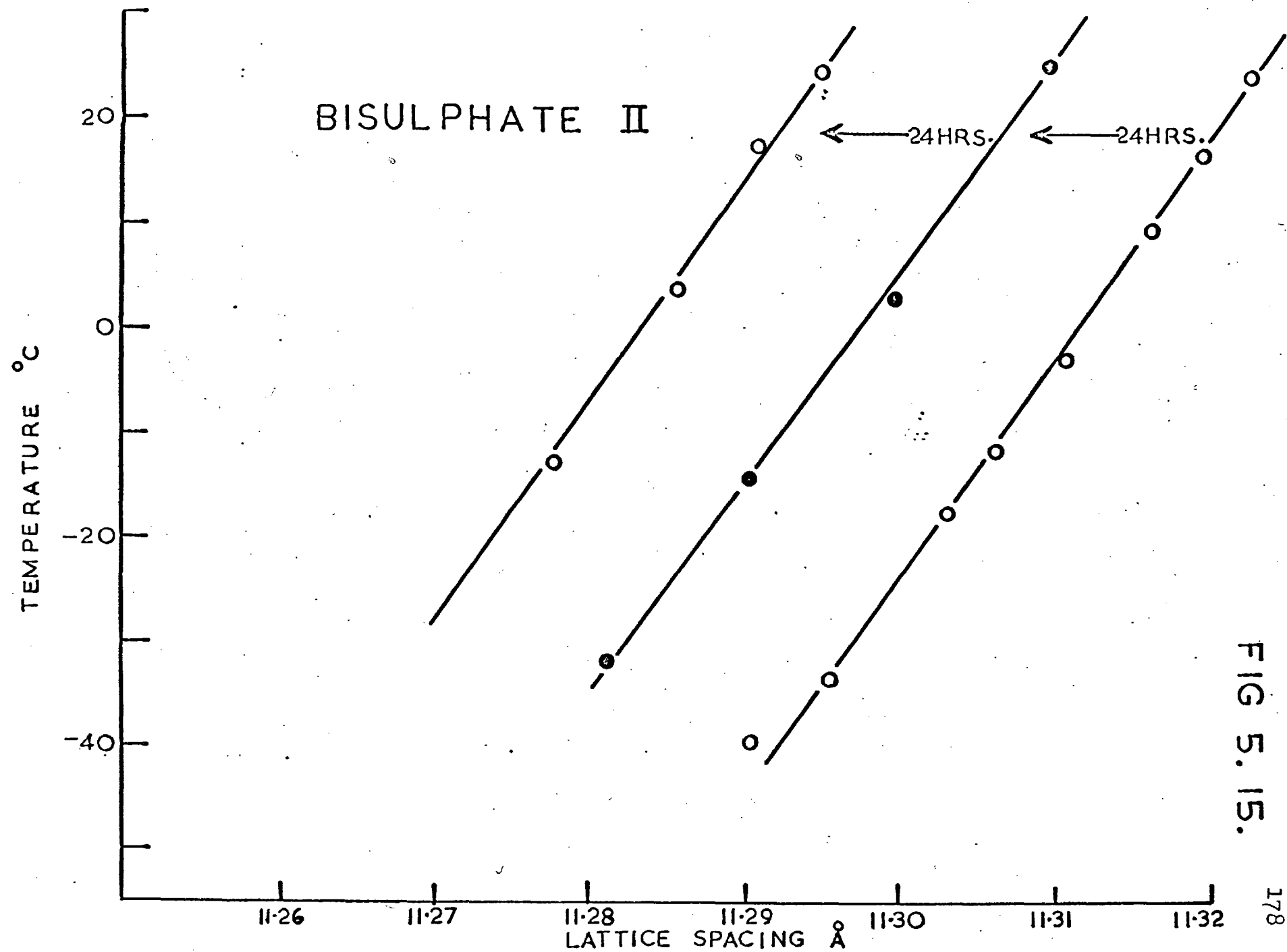


FIG 5. 15.

BISULPHATE II

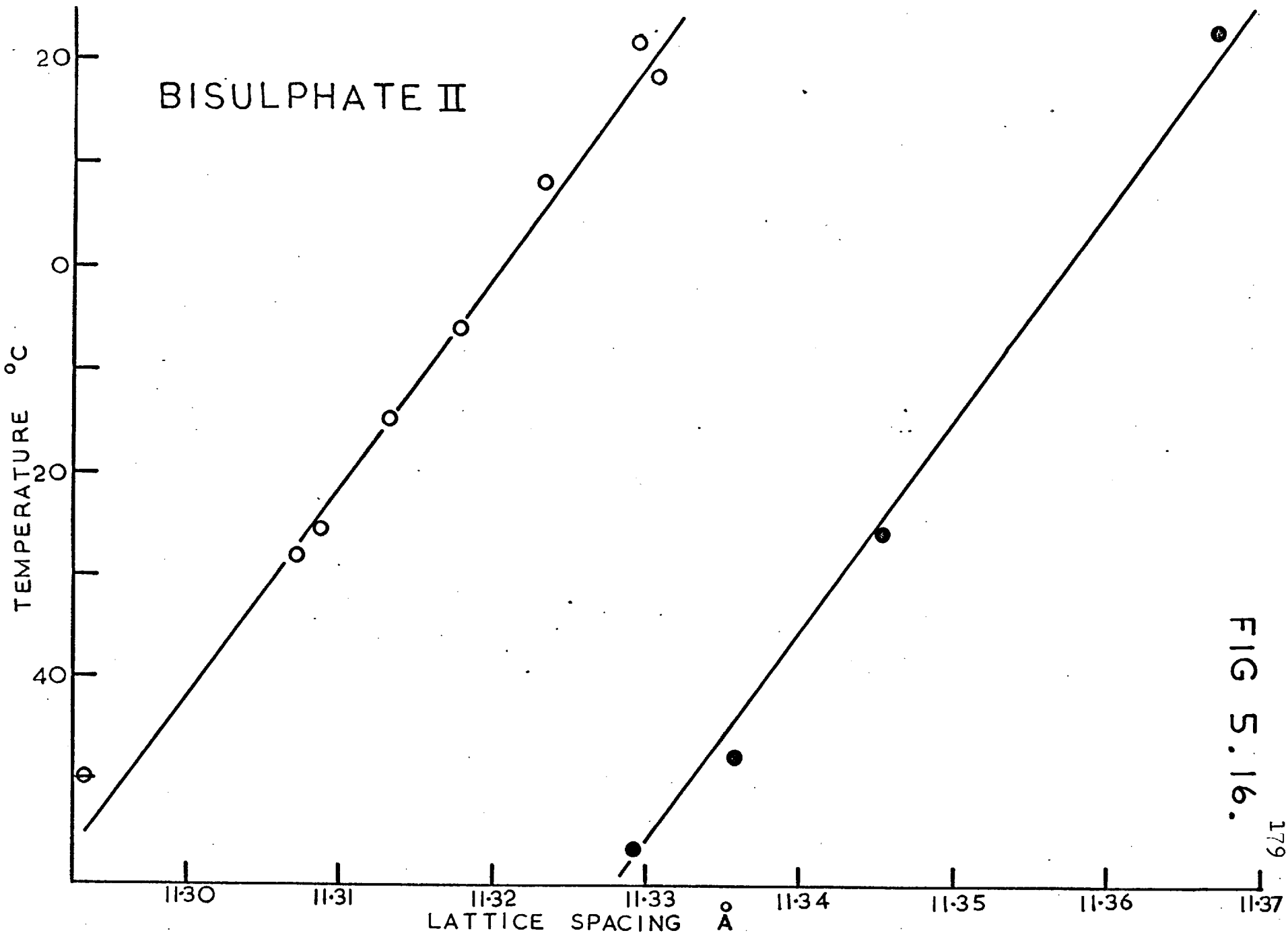


FIG 5.16.

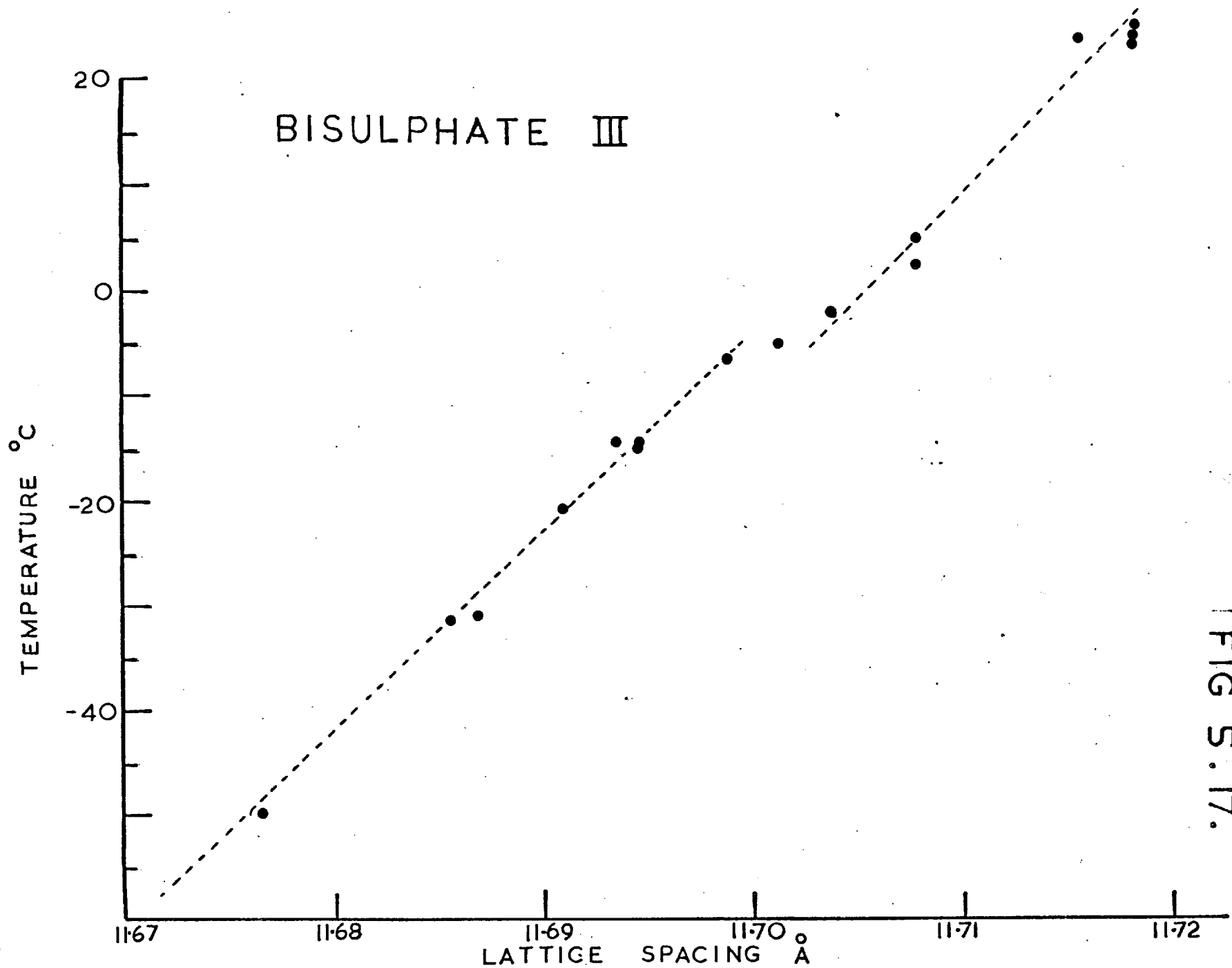


FIG 5.17.

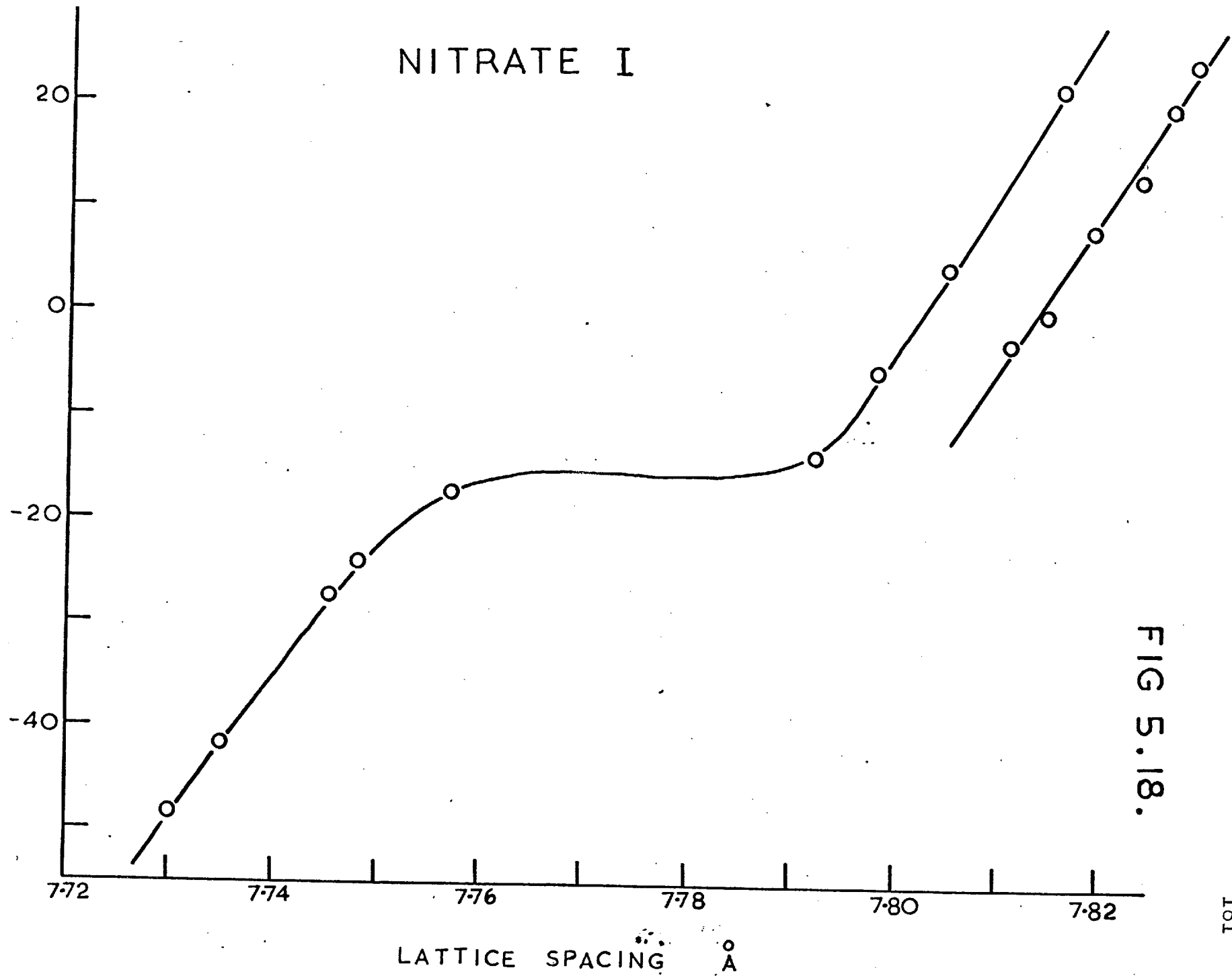


FIG 5.18.

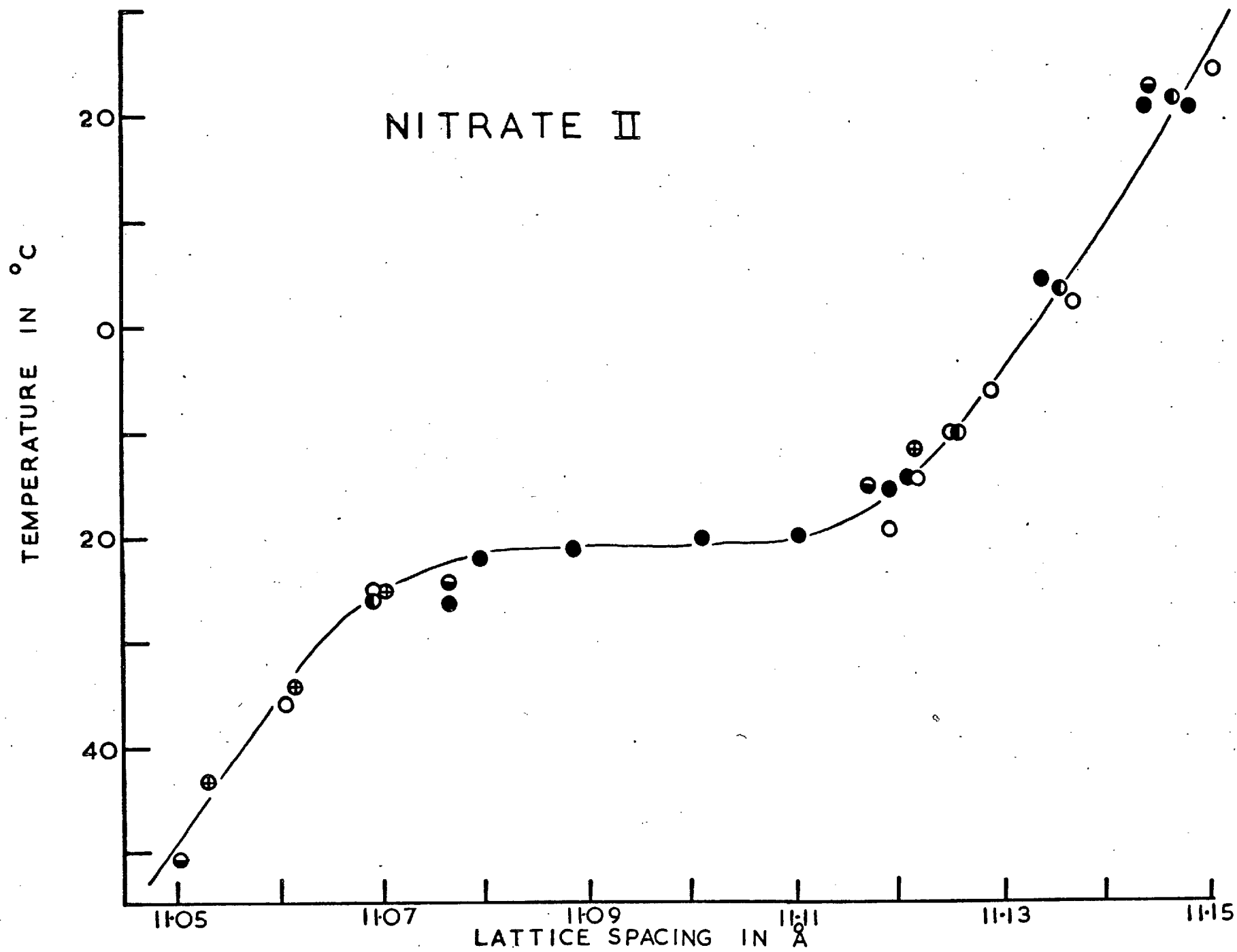


FIG. 5.19.

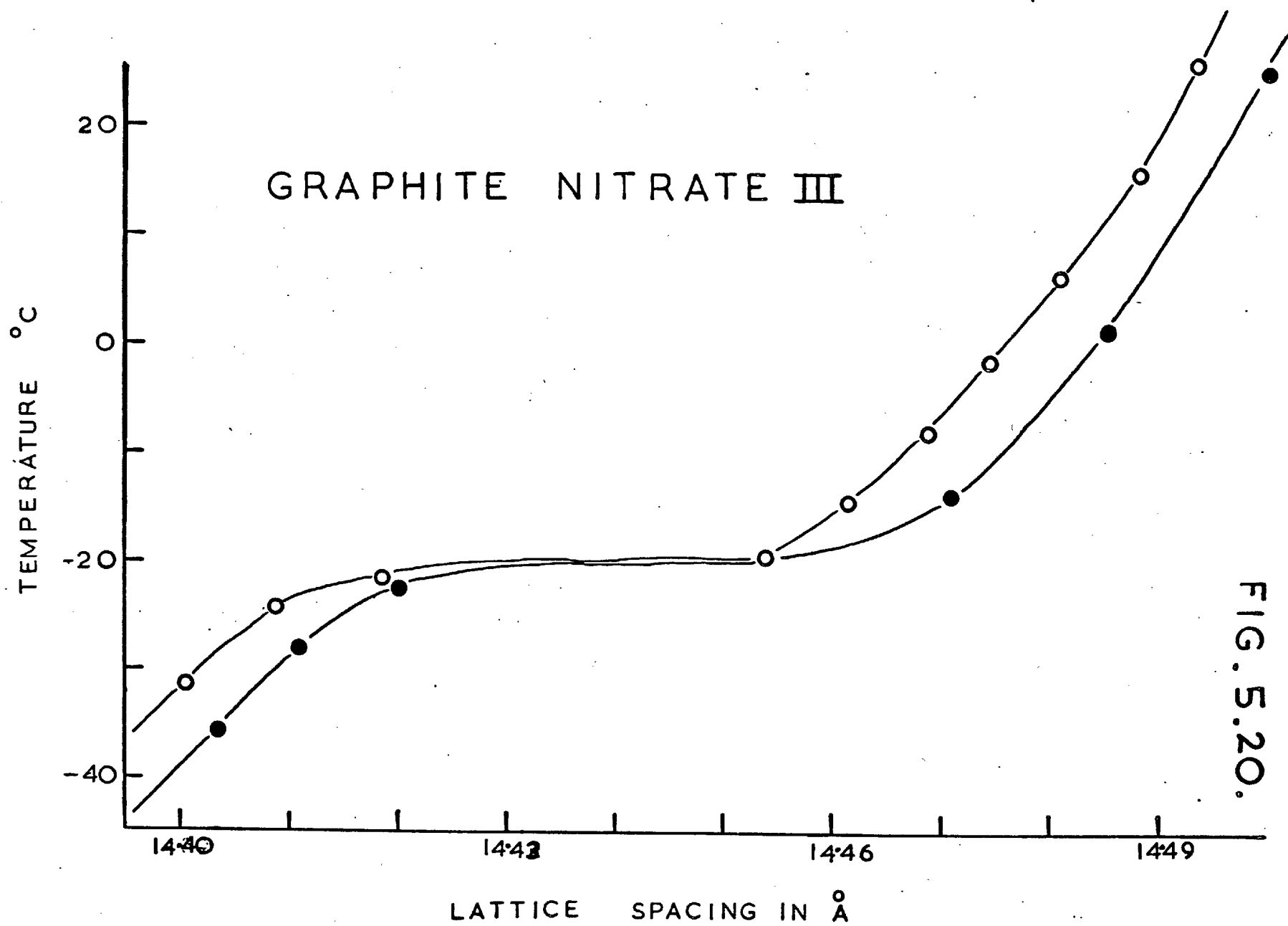


FIG. 5.20.

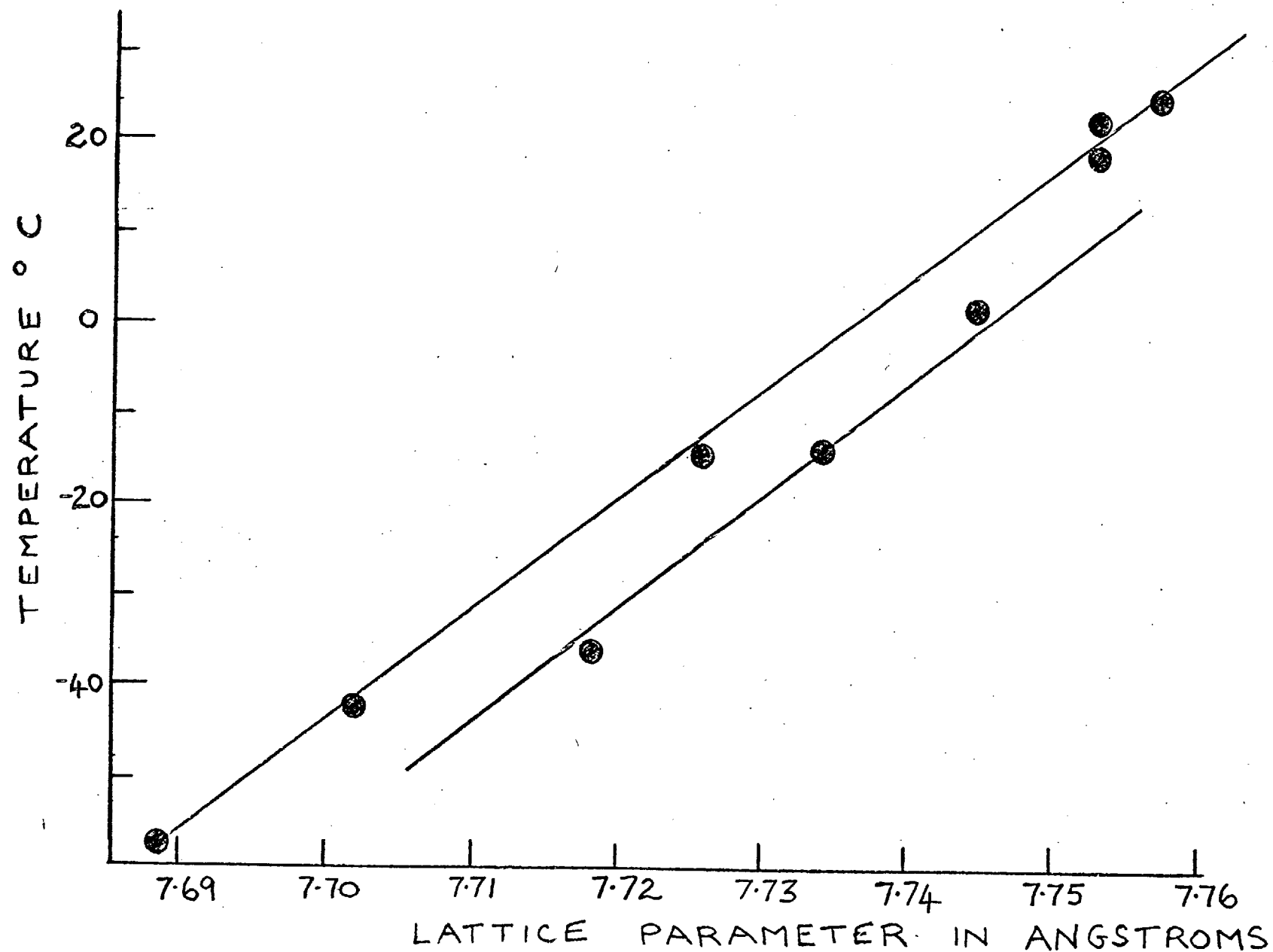
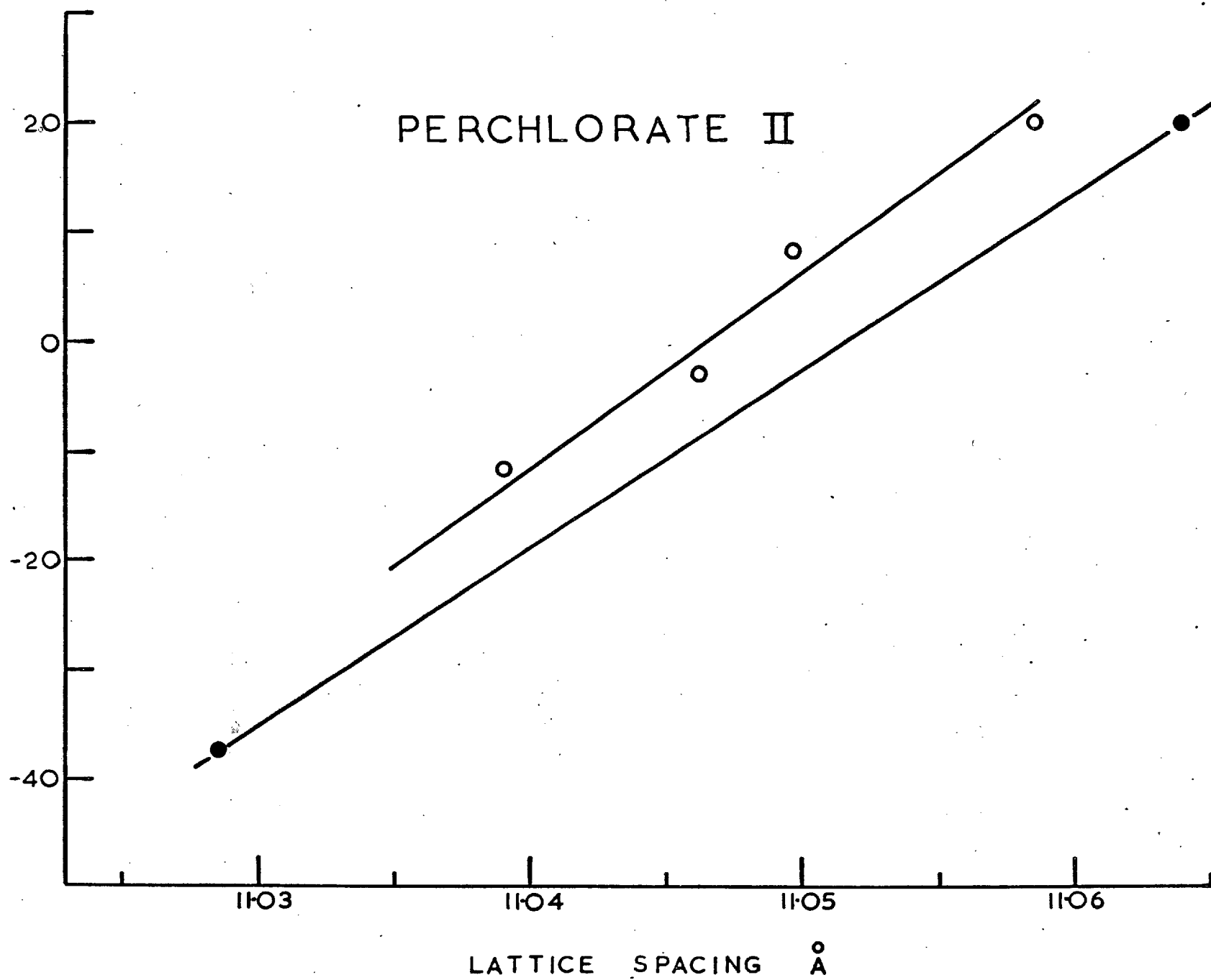


FIG.5.21. THERMAL EXPANSION OF GRAPHITE



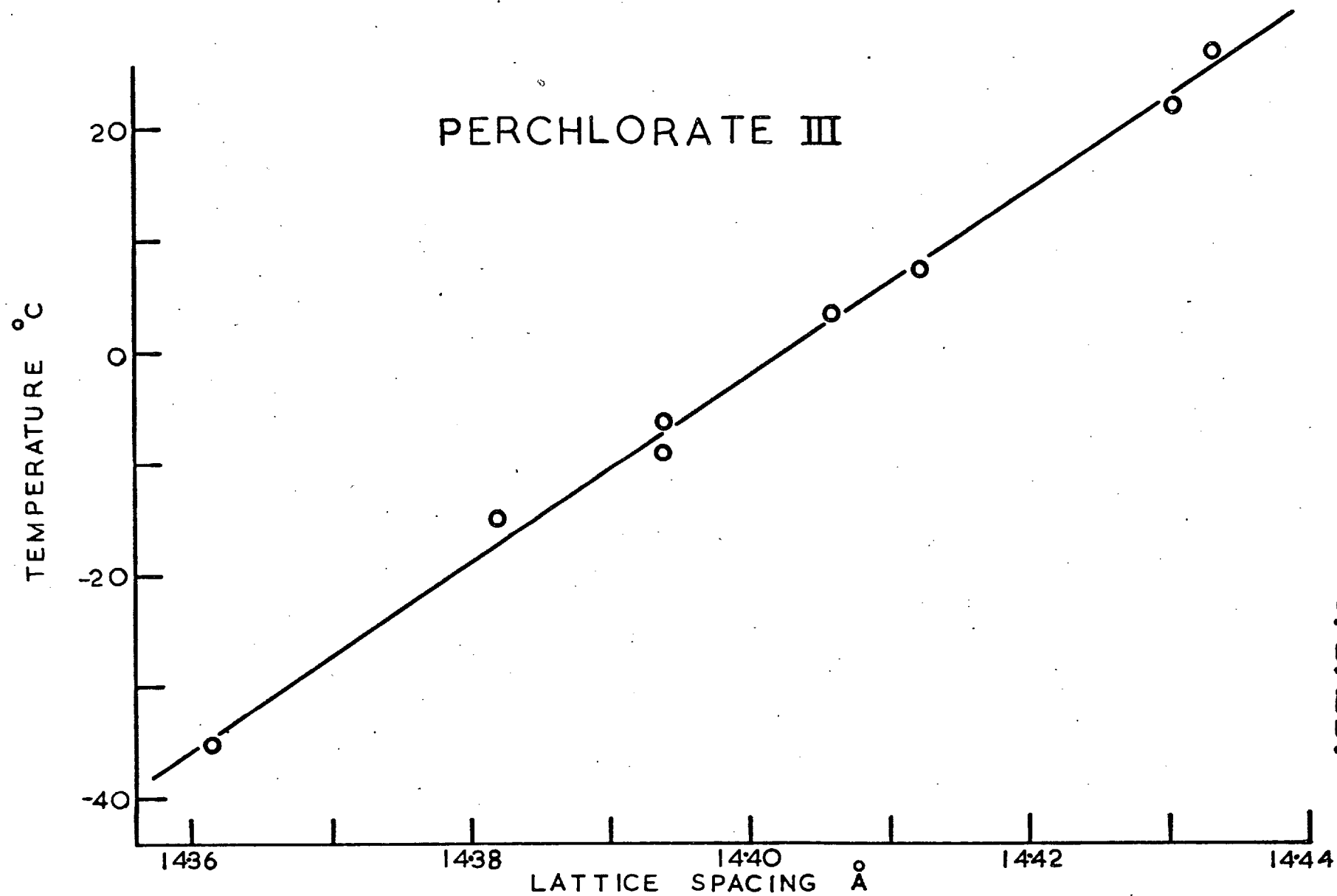


FIG. 5.23.

SHAPE OF PERCHLORATE III OO14 REFLEXION

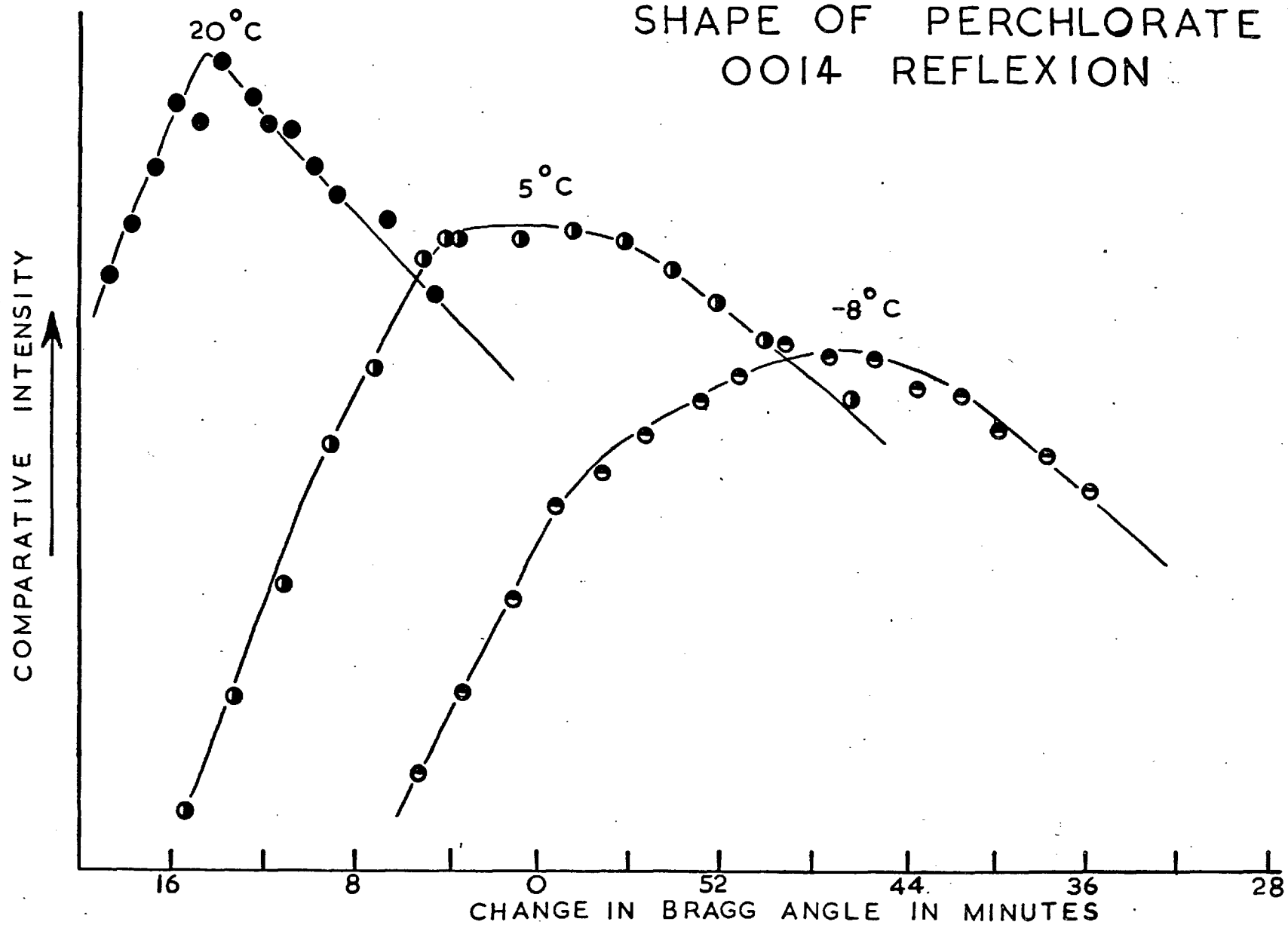
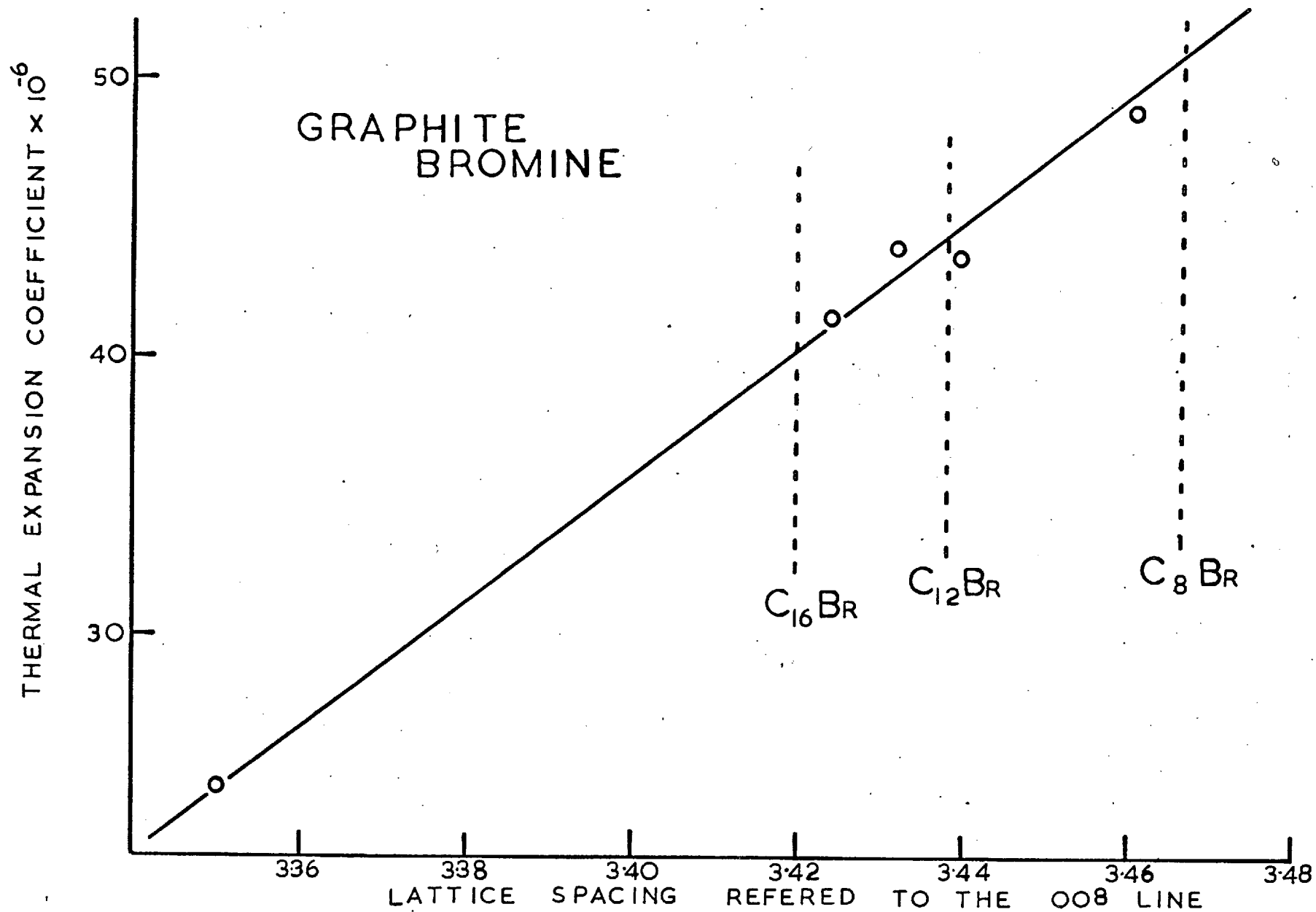


FIG. 5.24.



POTASSIUM GRAPHITE

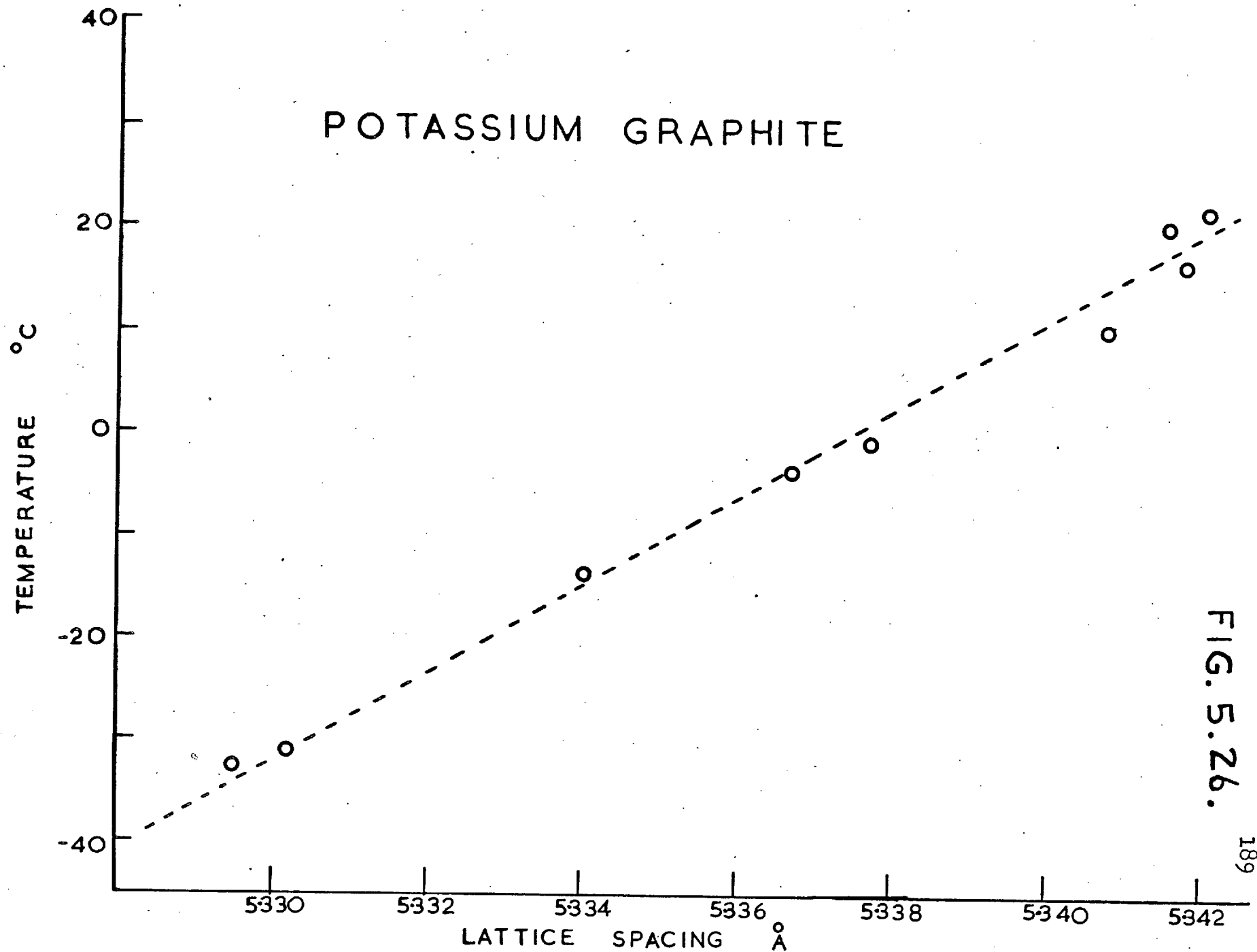


FIG. 5.26.

CAESIUM GRAPHITE

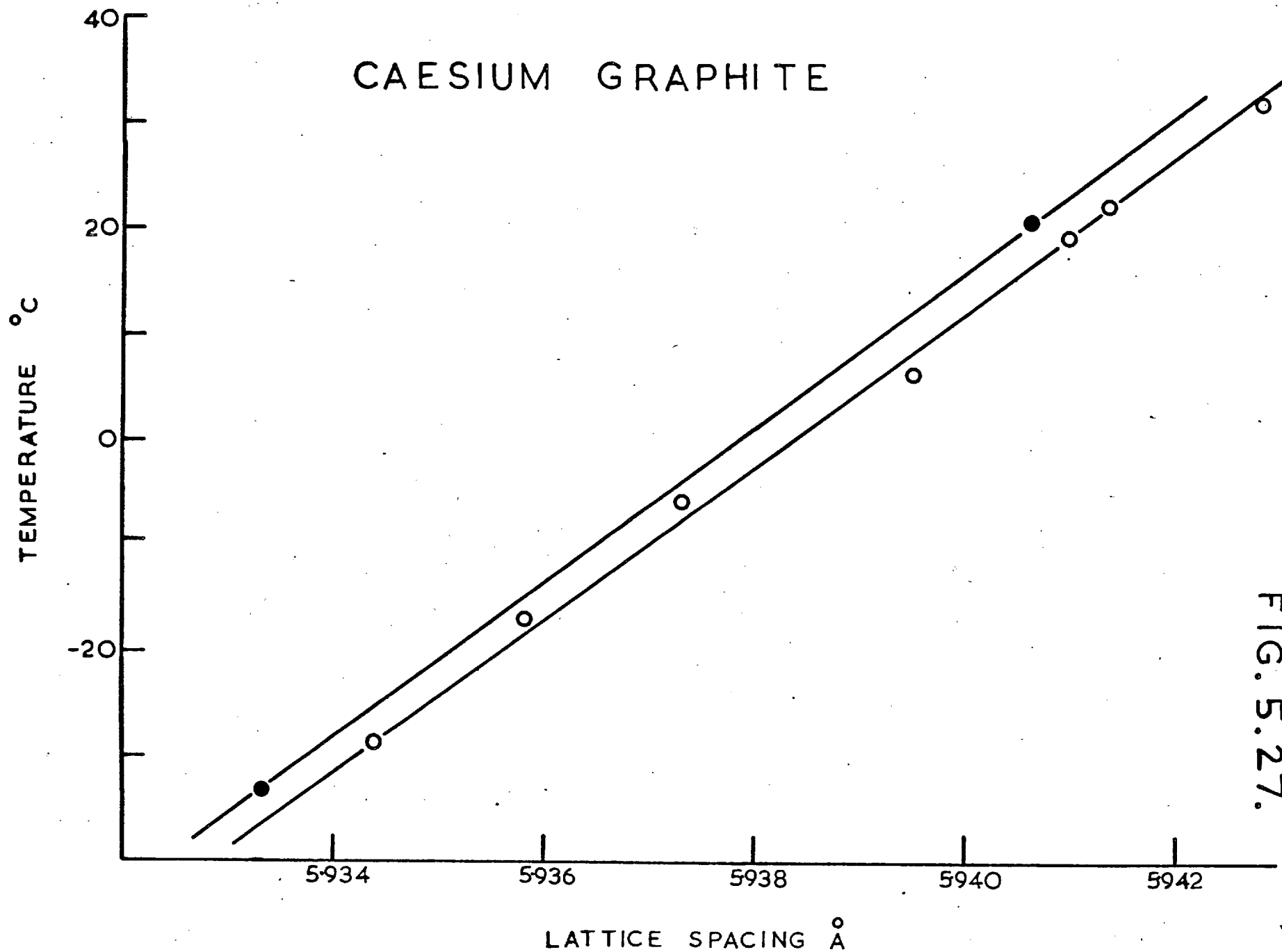


FIG. 5.27.

Chapter 6: DISCUSSION

6.1 The preparation of graphite compounds from pyrolytic graphite

In general there was little difference between the reaction of pyrolytic graphite and the powdered or flake graphites which had been studied previously. For the alkali metal and metallic chloride compounds similar methods to those reported for powdered graphites were completely successful in forming compounds. The formation of a bromine compound from pyrolytic graphite was studied in some detail and it seems likely that the reaction takes place in two steps. Firstly, an absorption step in which the expanded graphite matrix is filled with a random arrangement of bromine species. Secondly, an ordering process of some kind which stabilises the intercalated bromine. At low bromine concentrations such as those found in the vapour then the second process appears to occur at a comparable rate to the intermediate step. The occurrence of "picture frames" in the bromine compound and also in FeCl_3 (Hooker, 1964) supports the idea of formation in two distinct steps but at present the nature of these two steps is uncertain.

In the case of the acid salts of graphite the use of pyrolytic graphite resulted in a considerable extension of the electrochemical method of preparation. This method has not been used except to a limited extent for the preparation of graphite bisulphate; the principal limitation being the crumbling of the polycrystalline

electrodes as the compound formed. Pyrolytic graphite is ideal for this method of preparation because all the expansion during compound formation takes place in one direction and no crumbling of the electrode occurs. The method has the additional advantage that it can be carried out at room temperature whereas some chemical preparations require higher temperatures. Further, it is fairly simple to follow the course of the reaction by using a reference electrode and recording the potential between the reference electrode and the sample of compound. Knowledge of the extent of the reaction is very useful in the preparation of lower sequence compounds and this method is particularly suitable for these compounds. One of the principal disadvantages is that the oxidation may be carried too far. This produces decomposition of some compounds, notably the perchlorate and selenate; it is best overcome by using a low driving potential.

The method has proved particularly useful for the preparation of the bisulphate, perchlorate, selenate, chlorosulphate and fluorosulphonate, but it could be extended to the preparation of any acid salt which can be prepared chemically. In addition, the preparation of the complex alkali metal amine compounds should also be possible. (Preliminary studies on the lithium methyl amine system indicated that this method could be applied but that very dry conditions would be necessary.)

6.2 The structure of graphite compounds prepared from pyrolytic graphite

As a result of the development of preparative techniques for the graphite compounds it was often necessary to take x-ray diffraction photographs to characterise the samples. These photographs have yielded some interesting new information about the structure of some graphite compounds for which previous work was limited to results obtained on powder samples.

The nature of the pyrolytic graphite enables photographs to be taken which are very similar to single crystal rotation photographs with the axis of rotation parallel to the c-axis. The details which have been noted in the various groups of compounds are discussed below.

6.2.1 The Acid Salts

Good diffraction photographs were taken of the bisulphate, perchlorate and nitrate compounds. In all these photographs, hkl reflexions were well defined and indicated ordering of the graphite layers with respect to each other. Thus all the acid salts consist of an expanded graphite matrix which maintains an ordered stacking sequence. In the nitrate and perchlorate compounds only a diffuse band parallel to the c-axis is observed with a larger spacing than the hkl reflexions corresponding to the a-axis graphite spacing. Thus no three dimensional ordering of the intercalate appears to be present in these compounds. In the case of the bisulphate first

sequence however, an additional row of spots with an a-axis spacing larger than that of graphite is clearly visible (Plate 4.1b). Thus the structure of the first sequence bisulphate consists of intercalate layers which are ordered with respect to each other. This is in agreement with the structure previously reported for samples of the same compound prepared from powdered graphite (Rüdorff, 1939). The lower sequence bisulphate compounds do not show the "ordered intercalate" reflexions and appear to have similar structures to the nitrate and perchlorate compounds.

In the second sequence nitrate compound there is an interesting splitting of one of the reflexions associated with the graphite matrix. This splitting means that the unit cell proposed by Rüdorff, with a c-axis repeat distance of $2 \times 11.13 \text{ \AA}$ cannot completely represent the actual structure found in this work. This double reflexion, which occurs in all photographs of the second sequence compound would require a more complicated c-axis stacking sequence than the expected ... ABIBAIABIBA ... The first sequence compound does not show any additional reflexions and it seems likely that the graphite matrix has the ... AAAA ... stacking postulated by Rüdorff.

6.2.2 The Alkali Metal compounds

The x-ray diffraction photograph of the first sequence potassium compound shows very clearly the extra super-lattice reflexions which conform to a lattice repeat distance in the a-axis which is

twice that of graphite. This is in complete agreement with the previous results for powdered graphites and supports the three dimensional ordering of the intercalate layers. In the second sequence compound there are no discrete super lattice reflexions, but a diffuse band parallel to the c-axis is clearly defined (Plate 3.1c). Thus in the second sequence the intercalate layers are not ordered with respect to each other; only the graphite matrix is ordered. The rubidium and caesium first sequence compounds which had previously been thought to be very similar to the potassium compound did not show the same pattern of super lattice reflexions. Instead of systematic absences in the superlattice pseudo layer line for $l = 4n$, there were systematic absences for $l = 3n$. This result suggested that the intercalate layer arrangement might repeat every three layers instead of every four layers. A detailed consideration of the evidence for the fourfold repeat in the caesium and rubidium compounds showed that the observed powder pattern (Schleede and Wellmann, 1932) could also be fitted to a three fold repeat. Thus the first sequence caesium and rubidium compounds have a threefold repeat unit in the c-axis resulting in a unit cell of about $17 \overset{\circ}{\text{A}}$. There is no obvious reason for a change in stacking sequence in these compounds; the larger cations have still a considerable separation in the c-axis direction. Both the potassium and caesium structures were stable for the respective compounds between -150°C and $+150^{\circ}\text{C}$ and it was not possible to induce a transformation

from one form to the other.

6.2.3 Molecular compounds

The second sequence ferric chloride graphite compound, which is the only compound with the metallic chlorides that has been studied in detail, appears to contain an ordered graphite matrix. This does not agree with the previous reports of the structure (Cowley and Ibers, 1956) which indicated a completely random arrangement of the carbon layers. The x-ray diffraction photograph does not show any discrete super lattice reflexions but there is a diffuse pattern of scattering. This has been explained by Cowley and Ibers as resulting from preferred positions of the chlorine atoms with respect to the graphite matrix. The photographs obtained in this work do not support this and the origin of this diffuse scattering appears to be the individual sandwiches of chlorine-iron-chlorine which make up the intercalate layers.

The structure of the bromine compound is still not completely understood. The a-axis repeat distance is large; spacings up to 8.5° Å have been recorded for compounds using pyrolytic graphite as starting material and recent work (Eeles, 1964) suggests that the largest a-axis spacing is 17° Å. Diffractometer studies of the 001 reflexions showed the existence of third and fourth sequence compounds which have not previously been reported.

In conclusion it must be stated that some of the above discrepancies between the structure of compounds formed from pyrolytic

graphite and other forms of graphite may have arisen as a result of the difficulties of analysing powder diffraction photographs for such complex crystals (of the caesium and rubidium compounds and the second sequence nitrate compound). Taking the specific example of the splitting of the reflexion in the second sequence nitrate compound, it is unlikely even if this reflexion was in fact split that this would be apparent from a powder photograph. There is considerable scope for the study of some of these compounds in more detail. Specifically, the caesium compound prepared from single crystal graphite would provide confirmatory information for the stacking sequence proposed. Similarly an investigation of the molecular compounds prepared from various types of graphite might help to clarify the point as to whether different graphites result in different compounds.

6.3 Thermal Expansion

6.3.1 The Thermal Expansion of Graphite

The values for the thermal expansion coefficient of pyrolytic graphite obtained in the two cells are compared with previous workers in Table 6.1

TABLE 6.1

Details of Sample and results	Temperature range	Thermal Expansion Coefficient $\times 10^6$
Hot-pressed pyrolytic graphite in cell 1	$30^{\circ}\text{C} - -50^{\circ}\text{C}$	25.2
Inner layers of thick deposit in cell 2	$30^{\circ}\text{C} - -50^{\circ}\text{C}$	24.7, 24.9
Extrapolated value from theoretical calculations of Riley (1945)	extrapolation of smoothed curve to 0°C	24.5
Steward and Cook, 1960	$15 - 800^{\circ}\text{C}$	28.4
Matyama, 1955, 1958	at 0°C	24.6
Entwisle, 1962 Pyrolytic graphite	$-196^{\circ}\text{C} \pm 20^{\circ}\text{C}$ $20^{\circ}\text{C} \pm 120^{\circ}\text{C}$ $100^{\circ}\text{C} - 700^{\circ}\text{C}$	19.5 24.6 28.3

The most valid comparison with the present work are the results of Entwisle (1962) which were obtained by macroscopic measurements on pyrolytic graphite. For the range of the present results ($-50^{\circ}\text{C} - 20^{\circ}\text{C}$) a value of $22-23 \times 10^{-6}/^{\circ}\text{C}$ was found and this is in fair agreement with the values of $25 \pm 1 \times 10^{-6}/^{\circ}\text{C}$ determined in the present work. If the graphite contains any macroscopic defects or misalignments, then a slightly higher value might be expected from the x-ray method.

In the present work measurements made on Type AB and on hot

pressed material gave essentially the same results. The principal difference between these two graphites is in the orientation of the crystallites in the c-axis. Thus type AB has a spread of c-axes of the crystallites of about $10-15^{\circ}$ whereas hot pressed material has a spread of only $1-2^{\circ}$. The carefully selected Type AB inner material can be expected to be better than the average but a spread of $5-10^{\circ}$ might still exist. As the x-ray method of measuring thermal expansions selects only those crystallites that are in the correct orientation this close agreement is not unexpected. There may be a slight difference in the c-axis expansion of these two materials if macroscopic measurements were to be compared.

6.3.2 The thermal expansion of graphite compounds

The consideration of the thermal expansion of the graphite compounds can be broken down into three sections:

- (a) The comparative values of the expansion coefficients of various compounds
- (b) The comparative values of the expansion coefficients of various sequences of the same intercalate
- (c) Any anomalies, either arising from thermal effects or from other sources.

Discussion of the second group of results is best considered before the others.

6.3.2.1 The thermal expansion of different sequences of the same compound.

The good agreement of the lattice spacings of the lower oxidation state compounds with theoretical values calculated by addition of the first sequence spacing and n graphite spacings has suggested the hypothesis that graphite compounds can be considered as composed as layers of atoms, each layer retaining its own properties. Thus the assumption of a general expression for the lattice spacing of the n^{th} sequence compound C_n given by

$$C_n = C_1 + (n-1)3.35$$

where C_1 is the spacing of the first sequence compound, tests this hypothesis at a simple level. In Table 4.1, the reduced lattice parameter $C_n - (n-1)3.35$ which should be constant is listed for various compounds. The consistency of the reduced parameter is good, but deviations do occur, particularly noticeable are the discrepancies in the reduced parameters of Rüdorff's values for the perchlorates. The present values fit in much better, but as discussed later, the perchlorate compound appears to behave in anomalous ways at times and the spacings found by Rüdorff cannot be considered as suspect.

As a further extension of this idea, the first sequence compound can be considered as being composed of the intercalate and of graphite. Thus in the ferric chloride compound, good agreement is obtained between the spacing of one ferric chloride layer and

one graphite layer $5.80 + 3.35 = 9.15 \text{ \AA}$ and the actual compound spacing, $9.4 \text{ \AA}$. However this does not apply in general and in the alkali metal compounds considerable deviations are found, see Table 6.3. Thus the intercalate sandwich can only be considered as composed of an intercalate layer and a graphite layer when the interaction between the two is very weak i.e. in the molecular compounds. In all other cases the more general model which assumes additivity of filled and empty layers must be resorted to.

The agreement of the calculated and experimental values of the lattice parameters for the compounds based on this model suggests that the expansion of a filled layer is independent of the sequence of the compound as far as can be determined at the present level of accuracy. A logical extension of the hypothesis is to check the agreement between the experimental values and similar calculations for the thermal expansion. Here it is necessary to assume that the expanded or filled layer has an expansion α_I and that the graphite layer pairs retain the expansion of graphite $\alpha_G = 25 \times 10^{-6}/^\circ\text{C}$. Hence we have for the expansion coefficient of an n^{th} sequence compound $\alpha_n = \frac{C_0 \alpha_I + 25 \times 3.35 \times (n-1)}{C_n}$

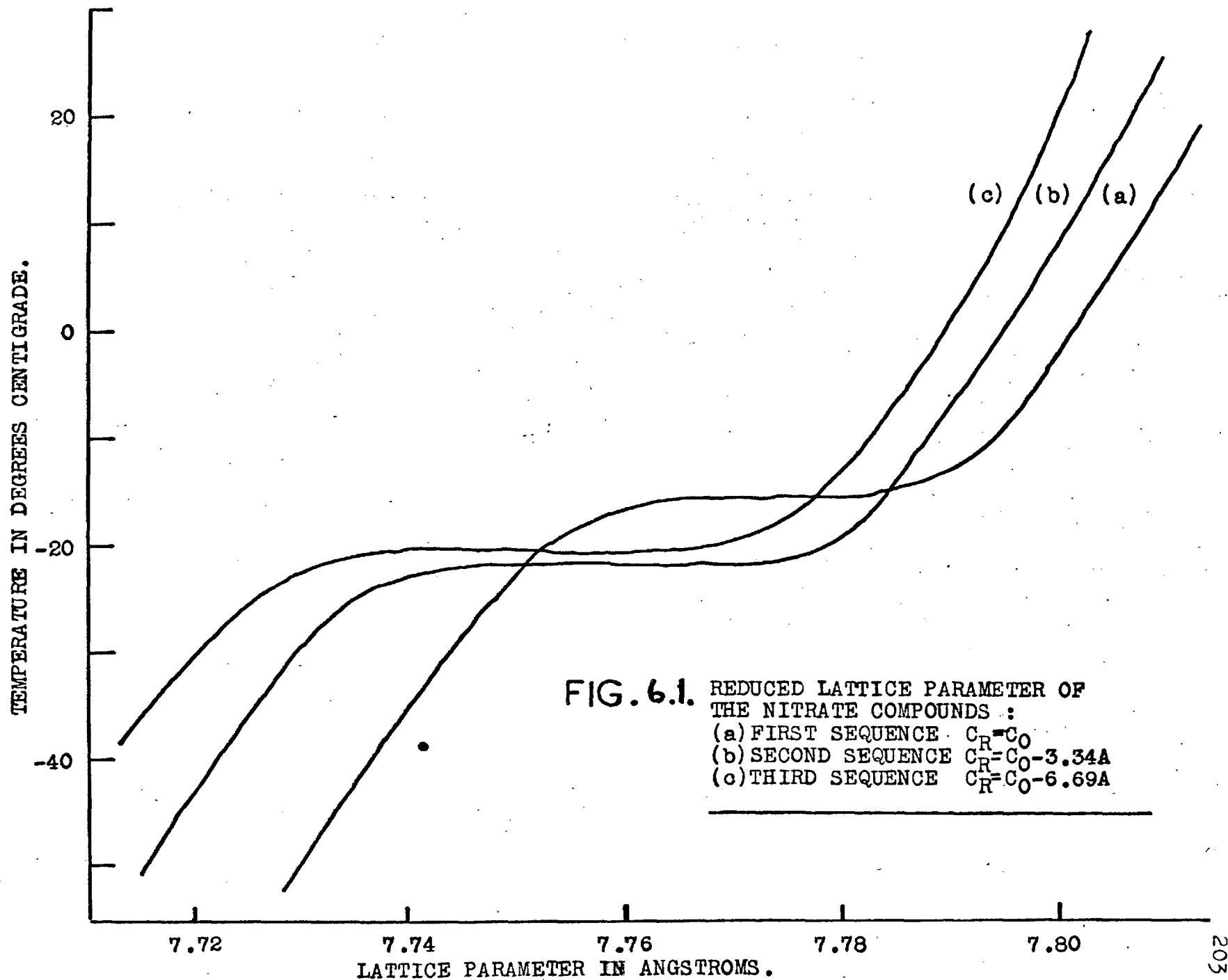
where C_0 is the lattice spacing of an intercalate layer and can be taken as the mean value of the reduced lattice parameter for that compound. Thus a reduced thermal expansion coefficient can be calculate equal to $\frac{\alpha_n C_n - 25 \cdot 3.35 (n-1)}{C_0}$ and this is strictly

comparable for a series of compounds of a given intercalate.

The reduced thermal expansion coefficients are listed in Table 6.2 for the nitrates, bisulphates and perchlorates. The reduced lattice parameters are also plotted against temperature in Fig. 6.1 and 6.2 for the bisulphateⁿ and nitrate respectively.

TABLE 6.3.

	Li	Na	K	Rb	Cs
C-axis spacing	-	4.58	5.34	5.65	5.94
Ionic Diameter	1.56	1.96	2.66	2.98	3.30
Atomic Diameter	2.66	3.14	4.06	4.32	4.70
C-M	-	2.62	2.68	2.67	2.64
C-M	-	1.44	1.28	1.33	1.24
Compound	-	-	44	36	25
Fluoride	34	36	37	-	32
Chloride	44	40	38	36	50
Bromide	50	43	40	38	60
Iodide	59	48	45	43	55



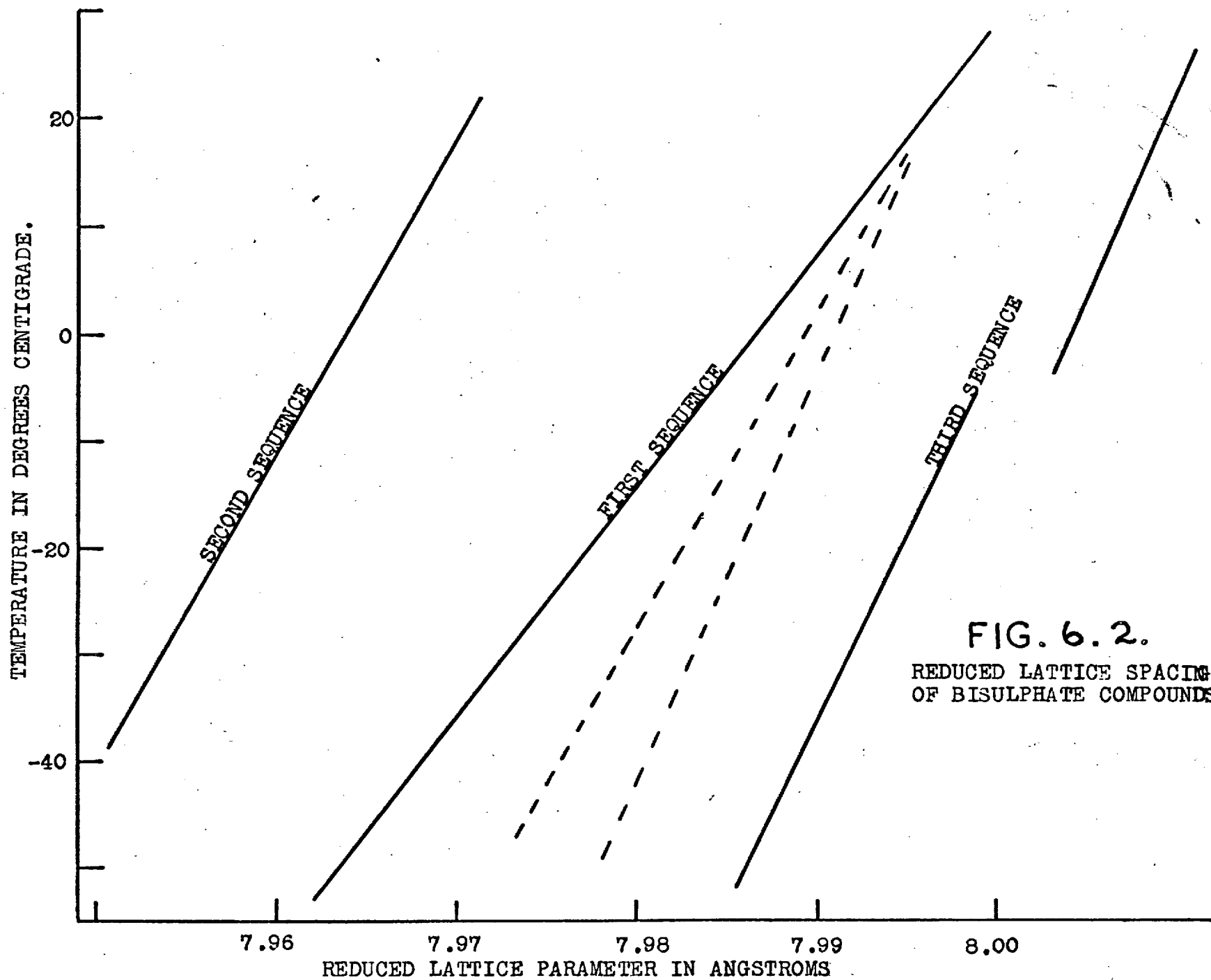


TABLE 6.2

	n	Nitrate above -20°C	below -30°C	Bisulphate	Perchlorate
First sequence	1	84	94	61	95
Second sequence	2	78	92	50	67
Third sequence	3	81	99	44 38	

It is apparent from the reduced lattice parameter plots that in the nitrate the additivity model holds and the general behaviour of the intercalate layer is similar irrespective of the sequence of the compound whereas in the bisulphate considerable differences exist. This is supported by the reduced thermal expansion values in Table 6.2. Unfortunately in the case of the alkali metal compounds it is not possible to apply this treatment as the expansion coefficients are too close to that of graphite for any definitive conclusions to be drawn (see earlier).

It appears from the above discussion that there is a gradual transition from the case of the ferric chloride compound where only weak interactions are present between the intercalate layer and its adjoining graphite layers, to the bisulphate compound where strong interactions of an intercalate layer both with the graphite layers and the adjacent intercalate layers must exist. The presence of long range forces is not altogether surprising in consideration of the formation of 'sequences' in these compounds. For a regular stacking of filled and unfilled layers to occur

there must be some interaction between intercalate layers.

This is emphasised even more by the formation of three dimensionally ordered compounds.

6.3.2.2. The Thermal Expansion of First Sequence Compounds

The thermal expansion of graphite compounds can only be given limited interpretation in the absence of data regarding the C-axis compressibility and the specific heat. Even with the present range of data there are however some points which can be made. Perhaps the simplest interpretation which could be given is that the expansion is proportional to the separation of the graphite layers. In Fig. 6.3 the graphite layer separation is plotted against the expansion coefficient for those compounds studied. There is obviously no simple relation between these quantities and although those compounds with larger spacings tend to have larger expansions than those with smaller spacings the alkali metal compounds contradict this. The c-axis lattice parameter may therefore have some influence on the thermal expansion but it is not the overriding factor.

The overall interpretation of the results is very difficult; it therefore seems logical to consider the series of alkali metal compounds apart from the others to see if any conclusions can be drawn from this relatively simple series.

When the thermal expansions of these three compounds are compared with those of the alkali halides there is a considerable

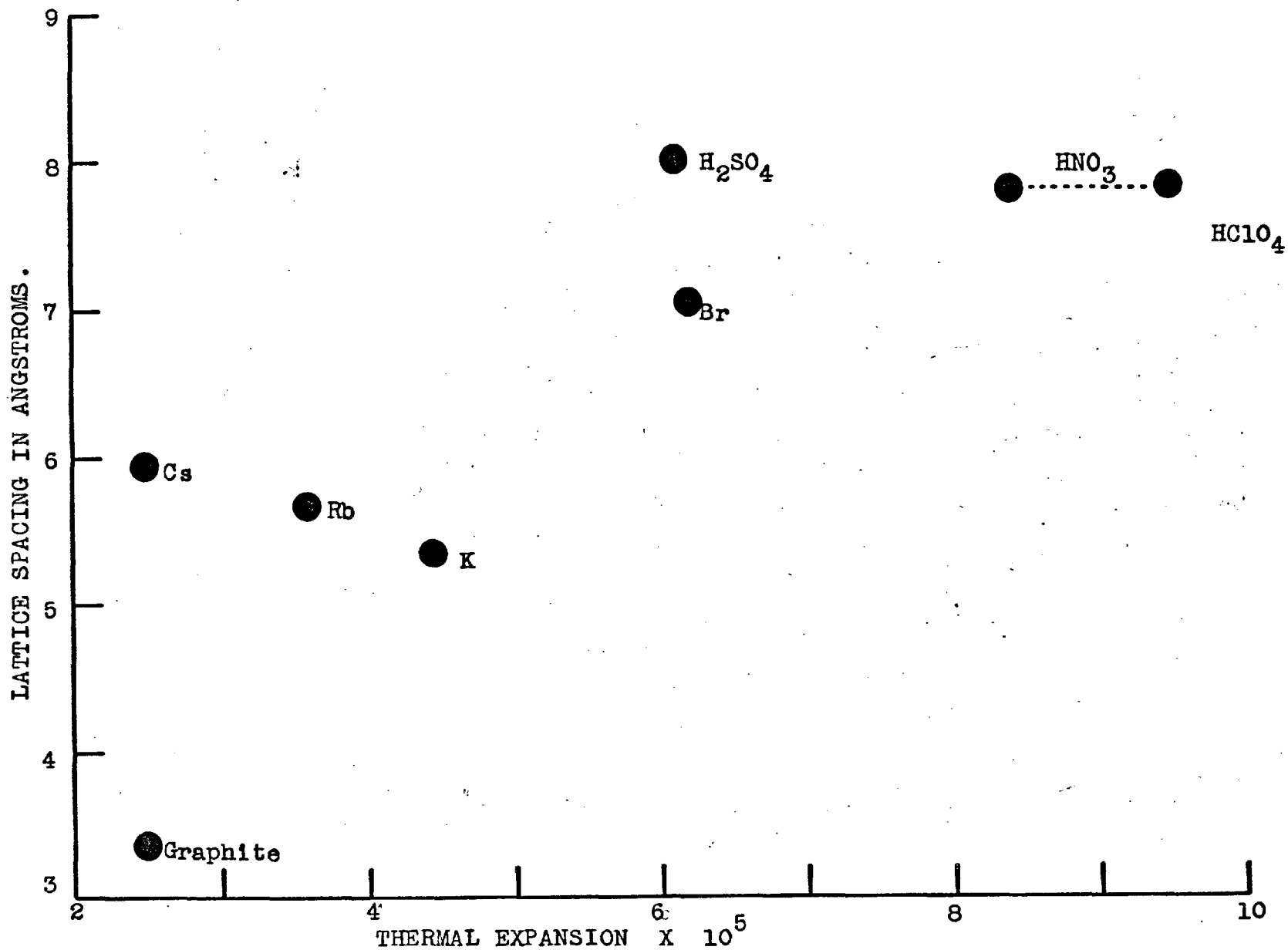


FIG.6.3. THERMAL EXPANSION COEFFICIENTS PLOTTED AGAINST LATTICE SPACING

difference in the range of expansion coefficients. The change in expansion from potassium to caesium in the compounds is much larger than in the alkali halides. However the consistent value of $C - M^+$ for the compound of approx. $2.65 \text{ \AA}$ suggests that no radical change in bonding takes place and thus the large difference cannot arise from this source. Further it indicates that macro anions of approximate thickness $2.65 \text{ \AA}$ exist (this is in reasonable agreement with the analogous F^- with a diameter of $2.72 \text{ \AA}$). However it has been suggested that only about one third of the intercalate species are charged (Hennig 1956) and therefore the straightforward model of carbon macro anions with the intercalate as cations is not totally acceptable. If the bonding in the three compounds is similar then the general shape of the potential well in the energy versus atomic separation curves should also be similar. However the differing values of the thermal expansion indicate that this is not the case and that the caesium compound has a much narrower potential well than the potassium compound.

One way in which a narrower potential well can arise, apart from a direct change in force constant, is when the attractive forces obey a higher order relation than the $\frac{1}{r}$ of the ionic attraction. Thus if the repulsion forces are taken to be of the general form A/r^n where n is approximately 10 - 12 then a resultant potential of the form $A/r^n - B/r^m$ will have a narrower well than the resultant potential of the ionic attraction $A/r^n - C/r$ and

hence will have a smaller thermal expansion. This is shown graphically in Fig. 6.4 where the functions $\frac{1}{x^{12}} - \frac{1}{x}$ and $\frac{1}{x^{12}} - \frac{1}{x^6}$ are plotted. The general curve $\frac{1}{x^{12}} - y \cdot \frac{1}{x} - (1-y) \frac{1}{x^6}$ where y is less than one must lie between these two limiting curves.

Thus the potential well will become narrower if the Van der Waals bonding increases and the ionic bonding decreases. Hence although the overall strength of bond may remain very similar the thermal expansion may be considerably altered.

The occurrence of an attractive force with a potential of the type $\frac{1}{r^m}$ is to be expected in all compounds for the dispersion or Van der Waals forces. These forces were first considered by London 1930 and principally arise from dipole - dipole attractions but also involve terms due to dipole - quadrupole and quadrupole - quadrupole attractions. The general form of this interaction is $\frac{p}{r^6} + \frac{q}{r^8} + \frac{r}{r^{10}} \dots$ and is a close approach to the type of potential required to narrow the potential well.

The dispersion forces normally however play a relatively small part in the crystal energy of ionic crystals; approximately 2% in the alkali halides and up to 10% in the silver halides. In the graphite compounds in which the ionic bonding is relatively weak these forces may play a considerably more important role and a contribution up to 50% might be possible.

If the contribution of these forces increased from the potassium compound to the caesium compound then the narrowing of the

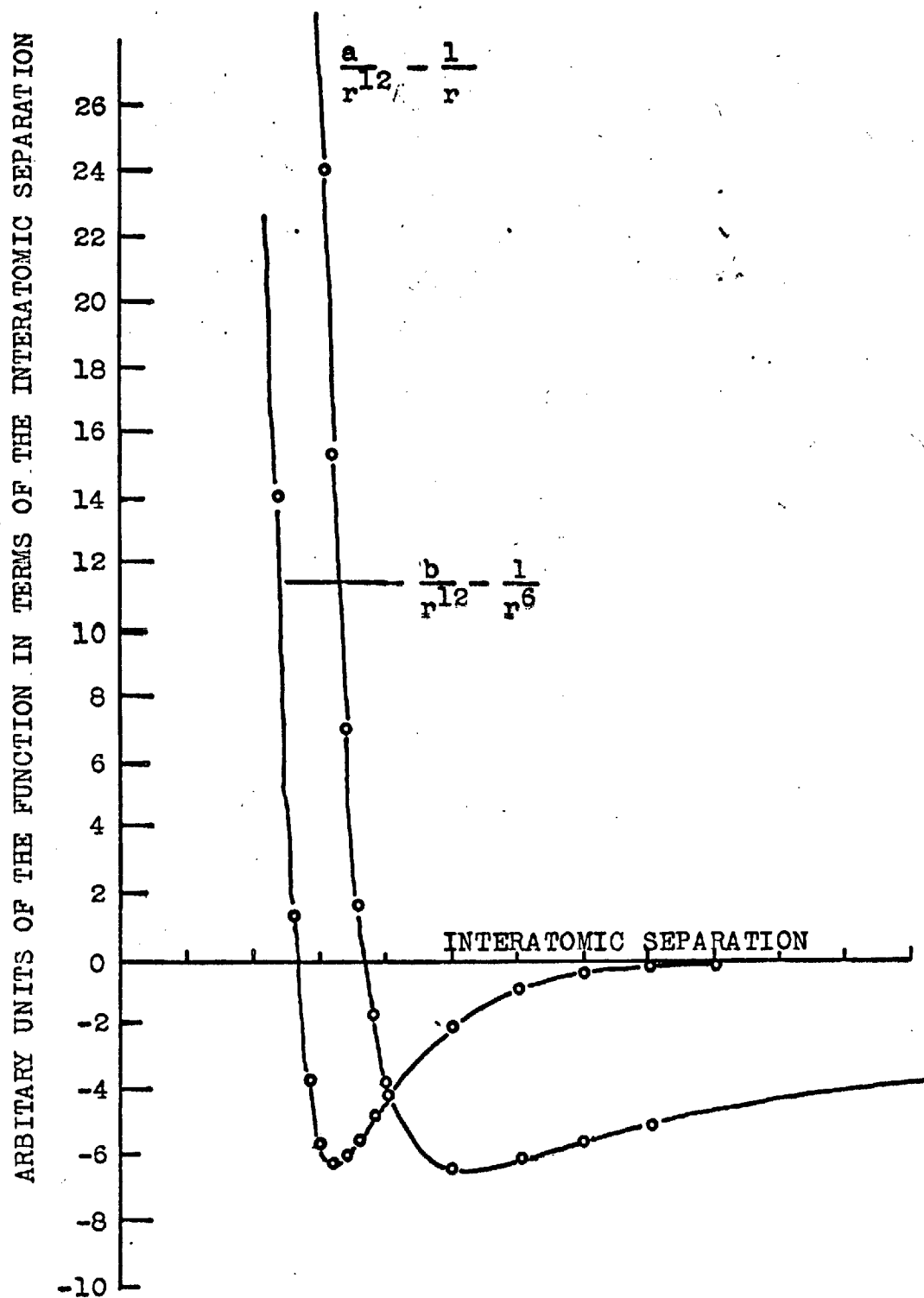


FIG. 6.4. CURVES OF THE GENERAL FUNCTION $\frac{a}{r^{12}} - \frac{1}{r^n}$

potential well which the experimental results suggest can be explained. Thus an assessment of the relative contributions of Van der Waals forces in these compounds is required. This can be obtained approximately by a consideration of Van der Waals force constants for the rare gases; these are Ne 4.67 A 55.4 Kr 107 Xe 233 x 10⁻⁶⁰ ergs cm⁶. It is immediately apparent that the Van der Waals contribution to the energy is larger in the heavier rare gases. The contribution of the Van der Waals energy between two atoms is given theoretically by $3 \frac{\mu_a \mu_b}{2R^6} \frac{U_a U_b}{U_a + U_b}$

where μ_a and μ_b are the polarisabilities of the atoms and U_a and U_b can be related to the ionisation energies of the atoms (Pitzer 1959). For the graphite compounds where μ_a and U_a are constant this reduces to:-

$$\text{Const.} \frac{\mu}{r^6} \frac{U_a U_b}{U_a + U_b}$$

where μ is the polarisability of the alkali metal species.

No quantitative relation between this formula and the thermal expansion can be expected because the Van der Waals forces are not the only attractive forces involved in the compounds.

There should however be some qualitative connection between the quantity $\frac{\mu}{r^6}$ and the reciprocal of the thermal expansion if this bonding is important. The term $\frac{\mu}{r^6}$ is plotted against the reciprocal of the thermal expansion in Fig. 6.5 using the polarisabilities due to Fajans & Joos (1924) K⁺ 0.88 R_b⁺ 1.56 C_s⁺ 2.56.

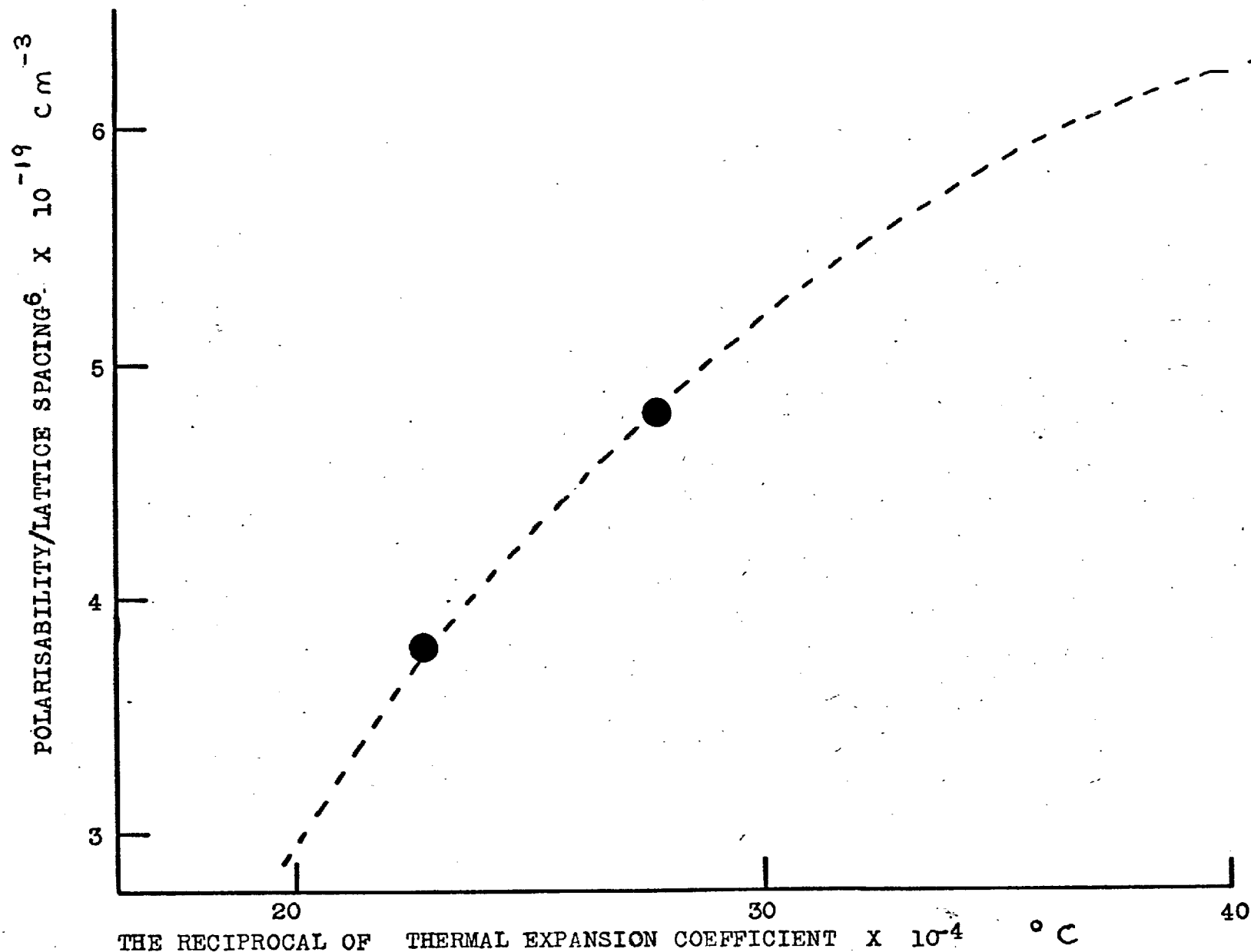


FIG. 6.5. THERMAL EXPANSION PLOTTED AGAINST POLARISABILITY.

Thus the thermal expansion behaves as an inverse function of the term $\frac{M}{r^6}$; the considerable change in thermal expansion coefficient in this series of compounds can therefore be explained by a variation in the Van der Waals contribution to the overall attractive forces. This discussion is at present only extended to the ionic intercalate between large carbon anions. However it has previously been noted that the structure of the alkali metal compounds cannot be considered as wholly ionic.

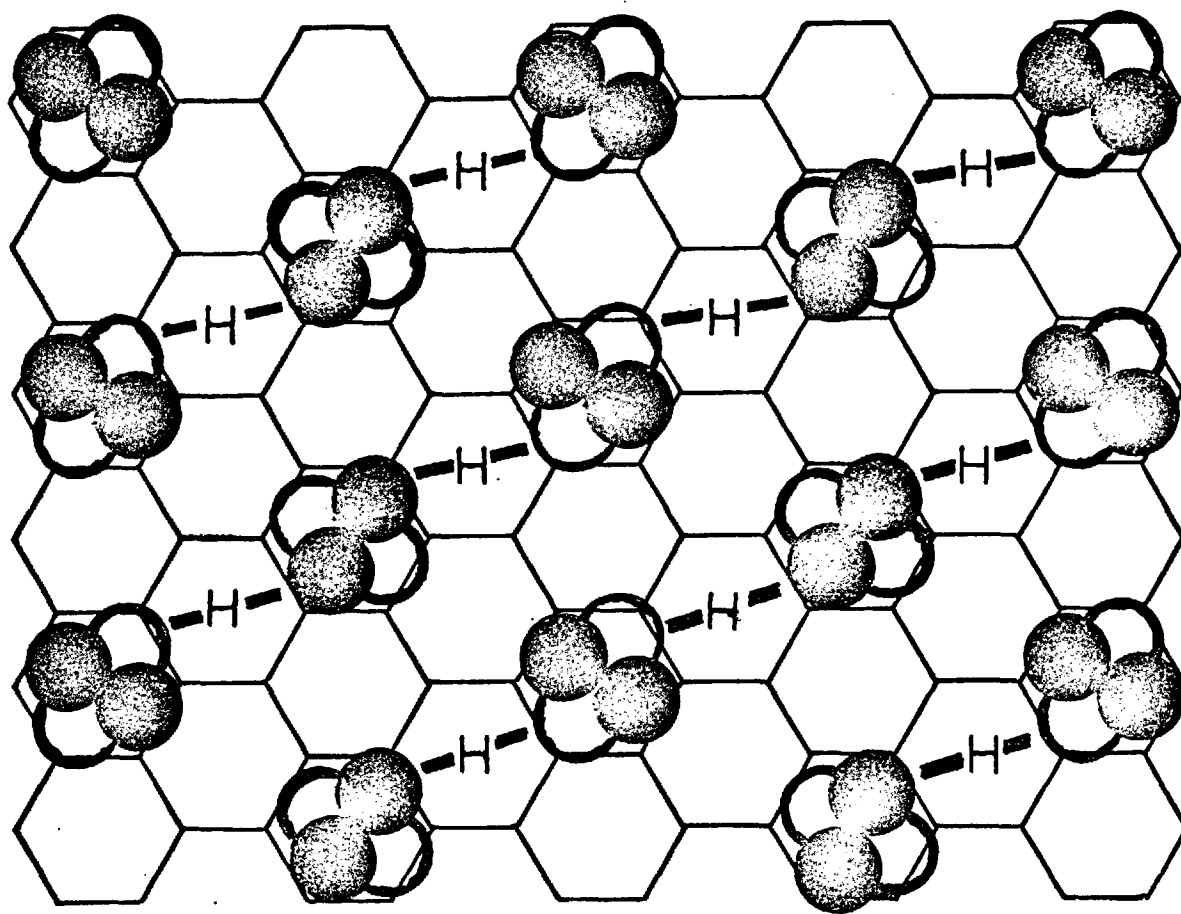
This point opens a new problem in that the polarisabilities of the atoms are much higher than the polarisabilities of the ions. The values quoted are not consistent (Leibfried Vol. I Pt. I 401) but are 20 - 40 times the ionic polarisabilities. Although some of this increase will be offset by a corresponding decrease in ionisation potential there will be a considerable difference in the Van der Waals forces operating between the carbon layers and ions or atoms in the intercalate layer. This means that if the ratio of atoms to ions, which has not yet been accurately investigated, varied from the potassium to the caesium compound then this could influence the strength of the Van der Waals bonding to quite a large extent. Very little extension of this point can be made as neither the ratio of ions to atoms is known nor is the ionisation potential of a graphite layer available.

A much simpler interpretation of the decrease in thermal expansion from potassium to caesium can be obtained from a

consideration of the nature of these compounds as large heavy layers of carbon atoms separated by relative light atoms of the intercalate. The intercalate atoms will be able to 'rattle' between the layers; the extent of the rattling will depend on the force constant in the C-axis direction. The increase in Van der Waals bonding in the caesium compound will increase the force constant and hence decrease the amplitude of oscillation of the intercalate. Although the thermal expansion does not directly depend on the amplitude of vibration the anharmonicity of the vibration is limited to a first approximation by the amplitude. This argument can be extended to the acid compounds of graphite whereas the previous theory is difficult to extend to these salts.

A similar large difference to that noted above is noticeable in the thermal expansion coefficient of the bisulphate and perchlorate compounds. These two salts are reported to have similar structures and in view of this large difference in thermal expansion is unexpected.

A possible source of this difference in behaviour lies in the properties of the intercalate layer. In the hypothetical bisulphate compound $C_8 HSO_4$ it is possible to produce a hydrogen bonded structure with long chains of molecules (Fig. 6.6). With the actual structure $C_{24} HSO_4 \cdot 2H_2SO_4$ the extra hydrogen bonds available will allow cross bonding of these chains and a bonded network parallel to the graphite planes will be formed.



THE STRUCTURE OF THE HYPOTHETICAL
 FIG. 6.6. COMPOUND $C_{24}HSO_4 \cdot 2HSO_4$ SHOWING
 POSSIBLE HYDROGEN BONDS

It is not possible to produce a cross bonded network with less than one hydrogen bond per molecule. Therefore the perchlorate and nitrate cannot have this type of bonded network as the maximum number of hydrogen bonds is only one for the intercalation of pure acid i.e. $C_8 HNO_3$ and $C_8 HClO_4$. (The probable number of hydrogen bonds is in fact less than one per molecule to be consistent with the formulae $C_{24} NO_3 \times HNO_3$ and $C_{24} ClO_4 \cdot y HClO_4$). Thus in the perchlorate and nitrate a rather similar pattern exists to that in the alkali metal compounds. There is the possibility of single molecules or small groups of molecules 'rattling' between the carbon planes. In the bisulphate the model is considerably different in that the intercalate is probably also a macro-ion. The thermal expansion of this model is more likely to be influenced by the overall lattice vibrations in the c-axis rather than the vibrations of the intercalate species and this could account for the much smaller thermal expansion coefficient of the bisulphate compounds. This difference in the nature of the vibrations which contribute to the thermal expansion could also influence the additivity of thermal expansion in the lower oxidation states. The overall lattice vibrations are likely to be influenced by the c-axis stacking whereas the vibrations of an intercalate species are not. Thus the graphite bisulphate thermal expansion in the lower order compounds would not necessarily be expected to be the sum of its

constituent parts. The perchlorate compounds do not fit in to this scheme of analysis particularly well. There is however a considerably greater spacial requirement for the perchlorate species as compared with the nitrate species which are flat and hence the rattling of the perchlorate species may be influenced by intercalate species in adjacent layers to a greater extent than in the nitrate compounds.

There is a second point which may be of some importance in these lamellar compounds and this is the Poisson effect. The expansion in the c-axis (α_c) can be expressed in the form:-

$\alpha_c = 2S_{13} q_x + S_{33} q_z$ where q_x and q_z are the thermal pressures in the respective directions. The second term is the intrinsic expansion in the c-axis direction whilst the first term is due to the Poisson contraction which arises from the intrinsic expansion in the a-axis direction. This Poisson contraction does not depend on the measured a-axis expansion which might be expected to be small but on the intrinsic a-axis expansion which may be relatively large compared with the measured value. The magnitude of this effect is difficult to calculate but for graphite Riley has calculated a contribution of the order of 50% of the measured c-axis expansion.

The Poisson contraction will depend on the a-axis arrangement of atoms and although in the crystal structure the intercalate atoms are 'tied' to the graphite layers in most

compounds the intercalate layer will have some influence on the a-axis mechanical properties. There is a considerable difference in the closeness of packing in the case of the alkali metal compounds (Table 6.4)

TABLE 6.4

	Distance of centres	less ion diam.	less atom diam.
K	↑	2.26	0.86
Rb	4.92	1.94	0.60
Cs	↓	1.62	0.22

and this difference may considerably influence the Poisson contribution to the c-axis expansion but it is not possible to estimate this effect. Similar arguments can be applied to the acid compounds where the hydrogen bonding will influence the Poisson contribution to the c-axis expansion.

The thermal expansion of the bromine compound is the only one which has been measured previously (Brocklehurst 1962, Martin & Brocklehurst 1964). These workers have studied the macroscopic thermal expansion of 'residue compounds' with approximate formulae $C_{50}Br$ but much of the work has been concerned with the exfoliation of graphite bromine which appears to start at about 100°C. Below this temperature the expansion was not measured accurately but a value of about 3 times that of graphite was estimated. This is

considerably higher than the present work would suggest for such a low oxidation state and is probably due to the onset of exfoliation at temperatures below 100°C. Results for the thermal expansion of graphite compounds obtained by macroscopic measurements will be subject to considerable error in some of these compounds because of their 'spongy' nature. In many cases the expansion measured macroscopically may largely be due to expansion caused by a similar mechanism as exfoliation or alternatively may be caused by expansion of the free acid in macroscopic pores and cracks in the compound. Thus the microscopic measurements of lattice expansion should prove to be far more reliable than macroscopic measurements.

6.4 Anomalies in the Thermal Expansion of Graphite Compounds

From the reduced lattice parameter of the nitrate compounds it is apparent that a transition of some type is taking place at a temperature of about -25°C.

The change in spacing of the intercalate layer for the three compounds is $.039\text{\AA}$, $.046\text{\AA}$ and $.048\text{\AA}$ respectively for the first, second and third sequences. The fact that the transition occurs at approximately the same temperature (-20 to -25°C) and produces the same lattice parameter change suggests that the anomaly is associated with the intercalate layer. If it was associated with a change in stacking sequence then the different number of graphite layers in each compound would be expected to have a considerable effect.

As the intensities of the $00\frac{1}{2}$ reflexions do not change drastically at the transition no appreciable alteration in the z -parameter of the nitrate molecules seems likely. Thus a rearrangement of the nitrate layer appeared to be a likely reason for this spacing anomaly and recent detailed study has shown that an order - disorder transition in the layer does indeed take place.

The thermal expansion of the nitrate compounds is slightly larger below the transition than above it. This may be a real effect or it may be associated with a premonitory change in the nitrate layer. The first and second sequence nitrate show a constant, but different, value for α both above and below the transition so it seems unlikely for these two compounds that the expansion is influenced by effects of this kind. The third sequence nitrate however does show a much more gradual transition to which premonitory change may contribute significantly. The more gradual change in this compound may be associated with the large separation of the intercalate layers which will reduce the possibility of a cooperative effect taking place.

Apart from this well defined anomaly there is also strong evidence of a thermal anomaly in the third sequence bisulphate. Here the lattice spacing change is very much smaller ($\sim 0.005\overset{\circ}{\text{\AA}}$) but it is associated with an intensity change in the 0026 line. This transition is reversible on warming and does not appear to occur in the other bisulphate compounds. As this anomaly is

associated with an intensity change in the 0026 reflexion it may be associated with a change in stacking sequence. However as the interactions between the intercalate layers and graphite layers vary in the bisulphate from one sequence to another, the possibility of a rearrangement in the layer itself cannot be ruled out.

6.5 Non-Thermal Anomalies in the Graphite Compounds

Apart from the anomalies discussed above which were associated with thermal cycling of the sample there were found to be two compounds which showed two different spacings at room temperature. In the first sequence perchlorate the normal spacing found was $7.73\text{\AA}$ but one sample showed a spacing of $7.94\text{\AA}$. All the samples prepared by Rüdorff had a spacing of $7.94\text{\AA}$. The chief differences between these two researches were the method of preparation and the graphite used. It is possible that the type of graphite used may lead to this difference but in view of the fact that the one sample of spacing $7.94\text{\AA}$ on further electrolysis gave a spacing $7.73\text{\AA}$, it seems more likely that the $7.94\text{\AA}$ spacing is associated with a slightly lower oxidation state. This would explain the formation of this $7.94\text{\AA}$ compound by chemical oxidation which is probably less vigorous than the electrochemical method.

An analogous difference in spacing was observed in the potassium compound which normally had a spacing of $5.36\text{\AA}$ but one

sample gave a spacing of $5.40\text{\AA}$. Again it is interesting that "Rudorff always found a value of $5.40\text{\AA}$ whereas other workers in general agree with the lower value, see Table 3. 1. This difference in spacing is as yet unexplained.

There is a further spacing change which merits mention; this is the gradual variation of lattice parameter with time noticed in the first and second sequence bisulphate compounds. There is very little change in the appearance of the 00ℓ reflexions in the traces before and after thermal expansion measurements so this drift must be associated with only a slight change in structure. If a sample of the bisulphate is stored in contact with sulphuric acid for a length of time then it is usually noticed that the acid becomes brown. This may be due to the formation of small quantities of graphite oxide from decomposition of the compound. It appears likely that this type of decomposition of the bisulphate compound may be responsible for the slow change in lattice spacing which takes place on standing.

Very little work has been carried out in this direction but it seems possible that many of the graphite compounds are inherently unstable in contact with the acid medium and slowly decompose to lower compounds. These changes in lattice parameter do not appear to influence the thermal expansion results within the accuracy of measurement as samples of the second sequence

bisulphate which were 'drifting' in opposite directions gave essentially the same thermal expansion. Thus in the calculation of the results, these drifts were eliminated mathematically and satisfactory agreement was obtained between duplicate samples.

6.6 Summary

The measurement of the thermal expansion of graphite compounds has proved successful in almost all cases where it has been possible to prepare a compound which would give clearly defined 00ℓ reflexions. The work has been limited by two principal factors; firstly some of the compounds, notably the molecular compounds, do not give sharp 00ℓ reflexion under the present conditions of preparation. Secondly, methods of preparation from pyrolytic graphite have had to be developed for the acid compounds. Further to these limitations to the preparation there are apparent discrepancies between the structure of compounds prepared from pyrolytic graphite and from powder graphites.

For a more detailed interpretation of the thermal expansion results it is important to investigate these discrepancies in order that a fuller understanding of the structure of the graphite compounds may be obtained. Thus there is considerable scope for detailed structural studies on the graphite compounds, especially the metallic halide compounds

which are at present poorly characterised. One aspect of the structure of the compounds which has not been studied except in a very few cases is the arrangement of species in the intercalate layer. This is a particularly important point in the acid salts where the amount of free acid present is not definitely known. X-ray diffraction does not yield much information about this arrangement especially when the intercalate layers are not ordered and it seems probable that any information about the a-axis must come from electron diffraction which up till now has not been applied to these compounds.

Apart from the obvious work necessary on the structure of these compounds there is now available graphite of a suitable c-axis thickness (2 - 3 mm) to make the measurement of compressibility by velocity of sound methods a feasible project. As these measurements are of great importance in elucidating the force fields this seems the logical step in expanding the data available for the graphite compounds.

APPENDIX 1: THE COMPOUNDS OF GRAPHITE WITH METAL CHLORIDES

The compounds formed between the metallic chlorides and graphite are good examples of the molecular compounds where there is only a weak interaction between the intercalate and the graphite layers. The thermal expansion of these compounds would make an interesting comparison with that of the alkali metal compounds and of the acid salts. Thus attempts were made to prepare these molecular compounds from pyrolytic graphite in order to measure the expansion.

1. Preparation

Four compounds were investigated; these were the graphite compounds of ferric, gallium, indium and aluminium chlorides. In the preparation of ferric chloride graphite the salt was placed in the reagent section of a reaction tube (Fig. 3.3.b) with the graphite in the other section. The tube was then evacuated and sealed off. For the other three salts a similar procedure was adopted except that the tube was evacuated and filled with chlorine at 1 atmosphere before sealing off. All the preparations were carried out by heating the reaction tubes in the zone furnace at various temperatures.

2. Results

The metallic chlorides appeared to form graphite compounds with pyrolytic graphite under similar conditions to those reported for other types of graphite (Rüdorff and Schulz, 1940; Rüdorff and Landel, 1958). The products were less compact than the compounds formed with the alkali metals; macroscopic cracks were always visible in the edges of the samples. The preparation time required for these compounds was also very long compared with the alkali metal compounds (see below); this is especially so for the ferric chloride compound.

The compounds did not give suitable 001 reflexions from which to determine the thermal expansion. The reflexions were either very weak or present only at low angles, i.e. less than 50° in θ . For the separate compounds the following results were observed.

2.1 Gallium and Aluminium Chlorides

With graphite temperatures of approximately 200°C and the salt at $150\text{--}180^\circ\text{C}$ a blue compound was formed. Because of the sensitivity of these compounds to air, the weight uptake could not be determined. When both these compounds were investigated on the diffractometer, their diffraction pattern consisted of a very weak series of 001 lines. The calculated spacing for the gallium chloride compound was

9.6 Å in good agreement with that of Rüdorff, 9.54 Å.

2.2 Indium Chloride

The preparation of this compound required much higher temperatures than the two previous salts. Both the graphite and salt were heated to about 500°C but after 72 hours the samples were still black. These samples were weighed and showed only 5-10% of indium chloride had been intercalated. Because of this low uptake no further investigation was attempted on this compound.

2.3 Ferric Chloride

This compound was investigated in rather more detail because its greater stability enabled diffraction photographs to be taken. A sample of graphite heated at 200°C for 72 hours took up only 8% ferric chloride. A second sample was heated at 305°C for 17 hours and the uptake was 50.4% FeCl_3 ; this sample was sealed up with further FeCl_3 and heated for a further 22 hours at 310°C, the uptake was then 129% FeCl_3 . This corresponds to 56% FeCl_3 by weight, compared to 69% for the theoretical first sequence compound assuming completely filled layers. Three further samples of different weights were heated in the same tube with FeCl_3 at 320-340°C and the percentage of FeCl_3 in the resultant compounds was 53.5%, 53.0%, 52.5%.

The flat-plate diffraction pattern of the sample

containing 8% FeCl_3 was very similar to that of graphite.

There were two diffuse bands parallel to the c-axis corresponding to spacings of approximately $5.1 \overset{\circ}{\text{\AA}}$ and $2.7 \overset{\circ}{\text{\AA}}$ in the a-axis direction which did not occur in graphite.

The photographs of the compound containing approximately 55% FeCl_3 are very complex.

An attempt to reproduce the main features has been made in Plate A1.1, but as some detail is lost in this photograph a stylised representation of the pattern obtained is shown in Fig. A1.1. The discrete reflexions are indexed on this diagram on the basis of a hexagonal unit cell with $a = 2.46 \overset{\circ}{\text{\AA}}$ and $c = 12.7 \overset{\circ}{\text{\AA}}$. The diffuse scattering is associated with two dimensional ferric chloride reflexions and are indexed accordingly (see discussion).

An examination of the 00l reflexions on the diffractometer showed, for the samples containing 55% FeCl_3 , a series of lines corresponding to a c-axis spacing of approximately $12.7 \overset{\circ}{\text{\AA}}$. The highest order observed was the 0012 at 57° ($\text{Co K}\alpha$) but this was very weak and the strongest high angle line was the 0011 at 51° . This reflexion was not resolved into $\text{K}\alpha_1$ and $\text{K}\alpha_2$ so no thermal expansion measurements were carried out.

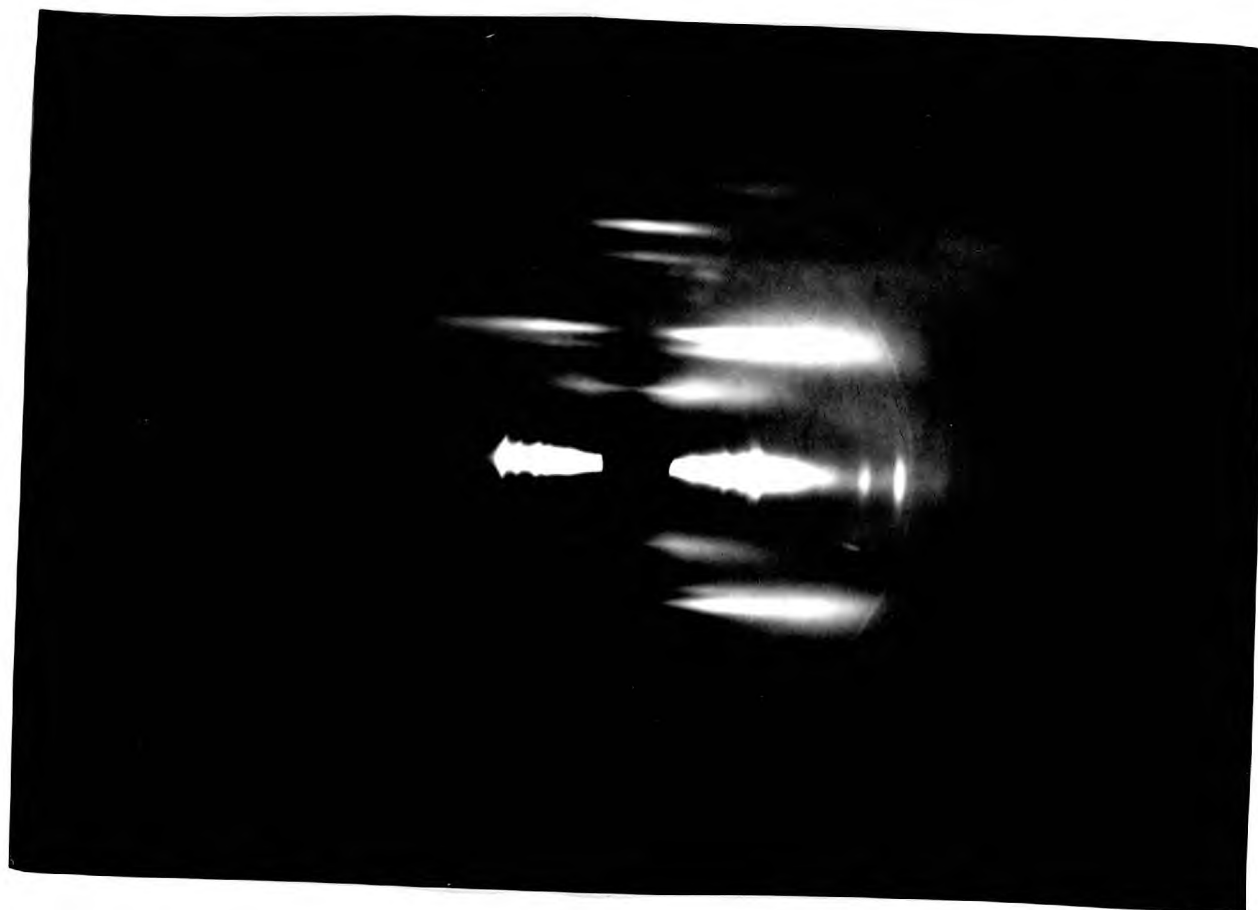


Plate A1.1. X-ray diffraction photograph of
ferric chloride graphite.

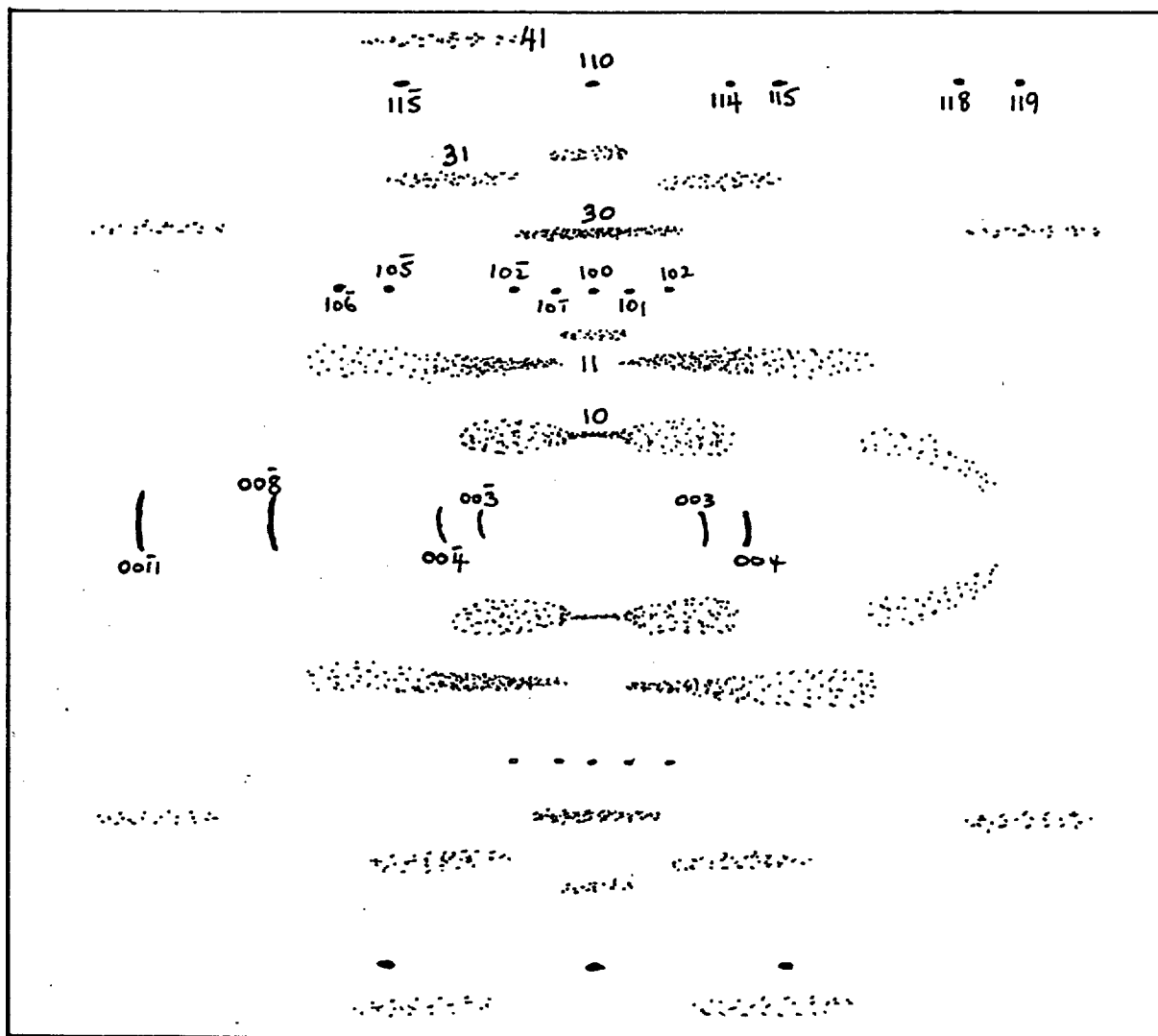


FIG.A1.1. Diagrammatic representation of Plate A1.1.
 showing additional reflexions and scatter. Three dimensional
 indexing on a hexagonal unit cell $a = 2.46\text{\AA}$ and $c = 12.7\text{\AA}$

3. Discussion

A detailed study has been made previously of the FeCl_3 compound containing 55% FeCl_3 (Cowley and Ibers, 1956). The conclusions of these workers were that this compound was a mixture of graphite and a FeCl_3 /graphite compound with one ferric chloride layer between each graphite layer, i.e., a first sequence compound. The compound was said to contain about 17% graphite and the c-axis spacing in the compound was $9.41 \text{ \AA}$. Further, it was claimed that as the percentage of ferric chloride in the compound decreased then the amount of free graphite increased. In addition, the fraction of ferric chloride per ferric chloride layer decreased.

The present work is not in agreement with these general conclusions; for the samples containing 50-55% FeCl_3 there is firm evidence of the existence of a second sequence compound of spacing $12.7 \text{ \AA}$ (in good agreement with the expected value $(9.41 + 3.35) \text{ \AA}$). Further, the 001 traces showed no lines corresponding to the 002 or 004 lines of graphite.

The presence of a second sequence compound is confirmed by the flat-plate photograph (Fig. A1.1) where the discrete sharp hkl reflexions are also consistent with a unit cell with a c-axis repeat distance of $12.7 \text{ \AA}$. Thus this confirms the existence of three dimensional ordering

between the graphite layers as occurs in all the other compounds of graphite. The indexing of the 101 and 001 reflexions on the same c-axis repeat distance indicates that the graphite layers are arranged AB on either side of the intercalate layer. Thus the stacking sequence is ...ABIABIA..., whereas in a typical acid salt the sequence would be ...ABIBAIABIBA...

The pattern of diffuse scattering which consists of streaks parallel to the c-axis direction arises from the individual ferric chloride layers in the intercalate. The spacing of these diffuse reflexions calculated from the projection on to the zero layer line is in good agreement with the expected spacings in a single ferric chloride layer (Table A1.1)

TABLE A1.1

Index of two dimensional spacing	Calculated spacing	Measured spacing by projection on to zero layer line
10	5.17	5.06
11	2.90	2.93
20	2.62	2.64
30	1.76	1.72
31	1.46	1.49
41	1.14	1.18

There is no modulation of these reflexions to suggest the ordering of the intercalate layers with respect to each other as was suggested by Cowley and Ibers. It seems that the compound from pyrolytic graphite differs considerably from that reported previously.

APPENDIX 2: BROMINE GRAPHITE

The expansion of bromine graphite was of considerable interest as the compound has a simple negative intercalate and a comparison with the expansions of the alkali metal compounds, with a simple positive intercalate, was of interest. By simple immersion of graphite in bromine it was not possible to prepare compounds that gave well defined 001 reflexions suitable for expansion measurements on the diffractometer. Some work was therefore carried out on the kinetics of the bromination of pyrolytic graphite, in addition the x-ray diffraction patterns were studied in some detail to determine if thermal expansion measurements were possible.

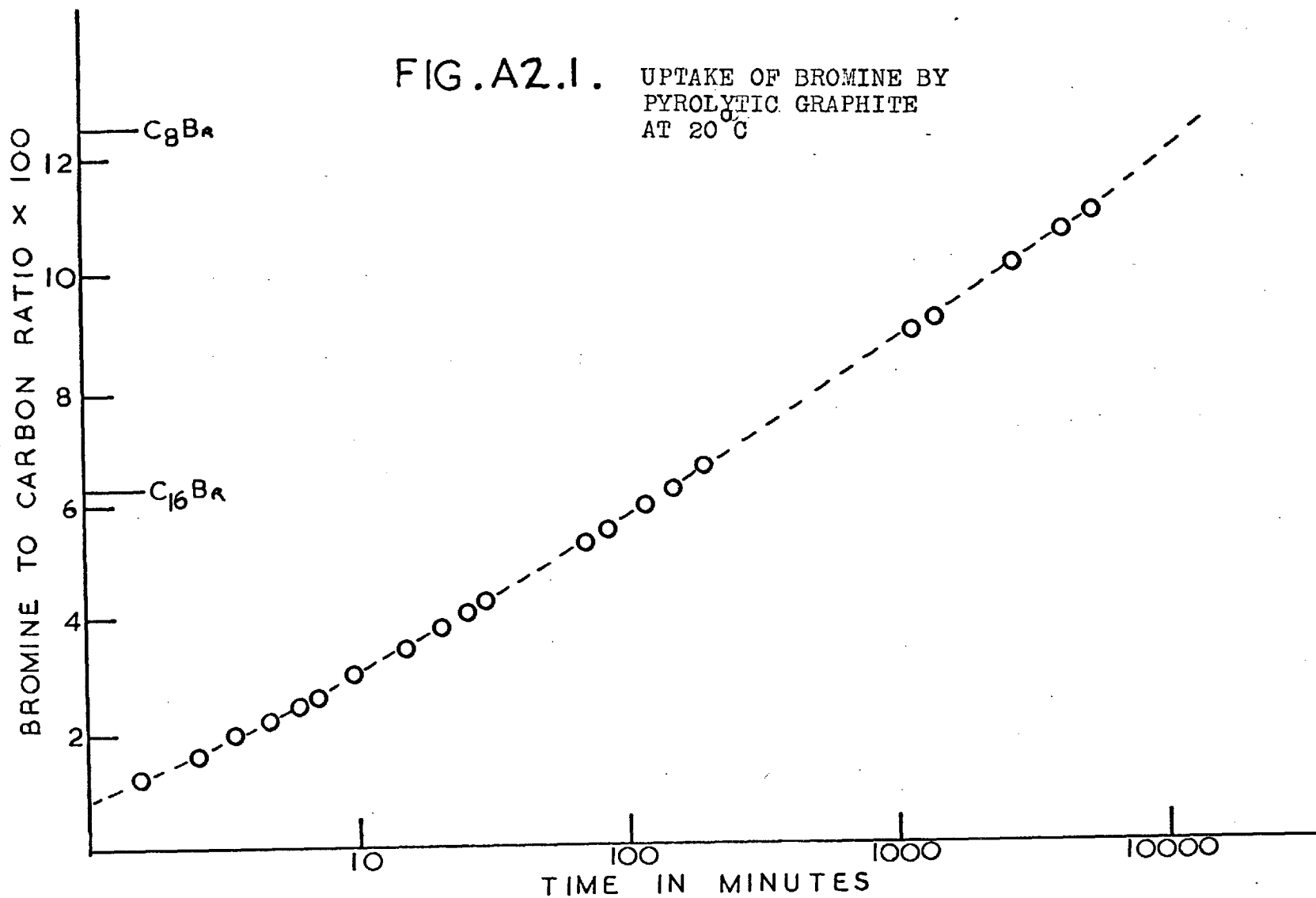
1. Results

Analard bromine was used for all the experiments recorded below. The pyrolytic graphite was prepared by cracking methane at 2150°C and then annealing at 3100°C for one hour. A series of short experiments was carried out to determine the influence of sample size, bromination rate and temperature on the kinetics of bromination.

(a) Samples of graphite were suspended on quartz spiral springs in an atmosphere of bromine and the weight uptake was calculated from the extension of the spring.

This uptake is plotted against time for a typical sample in Fig. A2.1. The uptake is approximately a logarithmic function of the bromination time. The time required to reach C_8Br can be estimated to be about 10 days. Brominations were also carried out in liquid bromine; in this case the weighed samples were immersed in liquid bromine for specific times then taken out and the surface bromine removed and the sample reweighed. The uptake was very rapid and most samples reached a composition C_8Br in about 10 minutes. The bromine content of the samples did not however exceed the approximate composition C_8Br . Most of the bromine taken up in the liquid was lost very rapidly on being removed from the bromine as can be seen from Fig. A2.2, where the loss of bromine is plotted against time. In order to investigate the amount of bromine which was not lost rapidly three sizes of sample were brominated in liquid bromine for times from 1 to 360 hours. These samples on being removed after bromination had the approximate composition C_8Br but after being allowed to lose bromine for 48 hours the compositions were quite different. The composition of these samples is plotted against time in Fig. A2.3 where the approximate composition expected from bromination in vapour is also indicated. It is easily seen that the amount of bromine

FIG. A2.1. UPTAKE OF BROMINE BY
PYROLYTIC GRAPHITE
AT 20 °C



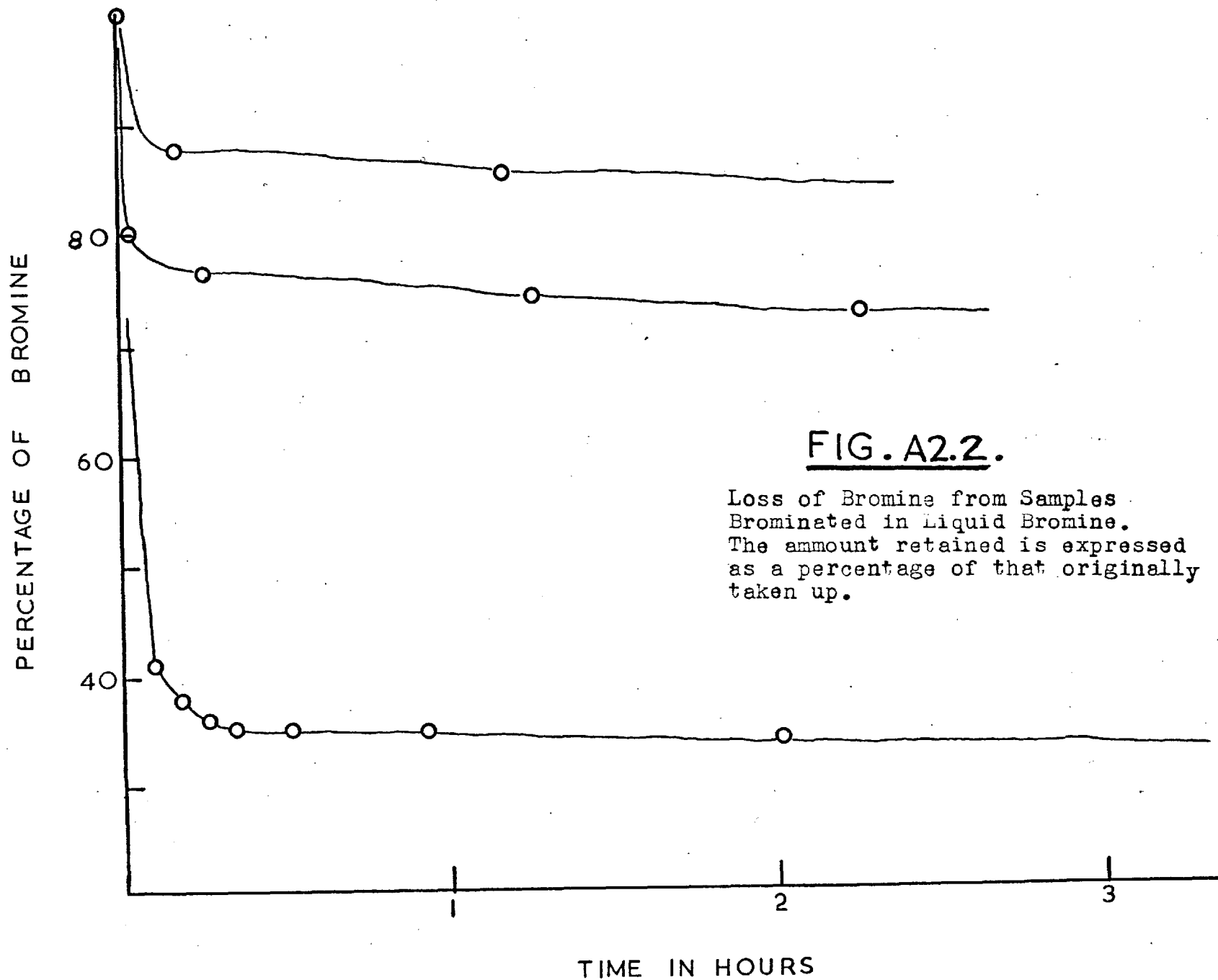


FIG. A2.2.

Loss of Bromine from Samples
Brominated in Liquid Bromine.
The ammount retained is expressed
as a percentage of that originally
taken up.

PERCENTAGE OF BROMINE RETAINED AFTER 48 HOURS

FIG
A2.3.

VAPOUR CURVE

SAMPLE SIZE

1 cm x 1 m.m. x 1 m.m. ●

1 cm x 1 cm x 1 m.m. ○

1 cm x 1 cm x 0.1 m.m. ⊙

60
50
40
30
20
10

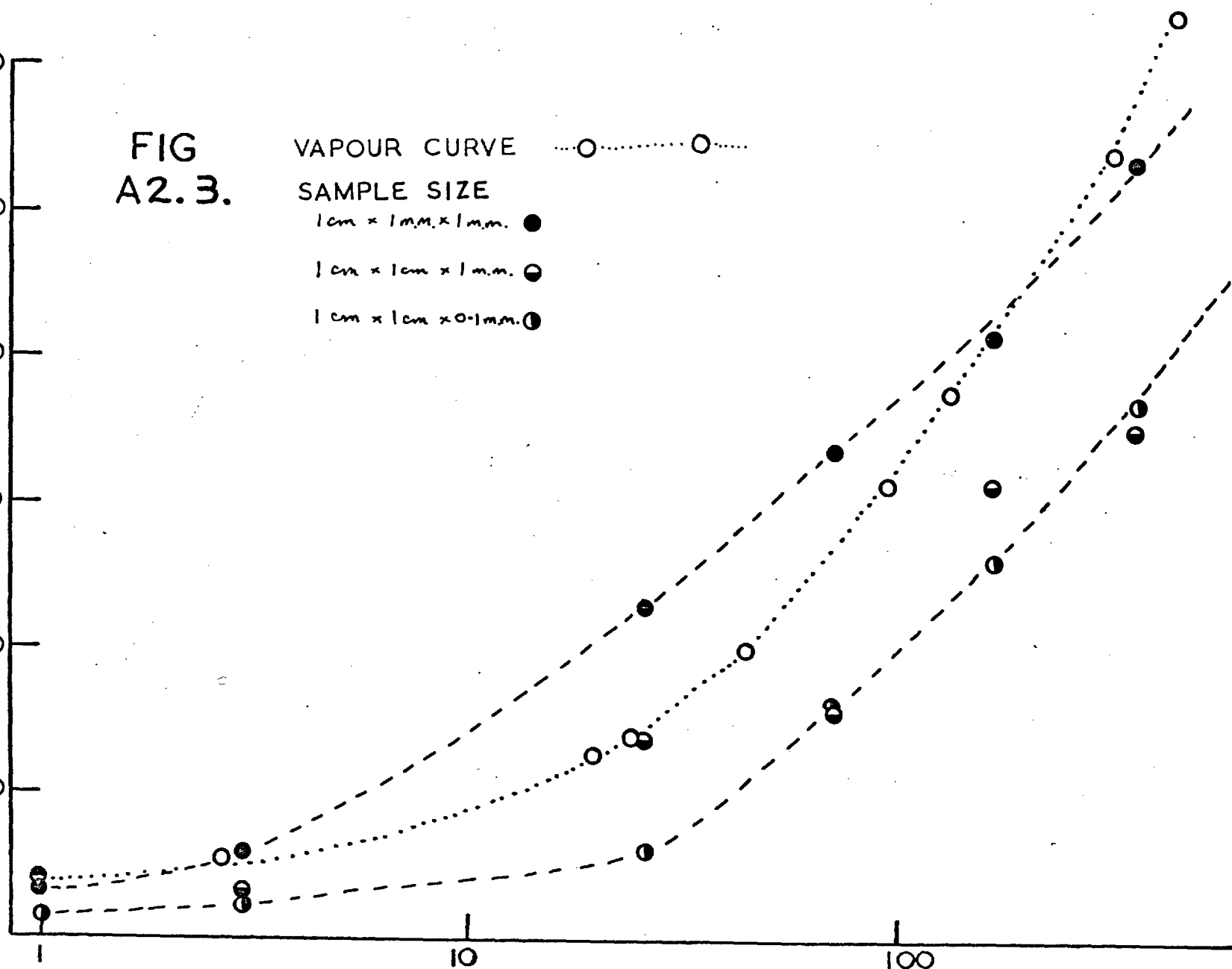
1

10

100

BROMINATION TIME IN HOURS

237



retained more strongly is a function of the time of bromination and approximately agrees with that predicted for bromination in the vapour.

(b) The difference in the curves of the three different shaped samples in the last experiment indicated that the shape of sample could influence the rate of bromination. This was investigated by two experiments: samples of the same a-axis dimensions but of different c-axis thickness were brominated for the same time, and secondly, circular samples of the same c-axis thickness but of different a-axis diameters were also brominated for the same time. The samples were allowed to debrominate and the percentage of bromine in the samples was measured periodically by weighing. The results for varying c-axis parameter are shown in Table A2.1 and those for varying a-axis parameter in Table A2.2. The bromine retention of the discs is also plotted in Fig. A2.4. The c-axis dimension appears to have little effect on the uptake but the a-axis dimension strongly influences the uptake (see discussion).

(c) Samples of approximately the same size were brominated at different temperatures; the samples were then weighed after the initial bromine loss and allowed to lose bromine slowly in air. The loss of bromine is plotted against time in Fig. A2.5. The relative rates of bromination

T A B L E A 2 . 1

Thickness
of sample
in m.m.

Percentage of bromine retained after:-

	0 hr.	1 hr.	24 hr.	125 hr.	500 hr.
1.75	55.9	9.9	7.1	5.4	4.5
1.37	66.6	10.2	7.2	5.4	4.4
0.78	54.3	11.0	7.6	5.8	4.8
0.57	52.3	10.4	7.2	5.5	4.8
1.06	54.2	12.5	8.1	6.1	5.5
0.46	24.9	12.6	8.2	6.0	5.2
0.34	25.3	15.6	11.2	8.6	7.2

T A B L E A 2 . 2

Diameter
of Disc
in m.m.

Percentage of bromine retained after:-

	4 hr.	24 hr.	48 hr.	100 hr.	400 hr.
15.55	26.9	23.1	21.2	18.7	15.0
12.91	29.7	25.8	23.0	19.9	16.5
9.32	41.5	34.5	31.2	26.2	21.4
7.27	43.4	37.5	34.6	30.6	24.1
4.82	56.8	47.9	43.7	37.7	29.1
2.80	74.2	61.7	58.3	45.0	31.7

FIG. A2.4.

Loss of Bromine from Discs of
Different Diameters which had
been Brominated for the same
Time in Liquid Bromine.

PERCENTAGE OF BROMINE

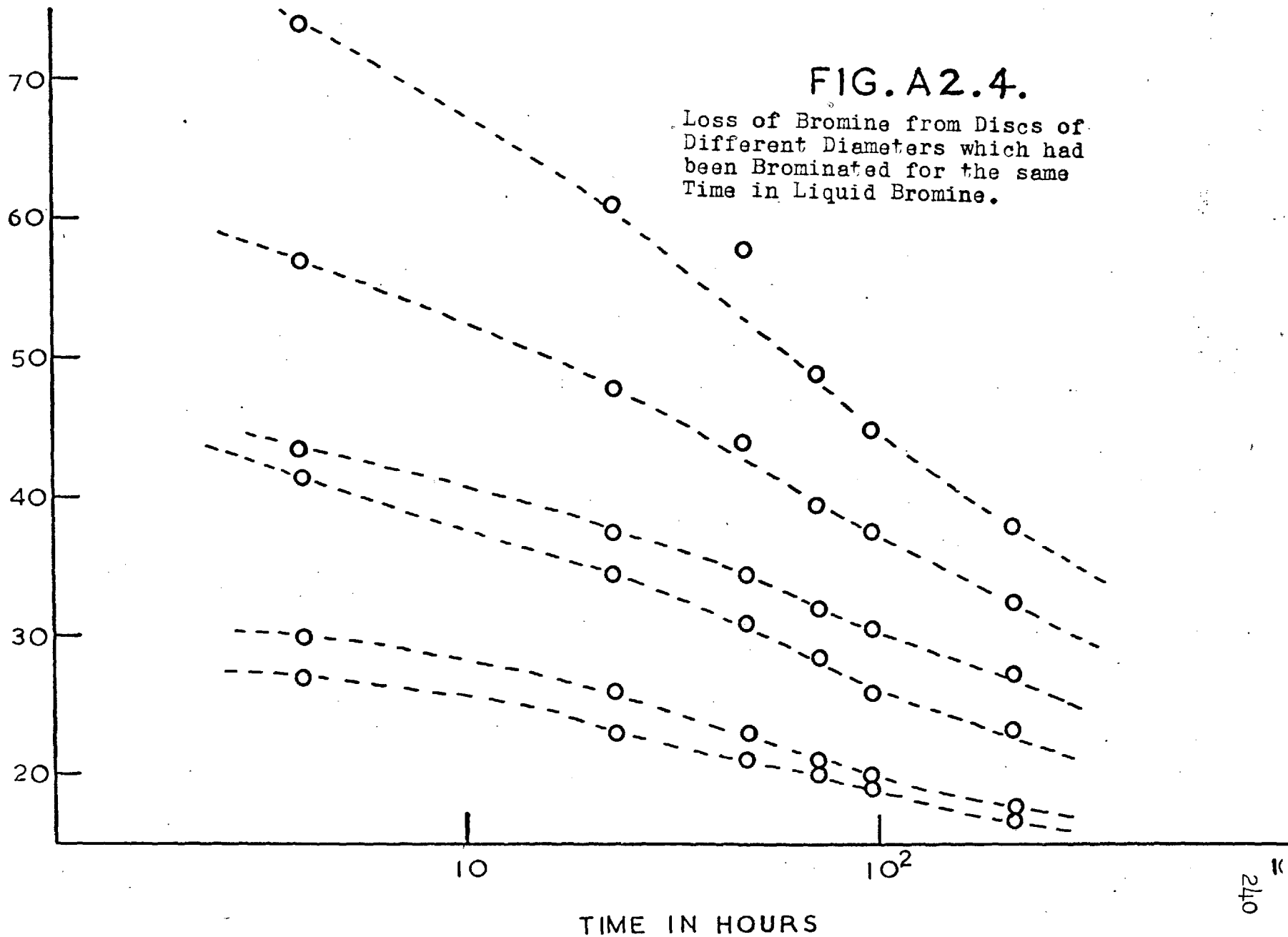
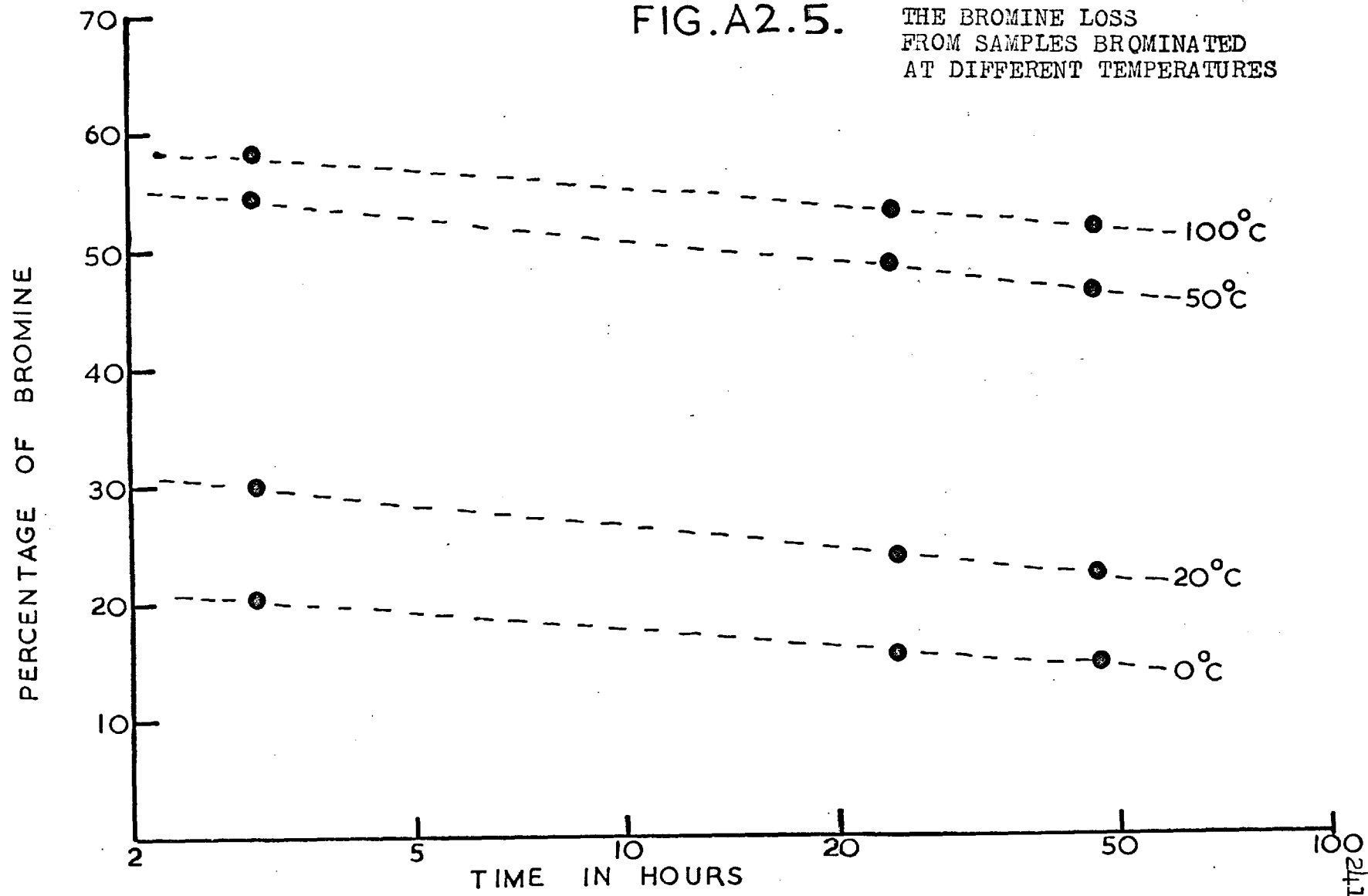


FIG.A2.5.

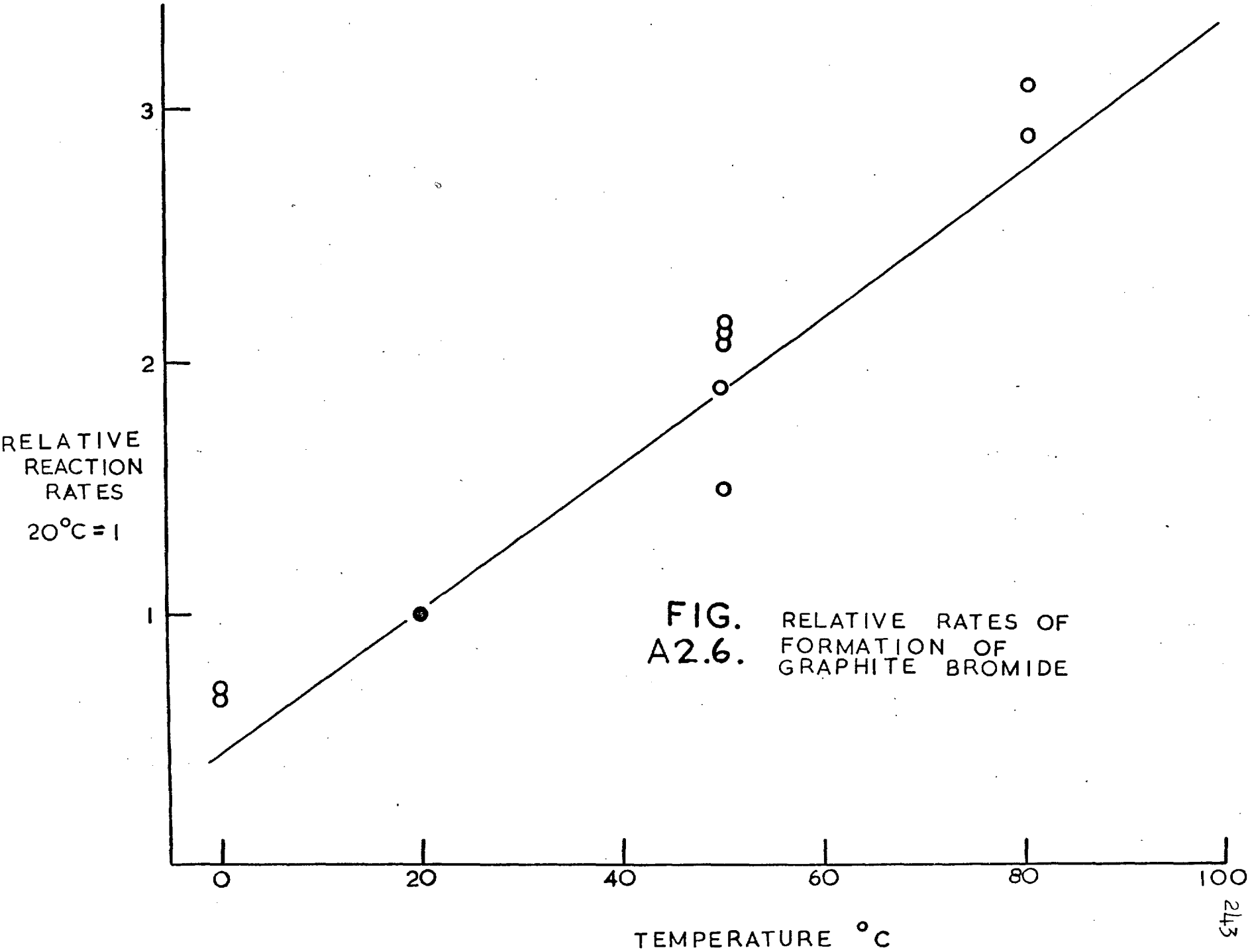
THE BROMINE LOSS
FROM SAMPLES BROMINATED
AT DIFFERENT TEMPERATURES



at four temperatures were plotted in Fig. A2.6. The room temperature rate of bromination being taken as unity.

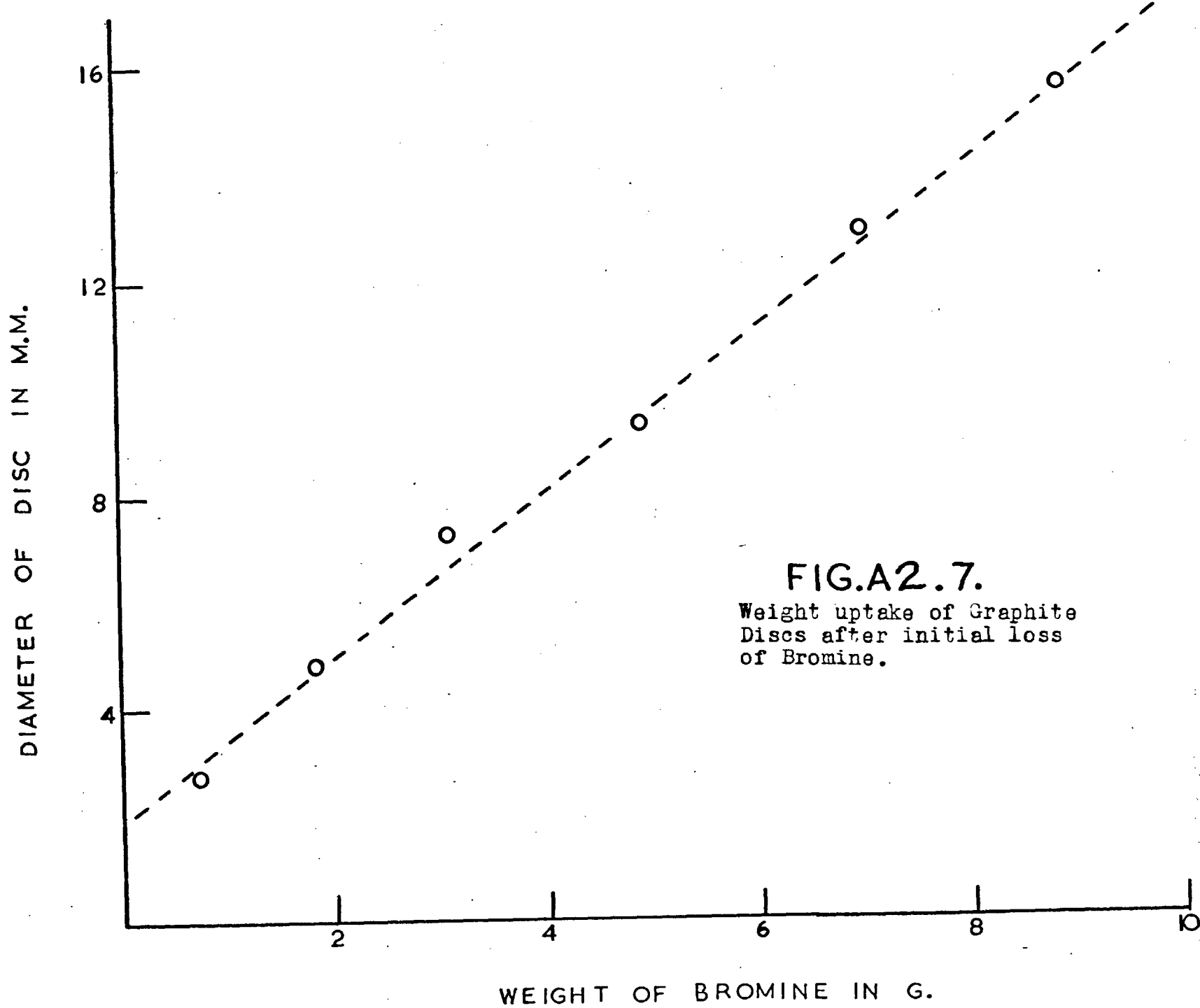
2. Discussion

Uptake of bromine from the liquid is very much faster from the vapour but all the bromine taken up from the liquid is not tightly held and much of it is lost immediately on removal from the liquid (Fig. A2.1). The amount of bromine retained strongly is roughly comparable with that which would have been absorbed had the bromination been carried out in the vapour. This is consistent with the reported mechanism of formation of bromine graphite (Saunders, Ubbelohde and Young, 1963). Their work shows that the expansion of the layer planes takes place more rapidly than the rate of bromine uptake would suggest. Thus expanded layers which are not completely filled with bromine will exist and the weakly held bromine can be absorbed in these layers. Because of the very rapid initial loss of bromine from samples brominated in the liquid, the actual uptake of bromine before this initial loss is not particularly meaningful. The results on the samples of different thicknesses (Table A2.1) showed that the thickness has a negligible effect on the percentage of bromine retained (the one result which differs is probably because of inaccurate weighing of the smallest sample).



The bromination of the discs showed that the samples with smaller diameters retained relatively more bromine than those with much larger diameters. The weight of bromine retained was corrected for the slight differences in thickness of the discs (Fig. A2.7). The resulting straight line suggests that the strong retention of bromine is in some way associated with a process which originates at the circumference of the sample. This is supported by an interesting observation on some of the samples of a raised picture frame at the edge of the sample (Plate A2). This effect was noticed on numerous samples but it was particularly noticeable with the samples brominated at higher temperatures. This effect has also been reported for ferric chloride graphite (Hooker, 1964).

The experiments on bromination at different temperatures showed that up to 80°C the rate of bromination increased. The one point obtained at 112°C did not brominate as fast as those at 80°C . This suggests a maximum in the bromination reaction rate at about $80-100^{\circ}\text{C}$ which is similar to the maximum reported in the chlorination of graphite at -16°C (Juza, Jönck and Schmeckenbecher, 1957). From the slope of Fig. A2.6 an approximate calculation of the heat of formation of graphite bromine in liquid bromine can be made and the value found is 3.8 k.cals. per mole. A value



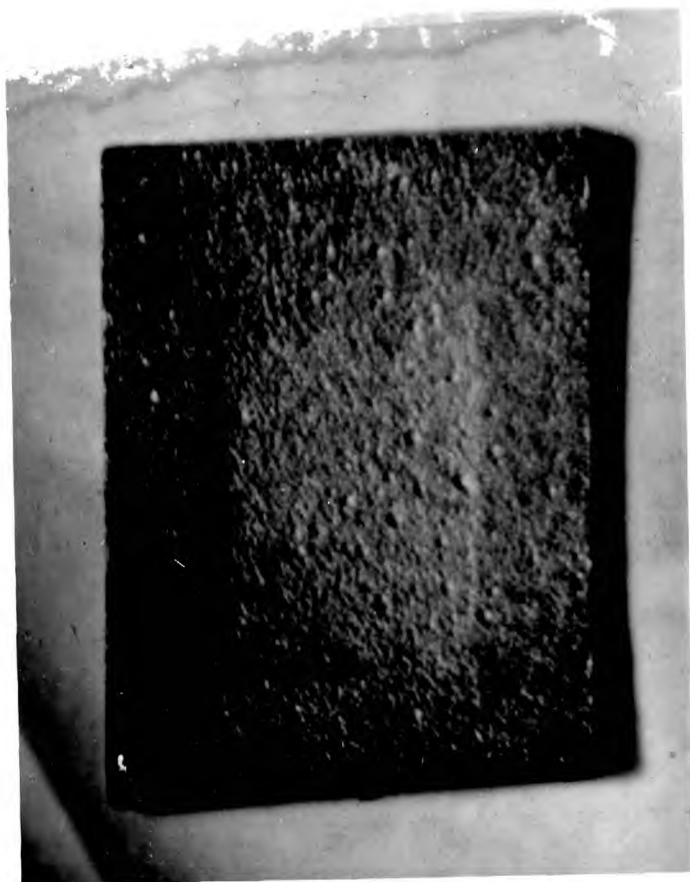


Plate Enlarged photograph of a piece of graphite bromine
A 2.1 compound which clearly shows a raised ridge about
 $\frac{3}{4}$ " in from the outer edge (The sample size is about
 10 m.m. x 8 m.m.)

of 7.5 k.cal./mole has been estimated previously (Saunders, Ubbelohde and Young, 1963).

From Figs. A2.4 and A2.5 it is apparent that compounds containing a higher percentage of bromine lose bromine at the same rate if they are prepared at the same temperature. However, compounds prepared at high temperatures although containing more bromine than those prepared at lower temperatures retain this bromine more strongly. It seems, therefore, that bromine graphite prepared at higher temperatures is more stable; this may be because of a higher degree of ordering.

3. X-ray studies on graphite bromine

Samples of graphite were sealed in cells, similar to those described later for the preparation of acid salts, along with some liquid bromine. Two samples were studied; the first was brominated in liquid bromine and during the bromination 001 lines of a second sequence compound with some weak lines corresponding to a fourth sequence compound. A second sample was brominated in careful controlled stages, firstly for 96 hours in bromine vapour. It had by the end of this time a composition $C_{14.7}Br$ and showed 001 lines for a second sequence compound with the strongest lines of a fourth sequence compound superimposed. The sample was then transferred to liquid bromine for 72 hours and reached

a composition $C_{13.7}Br$. It still showed predominantly a second sequence pattern, but with subsidiary fourth sequence lines. (The observation of a dominant second sequence compound pattern and a weaker fourth sequence compound was also observed for three other samples.) The sample was then removed from the liquid and replaced in an empty cell. After 2 hours the pattern was purely second sequence compound and after 65 hours in the empty cell a very clear series of 001 lines for the second sequence compound was obtained. It showed all the 001 lines up to 0012 at 63° including the very weak 0010 and 0011 lines not observed by Rüdorff. The cell was then left open to the atmosphere for 72 hours; the diffraction pattern was now complex and showed relatively sharp lines 001, 002, 003, 004, 005, (006), (007), 008, 0010, 0011, 0012 and 0016 for a third sequence compound and, superimposed, a rather broader sequence of lines 001, 002, 003, 004, 005 for a fourth sequence compound. A second sample which had been allowed to dehydrate for 170 hours showed a diffraction pattern corresponding to a fourth sequence compound with no other lines present. A further sample which had been brominated at $100^\circ C$ and then residued showed a fourth sequence pattern but also showed two very sharp subsidiary peaks to the strong 005 peak. These peaks resemble "ghost" peaks and suggest a larger unit cell

repeat than the expected fourth sequence distance of 7.05 + 3.3.35 ^o Å (these peaks can also result from periodic disorder in the lattice).

In addition to the diffractometer studies, photographs of both residue compounds approximating to C₈Br have been taken. These photographs suffer from the heavy background scatter caused by the fluorescence of the bromine atoms, but it is nevertheless apparent that no strong hkl lines are present.

The photographs with the x-ray beam perpendicular to the c-axis show only the 00l reflexion as reasonable sharp spots and diffuse rings which correspond to the following spacings 4.25 Å, 2.84 Å, 207 Å. One photograph shows also a ring corresponding to a spacing of 8.5 Å. If these are repeat distances in the a-axis direction then a minimum repeat distance of 8.5 Å would be necessary. Recent work (Eeles, 1963) suggests that the structure of graphite bromine is complex and that a large repeat distance of about 17 Å within the intercalate layer probably exists. This is in good agreement with the spacings observed.

4. Summary

The problem of graphite bromine is interesting; the first weak absorption of bromine from the liquid gives a weight uptake close to C₈Br but only after a very long

period does this bromine become firmly held in the graphite framework. It does appear that graphite can absorb bromine, which is just as readily desorbed, but that there is also a stable bromine compound in which the bromine species becomes ordered in the intercalate layers. The influence of the a-axis dimensions on the rate of bromination is difficult to understand and requires more detailed study before any definite conclusions can be drawn.

APPENDIX 3 Recommended Methods for the Preparation of the Acid Compounds of Graphite.

(a) Bisulphate compounds-100% sulphuric acid should be used for all the preparations and a low voltage i.e. 3-6V gives the most satisfactory results.

The end point of the formation of the various sequences is best determined as follows:-

(i) First sequence-by observing the start of the final voltage plateau, usually at about 1.0-1.1V.

(ii) Second sequence-by observing the start of the penultimate voltage plateau at 0.5V and also by the rapid change in colour of the sample from black to blue.

(iii) Third sequence-and lower sequences-by calculation of the theoretical current required to produce the particular oxidation state.

(b) Chlorosulphonate compounds-100% chlorosulphonic acid should be used for all the preparations and a high driving voltage is recommended (40-60V). The end point of formation of a given sequence is best determined by observation of the voltage plateaus.

(c) Selenate compounds -100% selenic acid diluted with distilled water until just liquid at 25°C is recommended. The preparation should be carried out

at 25°C using a low driving voltage and similar methods for determining the end point of the reaction as for the bisulphates are suggested. (the preparation of selenate compounds by electrochemical methods does not appear to be as satisfactory as other graphite compounds)

(d) Fluosulphonate compounds-100% redistilled fluo-sulphonic acid using the same methods as for the ~~chlorosulphonates~~ chlorosulphonates.

(e) Perchlorate compounds -70% perchloric acid is recommended but if stronger acid is available it could probably be used with better results. The end point of the preparation of the different sequences can be determined as for the bisulphates but great care is necessary in preparing the first sequence compound as overoxidation even to the extent of 5-10% can lead to complete breakdown of the sample.

(f) Nitrate compounds -electrochemical methods of preparation are not recommended for these compounds. All the nitrates can be conveniently prepared by immersing the graphite in nitric acid of the necessary strength i.e.

First sequence-50 parts HNO_3 (fuming) S.G.1.52
50 parts N_2O_5

Second sequence-100 parts HNO_3 (fuming) S.G.1.52

Third sequence -60 parts HNO_3 (fuming) S.G.1.52
40 parts HNO_3 (conc.) S.G.1.42

APPENDIX 4 DATA FROM THERMAL EXPANSION WORK.

COMPOUND	PAGE NO.	GRAPH NO.	BRAGG ANGLE	LATTICE SPACING	TEMP.
BISULPHATE 1	161	5.11	74 $26\frac{1}{2}$	8.0380	18.00
		5.12	75 1	8.0164	-30.00
		5.13	74 $21\frac{1}{2}$	8.0416	18.50
		5.14	75 $10\frac{1}{2}$	8.0105	-43.50
			74 $18\frac{1}{2}$	8.0436	25.00
			74 36	8.0322	2.00
			75 5	8.0139	-38.00
			74 21	8.0420	18.00
			74 $38\frac{1}{2}$	8.0306	-3.00
			74 $27\frac{1}{2}$	8.0377	10.00
			75 $40\frac{1}{2}$	7.9924	19.50
			76 00	7.9809	-5.00
			76 17	7.9712	-26.00
			76 $43\frac{1}{2}$	7.9564	-50.00
			75 35	7.9956	18.50
			75 53	7.9850	-5.00
			75 33	7.9968	18.50
			76 $5\frac{1}{2}$	7.9771	-22.50
			75 25	8.0016	32.00
			76 38	7.9594	-54.50
			76 $26\frac{1}{2}$	7.9658	-42.50
			76 14	7.9729	-30.00
			76 $00\frac{1}{2}$	7.9806	-16.00
			75 31	7.9980	17.00
			75 $40\frac{1}{2}$	7.9923	4.00
			75 26	8.0010	20.00
			75 $21\frac{1}{2}$	8.0037	19.00
			75 $19\frac{1}{2}$	8.0050	20.00
			75 $15\frac{1}{2}$	8.0086	20.50
BISULPHATE 2	162	5.15	70 7	11.32282	24.00
		5.16	70 $12\frac{1}{2}$	11.31628	9.50
			70 17	11.31097	-1.75
			70 21	11.30626	-11.50
			70 $9\frac{1}{2}$	11.31984	17.00
			70 $23\frac{1}{2}$	11.30333	-17.50
			70 $34\frac{1}{2}$	11.29051	-40.00
			70 30	11.29574	-33.75
			70 18	11.30979	25.50
			70 $26\frac{1}{2}$	11.29982	3.25
			70 $34\frac{1}{2}$	11.29051	-14.25
			70 $42\frac{1}{2}$	11.28129	-32.00
			70 $30\frac{1}{2}$	11.29156	24.75
			70 $38\frac{1}{2}$	11.28589	4.00

			70	45 $\frac{1}{2}$	11.27785	-12.75
			70	51	11.27156	-34.50
			70	59	11.26250	-53.50
			70	34	11.29109	17.75
			71	4 $\frac{1}{2}$	11.25630	-45.50
DISULPHATE 3	163	5.17	58	46 $\frac{1}{2}$	14.71551	24.00
			58	55	14.69353	-14.50
			58	45 $\frac{1}{2}$	14.71811	23.75
			58	54 $\frac{1}{2}$	14.69482	-14.50
			58	58	14.68581	-31.50
			58	45 $\frac{1}{2}$	14.71811	24.75
			58	49 $\frac{1}{2}$	14.70774	5.00
			58	53	14.69869	-6.50
			58	45 $\frac{1}{2}$	14.71811	24.00
			58	49 $\frac{1}{2}$	14.70774	2.50
			58	51	14.70386	-2.00
			58	52	14.70127	-5.00
			58	54 $\frac{1}{2}$	14.69482	-15.00
			58	56	14.69096	-21.00
			58	57 $\frac{1}{2}$	14.68710	-31.50
			59	1 $\frac{1}{2}$	14.67683	-50.00
NITRATE 1	165	5.18	66	4	7.82882	25.25
			66	6	7.82680	21.00
			66	9	7.82377	14.25
			66	13 $\frac{1}{2}$	7.81926	9.25
			66	18	7.81476	1.00
			66	21 $\frac{1}{2}$	7.81127	-2.00
			66	16 $\frac{1}{2}$	7.81625	22.50
			66	27 $\frac{1}{2}$	7.80532	5.25
			66	34 $\frac{1}{2}$	7.79842	-4.75
			66	40 $\frac{1}{2}$	7.79254	-13.25
			67	17 $\frac{1}{2}$	7.76699	-17.00
			67	27	7.75806	-24.00
			67	30	7.74525	-27.25
			67	32 $\frac{1}{2}$	7.74292	-30.50
			67	46 $\frac{1}{2}$	7.72997	-48.50
			67	41	7.73504	-41.75
NITRATE 2	165	5.19	60	17	11.14564	22.25
			60	29 $\frac{1}{2}$	11.12263	-11.50
			60	58	11.07106	-25.00
			61	3	11.06215	-34.25
			61	8	11.05327	-43.25
			61	13	11.04443	-52.50
			60	18	11.14379	21.00
			60	23	11.13457	4.75
			60	30	11.12172	-14.25

			60	31	11.11990	-15.25
			60	36	11.11076	-19.75
			60	41	11.10168	-20.10
			60	48	11.08902	-21.00
			60	53	11.08003	-22.00
			60	54 $\frac{1}{2}$	11.07733	-26.25
			61	8	11.05327	-56.75
			72	54	11.14032	23.00
			73	17	11.11768	-15.00
			74	00	11.07694	-24.25
			74	29	11.05060	-50.75
			72	46	11.14833	21.50
			73	7	11.12745	-9.00
			73	59	11.07786	-25.50
			61	8	11.05327	-47.25
			60	19	11.14195	16.75
			72	47	11.14732	21.75
			72	58	11.13634	3.75
			73	8	11.12647	-10.00
			74	8	11.06958	-26.00
			72	43	11.15135	24.50
			72	57	11.13733	2.50
			73	5	11.12942	-6.00
			73	9	11.12549	-10.00
			73	12	11.12255	-14.25
			73	15	11.11963	-19.25
			74	8	11.06958	-25.00
			74	18	11.06048	-35.75
NITRATE 3	165	5.20	73	3 $\frac{1}{2}$	14.4936	25.50
			73	8	14.4878	15.50
			73	13 $\frac{1}{2}$	14.4808	6.50
			73	18 $\frac{1}{2}$	14.4744	-1.25
			73	23	14.4688	-7.75
			73	29	14.4613	-14.25
			73	35	14.4538	-19.50
			74	4	14.4485	-21.25
			74	12 $\frac{1}{2}$	14.4083	-24.00
			74	19	14.4007	-31.00
			72	58 $\frac{1}{2}$	14.5000	24.25
			73	10	14.4852	1.25
			73	21 $\frac{1}{2}$	14.4707	-13.25
			74	3	14.4197	-22.25
			74	10 $\frac{1}{2}$	14.4107	-28.00
			74	16 $\frac{1}{2}$	14.4036	-35.50
			74	32	14.3855	-52.50

PERCHLORATE 1	166	5.21	48 45 $\frac{1}{2}$	7.72394	-14.75
			48 30 $\frac{1}{2}$	7.75368	18.25
			49 3	7.68973	-57.25
			48 30 $\frac{1}{2}$	7.75368	21.50
			48 56 $\frac{1}{2}$	7.70237	-42.25
			60 56	7.75854	22.25
			61 4	7.74850	2.25
			61 14	7.73605	-13.50
PERCHLORATE 2	166	5.22	61 26 $\frac{1}{2}$	7.72063	-37.00
			61 5	11.05859	20.00
			61 10	11.04972	8.50
			61 12	11.04618	- 2.75
			61 16	11.03913	-11.50
			61 2	11.06392	20.00
			61 22	11.02859	-37.50
PERCHLORATE 3	166	5.23 5.24	69 52	14.43378	26.00
			70 6	14.41238	7.00
			70 18	14.39428	- 6.75
			70 26	14.38233	-15.25
			70 40	14.36166	-35.50
			69 54	14.43 70	21.00
			70 10	14.40632	3.00
			70 19 $\frac{1}{2}$	14.39203	- 9.25
POTASSIUM 1	168	5. 26	70 40	14.36166	-35.50
			80 33	5.34208	21.50
			80 38	5.34080	10.25
			80 50	5.33776	- .25
			81 5	5.33405	-13.50
			80 34	5.34183	16.75
			81 21	5.33022	-31.00
			80 35	5.34157	20.50
POTASSIUM 2	168	---	80 54	5.33676	- 3.50
			81 24	5.32951	-32.50
			80 3	5.34456	21.50
			81 7	5.33357	-26.00
			75 56	8.73473	21.00
			76 21	8.71907	-29.00

CAESIUM 1	168	5.27	77 50	5.94136	22.50
			77 55	5.93951	6.50
			78 1	5.93729	- 5.50
			78 9	5.93438	-28.50
			77 51	5.94099	19.50
			78 5	5.93583	-17.00
			77 46	5.94286	32.00
			77 52	5.94062	20.50
RUBIDIUM 1	168	---	78 12	5.93330	-33.00
			71 42	5.66979	22.00
			71 59	5.67900	-20.00
			71 45	5.66181	19.00
			72 14	5.67736	-60.00

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1083. *Electrochemical Preparation of Salts from Well-oriented Graphite.*

By M. J. BOTTOMLEY, G. S. PARRY, A. R. UBBELOHDE, and D. A. YOUNG.

With well-oriented pyrolytic graphite, electrochemical methods permit the convenient preparation of graphite salts. Methods are described for obtaining graphite compounds of sulphuric, chloro- and fluoro-sulphonic, selenic, perchloric, and nitric acid and the complex acid $\text{BF}_3 \cdot 2\text{AcOH}$. Progress of the reaction can be followed by measuring voltage differences; the nature of the end product can be studied by X-ray diffraction methods.

In a number of cases more than one stage of salt formation can be achieved by controlled electrolysis. Double decomposition can also be used to replace one acid, intercalated by electrolysis, to form a graphite salt of another acid. Qualitative observations indicate that similar methods probably afford other graphite salts, such as those derived from trifluoroacetic, arsenic, periodic, phosphoric, and pyrophosphoric acid.

ALTHOUGH salts of graphite with acids have been known for over a hundred years,¹ convenient methods of preparation are somewhat elusive. One reason is that a large increase in distance between the carbon-hexagon networks occurs on formation of any crystalline compound of graphite. This precludes the use of polycrystalline graphite as starting material for electrochemical methods, because the electrodes crumble before the higher stages of oxidation can be attained. Conventional methods using strong acids and various oxidising agents such as CrO_3 , Mn^{3+} , and HIO_4 , have led to the identification of various inorganic salts, prepared from flake or powdered graphite.² A study of their structure has been made, mainly by powder X-ray diffraction.³

The bisulphate and perchlorate have been prepared electrochemically by using well-oriented pyrolytic graphite,⁴ and natural single crystals of graphite have been used for electrolytic preparation of the hydrogen sulphate.² However both the above electrolytic procedures involved other conditions that are not relevant to the general preparative chemistry of these compounds. The present paper describes the electrochemical formation of a number of salts of graphite from well-oriented pyrolytic graphite, and illustrates the possibilities and difficulties. Progress of the reaction can be followed fairly simply and the compounds are obtained in a compact form convenient for study.

EXPERIMENTAL

Well-oriented pyrolytic graphite was prepared by pyrolysis of short-chain hydrocarbons at $\sim 2100^\circ\text{C}$, followed by annealing at higher temperatures,^{5,6} and consisted of crystallites of near-ideal graphite with random *a*-axis orientation but with good *c*-axis parallelism. Specimens ($1.0 \times 0.5 \times 0.01$ cm.) were used for preparative work only if they gave X-ray diffraction patterns near to those of a single-crystal *c*-axis rotation pattern (Plate a), and provided they showed a positive temperature coefficient of electrical resistance in the basal planes. The thermal expansions of such specimens along the *c*-axis were measured by X-ray diffraction and agree within 0.5% with values predicted for natural single crystals.⁷ Well-crystallised starting material was chosen because network disorder within the crystallites and disorder of their *c*-axes can obstruct crystal-compound formation⁸ and may affect some of the physical properties of the products.⁴ Disorder in the starting material is also likely to weaken or destroy the X-ray diffraction pattern used to characterise the products.

Selected specimens (0.02—0.05 g.) of graphite were weighed, measured, and placed in sliding contact with the 24-gauge platinum wire (B in Fig. 1), forming the anode. A thinner wire would help to reduce losses from electrolytic side reactions but is a less effective support. A second, larger piece of graphite C ($\sim 2 \times 1 \times 0.1$ cm.) was cut from a well-oriented deposit of pyrolytic graphite (not, however, specially selected), and served as a floating reference electrode. The anode and cathode compartments were separated by a sintered Pyrex disc (porosity 1); bright platinum foil was used as cathode at A.

Great care was necessary in controlling the composition of the electrolyte; the best conditions observed with each of the acids used are detailed under the individual compounds below. In general, if the electrolyte was allowed to absorb too much water, side reactions during electrolysis competed to an undesirable extent with the primary electrochemical reaction. Moisture also impaired the stability of the acid salts on storage after the completion of electrolysis.

The electrolytic reaction was carried out by one of two methods:

(i) A current, constant to $\pm 2\%$, was passed continuously through the cell, by applying a D.C. voltage (H.T. Battery) of 24–36 v to the cell, in series with a 10^5 ohm resistance inserted to render insignificant any changes of the internal resistance of the cell during electrolysis.

(ii) A fixed voltage, usually 1.5 or 3.0 v (from dry cells), was applied across the cell, with only a small resistance (5000 ohms) in series, as shown in Fig. 1. Both the cell current, and the voltage developed between the specimen B and the reference electrode C, were recorded continuously.

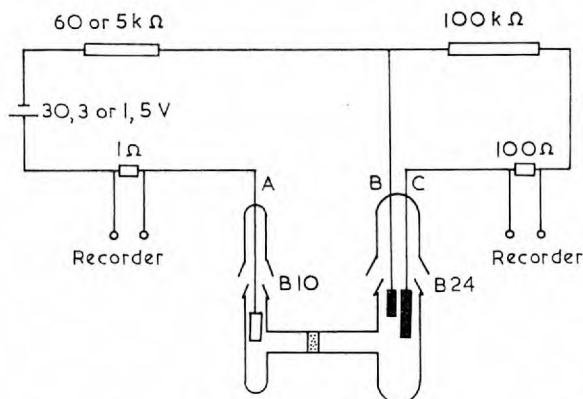


FIG. 1. Schematic diagram of preparation cell and associated electrical circuits.

Comparisons between runs at current densities of 500 and 50 $\mu\text{A}/\text{cm}^2$ showed very similar voltage-current plots in the case of the hydrogen sulphate. Rather better resolution of the plateaux observed in the early stages of compound formation was obtained with the lower current density, but this was normally used only when the formation of the lower oxidation states was of particular interest.

For the investigation of X-ray diffraction patterns, specimens were quickly transferred from the anode compartment to a satchel ($\sim 2 \times 1$ cm.) formed by heat-sealing polychlorotrifluoroethylene foil (0.03 mm. thick). Acid carried over with the specimen in this transfer helped to maintain anhydrous conditions inside the satchel. Photographic examination of the X-ray diffraction patterns from specimens prepared in this way normally showed no deterioration for up to 2 weeks, provided the acid salt itself did not decompose spontaneously.

For more accurate measurements of lattice spacings, the salts were prepared *in situ*, in the same electrochemical conditions, but with the graphite held in a special cell which could be mounted directly on a proportional-counter X-ray diffractometer. These studies are being described elsewhere.

Chemical Composition and Nomenclature of the Salts of Graphite and Acid.—In accord with Rüdorff and Hofmann's proposals,² crystal compounds in which every layer between the carbon-hexagon networks is filled are designated in the present paper as "first sequence" ("erste Stufe"); when every second layer is filled the compounds are designated as "second sequence," and so on.

Accurate chemical analysis of these crystal compounds proved difficult; if completely separated from the circumambient strongly acidic electrolyte, they decomposed quite rapidly. Mere immersion of the graphite compound in the analytical reagents is not adequate to remove all the intercalated species.⁸⁻¹⁰ Accurate chemical analysis thus requires destruction of the graphite networks and does not always lead to meaningful results in view of the instability of the compounds during handling. On the basis of special analytical techniques, the formula $\text{C}_{24}^+\text{HSO}_4^-(2\text{H}_2\text{SO}_4)$ has been put forward for the first-sequence bisulphate.² In this formula, the oxidation state of the graphite can be established with fair accuracy, but even if

the above limiting chemical formula describes the oxidation state correctly, the precise number of additional H_2SO_4 molecules packed between the carbon-hexagon networks is less certain. By analogy with graphite-bromine⁸ the spatial arrangement of such additional molecules packed within each intercalated layer is likely to depend on the sequence of formation reactions used.

It therefore seemed unprofitable to attempt to determine what "acid of crystallisation" was present in the preparations. Instead, two other methods have been used for identifying the compounds obtained.

(i) Graphs showing the voltage difference between the compound and the reference electrode as a function of the integrated charge passed per g.-atom of graphite showed breaks which often coincided with colour changes in the product. When electrolytic side reactions had been eliminated (or allowed for) these breaks could be correlated with the coulombs per carbon atom needed to reach specific stages in the electrochemical oxidation. Such correlation permitted assignment of the composition of the oxidation product C_n^+A^- , where A is the anion, but did not, of course, give any direct information about the intercalation of additional molecules of acid between the layers. This question is left open in what follows.

Since the limiting-sequence compound for many of the acids investigated appears to lie at $\text{C}_{24}^+\text{A}^-$, the integrated charge per carbon atom at given times has been plotted as a fraction of the total charge required to form this compound in conditions where no loss occurred by side reactions during electrolysis.

(ii) X-Ray diffraction patterns of the crystal compounds were obtained in every case. The 00 ℓ spacings confirmed changes in the distance between carbon-hexagon networks due to intercalation of the acid anions, either directly, as in the case of the first-sequence compounds, or indirectly, as for compounds of other sequences, if we assumed unfilled layers to have the normal graphite separation. In most cases, hkl reflexions were observed, showing that the individual crystallites had some degree of three-dimensional order. Except in the case of the first-sequence bisulphate, no hkl superlattice reflexions were observed, but the question of whether the intercalated molecules are ordered relative to the carbon lattice is not relevant to the use of the technique for chemical identification, and will not be discussed here.

Graphite Bisulphate.—Preparation of this salt by other methods has been frequently described. Nevertheless it was considered desirable to explore optimum conditions for preparation by the present electrolytic techniques, in view of the accurate control of composition they permit under favourable circumstances, and also because salts with other acids can be prepared from the bisulphate by double decomposition (see below). Electrolysis was best carried out in 100% sulphuric acid (Griffin and George). Fig. 2 records a plot of the voltage measured between electrodes B and C against the quantity of electricity passed. Clear breaks can be observed at X (where the solid first suddenly acquires a blue colour) and at Y. X-Ray-diffraction photographs of samples electrolysed under similar conditions showed only the structure of the first-sequence compound $\text{C}_{24}^+\text{HSO}_4^-(2\text{H}_2\text{SO}_4)$ at Y (Plate b). No further change could be detected in the pattern, or in the 00 ℓ spacings, in the interval from Y to Z. This interval was found to vary without any obvious relation to the mass of the graphite used. Provisionally, it seems likely that the portion of the curve in Fig. 2 beyond Y refers to the build-up of an oxygen overvoltage, and not to the formation of an oxidation stage higher than $\text{C}_{24}^+\text{HSO}_4^-$.

The break at X corresponds to completion of formation of the second-sequence compound $\text{C}_{48}^+\text{HSO}_4^-(n\text{H}_2\text{SO}_4)$ and the onset of formation of the first sequence. Formation of the second-sequence compound was verified by X-ray diffraction; the diffraction lines were, however, too weak for reproduction here. A less distinct break at W (Fig. 2) is probably due to completion of a third sequence, $\text{C}_{72}^+\text{HSO}_4^-(n\text{H}_2\text{SO}_4)$; but no attempt was made to verify this by X-ray diffraction methods. Fig. 2 further indicates that when 24 v were applied across the cell, the total current passed was ~25% in excess of the theoretical quantity of electricity calculated for completion of the various sequences. This excess can be attributed (at least in part) to the evolution of oxygen or formation of peracids at the platinum anode surface above the graphite specimen.

In the absence of graphite, only a small current (5–10 μA) passed for an applied E.M.F. of 2 v (Fig. 3). When this low driving potential was used for the formation of bisulphates, the excess of coulombs passed beyond the quantities required for the formation of the crystal compounds corresponded quite closely to the discharge processes on the surface of the platinum

support. However, such small E.M.F.s, though necessary to establish the amount of charge transfer, were inconvenient and time-consuming for general preparative purposes. Fig. 3 shows the effect of increased driving voltages on the current flowing between bare platinum electrodes in various strong acids.

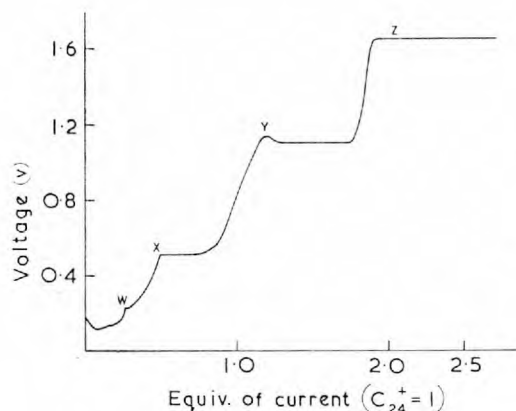


FIG. 2.

FIG. 2. Voltage-current curve for the formation of graphite hydrogen sulphate.

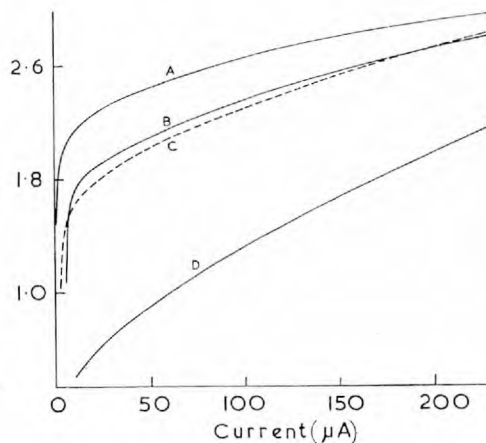


FIG. 3.

FIG. 3. Current flowing through cell, with bright platinum electrodes, as a function of applied voltage for various strong acids.

A, 100% H_2SO_4 ; B, HClO_4 ; C, 98% H_2SO_4 ; D, ClSO_3H .

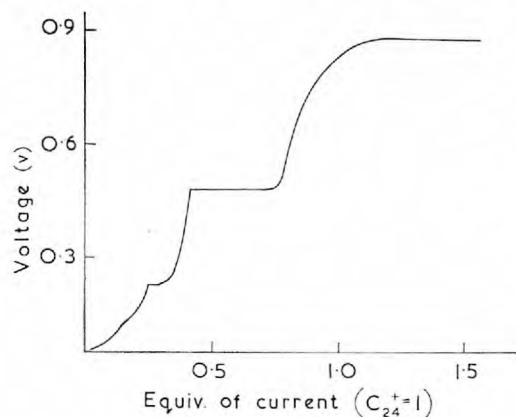


FIG. 4.

FIG. 4. Voltage-current curve for graphite chlorosulphonate.

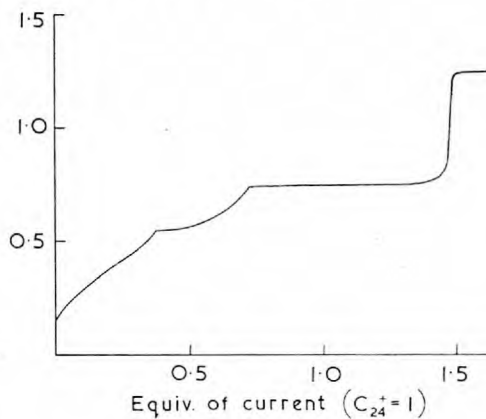
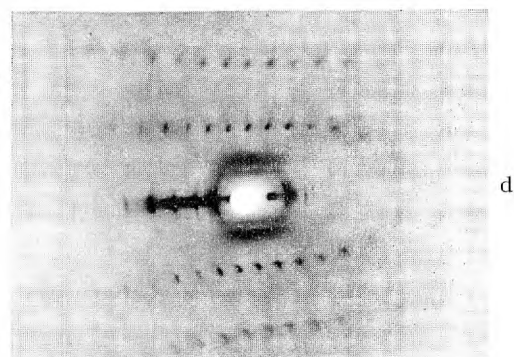
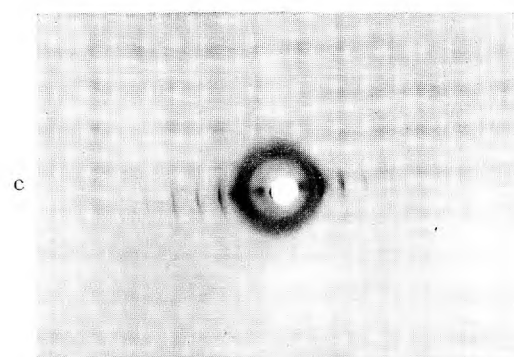
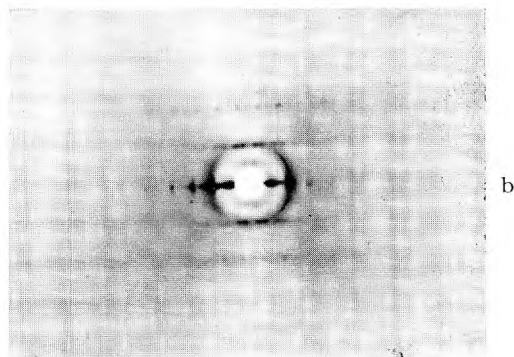
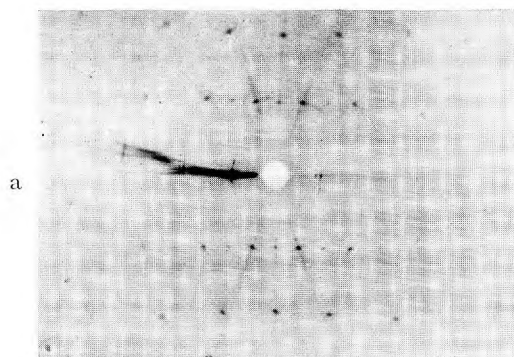


FIG. 5.

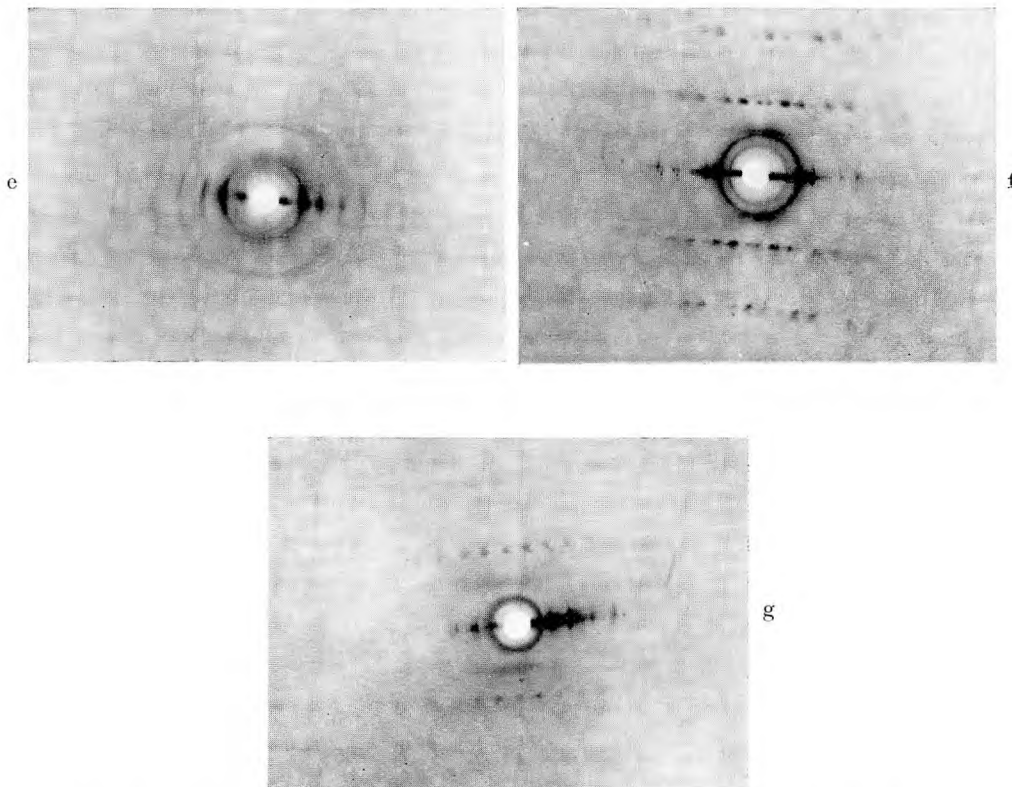
FIG. 5. Voltage-current curve for graphite selenate.

Graphite Chlorosulphonates.—With 100% chlorosulphonic acid (B.D.H.; 99.5% acid, 95% chlorine), the higher-voltage technique was more suitable, despite the fact that, with this electrolyte, application of 24 v led to a much larger excess current than with 100% sulphuric acid (cf. Fig. 3). This excess corresponds with a reduced efficiency of formation of graphite chlorosulphonate $\text{C}_{24}^+\text{SO}_3\text{Cl}^-n(\text{ClSO}_3\text{H})$ in the present apparatus. Fig. 4 shows the final plateau corresponding with $\text{C}_{24}^+\text{SO}_3\text{Cl}^-$, with breaks for the second- and third-sequence compounds. Formation of the first-sequence compound was verified by X-ray diffraction (Plate c).

Graphite Selenates.—Preparation of these crystal compounds by electrolysis called for particularly careful control of the conditions. At room temperature commercial 100% selenic acid crystallised in the cell, particularly around the sintered disc which provided numerous



[To face p.



Diffraction photographs of stationary specimens recorded with Mo-*K* radiation (Zr-filtered except for A) on flat film. In all cases the *c*-axis is approximately horizontal and perpendicular to the beam. The random *a*-axis orientation of crystallites in any specimen gives rise to a diffraction pattern that is effectively a *c*-axis rotation photograph of a single crystal.

- (a) Pyrolytic graphite, type AB, as used for preparations. (b) Graphite hydrogen sulphate, first sequence. The superlattice *hkl* reflexions are clearly visible. (c) Graphite chlorosulphate, first sequence. (d) Graphite perchlorate, first sequence. (e) Graphite perchlorate, first sequence. Double-decomposition preparation. (f) Graphite nitrate, first sequence. (g) Graphite nitrate, second sequence.

nucleation centres. Raising the temperature kept this electrolyte molten, but above 30° no first-sequence compound was formed, presumably owing to its instability at this temperature or to competitive side reactions at the graphite anode. As the acid was progressively diluted with distilled water, the efficiency of electrochemical oxidation decreased rapidly. A workable compromise was to add just sufficient distilled water to keep the electrolyte "liquid" at 25°, and to electrolyse at this temperature with an applied voltage of 1.5 v so as to minimise side reactions. As illustrated in Fig. 5, a charge-transfer efficiency of ~85% was achieved in these conditions; in some experiments, the sharp rise at the end of the preparation illustrated in Fig. 5 was sometimes more gradual. Other evidence suggests that this rise is a function of the structural perfection of the starting material.

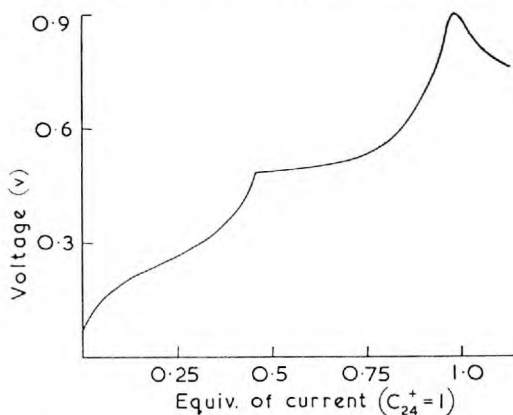
With this crystal compound it was important to stop electrolysis at the end-point, to avoid rapid exfoliation. As in the case of the acid sulphate, the final plateau observed in the plot in Fig. 5 was probably due to oxygen overvoltage. For both acids, a tentative hypothesis is that the peracid radical $[\text{SO}_3(\text{OOH})]^-$ or $[\text{SeO}_3(\text{OOH})]^-$ begins to intercalate between the carbon-hexagon networks when formation of the first-sequence compound is complete. However, this would be a highly unstable system, especially for perselenic acid. The exfoliation may be due to liberation of oxygen in this decomposition within the specimen.

The problem of stopping electrolysis before serious degradation of the sample takes place was not easily overcome for the selenate. Unlike the bisulphate and perchlorate, with which either a fairly sharp plateau or clear peak marked the completion of formation of $\text{C}_{24}^+\text{A}^-$, the selenate only rarely showed a break, apparently owing to the proximity of the overvoltage potential. This aspect of the preparation of graphite biselenate has not been examined further, mainly because X-ray-diffraction photographs of all preparations showed no hkl reflexions. By analogy with the preparation of graphite perchlorate, discussed below, the best route to graphite hydrogen selenate seems to be double decomposition of graphite bisulphate and selenic acid.

Fig. 5 also illustrates breaks which mark the complete formation of two crystal compounds with longer sequences than the first. It was interesting that the second-sequence compound was also blue, unlike most of these salts with acid but like alkali-metal derivatives of graphite.

Graphite Perchlorates.—When 70% perchloric acid and a driving voltage either of 24 v or 1.5–3 v were used, the preparation proceeded, with a loss in side reactions of 5–10% of transferred charge, to the stage where a peak corresponding with the first-sequence compound was

FIG. 6. Voltage-current curve for graphite perchlorate.



reached (Fig. 6). As in the case of the selenate, electrolysis beyond this stage led to rapid breakdown, probably involving decomposition of the perchlorate radicals within the specimen. Water liberated in such decomposition further accelerates breakdown, so that it soon becomes catastrophic. Attempts to lower the concentration of "free" water by adding anhydrous magnesium perchlorate reduced neither the side losses nor the decomposition beyond $\text{C}_{24}^+\text{ClO}_4^-$. X-Ray diffraction patterns were obtained for the first-sequence (Plate d) and higher-sequence compounds prepared by electrolysis.

Graphite Nitrates.—Immersion of well-oriented pyrolytic graphite in fuming nitric acid (d 1.52) led to the formation of the second-sequence compound directly, by chemical oxidation

(Plate g). Therefore, with the second-sequence compound as reference electrode, formation of the first-sequence compound (Plate f) could be carried out by electrochemical oxidation with fuming nitric acid partly dehydrated by phosphorus pentoxide, which resulted in the formation of some (about 10%) nitrogen pentoxide in solution. The graphite nitrate first-sequence compound did not appear to be very stable even in this acid (see below). It proved practicable to form the first-sequence compound by passing a fairly high current (500 μ A) with a 24 v driving potential and continuing the reaction until the E.M.F. referred to the secondary electrode ceased to rise. The correlation between the weight of sample and the total charge transferred was not good, probably because of the instability of the first-sequence compound in contact with nitric acid. Completely reproducible preparation of the first-sequence compound may demand the use of nitric acid containing some 50% of nitrogen pentoxide in which the compound is reported to be stable.² We have confirmed that direct formation of the first-sequence compound occurs when the graphite is immersed in this solution, but this preparation is much less convenient than electrolysis.

X-Ray diffraction photographs showed that at room temperature the second-sequence nitrate was stable indefinitely in contact with fuming nitric acid, but that in these conditions the first-sequence compound reverted to the second-sequence compound during 1–3 days. It may, however, be preserved if the excess of acid is drained away after completion of the electrochemical preparation and the solid is then stored in a sealed glass tube.

Graphite nitrates can also be prepared by double decomposition from the stage 1 hydrogen sulphates, as described below.

Formation of Salts with Other Acids by Electrochemical Oxidation of Well-oriented Graphite.—It seems likely that salts with a number of other acids can be prepared by similar electrochemical procedures, provided suitable electrolytes can be found. Mention is made here of preliminary studies which illustrate the kind of obstacles encountered.

Graphite Fluorosulphonates.—Anhydrous fluorosulphonic acid was prepared by distilling the commercial acid (kindly provided by Imperial Smelting Corporation) until a colourless fraction was obtained (b. p. 155–165°). Electrolytic preparation apparently gave only the first-sequence compounds as a distinct stage in the formation. No satisfactory X-ray diffraction patterns could be obtained, principally because of difficulties in handling the samples, which evolved hydrogen fluoride in large quantities.

Boron Trifluoride-Diacetic Acid.—As electrolyte, a 40% solution of boron trifluoride in glacial acetic acid was investigated. This contained a large fraction of the trifluoride in the form of the above complex.¹¹ Electrolysis led to the formation of a blue compound, probably third-sequence $C_{32}^+A^-$, and there were also indications of a fourth-sequence compound $C_{64}^+A^-$.

Acids, CF_3CO_2H , H_3PO_4 , H_3AsO_4 , HIO_4 . With each of these acids, a cathetometer was used to follow swelling during anodic oxidation of well-oriented graphite. X-Ray-diffraction patterns gave indications of an expansion of the layers and the formation of crystal compounds, in the case of periodic and arsenic acid, but no detailed X-ray examination of any of these compounds has yet been practicable.

For trichloroacetic and dichloroacetic acids, no suitable electrolyte composition has yet been found. Possibly these acids are too weak to permit the formation of salts of graphite by the method.

Cathodic reactions during electrolysis. Cathodic hydrogen may lead to reduction products, especially with strong acids when very concentrated. Thus concentrated sulphuric acid gave some hydrogen sulphide and sulphur; selenic acid gave finely divided selenium; but the sintered disc reduced the rate of diffusion of any such products into the anode compartment and no serious disturbances were experienced.

Indirect Formation of Salts by Double Decomposition.—From the present experiments, it seemed likely that obstacles to a generalisation of these direct electrochemical methods might include the following:

(i) Water in solution tends to promote side reactions during electrolysis and to reduce the stability of the salt. It is tempting to interpret the first step in the degradation of graphite salts as a hydrolysis, e.g.:



followed by proton switching and valency rearrangements in the graphite-hydroxide system,

leading eventually to alicyclic types of network and conversion into graphite oxide. For various reasons, unfortunately, water cannot always be entirely eliminated from the electrolyte.

(ii) Some acids may be too unstable or too weak to conduct an adequate current at room temperature. Rise of temperature may promote degradation and cannot generally be used to increase electrical conductivity. Cooling, to improve stability, may reduce the conductivity to an undesirable level.

(iii) The affinity of the process



and of similar oxidative processes for higher-sequence derivatives may require very high driving voltages and cause deleterious side reactions to take place during electrolysis.

Such difficulties indicated the desirability of exploiting an indirect electrochemical route for obtaining these salts. Graphite bisulphates are readily and reliably prepared by the electrochemical method; starting with well-oriented pyrolytic graphite, the products are coherent, and the sulphuric acid electrolyte can readily be replaced *in situ* by a range of other concentrated acids. Provided that thermodynamic and kinetic conditions are suitable, repeated washing can lead to the formation of salts of other acids by double decomposition:



here mass-action principles can be applied to remove the sulphate from the compound, if necessary by repeated washings.

This procedure has been tested for the bisulphate first-sequence compound, in double decomposition with 70% perchloric acid. First-stage graphite perchlorate $\text{C}_{24}^+\text{ClO}_4^-$ was obtained, and the hazards of overoxidation encountered in the direct electrochemical oxidation as described above were obviated at the expense of a rather less well-oriented product (see below).

Problems of electrochemical instability limit the usefulness of this procedure. Thus graphite nitrate was obtained only as a second-sequence compound by washing the first-sequence hydrogen sulphate with fuming nitric acid until all traces of sulphate ion had disappeared. Presumably the first-sequence nitrate was too unstable to survive these operations.

Though they verify that double decomposition has occurred, *X*-ray-diffraction measurements do not, of course, guarantee that this indirect route removes the final trace of anions intercalated in the direct preparation, which may be stubbornly retained as "residue compounds."⁸⁻¹⁰ In this connexion it may be significant that graphite perchlorate formed by double decomposition (Plate e) showed the correct 00 l spacings but with increased *c*-axis misorientation, compared with the crystal compound prepared by direct electrolysis (Plate d). (The graphite used as starting material in this reaction sequence was of the same high degree of order as in that which yielded Plate b.)

Double decomposition is thus to be used with caution; careful chemical analysis is advisable in cases where such retentions could lead to error. Nevertheless, double decomposition offers a very promising route where direct electrochemical oxidation is unpracticable.

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Thermal expansion of some salts of graphite

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X-ray methods have been applied to measure *c* axis thermal expansion of nitrates, perchlorates, and bisulphates of graphite. Three different intercalation sequences were prepared from each of these acids, stress-annealed graphite being used as starting material. Positions of high angle 00 ℓ diffraction peaks were recorded over the temperature range +25 to –60 °C, by means of a proportional counter diffractometer.

Thermal expansions of all these salts in the *c* axis direction, are up to three times as large as in the parent graphite. In addition, the three nitrates show a thermal expansion anomaly at about –20 °C and one of the bisulphates shows a small anomaly at –3 °C. These may be due to λ -type transformations in these salts.

INTRODUCTION

As is well known, graphite forms a considerable range of crystal compounds, by intercalation of a diversity of molecules between the carbon hexagon networks. X-ray evidence (see, for example, Rüdorff 1939) indicates that intercalation leads to an expansion of the spacings between the planes of carbon hexagons, but has no detectable effect on carbon–carbon bond distances within any network. Nevertheless, transfer of charge between the aromatic networks and the intercalated molecules can be inferred from the profound modification of electronic properties of the parent graphite when it is transformed into a variety of crystal compounds (cf. references quoted in Ubbelohde & Lewis 1960). However, even in graphite itself, the nature of the interaction between planes of carbon atoms in the direction of the *c* axis is not completely understood. Fuller understanding of interaction forces between the intercalates and the macro-aromatic molecules, is likewise needed, to interpret some highly interesting properties of the crystal compounds in the direction of the *c* axis.

These considerations give special interest to studies of crystal properties dependent on the force fields in this direction. In this connexion, the present paper deals with measurements of thermal expansion.

By stress recrystallization at high temperatures of pyrolytic graphites prepared by cracking methane at about 2180 °C (type AB, Blackman & Ubbelohde 1962; cf. Moore, Ubbelohde & Young 1963), synthetic graphites can be obtained in which the *c* axes are closely aligned. A variety of crystal compounds can be formed from these graphites, without distortion of the alignment. For example, many salts of graphite can be prepared by electrochemical oxidation methods (Bottomley, Parry, Ubbelohde & Young 1964). A survey of these products by X-ray methods has shown that salts of nitric, sulphuric and perchloric acids are formed in clearly defined oxidative states, with sufficient structural perfection to enable diffraction effects to be observed from planes whose spacing is about 1 Å. Samples can be

prepared with dimensions up to 1 cm square which so far as the 00l reflexions are concerned are almost single crystals, and yet allow the use of Bragg-Brentano focusing geometry for measurements of *c* axis thermal expansions by diffractometer techniques. With the precautions described below, such samples have been found to have an adequate stability when subjected to cycles of temperature in repeat determinations.

An interesting feature of the results recorded in the present paper is the prominent anomaly of thermal expansion in each of the three sequences in the nitrates of graphite, which may be due to a λ -type transformation in the crystals.

EXPERIMENTAL

Apparatus

In view of the easy deformability of graphite salts and of their decomposition by moisture, sample preparations were carried out *in situ* in a specially designed X-ray diffraction cell. It was decided to measure thermal expansions by cooling, since these salts of graphite become progressively less stable when heated above room temperature, and since cooling enhances the intensity of the rather weak high-order 00l reflexions. With the sample enclosed in the rather bulky electrolytic cell used, cooling by gas flow was impracticable. Instead, it was necessary to pump a thermostatically controlled fluid through a cooling jacket on the cell.

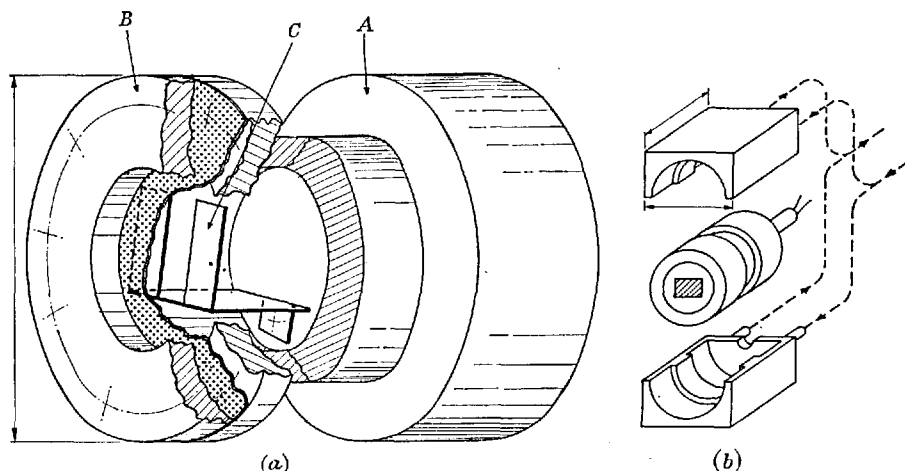


FIGURE 1. (a) Cell used for measurements of thermal expansion on diffractometer. A, Teflon body of cell; B, brass ring clamping window to cell body; C, platinum clip to hold sample. (b) Copper locating block, showing schematic flow of cooled petroleum ether.

The electrolytic cell (A) used for the majority of the results described in this paper is illustrated in figure 1. Its central parts were constructed of Teflon, made gas-tight by a film of Teflon 0.002 in. thick, firmly held in place against a circular ridge on the front face of the cell body by the outer brass ring (B), secured to the body by eight 8 B.A. brass bolts. A 24-gauge platinum electrode (C), the back surface of which defined the specimen plane when the cell was mounted on the

diffractometer, was likewise screwed to the body of the cell, and the graphite sample was held against this surface by light pressure from a Teflon spring (not shown).

During electrochemical oxidation, the thin graphite sample expanded against the Teflon spring with its front surface still in contact with the platinum anode, *C*, and thus satisfying the geometrical requirements for focusing. In trial removal and replacement of the cell on the diffractometer, uncertainties of location of this surface did not lead to errors greater than 5' of arc in the Bragg angle. These could be neglected in the thermal expansion measurements as no systematic trends or abrupt changes in location could be detected in the course of a temperature cycle. Absence of systematic trends was further verified by the close correspondence between thermal expansions of type AB graphite measured in the apparatus described, with values derived from other work (table 1). Absence of abrupt changes was verified from the reproducibility of the expansion curves obtained in repeat runs, and with different samples and different cells.

TABLE 1. THERMAL EXPANSION COEFFICIENTS OF GRAPHITE

authors	temperature range, etc.	expansion coefficient $\times 10^6$
present work		
cell 1	-40 to +30 °C	25.2 (mean)
cell 2		
sample 1	-40 to +30 °C	24.7 (mean)
sample 2	-40 to +30 °C	24.9 (mean)
Nelson & Riley (1945)	extrapolation of smoothed curve to 0 °C	24.5
Steward & Cook (1960)	15 to 800 °C	28.4 (mean)
Matuyama (1955, 1958)	0°C	24.6

In the present results any curvature in the plot of lattice spacing against temperature could be neglected so that mean thermal expansions may be directly compared with other values of $(dd/dT)/d$. Cell 1 is that described in the text. Data obtained with cell 2 (an earlier design) are quoted separately to illustrate the order of reproducibility.

Procedure

The complete assembly was tested from time to time with a specimen of stress recrystallized type AB graphite to check that the resolution of the peak profiles was being maintained.

The temperature of the specimen was controlled to ± 0.25 degC within the range +25 to -55 °C, and was measured by a thermistor encapsulated in a thin glass sleeve, passing through the back wall of the cell and rigidly fixed to it so that the thermistor tip was located within 0.5 mm of the rear surface of the specimen. To maintain various temperatures, petroleum ether was pumped from a low temperature thermostat, through a series of narrow channels in the split copper block (figure 1(b)) surrounding the cell. Location of the cell to 0.1 mm within this block was ensured by careful machining of all the parts. Thermal insulation between the copper block and the worm wheel of the standard sample holder on the Berthold diffractometer was ensured by a spacer plate of pyrophyllite $\frac{3}{4}$ in.

thick which was screwed to the worm wheel. Optical methods were used to ensure that the surface of the sample lay in the specimen surface of the diffractometer, and the copper block was then firmly glued to the pyrophyllite with Araldite. Sealed X-ray tubes, selected to give radiation of suitable wavelengths (cf. table 2) were supplied from a stabilized high voltage generator. A Xenon-filled proportional counter detector received the diffracted beam, and was connected through an amplifier and pulse-height analyzer to a conventional scaler, ratemeter and chart recorder.

TABLE 2. SALTS OF GRAPHITE

salt	sequence	reflexion used	radiation $K\alpha_1$	θ $\pm 1'$	layer thickness Å	
					observed at 20 °C	Rüdorff (1939)
nitrate	I	008	Co	66° 15'	7.82 7.83	7.84
	II*	0020 0022	Fe	60° 18' 72° 46'	11.15	11.14
	III	0018	Cu	73° 3'	14.48 14.49	14.49
	I	008	Fe	74° 30'	8.01	7.98
	II*	0022	Fe	70° 15'	11.32	11.33
bisulphate	III*	0026	Fe	58° 45'	14.71	14.68
	I	006	Cu	48°	7.73 7.94	7.94
	II*	0020	Fe	61°	11.06	11.12
perchlorate	III	0014	Fe	69° 50'	14.43	14.30
Fe $K\alpha_1$ 1.93597 Cu $K\alpha_1$ 1.54051 Co $K\alpha_1$ 1.78892 Å						

The layer thickness gives the distance between successive carbon hexagon networks. For the first sequence it refers to a single filled layer, for higher sequences it combines the thickness of filled and empty layers. When the stacking in successive filled layers follows the sequence *abab...* instead of *aaa...* this is indicated by an asterisk and the 00*l* indices are doubled accordingly.

For each preparation of any desired compound, a preliminary survey was recorded of the diffraction pattern at room temperature in the range of Bragg angles from 20 to 80°. Only specimens free from other compounds and giving well-defined sequences of maxima, with good resolution of $K\alpha_1$ and $K\alpha_2$ peaks were studied further. Positions and intensities of the 00*l* maxima were, when possible, tested by comparison with X-ray powder diffraction data on graphite salts prepared by chemical means (Rüdorff 1939). The $K\alpha_1$ peak of highest attainable angle was next located with high precision, by scalar counting for 100 s at successive intervals of 1'. When the position of the peak maximum had been established, the temperature of the cell was lowered, usually by 10 to 15 degC, and the position of this maximum was again recorded. At each temperature the sample was left until the X-ray diffraction record showed that it was in thermal equilibrium with the cell. Approach to thermal equilibrium was followed by setting the counter on the edge of the peak, where the counting rate is very sensitive to changes

in position of the peak maximum. Times of the order of $\frac{1}{2}$ h were required to reach steady conditions after each change of temperature. Reflexions were recorded at more frequent temperature intervals near the λ -type change in graphite nitrates; the time necessary for equilibration was not found to alter to an extent which might indicate marked hysteresis.

After reaching the lowest temperatures conveniently attainable by pumping fluid from the reservoir thermostat, the cell was brought back to room temperature and a second complete diffraction pattern was recorded to verify that no structural or chemical deterioration of the sample had occurred. Accidental changes of location could also be detected in this way and were found to be less than the counter vernier error of $\pm 1'$ in Bragg angle. It is estimated that absolute values of lattice spacings observed with different specimens of the same material were reproducible to $0.01 \text{ \AA}$, whereas the estimated standard deviation (e.s.d.) for thermal expansion coefficients quoted in table 3, is around $\pm 5\%$ varying somewhat with the reflexion used.

Preparation of specimens

Electrolysis, or in the case of the nitrates, direct attack by the acid of appropriate strength, was carried out *in situ* with the cell tipped up so that the graphite lay at the bottom, and could be covered by electrolyte. For acid sulphates, the electrolyte was 100% H_2SO_4 , and for perchlorates 70% HClO_4 . For nitrates, third-sequence intercalation was obtained by direct immersion of the graphite for 12 h in a mixture containing 40% by volume of HNO_3 (s.g. 1.42) with 60% by volume of HNO_3 (s.g. 1.52). Second-sequence intercalation was achieved by direct immersion in HNO_3 (s.g. 1.52). First-sequence nitrates could only be obtained by use of a mixture of 50% HNO_3 (s.g. 1.52 by weight) with 50% N_2O_5 directly prepared by distillation from HNO_3 and P_2O_5 . In the electrochemical preparations, bright platinum wire was used as cathode (not shown in figure 1). General features of these preparations and determinations of composition have been previously described (Bottomley *et al.* 1963). In the present researches, the pieces of graphite used were approximately $10 \times 5 \times 0.1 \text{ mm}$; they were weighed before being placed in contact with the anode *C* and were electrolyzed at current densities of about 200 to $500 \mu\text{A}/\text{cm}^2$. After the desired intercalation stage had been reached, the platinum cathode and most of the electrolyte were removed. The front of the cell was clamped in place to make an airtight seal, before proceeding to the X-ray diffraction experiments. It was found desirable to leave a small gap (about 0.5 mm) between the electrode *C* and the thin Teflon window of the cell, so that there was no tendency for the electrolyte remaining in the cell to be drawn up over the front surfaces of the sample by capillary action when the cell was in place in the diffractometer.

Except where otherwise stated, each intercalation sequence of any salt was studied in two different preparations and each preparation was subjected to repeat thermal cycles to determine its thermal expansion. Table 2 records calculated mean values of the observed lattice spacings d in the c direction and table 3 the values of the mean thermal expansion coefficients over the temperature range

specified. For all the salts except the three nitrates and one of the bisulphates, the results could be accurately described by calculating the line of closest fit whose gradient gives the quoted thermal expansion. For the three nitrates, a prominent anomaly in thermal expansion was observed around -20°C . In order to record these anomalies with greater precision in figure 2, changes of spacing are plotted after subtracting the spacing at 20° at the beginning of a thermal cycle, which

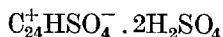
TABLE 3. THERMAL EXPANSIONS OF GRAPHITE SALTS

salt and sequence	sample	thermal expansion coefficient		
		temperature range ($^{\circ}\text{C}$)	$(dd/dT)/d$ ($10^{-6} \text{ degC}^{-1}$)	(e.s.d.)
nitrate 1	1	25 to -15	83.5	4
	2	25 to -15	85	1.5
	2*	-25 to -50	94	1.5
nitrate 2	1, 2	25 to -15	62	4
	1,* 2*	-25 to -50	72	—
nitrate 3	1	25 to -15	55	—
	1*	-25 to -50	66	—
bisulphate 1	1	30 to -50	62	—
	2	30 to -50	61	2
bisulphate 2	1	25 to -50	43.5	1.2
	2	25 to -50	41.5	—
bisulphate 3	1	25 to -5	32.3	3.4
	1	-5 to -50	36.0	1.3
perchlorate 1	1	25 to -50	98	—
perchlorate 2	1	25 to -50	55	—

* Below transformation.

thus serves as a reference zero. Other information about the nitrates is recorded in table 4. Special features in some of the experiments were as follows:

Bisulphates. The first sequence compound, to which the formula



has been attributed (Rüdorff 1938), showed little tendency to revert spontaneously to lower oxidation states. No traces of longer-sequence compounds were observed in the diffraction patterns of samples kept in the cell for several weeks. However, a very slow drift with time was observed in some of the peaks studied. For the first-sequence compound, measurements made over several days pointed to an expansion of about $0.004 \text{ \AA/day}$. Since this drift was apparently quite uniform a small correction was made for it before calculating expansion coefficients from results of thermal cycles with this salt. With the second-sequence compound, a contraction was observed of about $0.012 \text{ \AA/day}$. Unlike the first-sequence compound, however, this compound showed no drift of its lattice spacing so long as the salt was kept cool, e.g. during actual observations. Gradual contraction was observed when the specimen was allowed to attain room temperature, e.g. at

night. With this salt, no correction was therefore made to the spacings recorded during any one consecutive run. Data for different days were fitted to a family of parallel lines by least squares methods (Ergun 1956). With the third-sequence compound no variation of spacing with time was detected, but the results could not be adequately represented by a single straight line, since there was evidence of a thermal expansion anomaly for this salt at about -3° . This was, however, much smaller in magnitude than for the nitrates, involving a contraction of about $0.005 \text{ \AA}$. Although this change is small compared with the drifts observed with the other two sequences, it appears as a distinct feature both in graphical plots of peak position against temperatures, and in the height of the diffraction peak.

TABLE 4. SPACING PARAMETERS (EQUATION (1)) FOR GRAPHITE SALTS OF VARIOUS INTERCALATION SEQUENCES (IN ÅNGSTRÖMS) AT 20°C

anion	r	s	values quoted by Rüdorff (1939)
parent graphite	3.35	—	—
nitrate I	3.35	7.82	7.84
II		7.80	7.79
III		7.78	7.79
perchlorate I	3.35	7.73 (7.94)	7.94
II		7.71	7.77
III		7.73	7.60
acid sulphate I	3.35	8.01	7.98
II		7.97	7.98
III		8.01	7.98

Nitrates. The relative instability of the first-sequence nitrates ($\text{C}_{24}\text{NO}_3, x\text{HNO}_3$) made it necessary to complete the thermal cycles within about 8 h and reduced the number of readings conveniently obtainable. As seen in figure 2, all three sequences showed a pronounced anomaly in the change of spacing with temperature at around -20°C . In thermal cycles, the repeatability of the spacing calculated at 20°C before and after passing through this anomaly was not so good as for the bisulphates, possibly due to undetected small hysteresis effects with the nitrates. As illustrated in table 2, the third-sequence nitrate showed rather a more gradual transition than the other two salts; this has been allowed for in tables 3 and 5.

Perchlorates. With this compound first and second sequences were found to behave normally. No anomalies were observed; thermal expansion coefficients calculated from the results are shown in table 3. For the third-sequence perchlorate the lattice spacing could still be determined (table 2), but unfortunately no resolution between $K\alpha_1$ and $K\alpha_2$ could be detected. This prevented evaluation of the thermal expansion for this sequence. In the present research, most of the preparations of the first-sequence perchlorate studied gave a 'filled layer' parameter s (see equation (1) below) corresponding with that of the longer sequences. However, as shown in table 4, one preparation gave a different value (7.94) of this parameter. A similar value has been reported by Rüdorff (cf. Ubbelohde

& Lewis 1960). This variant may possibly be due to a polymorphic rearrangement of perchlorate groups within an intercalated layer, or to an actual change in the chemical composition of the layer. At present this question must be left open; one of the difficulties is that only the anion content and not the total acid

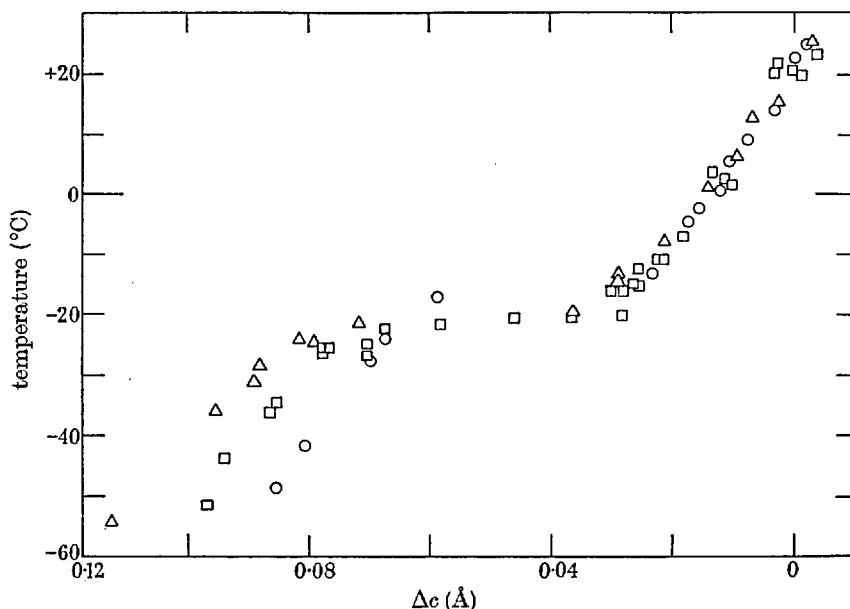


FIGURE 2. Thermal changes in lattice parameter (Δc) for graphite nitrates. O, First sequence: reference spacing at 20 °C = 7.84; □, second sequence: reference spacing at 20 °C = 11.14; Δ, third sequence: reference spacing at 20 °C = 14.49 Å.

TABLE 5. THERMAL EXPANSIONS OF SEPARATE LAYERS BASED ON THE HYPOTHESIS OF INDEPENDENCE

anion	sequence	observed $10^3(dd/dT)$ (Å/degC)	$10^3(dS/dT)$ derived from equation (2)	temperature range
nitrate*	I	0.657	0.657	25° C to λ-transition
	II	0.691	0.605	—
	III	0.800	0.628	—
nitrate*	I	0.735	0.735	-50 °C to λ-transition
	II	0.803	0.717	—
	III	0.950	0.778	—
perchlorate	I	0.734	0.734	—
	II	0.605	0.519	25 to -50 °C
	III	—	—	—
bisulphate	I	0.492	0.492	—
	II	0.482	0.386	25 to -50 °C
	III	0.470	0.298	25 to -5 °C
		0.529	0.357	-5 to -50 °C

* Estimated at some distance from the curvature produced by the transition.

content of an intercalated layer could be completely determined by the present method of sample preparation.

Further insights into this problem could in principle be obtained from measurements of density of these salts. By using the layer thicknesses observed (table 2) it may be calculated that densities change appreciably if additional acid is incorporated in the salt. This may be illustrated with reference to bisulphates and nitrates (table 6).

TABLE 6. CALCULATED DENSITIES OF GRAPHITE SALTS

salt	no acid	1 mole acid per anion	2 moles acid per anion	observed
bisulphate, sequence I	1.267	1.584	1.901	(1.84)
nitrate, sequence II	1.510	1.659	1.808	1.98

Handling of these salts without decomposition involves keeping them wetted with the strong acid in which they were formed. For density determinations, access of moisture to this acid must be prevented. In the case of the first-sequence bisulphates, it was observed that seven out of ten preparations sank in conc. H_2SO_4 of density 1.84 g/cm^3 and three floated. This indicated a density near 1.84 g/cm^3 and confirmed at least approximately the chemical evaluation made by Rüdorff, which gave $\text{C}_{24}\text{HSO}_4^+ \cdot 2\text{H}_2\text{SO}_4$ as a likely figure.

For graphite nitrate II specimens were prepared by lowering weighed pieces of well-oriented graphite into conc. HNO_3 (s.g. 1.52), to convert them into second-sequence compound by direct oxidation *in situ*. These pieces were held in a silica stirrup, suspended from a calibrated quartz balance (extension 90 cm/mg). Sufficient excess of acid was used to be able to neglect any changes of its density due to reaction with the graphite. From Archimedes' principle, the mean density of four different samples was calculated to be 1.98 g/cm^3 . This points to a formula approximately $\text{C}_{48}\text{NO}_3 \cdot 3\text{HNO}_3$. It is not to be supposed without further evidence that these crystal compounds will necessarily show exact stoichiometric ratios between the anion and the excess acid incorporated, since the energy required to create defect sites in these crystals is likely to be only small.

DISCUSSION

Additive effects in intercalation sequences

For each of the three families of graphite salts studied in the present research, the largest observed spacing of the n th intercalation sequence in the direction of the c axis has been shown (Rüdorff 1939) to obey approximately the additive formula

$$d = (n-1)r + s; \quad (1)$$

r is the spacing between successive carbon hexagon networks when unfilled, and may be compared with the spacing between layers in the parent graphite; s is the spacing between a pair of networks expanded to permit intercalation. Table 4 gives values of r and s deduced from values of d recorded in table 2.

The additivity found is remarkable, since it suggests that the layer pairs in these crystal compounds of graphite behave in this respect as though they had no effect on one another. Although a 'two-dimensional' model for the physical and electronic properties of these substances has often been used (see, for example, Blackman, Mathews & Ubbelohde 1960), it leaves certain observations unaccounted for. For example, the hypothesis that different layer pairs of an intercalation compound behave independently does not explain why intercalation occurs at regular intervals in the higher sequences of these structures. Random sequences would be expected if there was no interaction between filled layers to keep each as far as possible from the neighbouring filled layers. The present results permit even more searching tests of the hypothesis of independent layers by showing to what extent thermal expansions of layer pairs in the different sequences, are likewise additive. If equation (1) applied accurately at different temperatures, differentiation would give

$$\frac{dd}{dT} = (n-1) \frac{dr}{dT} + \frac{ds}{dT}. \quad (2)$$

To test this possibility, dd/dT can be obtained directly from the present experimental observations on thermal expansion of the crystal compounds around room temperature, dr/dT is known from the thermal expansion of graphite, i.e. 25×10^{-6} per degC. Calculated values of ds/dT for the different sequences are illustrated in table 5. It will be seen that only in the case of the nitrate sequence is ds/dT even approximately independent of sequence. For the other salts, the thermal expansion ds/dT is seen to drop as n increases indicating a somewhat tighter binding in the layers for the higher sequences.

Even for nitrates, allowance has to be made for the steep change or jump in spacing at the λ -anomaly. In all, this anomaly corresponds with a shrinkage on cooling of about 0.044, 0.048 and 0.052 Å for the first-, second- and third-sequence nitrates.

From a theoretical standpoint, additivity of thermal expansions accompanying additivity of layer thickness could be accounted for fairly readily on the hypotheses that in these salts the spacings are determined by contact between repulsion envelopes of anion and cation, and that each of these repulsion envelopes changes independently owing to anharmonicity of internal vibrations. It seems plausible to regard vibrations of the carbon atoms perpendicular to the network planes in which the atoms lie, as largely determined by bond stretching and bond angle deformation potentials, within each aromatic macro-molecule. These would remain practically unaffected by the behaviour of carbon atoms some 3.54 Å or more distant, in neighbouring networks. Provided lattice vibrations within any one carbon network remains largely unaffected by the vibrations of carbon atoms in neighbouring planes, each macro-cation would thicken its repulsion envelope as the temperature rises.

However, the entropy of these salts may also change appreciably with changes of d , regardless of any vibrational effects. Shrinkage of the distance between the layers could, for example, result in changes of mutual orientation of anion and acid molecules, which may also be involved in the λ -effects reported. Any

contributions to changes in this entropy with layer separation could also affect thermal expansion, in view of the thermodynamic relationship (cf. Ubbelohde 1952)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$

An analogous equation for layer compounds would be, for changes in the direction of the c axis, keeping the composition n constant

$$\left(\frac{\partial S}{\partial P_c}\right)_T = -\left(\frac{\partial d}{\partial T}\right)_{P,n}. \quad (3)$$

With the acid salts, no further discrimination between vibrational and other possible sources of thermal expansion can yet be made. Similar studies in progress with alkali metal/graphite compounds should permit further discrimination between various interesting possibilities.

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