SURFACE POTENTIAL STUDIES IN CHEMISORPTION AND CATALYSIS

A Thesis submitted for the degree

Doctor of Philosophy

by

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ABSTRACT.

A static capacitor method has been developed for study of surface potential changes during adsorption on metal films. The metal film forms the outer cylinder of a cylindrical capacitor across which is maintained a constant field. Perturbation of this field by an adsorbed gas layer results in rapid automatic compensation by a servomechanism. The compensating voltage is equal to the contact potential change to within 0.2%, and is simultaneously displayed on a pen recorder.

The preparation and use of a new reference surface is described.

The rapid response of the measuring system has been utilised to examine transient surface potential changes occurring at the instant of interaction of a gas with a metal surface. These transient changes are identified with two phenomena

a) Formation of a weakly held 2nd layer which diffuses across the adatom layer and becomes chemisorbed, this behaviour is found for oxygen and hydrogen on nickel at 77°K and 90°K and for nitrogen on tungsten at 77°K. It is not found for CO on nickel and copper, or for oxygen on copper. Activation energies for diffusion have been derived and are of the order of 2-3 Kcal.

b) Addition of oxygen to nickel or copper films at temperatures greater than 90°K is accompanied by incorporation in the metal lattice. The kinetics of incorporation have been examined. It is suggested that the surface field is the controlling factor in incorporation.

Some preliminary experiments on nickel and copper
oxide are described as well as some on mixed gas studies. Surface potential changes on oxides are found to be small and positive.

Surface potential changes for nitrogen on tungsten show that the recorded S.P. depends on the temperature of measurement and the temperature of addition. An attempt is made to explain this behaviour in terms of the $\alpha$, $\beta$ and $\delta$ states.
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Some General Aspects of Adsorption on Metals.

The adsorption of gases on clean metal surfaces has posed complex problems. Even after some fifty years of effort the mechanism of interactions at metal surfaces is but imperfectly understood. In general, advances in knowledge have followed the introduction of new experimental techniques. This is particularly noticeable in the field of surface chemistry. The major obstacle to the understanding of gas-metal interactions has been to simplify a particular system so that it is perfectly defined. This means that the state of the metal surface must be well known, and at the same time the variables of the gas phase. The former is a difficult requirement because it involves the generation and maintenance of atomically clean surfaces. Because of this primary requirement, by far the greatest amount of work has been done on metals of the transition series. This group contains the only metals which can be cleaned by "flashing". Coupled with this of course is the catalytic importance of the group as a whole. The advent of ultra high vacuum technique and the use of evaporated
metal films has helped to extend investigations over a broader basis. These techniques are now commonplace and need no special comment.

The interaction of a gas with a metal surface was originally divided fairly neatly into two categories, physical sorption, and chemisorption. The former is very non specific, and occurs on all solids with all gases. It is characterised by low heats of adsorption, only slightly higher than the heats of liquifaction. Adsorption is only appreciable in a temperature-pressure range near condensation, and many layers may be formed reversibly. Accompanying physical adsorption of inert gases and other molecules on metals, is a large dipole, positive end outwards from the surface. The interaction is necessarily non dissociative.

On the other hand, chemisorption is quite different, occurring rapidly, with almost zero activation energy in most cases (1,2,3,4,) despite the frequent dissociation during adsorption. The heats of adsorption are high, up to several e V. Sticking coefficients are generally high, and lie in the range 0.1 to 0.5, and vary with coverage (5,3,4,) One of the most interesting discoveries of recent years, resulting from improved techniques, has been the existence of a multitude of so called weak binding states. As a result there is found to exist almost a spectrum of bonding energies lying in between what was formerly considered physisorption and chemisorption. These new states have been termed
weakly chemisorbed. Some general aspects of chemisorption will now be considered.

One of the basic macroscopic studies carried out on gas-metal systems has been the measurement of the differential heat of adsorption. Surprisingly, the heat is found universally to fall with increasing surface coverage (2, 6, 7, 8). Comparison of heats extrapolated to zero coverage yields a scale of values descending in the order

\[ \text{Ta} \gtrsim \text{W} \gtrsim \text{Cr} \gtrsim \text{Fe} \gtrsim \text{Ni} \gtrsim \text{Rh} \gtrsim \text{Cu} \gtrsim \text{Au} \] (8, 9)

This trend cannot be considered as precise since there is a good deal of variation from one worker to another. For example, the variation of maximum heats measured for oxygen on nickel ranges from 105 Kcals (10), to 150 Kcals (11). A similar wide variation occurs for iron and oxygen, namely 100 Kcals (12), to 130 Kcals (10), though these are some extreme examples. The general trend of heats of adsorption has been correlated (9, 13, 14) with the d character of the metallic bonds (15). This interpretation requires that the bond between metal and adatom be essentially covalent (16, 17, 18) which is in accord with all the experimental observations, excepting some alkali metals on tungsten (19, 20, 21), where the interaction is more ionic in character.

The importance of the d-band in gas-metal interactions is brought out quite neatly by the work of Couper and Eley (17) on the activation energy for the ortho-para hydrogen conversion on palladium. The activation energy
undergoes a sharp rise as the d-band is filled by alloying with gold. Again, Trapnell (22) concluded from studies of the chemisorption of several gases on a large number of metal films, that metals with vacancies in the d-band are very much more active adsorbents than other metals.

The detailed nature of the adsorption bond in chemisorption is still poorly understood. There have been relatively few quantum mechanical calculations, and these usually highly simplified (23). It has been suggested (24) that transition metals are active in chemisorption because of their ability to act as both donor and acceptor, due to their partly filled d-bands. The d-bands are narrow and correspond to fairly localised electrons. The d-electrons have a tendency to lower their energies by bonding which enables them to approach the bonding nucleus with a consequent decrease in potential energy. This is true only for partially filled bands. As filling nears completion, there is more overlap, and exchange within the band, and hence less external bonding activity. These early approaches to a theory of chemisorption have placed most emphasis on the electronic structure of the surface and adsorbed gas.

The advent of new microscopic techniques, field emission and field ionisation, together with flash filament studies, has demonstrated the importance of surface heterogeneity and specificity. These results for some simple molecular gases will now be considered.
Weak Binding States and Surface Diffusion.

Originally the decrease in the differential heat of adsorption was attributed to repulsive interactions between adsorbed entities, and later to surface heterogeneity, and consequent variations of binding energy. The latter explanation has gained much support from the discovery of weak binding states in chemisorbed metals. Suhrman (1) in 1929 concluded from photoelectric measurements that two sorts of hydrogen were present on the surface of platinum during chemisorption. It is not until the work of Mignolet (2) that more convincing evidence for multiple states emerges. From surface potential measurements Mignolet has reported the formation of a second layer of hydrogen on top of a layer already chemisorbed on nickel. Such a second layer has been found for hydrogen on tungsten. (3) (22)

Resistance measurements for hydrogen on nickel films (4) (5) (6), showed, when plotted against the hydrogen coverage, two peaks which were interpreted as indicating three surface complexes. However, since resistance is a bulk property it is probably not wise to rely too much on the evidence these measurements offer of a surface process.

The best demonstration of the existence of multiple states of binding was produced by Becker (32), and by Ehrlich from flash filament studies of the systems W-N₂ (7); W-CO (8); W-O₂ (31). Hickmott (9) has investigated the
system $W-H_2$ by the same technique. Further evidence for
the existance and behaviour of weakly bound surface states
has been produced, using the field emission microscope, by
Sachtler and van Reijen (10). These studies throw consid-
erable light on the complex nature of chemisorption, and
will be considered more fully.

Wiegman (3) has shown that hydrogen adsorbs on
tungsten at 100°K in much the same fashion as at higher
temperatures. However once this primary state has been fill-
ed, additional hydrogen goes into a second weaker binding
state. Mignolet (12) has confirmed this behaviour from
contact potential studies. He showed that the contact po-
tential of hydrogen on tungsten changed from -0.57V to
-0.41V at $3 \times 10^{-2}$ mm Hg and 77°K. Sachtler (10), from field
emission studies, has indicated the presence of four ad-
sorbed entities in the temperature range 77°K to 800°K
characterised as follows.

Strongly bound H atoms with heat adsorption 20-
46 K cal depending on crystal face, desorbing above 280°K.
Species with a positive dipole outwards, and heat of adsorp-
tion 15-20 K cal. Species with a negative dipole outwards
and heat of adsorption 8-14 K cal. Both these species show-
ing a preference for the 411 face. Lastly a weakly bound
positively polarised state, heat of adsorption 6-10 K cal,
found mainly on the 411, 111, and 320 faces. These results
have been interpreted by Sachtler in terms of a topographic
dependence of heat adsorption. The bond strengths have been correlated with the number of surface atoms contacted simultaneously, and with their degree of unsaturation. At low coverages the adsorbate is concentrated on the faces with the highest heats of adsorption, these faces becoming populated mainly by surface diffusion from less attractive faces. Only at very low temperatures where diffusion is restricted will there be uniform coverage over the crystal faces. While the importance of surface heterogeneity is pronounced, some species are the result of induced or polarisation effects, since they are only seen on faces covered with the adsorbate.

Carbon Monoxide on tungsten does not differ greatly from hydrogen on tungsten. Measurements of the absolute numbers of molecules in the primary binding states have been made. (8) The weakly bound entities constitute slightly more than one quarter of the surface population. Again a spectrum of heats of adsorption are found with accompanying surface specificity. Thus the heats fall from 100 K cal $\beta_3$ state, 70 K cal $\beta_2$ state; 52 K cal $\beta_1$ state to 20 K cal $\alpha$ state.

The behaviour of hydrogen and carbon monoxide on tungsten, is characteristic of adsorption in which equilibrium can be maintained, once the surface is filled in a way which ensures the maximum lowering of the free energy. Hydrogen on Platinum has been shown by Mignolet (13) and
Sachtler (10) to form two states having opposite dipole polarities. There is little evidence of any preferred surface sites for the two species.

In contrast, the adsorption of nitrogen on tungsten proceeds through the simultaneous filling of different binding states. Once again a spectrum of binding energies is found, ranging from 2 K cal for a probably physically sorbed state, to 9 K cal for the \( \alpha \) state, 20 K cal for the \( \alpha \) state, and 87 K cal for the \( \beta \) state. Studies in the field ion microscope (14) have revealed a very marked topographical dependence, so much so that the 110 face covered at low temperature, becomes bare at room temperature.

The exclusion of the (110) from adsorption processes involving nitrogen at room temperature is apparently a consequence of a relatively small difference in the binding energy of nitrogen atoms, 5.1 e.v. on the (110) compared with 6.7 e.v elsewhere.

The number of molecules in the \( \gamma \) state is in excess of that of the much stronger primary \( \beta \) state. This is a metastable situation, one in which the kinetics of formation dictates the instantaneous population distribution. That this is so can be demonstrated by experiment. For this system it is concluded that the two most populated states, \( \gamma \) and \( \alpha \) are immobile, in contrast to hydrogen on tungsten.

The mobility of adsorbed gas layers on metals has been demonstrated by Gomer (15), Ehrlich and Hudda (17) and
Klein (21) using the field emission microscope. Direct ob-
servation of the movement of boundaries on field emission
tips has enabled diffusion coefficients and hence activation
energies for diffusion to be measured. At least three types
of diffusion occur. For deposits in excess of a monolayer,
a sharp boundary moving almost uniformly over the field
emission tip, is observed at c.a. 27°K for oxygen and
20°K for hydrogen. The layer formed in this way is not mo-
bile if the initial deposit is insufficient for complete
spreading. The sharp boundary remains stationary to very
much higher temperatures unless more gas is added. This
type of diffusion shows an upper limit above which it will
not occur. These data have been used by Gomer to suggest
that gas physically adsorbed on top of an immobile chemi-
sorbed layer, can wander to the edge of the layer and be-
come trapped there, and so extend the monolayer. The upper
temperature limit corresponds to the evaporation of physi-
cally adsorbed molecules before their migration to the edge
of the monolayer and chemisorption on the bare surface. A
second type of diffusion occurs involving the chemisorbed
adatom layer. Atoms can migrate over planes such as the
110, but are trapped on the rough surface at it\'s edge. The
trap sites are presumed to consist of surface configurations
offering more near neighbours to a diffusing atom. Var-
iations are observed if the adatom is sufficiently large
to occupy an interstice between four atoms, creating a
surface on which migrating atoms can make contact with two atoms only, thus being less tightly bound. Such a situation is postulated for oxygen on tungsten. (15)

At low coverages diffusion from trap to trap becomes rate controlling when there is insufficient adsorbate to saturate the traps. This is found with hydrogen on tungsten.

Measurements of the ratio $E_d/E_{ad}$ (15), the activation energy for diffusion, to the heat of adsorption, shows that the ratio increases with $E_d$, that is with surface roughness. The potential structure of the surface imitates to some extent its physical one. On a perfectly smooth substrate diffusion would require zero activation energy, regardless of the energy of adsorption. A similar increase in ratio is demonstrated going from hydrogen to carbon monoxide on tungsten. This is probably connected with the number of formal bonds made with the surface. The small size of an H atom permits it to be in contact with almost its full quota of W atoms even during diffusion.

Studies on nitrogen (7) show that the weakly held $\sigma$ and $\pi$ states do not have an appreciable diffusion lifetime in the temperature range of their stability. The activation energy for conversion to a more stable state or to evaporation, must be comparable to the barrier that prevents hopping from one site to another. This type of behaviour is in line with adsorption on discrete singular sites, a con-
elusion supported by the absence of conversion between states in flash filament experiments. (7)

The nature of the sites on which weak bonding can occur has been discussed by Roberts (16), who pointed out that in the adsorption of a molecular gas on a surface, under conditions of low mobility, a random distribution of pairs of sites rather than single sites is obtained. In such a distribution a number of single sites will be completely surrounded by filled sites, and will therefore be available for weak binding only. In this way approximately eight out of every hundred sites are expected to remain empty. Roberts as well as Langmuir and Tomks (18), have considered a slightly different model in which adsorption on a given lattice site precludes adsorption on neighbouring sites. Accordingly, thirty seven out of every hundred sites are filled. Roberts original model is not physically realisable since even if at equilibrium the adsorbed layer is immobile, the two adatoms formed by dissociation of a single molecule need not go into adjacent sites on the surface.

However, Ehrlich (19) has shown that a model based on the notion of excluded sites can be applied to nitrogen on tungsten. On the assumption that each nitrogen adatom prevents occupation of an adjacent site by another adatom, and allowing each adatom one jump only, approximately 36% of the surface sites on the 100 plane can be filled with adatoms. The predicted behaviour from this model is in
good agreement with the experimental data. Thus the \( \gamma \) state can be identified with unavailable pair sites. It predicts a decrease in the number of \( \gamma \) molecules, as a tungsten film is annealed at high temperature following the removal of domain boundaries, as is observed. The filling of the surface depends on the crystal plane involved, with the result that some surface specificity will be observed, as is indeed found. The observation of weak binding states does not necessarily depend upon the presence of singular sites, since different crystal faces have a varying ability to bind gas. This may be more important with some systems.

The nature of the binding of weakly held layers is not yet resolved. Evidence from surface potential and field emission studies shows that the majority of weakly held states result in a decrease of the metal work function, or in other words they have a dipole with its positive end pointing away from the metal surface. Such a dipole arrangement is characteristic of a molecule, rather than an atom or ion, interacting with the metal surface. Independent evidence pointing to the molecular character of weakly bound states has been obtained for most of the systems discussed previously. It has been shown that adsorption at \( 77^\circ \)K of the rare gases on transition metals, produces high surface potential changes. (23, 24, 17)

Despite this fact adsorption energies appear to be "normal". The positive dipole has been interpreted in terms
of induced polarisation (25), charge transfer of the donor acceptor type (26), or surface defects. The foremost explanation relies on polarisation of the adsorbed molecule by the surface field of the metal. Molecules on the surface are incorporated partly in the metal double layer. The metal double layer is accepted as having its negative side out from the surface, (27) (28) (29), so that the polarised molecule will have a positive dipole outwards from the surface.

This explanation is most acceptable for large, easily polarisable molecules, such as the rare gases, but for a small molecule such as $\text{H}_2$, there are immediate objections. The second explanation, in terms of donor-acceptor interactions, proposes that since the transition metals possess d-orbitals of low energy, they will accordingly be good acceptors and yield high S.P.'s. This is found experimentally. For molecules, the donor acceptor interaction may also be relevant. For example, the high heats of adsorption of hydrogen molecules on hydrogen covered tungsten or platinum surfaces, 9 and 15 K cal/mole respectively, are difficult to account for by polarisation effects alone.

The importance of weakly bound, particularly physically adsorbed, molecules in the kinetics of chemisorption has been discussed by Ehrlich (20), and Kislink (30). Ehrlich has analysed the then available data on the adsorption of diatomic molecules on bare metal surfaces. He concluded that with perhaps the exception of hydrogen, molecules physically
adsorbed on the surface form a reservoir from which chemisorption can occur. Or, quite generally, that if the sticking probability is less than one, and the condensation coefficient is equal to one, any chemisorption process must involve the participation of physically adsorbed precursors. In view of the variety of binding energies found for surface states, the precursor to chemisorption does not necessarily need to be physisorbed in the strict sense, one of the weakly bound states could doubtless function as a precursor.
The Work Function and Contact Potential.

The concepts of the work function and contact potential are basic to the various methods of surface potential measurements, so it is important to define these terms clearly and unambiguously before discussing any of the experimental methods of surface potential measurement. The thermodynamic basis of work functions and thermionic emission has been reviewed comprehensively by Herring (1), while contact potentials are discussed in a series of papers by Chalmers, (2) and also by Koenig and Lange (3).

The work function of a metal is defined as the difference in energy between an electron at rest in a vacuum 10^{-4} cm outside a metal, and an electron at the Fermi level. Let this energy difference be represented by $|e| \phi$, where $\phi$ is the electrostatic potential difference and $e$ the electronic charge, then from the definition and (fig. 1)

$$e \phi = W_1 - \xi_{01}$$

The terms in this equation are energy and can be expressed in electron volts, $\phi$ is then in volts. The energy $\xi_{01}$ is kinetic, all electrons inside the box having potential energy $-W$. The potential step $W$ is an intrinsic property of the metal, though a complicated one. It depends partly on the structure of the surface, and also on the presence of a double layer. This double layer of sheets of positive
and negative charges, results from the unsymmetrical placing of the electrons of the surface atoms with respect to the positive ions. This displacement of charge arises from the discontinuous nature of the metal surface. If \( \sigma \) is the charge per unit area, and \( t \) the thickness of the double-layer, then its dipole moment per unit area is \( \sigma t \), and the potential step across it is \( 4\pi \sigma t \), the surface potential. This quantity is contained in \( W \); \( W \) must be expected to vary if the surface is contaminated with impurity atoms, and even in the absence of impurities will be different for different crystal faces on the metal surface. Thus the work function of a polycrystalline metallic specimen will vary from place to place. The areas of different work function are called "patches" and the average work function for the whole surface is defined by \( \bar{\phi} = \sum_i f_i \phi_i \) where \( \phi_i \) is the work function of patches of type \( i \), and \( f_i \) is the fraction of the total area they occupy. Before passing from the work function it should be mentioned that the reason for choosing a point \( 10^{-4} \) cm from the metal surface as the zero point, is based on the classical concept of an image force. If a charge \( q \) is placed at a distance \( x \) from the metal surface there is considered to be an equal but opposite charge at the position of the optical image, the image force between them is \( \frac{q^2}{4\pi x^2} \). This type of force is experienced by an electron escaping from a metal surface and the work done against it is a further contribution to
the work function. Experiments to test the Schottky equa-
tion show that at distances greater than $10^{-5}$ cm from the
surface, the image force is negligible.

The Contact Potential.

If two isolated, electrically neutral conductors are placed in electrical contact, then at equilibrium the
electro-chemical potentials of both metals are equal. If
the electrostatic potential just outside the metal is $V$, then the potential energy of an electron just outside is
$-|e|V$. The work function may then be defined by $|e|\phi = -|e|V - \mu$. The term $\mu$ can be split into two parts, $\mu$, the
chemical potential of the body, which depends only on the
constitution of the body and is equal to $\xi_o$ of the Fermi-
Dirac statistics, and $W$ which depends only on the electro-
static potential at which the electrons find themselves.

For two metals in equilibrium $\mu_1 = \mu_2$

Hence $V_2 - V_1 = V_{12} = \phi_1 - \phi_2$

The potential $V_{12}$ is the Volta or contact potential, the
electrostatic potential difference between points just
outside the metal surface. The electrostatic potential difference between points inside is $W_{12}$, this cannot be measured directly.

The contact potential between two faces of the same crystal will be proportional to the difference of double layer strength at the faces, or equal to the difference of surface potential $4\pi \sigma t$. These contact potential differences will give rise to patch fields at the surface. Patch fields can arise in other ways, preferential adsorption on various crystal planes, irregularities of surface geometry, or the localised character of adsorption complexes. The effect of these patch fields on the results of measurement of contact potential, or work function, will depend on the method of measurement.
Modification of Surface Properties.

1) Change in work function.

As has already been indicated the existence of an adsorbed layer on the surface of a metal can be expected to modify the inherent dipole structure. This effect can be measured in terms of the dipole moment produced by the adsorbed layer on the metal surface. When $\sigma'$ dipoles per unit area are aligned perpendicular to the surface of the conductor, the resulting system approximates to a double charge layer, one layer positive, the other negative, of density $\sigma'e$, and separated by a distance $d$. If cooperative adsorption effects are neglected, then the double charge sheet may be considered as a capacitor, whose potential is proportional to the number of individual dipoles per unit area.

The product $ed = M$, the dipole moment. There is no external field with a perfect double layer, so that from electrostatics there is a sharp potential drop across the double layer, equal to $\frac{1}{2}\pi \sigma M$. This potential drop contributes to the work function, thus a charge sheet with negative pole outwards will increase the work function. When the whole surface is not effected by the adsorbed layer the effect is smoothed out, and the change in work function is then given by:

$$\Delta \phi = 4\pi \sigma_m \Theta M$$

where $\Theta \sigma_m = \sigma'$ dipoles per cm$^2$, $\Theta$ being the fraction of the
total number of surface sites per $cm^2$, $\sigma_m$ available to the adsorbate.

2) Change in Contact Potential.

It has been shown that the contact potential between two metals in electrical contact is given by $V_{12} = \phi_1 - \phi_2$. If now a dipole layer is formed on metal (1) the work function will change accordingly to a new value. The change in work function is as above. The new contact potential will then differ from the old by $4\pi \sigma_m Q M$. The change in work function, or contact potential, arising from a deposited double layer is often termed the surface potential, and in the experiments described later it will be used for convenience. The true surface potential is the double layer at the metal surface resulting from the displacement of electrons. The quantities referred to above are more precisely the change in surface potential, or contact potential, and are equal in magnitude and opposite in sign, to the change in work function.

The importance of the measurement of surface potential changes lies in the information they give about the nature of the surface bond. Theoretically it might seem that they would offer a convenient route to the evaluation of surface dipole moments. However this can only be done if the charge separation distance is known precisely, which is not the case.

Nevertheless, an analysis of the type of surface
potential change which might be expected for different surface bonds will now be considered.

1) Physical Adsorption.

The adsorbed molecules are held by weak forces of the Van der Waal's or charge transfer type, and are polarised by the surface field. The resulting dipole is small, and has its positive pole outwards. The surface potential change is \( \Delta \phi = 4\pi \sigma_m \Omega M \) where \( M = ed_p \), \( d_p \) being the separation of positive and negative charges.

2) Ionic Adsorption.

For a completely ionised adsorbate on a conducting surface the change in surface potential is given by

\[ \Delta \phi = 4\pi \sigma_m \Omega M, \]

where \( M = ed_i \), \( d_i \) being the distance between the charge and the metal surface. This type of adsorption can result in positive or negative surface potential changes depending on the polarity of the ion.

3) Covalent Adsorption.

If it is assumed that effective metallic conduction begins at the metal surface, then the surface potential change is given by

\[ \Delta \phi = 4\pi \sigma_m \Omega M, \]

where \( M = c \frac{d_{MA}}{2} \), \( d \) is the distance between the adsorbate and metal atoms. Covalent adsorption very often results in negative surface potential changes, although the sign depends on the direction of the electron transfer.

The variation of surface potential change with coverage is never linear as predicted by simple theory.
The reasons for this deviation have been considered in some detail by Macdonald and Barlow (4).
Measurement of Surface Potential Changes.

The methods of measurement of the effects of adsorbed layers on work functions will now be considered. There are two main classes, (a) those yielding a work function average "weighted" in favour of certain crystal planes or patches, these include photoelectric, thermionic, and field emission methods. The latter yields fine scale information as well. (b) Those yielding an integrated effect over the surface and a true work function average, including contact potential difference methods and the space charge limited diode.

a) The Field Emission Microscope.

The presence of an external field $F$, $V/cm$ at the surface of a metal modifies the barrier to electron emission, so that there is a definite probability that electrons approaching the surface will tunnel through the barrier and be emitted. The electrons concerned are those with energies near $E_F$, and the tunneling probability is very sensitive to the applied field. The theoretical equation describing the electron emission is the Fowler Nordheim equation.

$$j = V^2 a b \exp (-6.34 \times 10^7 \phi^3/2kV)$$

where $j$ is the total current, $V$ the applied voltage, $a$ the emitting area, $k = F/V$. The constant $b$:

$$b = 6.2 \times 10^6 k^2 (E_F/\phi)^{1/2} / (E_F + \phi)$$

Quantitative tests based on absolute magnitudes of $F$ and $\phi$
have been carried out by Dyke and Dolan (5) over a very wide range of i, and show that the equation is obeyed quantitatively within the experimental uncertainties of F (15-20%), if the image potential is taken into account. The work function values obtained from the Fowler-Nordheim plots are an intensity average favouring those parts of the surface for which electron emission is high. The field emission microscope is comprehensively considered by Muller (6) and Gomer (7).

Thermionic Method.

For thermionic emission from a uniform surface, the maximum electron flux \( j \) across the uniform surface at a temperature \( T \) in absence of an applied field is given by

\[
j = A(1-\bar{r})T^2 \exp \left( -\frac{e\phi}{kT} \right)
\]

where \( \bar{r} \) is the mean reflection coefficient at the surface, assuming a Maxwellian distribution of velocities, and \( A \) is a constant.

The emission equation is valid for each of the patches on a non-uniform surface, but the total measured current from the various patches depends on the relative magnitudes of the collecting and patch fields, as well as on the work function. Thus the average work function for a polycrystalline surface measured thermionically may differ from the true average work function. This method is limited, unless systems where \( \phi \) is small are used. High temperatures are necessary before significant emission occurs. The adsorbed
layers are generally detached under these conditions. Use of the thermionic method is described by Becker (8).

**Photoelectric Method.**

The energy of photoelectrons liberated from a metal is given by the equation \( E = h(\nu - \nu_o) \) where \( \nu_o \) is the threshold frequency. If \( V_s \) is the voltage required to stop electrons when light of frequency \( \nu \) falls on the surface, \( \nu_o \) may be calculated from the relationship

\[
e V_s = h(\nu - \nu_o).
\]

In turn the threshold frequency is related to the work function at \( 0^\circ \text{K} \) by the Einstein equation

\[
h\nu_o = e \phi_0.
\]

This equation remains valid at room temperature. A plot of the photocurrent for monochromatic light of frequency \( \nu \), against the potential \( V \), intercepts the potential axis at \( V_s \) provided the emitter and collector are of identical composition.

The change of work function may be calculated using

\[
\phi_1 - \phi_2 = h(\nu_{o1} - \nu_{o2})
\]

In the photoelectric method the measured average work function is always less than the true average, since patches of high work function tend to be excluded from the emission process. Practical disadvantages of the photoelectric method are the effect of threshold frequencies lying in the untra-violet and the pressure limit of \( 10^{-4} \text{mm Hg} \) owing to gas ionisation by collisions. The work of Suhrmann (9) is typical of the techniques of the photo-
-electric method.

**Space Charge Limited Diode.**

The maximum current which can be drawn from the cathode is given by the thermionic emission formula. At low current densities electrons emitted from the cathode build up an electron atmosphere or space charge at the surface. This space charge presents an electrostatic barrier to electrons flowing to the anode. Since the electrostatic barrier is higher than the surface barrier, comprising the metal work function and $E_\circ$, the anode current is controlled by the space charge, which is a function of temperature alone. A detailed consideration of the diode has been made by Gysae and Wagner (10), who showed that the current flowing depended almost entirely on the anode work function. The shift of current voltage characteristics along the voltage axis represents the change of anode work function. The diode method has two experimental limitations, namely, a pressure limit of c.a. $10^{-4}$ mm, and the presence of a hot tungsten filament which has a disrupting effect on some gases. The exploitation of the diode is described by Tompkins et al (11)

**The Magnetron Method.**

The magnetron comprises a diode with an axial magnetic field which reduces the saturation emission current. Contact potentials are measured between the clean and covered surfaces, and a central tungsten cathode which acts as reference electrode.
The total potential $V$ between the anode and cathode is given by (12)

$$V = V_a + V_{AR} + V_t$$

where $V_a$ is the applied potential, $V_{AR}$ is the contact potential difference between cathode and anode, and $V_t$ is a temperature dependent term related to the kinetic energy of the emitted electrons.

The field strength $H_o$ required to reduce the anode current to half its original value is related to $V$ by

$$V = H_o^2 R^2 \frac{e}{8m}$$

(13)

$R$ is the radius of the cylindrical anode, $e/m$ is the charge/mass ratio of the electron. Consequently,

$$V_a + V_{AR} + V_t = k I_o^2$$

where $k$ is dependent on the geometry of the system.

Provided $V_t$ is known $V_{AR}$ can be determined. Once again measurements by this method have the same pressure limitation as the diode. Work using this method is described by Wilson and Weissler (14)

**The Capacitor Methods.**

1) **The Vibrating Capacitor.**

The potential difference between two conductors connected electrically by a circuit containing no e.m.f. is given by $V_{12} = \phi_1 - \phi_2$ as described. If a potential is applied between the conductors to bring them to the same
potential, then the applied potential can be assumed to equal $V_{12}$. Under any other condition there will be a charge $q$ on the conductors given by

$$q = \frac{V}{C}$$

where $C$ is the capacity, and $V \neq V_{12}$. If the capacity $C$ is varied, then so also must $V$ for constant $q$. However at the condition $V = V_{12}$ variation of the capacity will not cause current to flow. In the capacitor method the surface under consideration and the reference surface, form the plates of a capacitor. The reference electrode must not undergo any work function change when exposed to gas or vapour during the measurements. Oxidised Ni and Pt surfaces have been used in this connection (15).

When one capacitor plate is vibrated an a.c. potential will be produced unless and until the compensating potential $V$ equals $V_{12}$.

An elegant example of this technique is afforded by the classic work of Mignolet (16). The capacitor method has no experimental limitations provided the reference surface is truly inert.

An ingenious modification of the vibrating plate method is the rotating disc method of Pratt and Kolm (17). Here, instead of vibrating the plates back and forth to vary the capacity, the electrodes are slid past each other, one mounted on the face of a rotating disc, the other stationary. This method is more sensitive than the vibrating
plate method, since the total variation in capacity is much greater. Contact potential changes of 1mV can be measured. The surface potential change obtained by this method is the true average value, provided the plate separation is large compared with the patch size.

Detailed accounts of the various methods of surface potential measurement and their results are contained in the reviews by Eberhagen (19), and Culver and Tompkins (20).
The Static Capacitor.

A further modification of the capacitor technique has been put forward by Eberhagen (18). This method was originally used to measure the change in contact potential during the outgassing of massive metal. In its original form this method had limited application since it was not possible to use it to study adsorption on metal films.

In theory the method involves the detection of the flow of charge in the external circuit from one plate of a capacitor to the other, as gas adsorption takes place. This charge flow results from the transfer of electrons from one plate to the other, to maintain the equivalence of the Fermi levels. At the instant of detection of charge flow, a compensating potential is introduced into the circuit to bring the charge flow to zero. If the compensating potential is introduced sufficiently quickly, so that no appreciable fraction of the charge has flowed, then the compensating or backing off potential will be practically equal to the change in contact potential. The measured change in contact potential is a true average. Once again one plate of the capacitor must remain inert to the influence of gases and vapours. This method will not measure a contact potential per se, only a contact potential change, since once the electrons have transferred from one plate to the other, there is no current flowing in the external
It is only if the opposing surfaces of the plates are brought into contact and then separated, that a contact potential will be measured. In practice this is not usually possible. One of the inherent drawbacks to the method is that it does not distinguish the source of charge flow, and consequently is prone to electrical interference, which introduces arbitrary zero shifts. A more serious difficulty is that measurements must be made all at one time, it is not possible to make related measurements on the same system once the apparatus has been switched off. This is a consequence of being a difference method only. However in the present work this method has been refined and improved for use as a method of measuring surface potential changes for gases adsorbing on metal films, together with the introduction of a new reference surface. By virtue of its inherent need to respond quickly to S.P. changes to give good accuracy, it enables rapid S.P. variations to be followed.

In the detailed consideration of the design of the static capacitor which is introduced in the following section, the formation of a dipole layer will be considered as equivalent to the instantaneous formation of a charge layer. This equivalence is not exact, because a dipole layer is immobile in the electrical sense, while a charge layer is mobile. The potential resulting from the deposition of a charge onto the plates of a capacitor, will
decay with time whereas the potential change following the formation of a dipole layer will not. However the conditions governing the transfer of charge from one plate to another are identical in both cases, thus enabling the measurement error and optimum design arrangements to be predicted theoretically using the charge layer model.
The Theory and Design of the Static Capacitor Method.

In the ordinary way it is difficult to measure the potential present between the plates of a capacitor since the measuring device will cause the potential to decay exponentially. If the input impedance of the measuring device is $R$ ohms and the capacitor has a capacity $C$ farads, a potential $E_0$ appearing between the plates at time $t=0$ will decay according to the equation

$$E_t = E_0 \exp\left(-\frac{t}{RC}\right)$$

where $E_t$ is the potential present after $t$ secs. If the value of $RC$ is made large the potential will decay slowly enough for an estimate of $E_0$ to be made, but there remains considerable error. The error can be much reduced if the measuring device is arranged so that a voltage equal in magnitude but opposite in sign to the voltage originally present, is fed into the capacitor circuit in a time $t_r$, very short compared with the time constant $RC$. That is, if $\exp\left(-\frac{t}{RC}\right)$ is very nearly equal to one. The measuring instrument operates now as a null detector.

In practice this is an oversimplified picture since it does not consider the effect of experimental "stray" capacities, or that the regulating potential itself is a function of time. A more detailed analysis is now given.
for the true situation.

In fig. (1b)
c_1 - cell capacity;
c_2 - stray capacity between reference surface and earth;
c_3 - input capacity of measuring device;
u_3 - voltage across condenser;
v - voltage across resistor R;
p - regulating voltage;
q - condenser charge.

Considering the interval \( 0 < t < t_r \) (\( t_r \) regulation time):

\[ u = p + v \]

At \( t = t_r \), \( u = p \) since \( v = 0 \)

Also \( q = c_1 u + (c_2 + c_3)v \) and \( v = iR \)

Substituting \( i = -\frac{dq}{dt} \) and rearranging

\[ \frac{du}{dt} = \frac{1}{RC} (p - u) + \frac{c_1}{c_1 + c_2 + c_3} \frac{dp}{dt} \quad (1) \]

where \( c = c_1 + c_2 + c_3 \)

The general solution of eqn. (1) is

\[ u = k \exp(-t/RC) + \frac{p - c_1}{c_1 + c_2 + c_3} \exp(-t/RC) \int_0^t \exp(t/RC) \frac{dp}{dt} dt \quad (2) \]

where \( k \) is a constant of integration.

The solutions for the two experimentally most likely types of function \( p \) are:-

The Linear Function \( p = \alpha t \) and constant \( 0 < t < t_r \)

\[ u_{tr} = u_o \frac{c_1 + c_2}{c_1} \left( 1 + \frac{t}{t_r} + \frac{t^2}{3! \frac{t_r}{RC}} + \ldots \right)^{-1} \quad (1) \]

The Exponential Function \( p = p_0 (1 - \exp(-\beta t)) \) and constant

\[ u_{tr} = u_o \frac{c_1 + c_2}{c_1} \left( 1 + \frac{t}{t_r} + \frac{(t_r)^2}{2! \frac{RC}{RC}} \right)\left( 1 - \beta \frac{RC}{2! \frac{t_r}{RC}} \right)^{-1} \quad (2) \]

The most accurate regulating function is (1). Comparison of the two series shows that (1) is always smaller than (2). Further, if the condition \( \frac{c_2}{c_1} = \frac{1}{2! \frac{t_r}{RC}} + \frac{1}{3! \frac{t_r^2}{RC}} + \ldots \) is fulfilled, the error for the linear regulating function becomes zero. The above derivations are only valid if the
insulation resistance of the capacitor is greater by a factor of at least ten, than the input resistance of the measuring device. It should also be noted that the input capacitance \( c_3 \) does not increase the error; instead it can be used deliberately to increase the effective time constant \( RC \). The form of the function \( p(t) \) is dependent on the method used to provide it.

In the present work it was proposed to use a servo-mechanism, that is, a control mechanism which is automatic and actuated by an error signal in the form of a closed loop cycle. (1) The loop is shown in fig. (1a), the error signal being the voltage \( v \).

The equation which will now describe \( p \) in terms of \( v \) is:

\[
\frac{1}{w_2^2} \frac{d^2 p}{dt^2} + T \frac{dp}{dt} + p = v
\]

where \( w, T \) are constants for any particular system. If the servomechanism is undamped the system will oscillate when disturbed by a step input voltage; this is the condition \( Tw = 0 \). While if \( Tw \) is greater than 2 the system is overdamped and the response time will increase unduly.

The actual form of this function is obviously more complex than either of the regulating functions already considered.

The conditions for accurate potential measurements may now be summarised as follows.

\[
\frac{t}{R} \ll R(c_1 + c_2 + c_3) \quad \text{and} \quad c_1 \ll c_2, c_3 \quad \text{any value}
\]

\[
0 < Tw < 2
\]

The amplifier must be of a special type which will operate
at low and zero frequencies, and have an input valve which will operate with a large value of RC connected across it. These conditions were met in the following way. R was fixed at $10^{12}$ ohms. $c_1$ was formed by a cylindrical capacitor in which the outer regulated cylinder was extended past the inner, to reduce $c_2$ to zero. $c_3$ had to be kept small since large values affected the stability and response time of the servomechanism. $c_1$ was 30pf in early work, but was increased to 100pf later. The servomechanism was operated with "phase advance" damping only. The condition $0 < Tw < 2$ was met by adjusting the conductance $G$ of the amplifier, since $Tw \propto \frac{1}{G^2}$. Using the figures quoted above the upper limit of error in the measurements is estimated at 0.6% and 0.2% respectively, while the actual error was probably smaller than this by a factor of two. The form of the regulating function as measured in response to a step input voltage is shown in fig. (1c). The product $Tw$ is here approximately equal to one.
Experimental.

1) The Vacuum System and Accessories.

The vacuum system fig. (C), plate (1) was housed in a simple, movable, rectangular box frame constructed from Dexion angle and measured 3ft. high by 2ft. by 2ft. 6ins. The top of this framework was covered with $\frac{3}{4}$in. thick asbestos sheet. Holes were cut in this sheet to allow the vacuum line through and where necessary to allow Dewars to be raised around the cell or cold traps. The items sited above the asbestos sheet were those which it was necessary to outgas at high temperature. For this purpose a furnace was constructed which could be lowered over the vacuum line to rest on the asbestos sheet. The furnace consisted of two open bottomed aluminium boxes placed symmetrically one inside the other leaving a 2ins. gap all round, but with their lower edges coplanar. The gap was filled with Vermiculite. The lower edges of the boxes were joined by an inverted "u" shaped channel and asbestos packing. The two boxes could thus expand independently of each other. Heat was provided by four 1 kW heating rods bolted onto spacers inside the oven. This power input raised the furnace temperature to about 420°C.
a.) **The Pumping System.**

The design of the pumping system was based on usual ultra-high vacuum practice and was found capable of an ultimate vacuum of $3 \times 10^{-10}$ mm Hg. It was constructed throughout in pyrex glass of minimum bore 25 mm. The ultra-high vacuum section comprising the cell, ion gauge, pirani gauge, glass valves and cold traps, sited on top of the asbestos sheet, was evacuated by a high speed annular jet mercury diffusion pump, the backing vacuum being supplied by a two stage rotatory oil pump. The cell could be isolated from the pumping system by a magnetically operated glass ball-joint valve; a similar valve isolated the cell from the dosing section. The cell was protected against condensable vapours by two conventional cold traps A, B, situated in the dosing line, both of which were baked, and a further two cold traps (a double rosebowl (C) and conventional pattern (D)) in the main pumping line, of these latter only the double rosebowl was included in the furnace. The vacuum ultimately obtained by the diffusion pumps after baking out the system was measured with a high sensitivity Alpert ion gauge type I G 3 H, situated adjacent to the cell. Pressures in the range $10^{-5}$ mm to $10^{-1}$ mm were measured with a Pirani gauge calibrated and operated at room temperature. The calibration was made in terms of the change of bridge "out of balance" current and indicated directly on a microammeter. The circuits used for the control of the ion gauge and Pirani gauge
are shown in figs. (4) and (5).

b) The Dosing System.

The dosing section was pumped independently by a two-stage high speed mercury diffusion pump backed by the same rotary oil pump as before. The dosing system comprised four glass stopcocks joined end to end, the first two separated from the last two by a glass bulb. The pressure of gas in the volume defined by the first two taps was measured on a mercury manometer. This volume (3.55ml) was then expanded into the large bulb (218.7ml) and a small volume (3.75ml) isolated in between the last two taps. This dose was then expanded into the vacuum system. The dose ratio was 1.94 x 10^16 molecules at 20^0C. for every cm. pressure at the inlet side, and each successive dose was 96% of the previous one. The gas supply to the dosing system was from 1 litre bulbs of spectroscopically pure gas. For hydrogen further purification was performed immediately before use by passage through a Palladium thimble.

c) The Cell.

The cell, fig. (6), Plate 2, was constructed entirely of Pyrex glass. The main outline of the body was ensured dimensionally reproducible and accurately colinear by forming the cell against a carbon template. The capacitor section comprised two concentric cylinders separated by a 1.5mm gap, the inner one being moveable vertically. The concentricity of the capacitor section was maintained by sitting the lower edge of the reference cylinder on a tapered
FIG 6  CELL
section of the cell, while the upper end was located by the iron lifting slug. The metal films were evaporated with the inner cylinder raised. Connection to the evaporated metal film was by a glass coated platinum wire, attached to platinum foil fused to the glass underneath the film and brought out through a tungsten-glass seal. The reference surface of the inner cylinder was connected to a similar tungsten-glass seal by a flexible nickel ribbon, which was spot welded to a strip of platinum foil fused to the glass under the conducting coating. It was found that the best way of arranging the inner reference cylinder to meet the experimental requirements was to construct it around a second cylinder of 2 cm. diameter which was flared out at its lower end to within 0.5 mm of the radius of the reference cylinder and extended a further 1.5 cm. in length. The reference surface was supported by the flared end of the inner cylinder when in position. This arrangement ensured a very long insulating path to meet the electrical requirements. When the reference cylinder was raised during the evaporation of metal films, the flared section also acted as a shadowing plate, preventing metal film from depositing on the reference cylinder.

The external glass surface around the high impedance connection to the reference cylinder was treated with a 2% solution of silicone fluid MS 1107 in carbon tetrachloride. The solution was applied to the glass with a clean pencil brush and allowed to dry for 10 minutes.
before the glass was baked at 400°C. for 10 minutes. It was important that the glass was thoroughly cleansed before the application. This treatment ensured that the insulation resistance of the glass was maintained at $\sim 10^{12}$ ohms cm$^{-1}$ even under adverse moisture conditions. The upper external surface of the cell was treated with a screening of "liquid" bright platinum, contact to which was made via a strip of platinum foil fused into the glass under the platinum coating, and extended out to a tungsten-glass seal and spot welded in position. This screening was earthed, and used as an earthing point for the throwing filament during experiments. The evaporation of the metal film completed the screening of the reference surface so all metal films had to have sufficient area to do this completely.

The reference surface was prepared by coating the outside of a glass cylinder with a mixture of stannous oxide and 1% antimony pentoxide using a modification of the method described by Gomer. (1) A small conical flask with a side arm joined on 1cm. above the base was filled with stannous chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to which 1% $\text{Sb}_2\text{O}_3$ was added. The flask was heated until white fumes were evolved when air was blown in through the side arm. These white fumes were played on to the surface of the glass cylinder which was heated to 400°C. by an electric heating spiral placed inside the glass tube. The area to be coated was defined by protective coatings of "aqua-dag" colloidal graphite. The resulting coating, slightly blue in colour was inert.
except to hydrofluoric acid or caustic alkali, both of which rendered it non conducting. A properly prepared coating had an average resistance of between 10 and 50 ohms depending on thickness.

The electrical capacity of the cell with an evaporated film was on average 30pf - 110pf depending on the cylinder spacing.

The pumping line to the cell passed through a vertical rectangular soft iron sheet which formed the back of the cell screening can. The cell was thus separated from the rest of the vacuum line. The position of the cell in space had to be carefully adjusted during attachment to the vacuum line in order that it lined up with the electrometer pre amplifier when that was in position, and at the same time allowed a Dewar to be raised around it.

d) Protective Devices.

The apparatus was protected against the failure of the water supply to the diffusion pumps by means of a thermistor detector. A Stantel thermistor type F23 was strapped to the water jacket of the Klemperer pump and monitored the temperature of the water jacket. The thermistor formed one arm of an a.c. bridge controlling a Sunvic hot wire switch in the electrical supply to the diffusion pump heaters. Since the pumps were arranged in series in the water supply any failure caused the electric power to be switched off. Simpler devices were used to protect the greased stopcocks from the heat radiated downwards during operation
of the furnace. For the most severely heated tap (E), water was passed continuously through the barrel, while for less severe cases wrapping with aluminium foil proved adequate.

2.) The Servomechanism.

A servomechanism was used to maintain a constant zero field between the capacitor plates. It comprised two distinct parts, the pre amplifier, (Plate 2), which was made to fit directly to the cell and the main d.c. amplifier and servomotor.

The pre amplifier was housed inside a brass tube flanged one quarter way along to take the mounting screws for attachment to the moveable section of the screening can. It contained a high insulation dielectric inset 2 inches at the cell end and carrying a small central socket. To this small socket was attached a short spiral of wire with a connecting block at one end. The connecting block could be screwed firmly to the tungsten rod of the cell. Access to this fixing point, which was normally totally screened and inaccessible was through a small rectangular hatch in the side of the pre amplifier tube which could be exposed by rotating a closely fitting sleeve having a corresponding opening. To the input socket also was attached the control grid of the triode electrometer type XE3 and the $10^{12}$ ohm resistor. The insulating surfaces were carefully
maintained free from dust and dirt and were never handled. All necessary cleaning was done with a clean pencil brush and pure cyclohexane.

The pre amplifier contained also the cathode follower output valve type EF37A, which was operated under electrometer conditions, and the drift control for backing-off the grid current of the XE3.

The output to the main amplifier was by a coaxial cable, the power supplies to the preamplifier being brought from the main amplifier via a six way screened cable and Plessey plugs. The main amplifier was constructed on an enclosed steel chassis. Extra screening was included around the main input.

**Power Supply.**

The H.T. power supply was obtained from a Racal 250mA stabilised power supply set to supply 260 volts D.C. The filaments of all valves except the XE3 and the output valves were supplied from the H.T. line with a 150mA supply via a dropper resistance which was conveniently formed from a 40 watt electric light bulb. The stabilised supply was stable to one part in four thousand and the ripple voltage was 5 mV approx. The filament and bias supply to the XE3 was from a 6 Volt accumulator and variable resistance which was adjusted to give correct bias conditions. The armature energising current for the servomotor was obtained by a full wave rectification of the output of a 50-0-50 V transformer. A 100 ohm 30 watt ballast resistor
was included in the D.C. supply.

The screen grids of the EL84 output valves were taken to a 300 volt point in the stabilised supply. This gave improved characteristics to the amplifier performance.

Theory of Operation of Servomechanism.

In the circuit shown in fig. (7) the output from the X.E.3 triode electrometer is directly coupled to an EF37A operating under reduced anode and filament potentials, and connected as a cathode follower. This low impedance output is directly connected to the main two stage d.c. amplifier using two ECC83's connected in the Miller drift compensating circuit. The amplified signal is directly coupled to a cathode follower output formed from one half of an ECC83. The other half is operated as a diode "clamp" to limit the positive excursions of the output to those below a pre-set level.

The amplified signal is fed to two EL84 output valves operating as a difference amplifier. The anode current of each valve energises one half of the split field winding of a Muirhead EF3A1D.C. servomotor, the armature of which is continuously energised from the 100 V D.C. supply. For zero input signal, identical anode currents flow in each of the output valves and the servomotor is stationary, but on reception of an input voltage the out of balance current effects rotation of the servomotor. The servomotor is directly coupled to a Beckman 7223, 10 turn,
precision, helipot through a small, light, friction clutch.

The helipot forms part of the potential regulator supplying the backing-off voltage to the cell. Calibration of the compensating circuit is achieved by switching in a 1.34 V mercury cell. Since a constant fraction of the regulating voltage is taken to a pen recorder, a potential calibration is directly available on the recording chart.

Four switched potential scales are available, namely, 3-0-3 V, 1-0-1 V, 0.3-0-0.3 V, and 0-1-0-0.1 V.

The overall performance figures for the amplifier when properly adjusted are as follows:

Current gain $2.5 \times 10^{10}$; Voltage gain 1,500; Conductance $G \sim 15$ amps volt$^{-1}$

Minimum input voltage required just to operate the servomotor was $\frac{1}{2}$ mV. or less, depending on the condition of the output valves and their operating point. The accuracy of the servomechanism is dependent on the drift stability of the amplifier. This is dependent on two further items: (1) the charging of the cell by the electrometer grid current, and (2) temperature variations and ageing in the amplifier and supply gear. The latter can be largely overcome by allowing the amplifier 5 or 6 hours to warm up before an experiment. Pre-aging of the valves before installation is also necessary. It is important that ambient temperature of the apparatus and supplies should not fluctuate markedly as this has an effect on the voltage of the stabilised supply. The nulling of grid current
charging is explained in the next section.

3) **Experimental Technique.**

Before any experiments were started the amplifier was allowed several hours in which to stabilise its zero. This was usually done concurrently with baking out of the vacuum line. A routine procedure was adopted for operating the servomechanism, as follows:

1) Set pre-amplifier input to zero.
2) Switch on electrometer filament supply having checked that 6 V accumulater was correctly charged.
3) Set bias + filament potential to correct value indicated on voltmeter scale.
4) Switch on electrometer anode potential and main amplifier power supply; allow 10 minutes to settle down.
5) Switch in regulating circuit followed by servomotor armature supply; allow to stabilise for 5 hours.
6) Immediately prior to the experiment switch off servomotor, switch off backing-off potential, and measure output voltage of amplifier; adjust to zero with zero control.

The effect of the grid current charging the cell capacity could be overcome in the present design by a very small, variable backing-off potential in the grid circuit. This potential was derived from a bridge circuit energised by a 1.34 V mercury cell, and could be made positive or negative as desired. The correct setting was found by
evaporating and sintering a film followed by stabilisation with gas at several cms. pressure.* Nitrogen is convenient for this purpose. The drift control is then adjusted until the output voltage shows no tendency to move steadily in one direction or another when the amplifier input is connected to the cell. Once set correctly, periodic checks were made to see if the setting required altering. The long term stability of this arrangement was good.

**Vacuum Procedure and Evaporation of films.**

The vacuum line was baked at 420°C, for several hours prior to every experiment. During bake-out the reference cylinder of the cell and glass valve F (fig. 6), were kept raised. Glass valve G was closed. The upper section of the cold trap D was heated to 200°C, with a heating tape while the lower half was kept in liquid nitrogen. After bake-out, the furnace was removed from the apparatus when the temperature had dropped to 150°C. At this time the ion gauge was outgassed by electron bombarding, and the throwing filament heated to just below evaporation point. When the glass had cooled to room temperature the cold trap D was completely immersed in liquid nitrogen, and the rose bowl trap C partly filled. Traps A, B were completely filled. As the vacuum improved the filling of the trap C was completed.

All metal films were evaporated from wires of spec-

*See end of section.*
-troscopically pure metal obtained from Johnson Matthey Ltd. Nickel films were evaporated either directly from 0.5mm wire, or from 0.1mm wire wound around a core of 0.3mm tungsten wire, previously cleaned by an A.C. electrolysis in NaOH. These wires were spot welded to 2mm tungsten rods which formed the bottom pinch seal in the cell. Nickel wires were outgassed for 12 hours at a temperature just below the evaporation temperature. The current setting required for this was found by increasing the current in increments of 0.1 ampere in the evaporation region, and waiting 15 minutes at each setting to see if any evaporation was occurring. When evaporation was just noticeable, the current was reduced by 0.1 amperes, and outgassing continued.

Evaporation of copper films was done from 36 S.W.G. wire wound closely around a 0.3mm tungsten core, all adjacent turns touching. Unless the evaporation was conducted extremely slowly, the copper melted into a globule and dropped off the wire, sometimes causing damage to the pinch seal. The copper filaments were heated to red heat in 1cm. pressure of hydrogen prior to outgassing, in order to remove the oxide coating always present. Outgassing was carried out for around 15 hours, less outgassing made it particularly difficult to maintain good vacua during evaporation. Tungsten films were evaporated directly from 0.1mm wire after 7 hours outgassing. The vacua obtained during evaporation of nickel films ranged from $5 \times 10^{-9}$
to $5 \times 10^{-8}$ mm Hg, while for copper the vacua was never better than $1 \times 10^{-8}$ mm. For tungsten, however, the vacua ranged from $8 \times 10^{-10}$ to $1.2 \times 10^{-9}$ mm Hg. Films were deposited at either 77°K or 90°K until the whole of the capacitor section of the cell was covered. (This is important since the film is also the electrostatic screen.) Films were sintered by thermal cycling over the range of temperatures expected. When necessary oxide layers were produced by baking a metal film at 300°C in several cm. pressure of oxygen for two hours, followed by pumping at the same temperature for one hour. After formation of the metal film, the reference cylinder was lowered, the screening can and pre-amplifier having previously been assembled and connected to the cell. The zero button on the amplifier was then released and the behaviour of the film observed. With nickel, and to a lesser degree copper, there was an initial zero drift which diminished after 10 or 15 minutes. The source of this drift is obscure because it could not be ascribed to gaseous contaminants since for nickel, for example, it was very often found to reach +2 Volts. It was concluded that this was due to some surface rearrangement since if allowed sufficient time it disappeared. If the zero was then re-set no further drift took place. The magnitude of the effect was irreproducible and unpredictable, but was in the order Ni > Cu > W. It was noticed that sintered films exhibited this behaviour very much less markedly. Once zero stability had been obtained the glass
valve (F) was closed isolating the pumping system, and doses of gas admitted by raising the glass valve (G). Each dose was typically $10^{17}$ molecules. The effect of each dose was measured on the pen recorder chart. A suitable voltage scale was selected prior to each experiment. The accuracy of the measurements is largely dependent on the cleanliness of the metal films. It was estimated that results were reproducible to within ±20 mV, the actual measurement error normally being less than this.

* In the correction of amplifier drift resulting from charging of the input capacity by the electrometer grid current, a more sensitive procedure is as follows. Set up amplifier according to the instructions, then with the pre-amplifier input disconnected, and completely shielded, adjust drift correction. The drift correction is now operating on the very small input capacitance which will charge much more quickly than the cell capacitance.

** The formation of ions by the throwing filament and their trapping on the metal film is a possible explanation of the initial zero drift at the commencement of experiments.
Experimental Behaviour of the Reference Surface.

The system nickel/oxygen at 77°K was selected to check the behaviour of the stannous oxide reference surface in terms of a gold reference surface. Identical experiments were performed using first a reference surface of glass covered with "liquid" bright gold, and then ore treated with stannous oxide. Oxygen was admitted in doses of approx. $10^{17}$ molecules until the saturation potential was reached. The experiments were repeated with the system Ni - Co at room temperature. In both sets of experiments the final surface potentials obtained agreed to within 30 mV. between themselves and the literature values of Mignolet. This was accepted as good evidence that at least in these two cases the stannous oxide surface was not significantly participating in either physisorption or chemisorption.

In all other systems studied a calibration experiment was performed under conditions which could be checked against the literature values for the same conditions. No significant divergence was found. It seems that the stannous oxide reference surface is completely satisfactory as a reference quite apart from its experimental convenience.
RESULTS AND DISCUSSION.

"Why, all the Saints and Sages who discuss'd
Of the Two worlds so learnedly, are thrust
Like foolish Prophets forth; their Words to Scorn
Are scatter'd, and their Mouths are stopt with Dust."

Omar Khayyám.

Results.

Hydrogen Nickel 77 - 90°K.

Hydrogen in doses of $1 \times 10^{17}$ molecules approx.

purified by passage through a Palladium thimble was added

to both sintered and unsintered nickel films at 90°K. The

initial doses resulted in the steepest rates of increase of

surface potential (S.P.) of 0.33V sec$^{-1}$. After the initial

dose, the second or third dose, depending on size of the

dose, yielded instantaneously a transient positive going

potential which decayed away to reach a new negative poten-
tial. The overall effect was of a more negative S.P.

(fig. 10) As the S.P. max of -0.35V was approached, the

magnitude and duration of the transient increased to a

maximum. After the S.P. max the transient did not decay

completely, so each dose had the effect of making the S.P.

less negative. At this juncture the mean lifetime or time

to fall to half its original value, was constant as well
as its magnitude. (fig. 10a) As the gas pressure over the film increased beyond $10^{-3}$ mm Hg, the magnitude of the positive transient began to diminish, and its mean lifetime increased slightly.

The variation in transient magnitude as a function of S.P. is plotted in (fig. 9) The onset of the transient occurred at 0.64 S.P. max for both curves even though the total amounts of gas which had been added in each case were significantly different, being $2.4 \times 10^{17}$ and $1.1 \times 10^{17}$ molecules for films 108 and 114 respectively. The maximum values of the transient varied. For the film of lower area the transient maximum was 90mV, while the higher area film yielded a maximum of 40mV.

The variation of S.P. with coverage is plotted in (fig. 13) for two films of different areas. At high ambient pressures viz $10^{-3} - 10^{-2}$ mm Hg the S.P. could be made to approach zero.

Pumping such a saturated surface at $90^\circ$K changed the S.P. to $-0.11$V, while warming to $178^\circ$K changed the S.P. to $-0.35$V with the evolution of $2.35 \times 10^{17}$ mols of hydrogen. Further warming to $298^\circ$K caused no change of S.P. but $12.6 \times 10^{17}$ mols of hydrogen were evolved. Recooling to $90^\circ$K did not result in the recovery of the original potential of $-0.11$V, and only $8.8 \times 10^{17}$ mols of gas were read sorbed, see (fig. 13) inset. The addition of hydrogen past the S.P. maximum resulted in a slightly "stepped"
S. P. VOLTS (–).
0.1 V divs.

Ni–H₂  90°K  Ex 108

FIG 10 a

0  1  2  3  4  5  6  7  8  9  10  11  12  13

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curve instead of the smooth curve which might be expected. The steps were not so evident for film 114. The behaviour of the nickel/hydrogen system at 77°K was not significantly different in any particular from the results quoted for 90°K. Hydrogen added to nickel films at room temperature showed no sign of the positive transient, and gave S.P. \(-0.34 -0.36\)V max in agreement with the literature. The S.P. was stable at room temperature and unaltered by pumping.

It was found in exps. 94 - 97 that the low temperature addition of hydrogen to nickel films yielded a S.P. of \(-0.15 -0.2\)V although there was no reason to suspect surface contamination. The S.P. maximum was reached after the addition of roughly the same number of molecules as were added to similar films which had yielded S.P. \(-0.35\) and the positive transient was still present (fig. 15) Saturation of the surface once again changed the S.P. to a small negative value. Pumping at low temperature caused the S.P. to become more negative by approx. \(-0.05\)V, whilst warming changed the S.P. to \(-0.28\)V passing through a maximum of \(-0.34\)V while still below room temperature (fig. 14).

Discussion.

The adsorption of hydrogen on nickel at 77 or 90°K is characterised by the pressure of a positive going transient which is not detectable at higher tempera-
-tures. This transient, which appears immediately on addition of gas once a critical coverage is reached, can most probably be ascribed to the formation and dispersion of a second layer of a weakly bound species resting for a time on the chemisorbate, before migrating to clean surface and becoming chemisorbed. Ehrlich (8)

This species has a positive dipole outwards as the result either of polarisation by the surface field, or some kind of weak chemisorption. The gradual build up of this 2nd layer eventually reduces the S.P. to a less negative value once the first layer is fully occupied. The low temperature spreading of chemisorbed deposits observed by Gomer (1) in the field emission microscope has also been explained in terms of the movement of a second layer.

The necessary condition for observation of this transient would seem to be that at the instant of addition, the gas should be distributed randomly between the 1st and 2nd layers in such a way that the potential change due to occupation of the 2nd layer exceeds that due to the 1st layer. If the occupation of the 1st layer is assumed proportional to \((1-\Theta)\) and that of the 2nd layer to \(\Theta\), where \(\Theta\) is the fraction of outer "visible" surface covered, then the S.P. change at the instant of addition will be the algebraic sum of two opposing S.P. If we assume that \(-\mu_1\) is the dipole moment of the 1st layer species and \(+\mu_2\) is the moment of the 2nd layer species, then a very simplified
expression for the magnitude of the transient $V$ is given by

$$V = -\mu_1 k(1-\Theta) + \mu_2 k$$

where $k$ is a constant of proportionality assumed equal for both species. If for simplicity we put $\mu_2 = k_1 \mu_1$ and insert the condition $V = 0$ we have

$$k_1 = \frac{1 - \Theta}{\Theta}$$

If $\Theta = 1$ corresponds to the S.P. max, then at S.P. = 0.64 S.P. max $\Theta \sim 1/5$ and $k_1 \sim 4$ Thus the dipole moment of the 2nd layer species is four times that of the 1st layer.

Mignolet (2) has stated from his results that the dipole moment of the second layer on Ni-H must be greater than that of the 1st layer, although he did not indicate the relative magnitudes. Equation (1) indicates that the transient should not be observed until a particular coverage and hence S.P., is reached, and that the transient will have maximum magnitude at $\Theta = 1$; this is in agreement with the observations.

It should be emphasised that $\Theta = 1$ is not the true surface maximum coverage, but only the outer surface maximum coverage as indicated by the S.P.

This may not be a perfect indication.

The Transient.

It has been shown in the preceding account that the positive transient is due to 2nd layer adsorption, the
amount of which may be estimated from the size of the transient. The disappearance of the transient will take place by a process of surface diffusion, provided the activation energy for diffusion is less than the heat of desorption from the 2nd layer. That the heat of desorption from the second layer is significant is shown by the stability of the second layer to pumping at 90°K. Gundry (3) has found that at the pressures and temperature used in this work, the heat is at least 5K cals, although it drops with increasing pressure.

Thus the 2nd layer can move over the chemisorbed adatoms by surface diffusion to the clean part of the film where it is itself chemisorbed. Each succeeding dose of gas encounters a greater area covered with chemisorbed atoms, so that the transient increases in size as does the $t^2$ value, since the average distance of travel over the adatom layer is greater, the larger the number of previous doses. The Einstein equation for the distance travelled by a particle in a random walk across a surface, gives the relation:

$$\frac{x^2}{x} = 2Dt$$

where $\frac{x}{x}$ is the mean distance travelled, D the diffusion coefficient, and t the time. The choice of a value for $x$ presents some difficulty. There is some evidence (4) that chemisorption occurs in bands on metal films evaporated on cylindrical substrates. One edge of the band located at the edge of the film, the other moving as chemisorption proceeds.
The value of \( x \) would here be determined by that fraction of the length of film known to be covered by chemisorbate. This value of \( x \) leads to a negative activation energies for diffusion. Clearly most molecules do not cross the whole band by surface diffusion. A better model, and one closer to reality, is to consider the surface as made up from many crystallites, here idealised as cubes with their outer faces aligned parallel. The linear dimensions of the cube edge can be calculated from the surface area and weight of the films.

If the chemisorbed layer is formed initially on the outer surface of a band of crystallites, then up to the S.P. max the transient will show a dependence on coverage, and the decay period will vary as molecules diffuse across crystallite surface faces and become chemisorbed. At the S.P. max chemisorbed molecules occupy their maximum outer surface coverage, and start to diffuse down the sides of each crystallite until the whole surface is covered by chemisorbed adatoms. The transient will now have constant magnitude and half life. After this stage, although chemisorbed molecules can disappear from the surface planes into the fissures, the build up of the 2nd layer has started and the surface concentration increases with successive additions of gas, until concentration of the 2nd layer can no longer be increased. Over this range the transient will diminish in magnitude. If the molecules in the second
layer are removed successively by diffusion to internal surfaces, then the distance they move to disappear entirely will be related to their number and hence to the maximum magnitude of the positive transient. Consequently a plot of the transient maximum magnitude against the square root of its duration for each successive dose, should be a straight line passing through the origin, and having slope \((2D)^{\frac{1}{2}}\), as indeed is found. (fig. 11) Using crystallite sizes of 1,160, 793 Å and assuming

\[ D = a^2 \nu \exp - \frac{E_d}{RT} \]

where \( a = 3^{\frac{1}{2}} \); \( \nu = 10^{12} \text{ sec}^{-1} \); \( E_d \) was estimated at 3.4 and 3.7 K cal for films 114 and 108 respectively.

The theory of diffusion can be applied more precisely when the outer layer of the cubes is covered with chemisorbed adatoms, i.e. at the S.P. maximum when the chemisorbed layer on the outer face of all crystallite cubes is complete; each succeeding dose of hydrogen therefore gives the same positive transient. This transient decays due to surface diffusion of these molecules to the sides of the cubes, where their chemisorption as adatoms does not affect the S.P., since they are not "visible" to the reference surface. The surface concentration \( C_t \) at any time \( t \) in the second layer is then given by:

\[ C_t = \frac{Q}{(Dt)^{\frac{3}{2}}} \]

where \( Q = C_0 h \); \( C_0 \) is the initial concentration at time \( t_0 \) and \( h \) is the average initial thickness in the direction
in which diffusive motion takes place. In this case half the average crystallite size. The same equation has been used by Bosworth (5) in the evaluation of the diffusion coefficients of Na and K on W ribbon. Thus during the decay, the magnitude of the positive transient at any time $t$ should be a linear inverse function of $t^{\frac{3}{2}}$, as is indeed found experimentally. (fig. 12) For the two films $h = 793/2$ and $1160/2$  \\ From the values of $D$ obtained above and using the formula:
\[
D = a^2 \nu \exp\left( -\frac{E_d}{RT} \right)
\]

$E_d$ is found to be 3 and 3.3K cals on the two films. The model predicts that a film with many crystallites will have a smaller external, but greater internal surface, than a film with fewer crystallites. The second layer will cause a smaller transient in the former case and diffuse less easily. These predictions are in complete agreement with the observations. The values of the activation energy for diffusion are high compared with Gomer's values for $O_2/OW$ and $CO/CO\ W$ of 0.9K cals (1) However it is not possible to state unequivocally that his measurements relate to a second layer, rather than a third or higher layer. From the manner in which his experiments were conducted, it seems probable that his values refer to a third layer in both cases. In the nickel-hydrogen system the value of $E_d$ for the third layer must certainly be less than 1K cal.

To summarise, the form of the transient and the
shape of the S.P. coverage curve at 77 and 90°K results from a weakly bound second layer. Gas impinging randomly on a band of crystallites is either immediately chemisorbed on clean metal, or forms a second layer which can diffuse across the crystallite faces. Up to the S.P., max diffusion is across the outer surfaces of the crystallites, while after the S.P. max diffusion occurs into the fissures of the film until the first and second layers are complete. The second layer has an activation energy for diffusion of 3.0K cal. The heat of desorption in the second layer is around 5K cal since it is stable to pumping at 90°K, but desorbs at 178°K.

**S.P. Coverage Curve.**

The high dipole moment of the second layer should have some bearing on the shape of the S.P. coverage curve (fig. 13). It is clear that the outer surface is not significantly covered with the second layer since invoking the additivity of dipoles this would reduce the S.P. much more than is observed. In fact the outer surface cannot be more than about 17% covered by second layer at the lowest S.P. of -0.11V. Even allowing that interactions between the two layers are of such a character as to prevent the simple additive treatment it is still impossible for the second layer to be completely occupied,
in the sense that it forms a continuous layer over the whole surface. In order to explain the discrepancy penetration away from the "visible" surface must be invoked. The gas which is removed by pumping at $90^\circ K$ and contributes the difference between $-0.11V$ and zero volts, is either a third layer of hydrogen molecules held on the surface by dispersion forces, each molecule having a small induced dipole, or part of the second layer less strongly held. The heat of adsorption might be expected to fall off with coverage. When the films are warmed to room temperature, gas is desorbed which cannot later be readsorbed simply by recooling the films to $90^\circ K$, neither can the S.P. be reduced again to $-0.11V$ even though the pressure in the gas phase is $1.8 \times 10^{-3}$mm Hg. This last result must reflect the effect of sintering; as crystallites aggregate and the surface area decreases, gas will be desorbed. Further, there will be an effect from the change in microtopography. If the resulting surface is less rough it will be more difficult to hold second layer molecules, since the opportunities for multiple interactions will be much reduced.

Although the character of the second layer species must remain a subject of speculation, it seems improbable that the surface field of the metal would be capable of producing such a large dipole in such a small molecule. The ease of polarisation of a molecule varies directly with its size, so that hydrogen would be the most difficult
molecule to polarise. However the behaviour of the second layer is very sensitive to the surface topography, and the partial surface coverage is more characteristic of adsorption in which the surface is filled in a way that ensures the maximum lowering of the free energy, i.e. filling of sites with high coordination, such as cracks and edges. Neither of these two types of behaviour is characteristic for example of a charge transfer type of interaction with the surface. Further a double charge layer will have an energy content in its own right merely from considerations of electrostatics. The energy of the double layer will vary with the inverse of its thickness for a constant potential across the layer. On this basis hydrogen will gain most stability from a double layer.

Comparison of the present results with those of Mignolet (2) show a large divergence unless the comparison is made for films which have undergone the same type of treatment. For films which have been warmed to room temperature and then recooled, the agreement is quite reasonable. Mignolet records a potential of $-0.26\text{V}$ at $2 \times 10^{-3}\text{mm Hg and } 77^\circ\text{K}$, compared with $-0.225\text{V}$ at $1.8 \times 10^{-3}\text{mm Hg and } 90^\circ\text{K}$. This latter difference may lie with the reference surface, although if the reference surface is participating in physisorption one would expect the change in S.P. to appear less than it should be.

The low values obtained on occasion and also
reported by other workers (7) are thought to be due to the presence of traces of oxygen as a surface contaminant, especially since the potential rises and then falls slightly on warming to room temperature. The positive transient appears at 0.65 S.P. max and the number of molecules added to reach the S.P. max is not characteristic of a surface containing few sites. It is more likely that the low value is due to the interaction between hydrogen and some species already present. It will be shown later that oxygen has a sensitive effect on the hydrogen surface potential.
Carbon Monoxide Nickel. Results.

The addition of doses of CO to nickel films at either 77 or 90°K yielded a maximum S.P. of -1.34V at an ambient pressure of $10^{-5}$ mm Hg. (fig. 18) During the addition of gas there was no sign of any transient positive potential similar to that found with hydrogen, thus demonstrating that the transient is not an experimental artefact. When the pressure over the film was increased to $10^{-2}$ mm Hg at either 77 or 90°K, the S.P. became slowly more negative to -1.50V, over a period of 16.5 mins. (fig. 16) This potential change was reversed by pumping at either temperature for around 15 mins.

Increasing the pressure over the film to 2mm at 298°K caused the S.P. once more to become more negative, this time to -1.44V, an increase of -0.13V (fig. 16) When the pressure of CO over a film maintained at 298°K was increased to 9mm Hg, after an initial rapid S.P. change to -1.40V, there commenced a slow change of S.P. reaching -0.95V after 40 mins. (fig. 17) This slow change could be arrested by cooling the film, or pumping off the CO in the gas phase.

It was found that nickel films covered completely with CO showed no S.P. change when hydrogen molecules were added, and a slow change of 0.05V to a less negative potential when $O_2$ was added. The latter could be entirely
Ni CO 298°K 9 mm Hg

FIG 17

S.P. VOLTS (V)

0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44

| MINS |

cooled to 77°K
removed by pumping.

Discussion.

In contrast to the behaviour of hydrogen, carbon monoxide shows no sign of a positive transient during the low temperature addition to nickel films. If one considers that a positive transient is simply due to physisorbed molecules, then there are two probable reasons why it is not observed with Ni-CO.

1) Extremely small dipole moment, making detection difficult.

2) Dipole of the second layer with negative pole outwards, which is the reverse of the arrangement usually found for physisorbed layers.

The last possibility would in turn explain the change to a more negative S.P. at high pressures and low temperatures, since this change has all the characteristics of a weakly bound physisorbed layer. It should be possible to recess further molecules in between the chemisorbed molecules, particularly if these latter are bonded in the bridge structure. However comparison of the S.P. coverage curves of Ni-CO and Ni-H show a rough equivalence of number of molecules added to reach the S.P. max, allowing for dissociative adsorption by $H_2$.

Thus it seems that the CO molecules are not joined to the surface in the bridge structure at high coverages,
this has been reported by Eischens also, but this would not prevent the insertion of extra molecules in the manner indicated below.

\[
\begin{array}{c}
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\end{array},
\begin{array}{c}
O^- \\
O^- \\
\vdots \\
\vdots \\
\end{array},
\begin{array}{c}
O^- \\
O^- \\
\vdots \\
\vdots \\
\end{array},
\begin{array}{c}
O^- \\
O^- \\
\vdots \\
\vdots \\
\end{array},
\begin{array}{c}
0^- \\
0^- \\
\vdots \\
\vdots \\
\end{array}
\]
\begin{array}{c}
C+ \\
C+ \\
\vdots \\
\vdots \\
\end{array},
\begin{array}{c}
C+ \\
C+ \\
\vdots \\
\vdots \\
\end{array},
\begin{array}{c}
C+ \\
C+ \\
\vdots \\
\vdots \\
\end{array},
\begin{array}{c}
C+ \\
C+ \\
\vdots \\
\vdots \\
\end{array}
\]
\begin{array}{c}
i Ni \\
i Ni \\
i Ni \\
i Ni \\
\end{array}

In view of the size of the CO molecule and the type of binding, it is likely that the 2nd layer molecules would be screened from the electron field of the metal double layer, which would then be of little significance in 2nd layer formation of the usual polarity. One can calculate the contribution to the overall S.P. of a layer of CO molecules having dipole moment 0.1D, assuming a one to one correspondence between physisorbed and chemisorbed species, and simple dipole additivity. The result is -0.37V. Although this value is higher than the increase, -0.2V actually found, it is not too divergent considering the simplicity of the model. At high pressures (9mm) and room temperature the formation of nickel carbonyl might be expected from infra red evidence (1) Nickel carbonyl has no permanent dipole moment (2) and exists as a tetrahedral molecule. It is a large molecule with a boiling point at 43°C. Both these properties should make it easily polarisable, resulting in a considerable positive S.P. The superimposition of the positive S.P. on a negative S.P. should lead to the
observed behaviour at high pressures.

Further evidence for the complete occupation of the metal surface by CO is afforded by the non interaction of either H₂ or O₂. This is a contrast to the work of Siddiqi (3) who found marked effects with hydrogen atoms on CO covered nickel surfaces. Presumably it is not possible for either H₂ or O₂ to dissociate on the CO saturated surface.
Nickel-Oxygen.

During the initial experiments with oxygen it was found that large doses of oxygen yielded apparent surface potentials as high as 7-8 volts. These large potentials were later discovered to be due to the Kramer Effect, or e electron emission. Electrons emitted during chemisorption cross the gap between the two capacitor cylinders, and appear as an equivalent current circulating in the input circuit of the servomechanism. However, provided the experiments were conducted in such a way that only small doses of oxygen were added (1 x 10^{17} mol), the Kramer Effect did not interfere with measurements. (See Appendix 1.)

To check the behaviour of the reference surface oxygen in doses of about 1 x 10^{17} mols was added to sintered nickel films at 77 and 90°K. The maximum potential achieved was \(-1.60^{+0.03}\) volts, in agreement with the literature, though the experimental spread of values was from \(-1.2\), \(-1.6\) volts. The S.P. coverage curve for Ni-O\(_2\) is shown in fig. (19) It is a smooth curve with a slight "foot" at the beginning. Close examination of the S.P. time trace showed the presence of a small positive transient commencing around \(-0.9\) V, and growing to 15mV at the S.P. max. Beyond the S.P. max the transient did not decay entirely, this behaviour caused the S.P. to become less negative until
finally, after saturation at \(1.6 \times 10^{-2}\text{mm Hg}\), the potential was \(-1.49\text{V}\) (fig. 19a.) Pumping for 5 mins restored the original S.P. max. The onset of the transient was at \(0.75\) S.P. max (fig. 20.) Thus the behaviour of the oxygen transient mirrored the behaviour with hydrogen. In this case the magnitude of the transient was so small compared with the overall S.P., that it was difficult to make estimates of the activation energy for diffusion with any accuracy. However in experiment 117, which will be discussed later, as a result of thermal cycling in the presence of oxygen, the crystallite size increased sufficiently to bring the transient magnitude up to \(40\text{mV max}\) (fig. 20a.) Consequently a plot of \(C\) against \(t^{-1}\) was made, (fig. 24a) and \(E_d\) estimated, following the same assumptions as for hydrogen, i.e. using the equation \(C_t = \frac{C_h}{(Dt)^{3/2}}\). The value of \(E_d\) was \(2.7\text{K cal}\). This value seems high since it was possible to remove the second layer by pumping for 5 mins at \(77^\circ\text{K}\). It is probable that not all of the second layer was removed by pumping, since on allowing the pumped film to warm to room temperature there was a small peak as the S.P. became momentarily more negative by \(0.06\text{V}\). The same peak was present when films saturated at \(90^\circ\text{K}\) were warmed up, see (fig. 21.)

In an attempt to measure the Ni-\(O_2\) S.P. at room temperature, nickel films saturated with oxygen at \(90^\circ\text{K}\) were suddenly warmed up to \(298^\circ\text{K}\). There was a sharp
S.P. VOLTS (\textdegree)
0.1 V. DIV.

Ni-O\textsubscript{2} 77\textdegree K FIG. 20a

Transient after thermal cycling

\( \text{gas added} \)
FIG. 21
S.P. changes following rapid temperature transitions

146°K
178°K
250°K
273°K

FIG. 22

O GUGGENHEIM
ΔE 0.78 K.CAL

\[
\log k = \frac{1}{T} - \ln a
\]
change to a less negative potential, no gas being desorbed during this time. This same experiment was repeated at temperatures between $90^\circ K$ and room temperature, and the resulting curves are shown in (fig. 21.) It was assumed that this result reflected the "switching" of surface oxygen into the metal lattice after the suggestion of Trapnell (1) The activation energy for this process was determined from the S.P. time curves, (a) from initial tangents, and (b) by Guggenheim's Method. The values obtained were 0.82K cals and 0.78K cals respectively (fig. 22.) These values are not accurate since they involve a thermal lag inherent in the method of changing the temperature, and a subjective error in the drawing of the tangents. A repeat series of experiments were conducted in which the gas was added to films maintained at fixed temperatures by baths of frozen organic solvents. Each dose of gas resulted in an initial negative step followed by a slow decay. (fig. 23) There was no sign of a positive transient at these temperatures. At the temperatures below $178^\circ K$ the decay was too slow to be useful. Under these conditions the final S.P. depended on the temperature and oxygen pressure, and lay in the range $-0.6V$ to $-1.6V$. However at $178^\circ K$ and above, the initial rates of decay could be measured and used to determine $\Delta H$, since the process obeyed 1st order kinetics. The value obtained was $2.05 \pm 0.5K$ cals (fig. 26) A different approach using the concept of a pseudo-equilibrium
Fig. 23

SP VOLTS

78°C K. Ex. 87

273°C K. Ex. 84

298°C K. Ex. 86

C. MINS
between the internal, and surface oxygen was used to determine equilibrium constants, from the curves of fig. (23). The sum of all the potential increments without decay (n) and the sum of the decay potentials (n₂) were plotted against the number of molecules added, for a set of temperatures. It was assumed that n = n₁ + n₂ and that V∝n, although in fact the method is self calibrating and does not really involve this latter assumption, since n₁ and n₂ are derived using the plot of n against number of molecules added as a calibration curve. If the pseudo-equilibrium is observed, the plot of n₁ against n₂ should be a straight line (fig. 24.) The actual results conform closely to this picture at low coverages, at higher coverages when the amount of incorporated oxygen had increased the relationship between n₁/n₂, which although still linear did not seem to be dependent so much on the temperature. It was ignored for the purposes of calibrating F. Plotting the pseudo-equilibrium constant, n₁/n₂ against 1/T yielded ΔF 2.0K cal (fig. 25).

The concept of a "switching" process suggests that sites originally occupied should become free after switching, and that these new sites should be very similar to the original. Accordingly a nickel film was sintered at room temperature, cooled to 77⁰K and saturated with oxygen. Oxygen remaining in the gas phase was removed by pumping. The film was warmed to room temp-
-erature, the potential changing from -1.24V to -0.3V. At this stage the film was recooled to 77°K and further oxygen added. The oxygen was adsorbed, and after 7 x 10^{17} molecules had been added the potential reached a maximum of -1.1V, further doses caused only a slight change to -1.07V with the presence of a positive transient reaching 40mV. This latter was ascribed to the build up of the second layer since it could be removed by pumping alone. The cycle was repeated twice more, the potentials reached at 298°K being -0.51, -0.66, and -0.82V respectively, after the addition of 7, 11, and 14 x 10^{17} molecules of oxygen. (fig. 27)

The original S.P. was not recovered at any stage during the thermal cycles. The S.P. coverage curves found during these cycles differed considerably from that obtained for the initial addition of oxygen. The initial slope in these cases was nearly seven times as great as before, and almost constant at about 0.4V per 10^{17} molecules, compared with 0.06V per 10^{17} molecules previously. The behaviour of the nickel oxygen system at higher temperatures was examined. A sintered nickel film was saturated with oxygen at 77°K. This film was then warmed to 25°C in a water bath. An oil bath at 84°C was then placed around the cell, whereupon the S.P. became less negative by 0.1V. Another oil bath at 130°C was placed around the cell. This causes the S.P. to change, slowly at first, but accelerating and finally approaching S.P. +0.61V slowly. (fig. 28.)
FIG 28a

Ni-O₂

Limiting S.P. values
Further heating has no effect. It was found that heating to 114°C would produce much the same result, (fig. 29.) the higher temperature not being absolutely necessary. On cooling to 77°C and adding further doses of oxygen \((5.4 \times 10^{17} \text{ mols.})\) the potential approached \(+ 0.025\text{V}\) (fig. 28.)

The steady S.P. values recorded on warming a closed Ni-O\(_2\) system are recorded in (fig. 28a.) These values do not represent the maximum values obtainable at a given temperature, since in all cases after a temperature transition further gas could have been adsorbed, they are instead limiting values.

**Discussion.**

**The S.P. Coverage Curve.**

The shape of the S.P. coverage curve for oxygen on nickel, differs markedly from the shape that might be expected from simple considerations of the formation of a double layer, even allowing for dipole depolarization. In fact, the initial slope of the curve in (fig. 1) would suggest a maximum S.P. around three times as great as is found. The influence of surface heterogeneity could be responsible, different crystal faces having different S.P. values. An alternative explanation lies in the way the metal films are prepared. The evaporation of metal from a small source situated on the axis of a cylinder, on to
the walls of the same cylinder has two drawbacks, (a) film is not distributed evenly along the length of the cylinder, and (b) there is a wide variation in the intensity of radiation along the cylinder. In the present cell design owing to the small cell diameter, the intensity of radiation is approximately 40 times greater in the middle of the film than at the ends. This will inevitably lead to considerable sintering occurring preferentially in the middle section of the film, while the ends will be very little sintered and consequently of high internal surface. The addition of gas in doses which are adsorbed in successive adjacent bands will cause the film structure to be reflected in the variation of S.P. with coverage. The steepest part of the curve will occur when gas adsorbs on the most heavily sintered section of film having least internal surface, where the efficiency of observation is highest. The shape of the S.P. coverage curve can thus be predicted as follows; initial foot as first molecules adsorb on surface with high internal surface area; succeeding section with steeper slope as molecules adsorb on middle section with low internal surface area; and final tail as molecules adsorb on highly porous surface.

The change in S.P. to a less negative value at high pressure and low temperature is attributable to the presence of a second layer. The positive transient being a manifestation of the initial stages of 2nd layer formation.
The presence of a positive transient during the addition of oxygen at low temperature, coupled with the depression of the S.P. at high pressures and low temperatures, suggests the presence of a second layer carrying a positive dipole outward. It is apparently possible to remove the second layer by pumping at 90°K, but warming such a pumped film reveals that the S.P. is still effected by the presence of a species with a positive dipole outwards. If one assumes that the second layer is composed of only one species, then the data suggests that the energetics of interaction change as more and more gas is added. Thus as the second layer becomes increasingly full, the heat of adsorption decreases. Adsorption at temperatures such that surface diffusion can occur rapidly compared with the rate of adsorption, yields an equilibrium distribution of ad-atoms over the surface, and initially the sites with the lowest potential energy are filled. As these are occupied the heat should diminish. For the calculated activation energy for diffusion to be meaningful, the maximum heat of adsorption in the second layer must be 4-5K cals. This heat is high considering the small polarisability of the oxygen molecule; and remembering that an easily polarisable atom such as Argon on Cu and Zu, yields heats of only 3K cal and 2.6K cal respectively.

A rough estimate of the relative magnitudes of the dipole moments of the first and second layers,
carried out in the same way as for hydrogen, suggests that this ratio is approximately unity. The concentration of molecules held with the heat of 4-5K cals must therefore be rather small, around 4%. The heat must fall rapidly with coverage, or alternatively, the maximum heat can be only slightly greater than $E_d$. With the fall in the heat of adsorption there must be an accompanying decrease in the magnitude of the induced dipole. This would account for the small effect on the S.P. of the addition of the last $24 \times 10^{17}$ molecules, some 0.1V, compared with 0.04 to 0.06V for the first $10^{17}$ molecules. Coupled with this there will be some disappearance of molecules away from the outer "visible" surface, so that not all of the molecules added are contributing to the S.P. change as measured.

The nature of the binding of the second layer on Ni-O is not clear. It seems unlikely that physical adsorption involving dispersion forces alone could be a sufficient explanation. An interaction of the no-bond charge transfer type is possible, especially as the heat of adsorption would be increased by transfer forces. However, as with hydrogen, the energy of the dipole layer may contribute some stability, so the latter explanation may not necessarily be involved.

The Incorporation Process.

The decay in the S.P. during additions of gas
at temperatures above $146^0K$ is considered to be due to incorporation of oxygen into the nickel lattice. It is estimated that between 1.4 layers are formed during room temperature adsorption. (2) (3) So at temperatures below this fewer layers will be formed. That penetration does occur is demonstrated by the presence of further sites for adsorption after films saturated at low temperature are thermally cycled. At the same time it is clear that these new sites differ in some way from the original Ni sites since

a) It is not possible to recover the original S.P. after a thermal cycle.

b) Comparison of the change in potential for the first dose on a clean film, and the first dose on an oxygenated film which has had one thermal cycle, shows that the latter is seven times greater.

To reconcile these data it is necessary to suggest that the change in environment of the nickel atoms following oxygen incorporation, modifies the interaction with further oxygen molecules, and that during the "switching" process the surface becomes more sintered. It is noticeable that even at 77 or $90^0K$ where no measureable "switching" occurs, there must be in fact, some incorporation. This follows from the observation that $2.4 \times 10^{18}$ molecules are required to reach the surface potential maximum, while $2.0 \times 10^{18}$ molecules of CO, or $1.0 \times 10^{18}$ molecules of H$_2$,
will suffice on films prepared in a strictly comparable fashion, and having similar weights.

The values obtained for \( \Delta F \), (2.0K cals) and \( \Delta H \), (2.05K cal) must mean that \( \Delta S \approx 0 \) for the switching process. This being so \( \Delta H \) for the reverse step, that of bringing oxygen from the metal out to the surface, would appear to require only 4K cal. On this basis the "switching" or incorporation of oxygen would be easily reversible. Such easy reversibility has never been demonstrated, presumably owing to the high heat of adsorption for \( O_2 \) on Ni.

An alternative explanation is that the activation energy for switching \( E \), is increasing with amount switched, so that the end of the process is where \( E \) is too high for corresponding \( T \). The gas goes on in a random fashion so that the proportion switched is independent of amount, unless there is a cooperative effect at high coverage.

On these assumptions we have:

\[
N \exp - \frac{E}{RT} = \text{rate of switch} = kN
\]

where \( k \) is the 1st order rate constant; \( \approx 10^{12} - 10^{13} \). 

\( E \), calculated using the values for \( k \) obtained from sudden temperature transitions, is tabulated in table (1).
Table (1).

<table>
<thead>
<tr>
<th>T⁰ K</th>
<th>k sec⁻¹</th>
<th>E(Kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>146</td>
<td>0.022</td>
<td>9.8</td>
</tr>
<tr>
<td>178</td>
<td>0.056</td>
<td>11.8</td>
</tr>
<tr>
<td>250</td>
<td>0.056</td>
<td>16.4</td>
</tr>
<tr>
<td>273</td>
<td>0.069</td>
<td>17.8</td>
</tr>
<tr>
<td>353</td>
<td>0.023</td>
<td>23.7</td>
</tr>
<tr>
<td>387</td>
<td>(0.002)</td>
<td>(28)</td>
</tr>
<tr>
<td>403</td>
<td>(0.0019)</td>
<td>(29)</td>
</tr>
</tbody>
</table>

Values shown in brackets ( ) are uncertain.

A plot of E against T shows a linear relationship up to 353⁰K. (fig. 30) At higher temperatures there is some divergence, but this may be due to the uncertainty in the value of k and hence E. One would expect that the upper limit to the value of E would be set by the activation energy for the motion of an oxygen ion into the metal lattice.

The positive S.P. recorded at temperatures around 114⁰C can easily be explained by the presence of Ni⁺⁺ protruding from the surface as the formation of a thin oxide layer takes place. It will be observed once the "switching" process has proceeded to such an extent that the contribution to the dipole layer from the positive ions in the surface layer exceeds that from the chemisorbed oxygen atoms. Similar positive S.P. values have been recorded for Ni-O₂ by Anderson and Klemperer (4), and by Burshtein (5). In both instances the same explanation has been
advanced. Although the positive S.P. was recorded for a closed system, i.e. no gas was added once thermal transitions had begun, the surface character was markedly different at this stage. It will be recalled that during thermal cycles between 77°K and 298°K, it was possible to recover almost all the original maximum potential once the surface was recooled, and further gas added. In this instance the S.P. could not be made negative, even though $5.5 \times 10^{17}$ molecules were readsorbed. This suggests that the dipole formed during the latter addition was very much smaller than that of Ni-O$_2$ chemisorption, or that the adsorbed oxygen is "buried." Any nickel atoms freed by "switching" have, during the high temperature treatment, lost their original metallic character.
Copper-Oxygen. Results.

With the object of investigating the switching process for copper, unsintered copper films were formed at 90°K and treated with doses of oxygen of c.a. \(10^{17}\) molecules. It was difficult to obtain good results from copper films since the copper itself was difficult to out-gas, and the films had very low surface area unless evaporated at low temperature, and left unsintered. The best S.P. values for Cu-O\(_2\) were -0.64 and -0.68V (fig. 31) in agreement with Mignolet, there was no sign of a positive transient. On warming such an oxygen treated film to room temperature, the S.P. became less negative by 0.1V. The lack of pronounced change suggested that the activation energy for the switching process is higher in the case of copper than it is for nickel. Accordingly films were dosed with oxygen at a series of temperatures, and the initial rates of reaction measured. It was not possible to make significant measurements below 250°K in contrast to Ni-O\(_2\). The activation energy for switching was estimated as 6.0 \(\pm\) 2 K cal. (fig. 32)

In a further experiment a copper film was saturated with oxygen at 77°K and then warmed to room temperature. The film was then recooled and further gas added. The second addition of gas did not restore the potential to its original value. The potential changing
FIG. 31

Cu-O₂  77°K

Warmed to 298 K

Recooled 577°K

O₂ added

FIG. 32

ΔH = 6.0 K cals
by only 0.025V. The small magnitude of the S.P. changes was thought to be due to the effect of sintering, both during the warm up and also throughout the switching process. A small quantity of gas desorbed from the walls of the cell would then obscure the true S.P. change on a surface having almost geometric area. Accordingly the experiment was repeated for a sintered Cu film. The change on warming to room temperature was to -0.32V. (fig. 34)

Discussion.

The data for the incorporation of oxygen in copper is only rather fragmentary, even so it is clear that incorporation is more difficult than in the case of nickel. Treatment of the results in the way used for nickel, i.e. putting the rate in the form \( n V \exp \left(-\frac{E}{RT}\right) \) yields table (2)

<table>
<thead>
<tr>
<th>( T^K )</th>
<th>( k \text{ sec}^{-1} )</th>
<th>( E \text{ Kcals.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>( 2.0 \times 10^{-3} )</td>
<td>20.7</td>
</tr>
<tr>
<td>273</td>
<td>( 1.67 \times 10^{-3} )</td>
<td>20.0</td>
</tr>
<tr>
<td>250</td>
<td>( 4.0 \times 10^{-4} )</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Plotting these data as \( E \) against \( T \) yields (fig. 33) A straight line can be drawn through the points, but this is in no way a decisive test of the data. The intercept is at 3.4 K cal. The data above depends on the "switching" process obeying 1st order kinetics. It is not certain
that this is so, however it seems a reasonable assumption.
The Incorporation of Oxygen in Nickel and Copper.

From the surface potential studies in this work and in the work of Quinn and Roberts (1) there emerges an order of "switching" for oxygen on some of the 1st row transition metals. The ease of switching lies in the order Cr > Fe > Ni > Cu.

Apparent activation energies for switching have been determined for only Nickel (1 - 2K cal) and Copper (6 K cal) but Roberts has shown that both Cr and Fe readily incorporate oxygen even at 77°C K. It should be noted that the activation energies quoted above are those calculated from plots of log k against $\frac{1}{T}$ and are probably not meaningful in the usual sense of an activation energy. This becomes clearer when it is remembered that the apparent activation energies for the "switching" process on Cr and Fe would be less than 1 K cal and the removal of incorporated oxygen would require an energy of the same magnitude, clearly improbable. Rather, these energies refer to the increase of E with T, or really the number switched. The true activation energy for switching is that determined by the equation rate = n exp - E/RT. Using this equation both Cr and Fe would yield a relationship with T cutting the temperature axis at some point above T = 0, contrast to Ni and Cu. A simple theory can be advanced which accounts for the observed behaviour with Ni and Cu quite
The energy term in the rate equation can be split into two components $Q$, the activation energy for the transfer of an oxygen ion from the surface into the metal lattice, and $q_a F$ where $q$ is the charge on the ion situated at distance $(a)$ from the metal, and $F$ the field operating at the metal surface. If one assumes a singly charged species then $q_a F$ is given by the surface potential expressed in electron volts. The new equation is then

$$\text{rate} = n \exp \left( \frac{Q - q_a F}{RT} \right)$$

(2)

Although S.P. data suggests that the dipole moment of the adsorbed oxygen is only $0.5 \text{D}$ this does not prevent the adsorbed species from carrying a single negative charge since the separation distance, or thickness of the dipole layer is not known. It is not impossible for the oxygen to be slightly recessed into the metal surface. There is other evidence that oxygen exists on the surface as $O^-$. 

Comparison of equation (2) with the data shows that $Q - q_a F$ must be a linear function of $T$. Since $Q$ will vary only slightly with temperature, $q_a F$ must itself be an almost linear function of $T$. This is in fact true over the temperature range $150 - 350^\circ \text{K}$. (fig. 28a.) It should be pointed out that in the present work the rates have been determined by putting a fixed number of molecules on the metal surface and then rapidly increasing the temperature to a new steady value. Under these conditions the surface
concentration of chemisorbed oxygen is reduced as the temperature is increased, thus the field operating at the surface of the metal is reduced correspondingly to some new limiting value. Graphical summation of $E$ and $qaF$ should yield a value of $Q$. This has been done, (fig. 35) and gives a value of $Q$ for nickel, falling from 32 to 31 K cal over the above temperature range, a very reasonable value. From the diagram it becomes clearer why at temperature around 390 - 400°K the S.P. moves easily more positive. Although the data for copper is very sparse it was thought worthwhile to pursue the same form of treatment. Accordingly the graphical sum of $E$ and $qaF$ was formed to produce an estimate of $Q$. The values found varied from 28 - 29Kcal over the temperature range 250 - 300°K. (fig. 36) Grimley and Trapnell have estimated that $Q$ for the transfer of a copper atom into a thin oxide layer is 26.5 K cal \(^{(2)}\) One would expect that an anion such as $O^-$ would require greater energy. The agreement is surprisingly good considering the paucity of the data and naivety of the approach. However, the picture formed for both Nickel and Copper explains the observed behaviour very well even though in some way it may be fortuitous. It seems safe to conclude that during the incorporation of the first layer of oxygen into either Nickel or Copper, the surface field is rate controlling. One might predict on the above theory that the S.P. of both Cr and Fe are unlikely to exceed 1.6V
unless the energy \( Q \) is very much higher in either case.

In fact the S.P. max. for iron is \(-1.6\) V, Cr reaches \(-2.0\) V suggesting that \( Q_{Cr} \) is larger than for iron.
Hydrogen and Carbon Monoxide on Nickel and Copper Oxide.

Results.

Some preliminary experiments were conducted on nickel and copper oxide formed by the oxidation of nickel and copper films as described in the experimental section, (p.58)

The addition of hydrogen to a nickel oxide layer at room temperature produced no S.P. change or any measurable adsorption. When the ionisation gauge was turned on there was an immediate S.P. change of +0.03V. This change was attributed to the formation of hydrogen atoms at the filament of the ion gauge, and their subsequent adsorption on the oxide surface.

The addition of carbon monoxide to a nickel oxide surface produced an S.P. of +0.09V. Again the uptake of gas was not measurable.

The addition of carbon monoxide to a copper oxide surface produced a more marked change, +0.115V. Pumping on the surface restored the potential almost to zero, while addition of more CO brought the potential to +0.11V.

Discussion.

The absence of a measurable S.P. for hydrogen molecules on nickel oxide confirms the findings of Roginsky (1)
The adsorption of hydrogen on bulk nickel oxide is reported to be zero, or very small, at temperatures below 120°C. The photo electric studies of Klemperer and Anderson (2) suggested that some adsorption with electron donation to the oxide does occur at room temperature. The results obtained in this work suggest that the adsorbed entity is an H\(^+\), rather than H\(_2\)\(^+\). Eischens in studies of hydrogen adsorbed on zinc oxide (3), found no evidence for the formation of H\(_2\)\(^+\); similarly with hydrogen on platinum (4), though Cotton and Fensham suggest that adsorption results in the formation of H\(_2\)\(^+\) (5).

The positive S.P. for CO on nickel suggests that adsorption is occurring with electron donation to the oxide. A similar positive trend is noticeable with CO on an oxygen covered nickel surface where the coverage is much higher, and consequently the S.P. change also. In view of the incorporation of oxygen into nickel, the resulting surface is likely to be of an oxide-like nature. The two systems might be expected to show parallel behaviour. Adsorption of CO on copper oxide occurs with electron donation by the gas. The reversible character is like a scaled down version of the interaction between CO and an oxygen covered copper surface. Considering the relative coverages the scaling effect is not surprising. The mechanism in the two cases may be closely similar with the CO adsorbing on top of surface oxygen. It is not intended to pursue the possible
mechanisms of adsorption on these oxide surfaces in detail, with the scanty data available.
MIXED GAS SYSTEMS ON NICKEL.


Addition of oxygen to a hydrogen covered nickel surface at 77 or 90°K. increases the negative S.P. from -0.79V (values for four experiments were 0.78, 0.79, 0.83, 0.75V) see (fig. 37.) The ratio of H₂ to O₂ is ill defined at this point, but there is certainly excess oxygen. Warming the system to room temperature produces a sudden S.P. change to +0.25V (average value from four experiments.) This change is largely complete in two minutes, but takes 15 minutes to reach a final steady value. During this time the pressure rises to 5 x 10⁻³ mm corresponding to 1.9 x 10¹⁷ molecules, and falls again to below 10⁻⁵ mm, while the S.P. drops back to +0.15V. The pressure rise does not accompany the most marked S.P. change, but occurs when the value is practically steady. The composition of the desorbed gas is not known, but it is surmised to be H₂.

Further addition of oxygen now at 298°K sends the S.P. more positive, finally reaching +0.75V, ±0.05V. After this point the S.P. becomes less positive, declining to c.a. +0.05V, while saturation with O₂ at 10⁻¹ mm gives
+0.2V, this last part being reversible since pumping removes it easily.

The room temperature behaviour is complex since it is time dependant. Each oxygen dose produces a sharp negative going transient which decays leaving an overall +ve S.P. gain. This behaviour holds up to the S.P. max. After this point the -ve transient does not completely decay, so the resulting S.P. moves negatively towards +0.05V. The last phenomenon depends on the size of the oxygen dose very markedly. Larger doses give an exceedingly pronounced "spike" in the negative direction. As more gas is added, each succeeding dose decays away less rapidly than its pre-decessor (fig. 40)

Low Coverage.

If the experiment is repeated at lower coverage that is O₂ added to a Ni surface only partially covered with H₂, then the behaviour has the same pattern, but potentials are shifted in the -ve direction. (fig. 39)

On warming the Ni-H₂-O₂ surface with S.P. of -0.6V there is a sudden change to +0.01V. Addition of oxygen is accompanied by a decay in the S.P. characteristic of oxygen adsorbing on Nickel, while the S.P. gradually moves to -0.03V. Saturation with oxygen changes the S.P. to -0.3V. However the warm up is not accompanied by a pressure rise in this case.
Room Temperature.

If the system Ni-H$_2$-O$_2$ is investigated at room temperature, addition of oxygen causes the S.P. to change from -0.2V (H$_2$-Ni) to +0.1V, and then alter again to 0.0V. Saturation at this point changes the S.P. to -0.36V. Pumping does not appear to reverse this change, the S.P. changing to -0.3V only. (fig. 38)

The interaction of hydrogen molecules with an oxygen treated surface was investigated. Oxygen was allowed to interact with a nickel surface at room temperature, and hydrogen was added in successive doses, causing the S.P. to change from -0.93V to +0.3V followed by a very slow change to 0.4V. The slow change was not followed to completion, so the true final value is not certain. (fig. 41)

Discussion.

The total number of molecules of hydrogen and oxygen adsorbed in (fig. 37) indicate that either much of the oxygen has become incorporated, the hydrogen desorbed and resited, or that the oxygen occupies quite separate independent sites on the surface, or all three. In view of the possibility that hydrogen can occupy an interstitial site the oxygen may be able to sit on the surface bound, independently of the hydrogen, to adjacent nickel atoms. In fact the S.P. (-0.78V), achieved after the addition of c.a.
$1.3 \times 10^{18}$ mols is 0.4V below the value for $O_2$ on a bare nickel surface, -1.18V, suggesting that at least some interaction between the oxygen and hydrogen has occurred, resulting in a species with a positive potential. This idea is supported by the change in S.P. on warming the film to room temperature. Instead of a change of 0.5 - 0.6V which might be expected, the actual change is 0.93V. The gas desorbed during the warm up, when switching is known to occur, is most probably hydrogen, some of which can re-adsorb on sites left vacant by the switched oxygen. This would account for maxima noted on warm up i.e. to +0.25, then dropping to +0.15V. The further addition of oxygen shows a transient negative potential which quickly becomes positive with time. The rate at which the potential becomes positive is not characteristic of a 1st order process, rather it would seem to be 2nd order where the concentration of one of the reactants is falling with continued addition of oxygen. One can surmise that the process is as follows. After warming to room temperature the surface is partly covered with oxygen and hydrogen. Some of the oxygen is on the surface, some has been incorporated. The hydrogen is either sitting in interstitial positions among four nickel atoms, or on top of chemisorbed oxygen, or both. The addition of further oxygen results in the adsorption of oxygen, followed by reaction with the hydrogen, either directly, or by desorption of the hydrogen first. The fact that oxygen tends to
become incorporated in the metal surface at room temperature forming an oxide like structure, leads to several possibilities. If the oxygen has become incorporated in association with a hydrogen atom, then both must be recessed in the metal surface to some extent.

$$\text{Ni H}^+ \text{ Ni H}^+ \text{ Ni}$$

0 0

The extreme sensitivity of a film of partially incorporated oxygen to attack by hydrogen molecules is demonstrated by (fig. 41). A similar sensitivity is displayed by an incorporated oxygen film on iron (2). These facts suggest that during the adsorption of oxygen at room temperature, hydrogen is desorbed and readsores on the oxygenated surface. Germer and Macrae (3) have shown by X-ray diffraction studies that oxygen can displace hydrogen from a nickel surface.

The interaction of hydrogen with the oxygenated surface can conceivably have two forms. 1) Nondissociative interaction of a hydrogen molecule with a surface oxygen leading to a species like a water molecule, bonded to the surface by the oxygen, but carrying a positive charge outwards, 2) Dissociative interaction with hydrogen bonded to a nickel atom and a surface oxygen, both of these hydrogen atoms carrying positive charges. Since some oxygen has become incorporated in the nickel lattice the surface nickel atoms will not have quite their original metallic character so that the formation of the positively charged hydrogen is
not impossible. Equally the hydrogen bonded to a surface oxygen could be expected to carry a partial positive charge in view of the high electronegativity of the oxygen. The addition of water to a nickel film leads to a negative surface potential (4), suggesting that dissociation occurs. Blyholder and Neff (5) find that water dissociates completely on supported iron, there being no trace of an OH band. These results tend to favour something like mechanism (2). Again if one draws an analogy with an oxide like surface the results of Eischens for zinc oxide tend to show that a dissociative mechanism is involved. Unfortunately it is not possible to establish the stoichiometry of the system from the amounts of gas added. Clearly some oxygen has reacted with the nickel surface, and become incorporated without interacting with hydrogen. The magnitude of the positive S.P. will probably depend on the amount of hydrogen available. As the addition of oxygen continues the point will come when the oxygen is reacting solely with the nickel surface, causing the potential to become more negative.
Oxygen - Carbon Monoxide. Results.

Addition of CO to Ni films partially covered (θ c.a. 0.6) with oxygen and maintained at 77°K, caused the S.P. to become less negative by 0.49V, when the S.P. due to chemisorbed oxygen was -0.93V. On warming to room temperature the S.P. became more negative by 0.18V, and 10¹⁷ molecules of gas were desorbed. Recooling to 90°K caused no change. The values reported here agree well with those found by Siddiqi. (1)

Discussion.

The results for O₂ and CO show that in contrast to H₂ - O₂ there is interaction between the two gases even at 90°K and this interaction produces either a species carrying a positive S.P., or converts the whole surface to a less negative species. On warming to room temperature the oxygen is unable to switch freely, instead the S.P. becomes slightly more negative. It is clear that CO must be bonded to the chemisorbed oxygen directly. The most probable configurations are:

(1) \[ \text{Ni} \quad \text{O} \]\n\[ \quad \text{C} \quad | \quad | \text{C} \]
\[ \quad \text{O} \quad \]
\[ \quad \text{Ni} \quad \text{Ni} \]

(2) \[ \text{Ni} \quad \text{O} \]\n\[ \quad \text{C} \quad | \quad | \text{C} \]
\[ \quad \text{O} \quad \]
\[ \quad \text{Ni} \quad \text{Ni} \]
Structure (2) would probably desorb CO on warming to room temperature thus accounting for the evolution of $1 \times 10^{17}$ molecules of gas.
Nitrogen - Tungsten. Results.

Some experiments were conducted on the system W-N$_2$ in view of the diversity of values and signs appearing in the literature. Nitrogen was added in doses of c.a. $9 \times 10^{16}$ molecules to tungsten films formed at 77°K. During the addition of gas at this temperature a small, positive, transient potential was apparent at S.P. greater than 0.4 S.P. max. (fig. 47) The small magnitude of this transient potential, 10 - 20 mV, made it impossible to estimate activation energies for diffusion with any precision, but using the transient data at the flat part of the S.P. maximum a rough estimate of 2 - 3 Kcal. was made, assuming a crystallite size of 1000 Å. Once again, as with hydrogen and oxygen, the observation of the transient potential is probably facilitated by the cell structure. Gas molecules can only reach the metal film through a narrow annular aperture at one end of the film. Incoming molecules are directed over surface already occupied.

The maximum value of S.P. obtained at 77°K varied from -0.15 to -0.2V, while increasing the pressure over the film to $2 \times 10^{-2}$ mm changed the S.P. to only -0.04V (fig. 46). The potential could be restored to its original value by pumping for 7 mins. at 77°K.

On warming a tungsten film covered with nitrogen at 77°K, the S.P. became more negative reaching -0.37,
-0.52V and then changing slowly to a final, less negative, value. The latter was irreproducible and varied from -0.35V to +0.09V.

Accompanying the peak in the negative S.P. there was an increase in pressure over the film. The pressure reached a maximum at the S.P. maximum, and then fell to a low value in the range $10^{-5}$, $10^{-7}$ mm Hg, at room temperature. The pressure rise corresponded to the desorption of 1.0, $1.3 \times 10^{16}$ molecules in the cases where pressure rise did not exceed the capacity of the measuring instruments. Gas added at room temperature was adsorbed without change of S.P. and the pressure remained at around $10^{-7}$ mm Hg. Addition of gas after warming and then recooling to 77°K did effect the S.P., changing it by +0.35V. The latter change could be reversed by warming the film to room temperature, whereupon the S.P. was restored to a slightly more negative value without passing through a maximum.

In experiment 137, after first warming and then cooling a nitrogen covered tungsten film, $6.66 \times 10^{17}$ molecules were added. This had the effect of making the S.P. less negative by 0.04V, addition of $5.6 \times 10^{17}$ molecules of nitrogen made the S.P. less negative by a further 0.04V. On warming the film the S.P. changed to -0.27V. The irreproducible character of the S.P. changes accompanying the adsorption of nitrogen on tungsten at various temperatures will be considered in greater detail.
To check the temperature variation of the $N_2$-W surface potential an experiment was conducted in which the temperature of the cell could be gradually raised from 77°K to room temperature. This was achieved by slowly boiling off the liquid nitrogen contained in a closed Dewar around the cell. A stream of warm, dry, nitrogen gas was passed through a copper spiral attached to a tight fitting copper jacket surrounding the cell. The whole arrangement was surrounded by the Dewar of liquid nitrogen. The temperature of the cell surface was recorded on a chromel-alumel thermocouple connected to a pen recorder. The S.P. and temperature could then be recorded simultaneously.

A tungsten film was evaporated at 77°K, warmed to room temperature, and finally recooled to 77°K. Nitrogen was added in doses of c.a. $9 \times 10^{16}$ molecules until the S.P. max was reached, after $6.2 \times 10^{17}$ molecules had been added. The pressure over the film was c.a. $10^{-7}$ mm Hg.

The warm up was begun and lasted over 135 minutes. The variation of S.P. with temperature is shown in (fig. 48). The maximum negative S.P. occurred at 190°K at which temperature the pressure had risen to c.a. $10^{-5}$ mm Hg. When the temperature had reached 290°K the S.P. had become steady at $+0.09 V$, while the pressure had fallen to $7 \times 10^{-7}$ mm Hg. The addition of further gas left the S.P. unaltered. This unusual behaviour was checked in a further series of experiments. It was not found possible to reproduce the above
behaviour, but all the succeeding experiments had the same general features. A film which had been saturated with nitrogen at $10^{-2}$ mm Hg and 77°K followed by pumping to remove the gas phase, produced a pressure peak too large to measure with the ion gauge viz $10^{-3}$ mm Hg, when the film was warmed rapidly to room temperature. The pressure was reduced to measurable dimensions by pumping for a few seconds. The S.P. change, after the maximum negative value, was least for this experiment, 0.14V. A repeat experiment using the same warm up time produced a similar effect. Although the starting S.P. was only -0.11V, 0.05V less than the previous experiment, the warm up curve followed that of the previous with a constant displacement of 0.05, 0.06V. The only significant difference between the experiments appeared to be the duration of heating. Accordingly in experiment 137 an intermediate heating period was used. 6.67 x $10^{17}$ molecules of N$_2$ were added to a tungsten film at 77°K giving a starting S.P. of -0.2V at $5 \times 10^{-7}$ mm Hg. When the film was warmed slowly to room temperature the S.P. rose to a maximum of -0.47V, and then fell to -0.1V. The S.P. change was again accompanied by a pressure burst, this time of $3.1 \times 10^{-4}$ mm falling quickly to $2.3 \times 10^{-5}$ mm, and then very slowly to c.a. $10^{-7}$ mm. The latter change occurred without S.P. change. The pressure rise corresponded to the desorption of $1.3 \times 10^{16}$ molecules N$_2$ (fig. 50).
Discussion.

The S.P. data for nitrogen on tungsten shows considerable complexity, which is perhaps not surprising in view of the multiplicity of binding states. The data is most conveniently analysed by comparison with the work of Ehrlich. At 77°K there appear to be two weak binding states unless the gas which desorbs during heating is also that responsible for the positive transient. Ehrlich (1) has shown that there are indeed two states of binding at low temperature. One, which comprises molecules held by dispersion forces, is mobile at T\sim 40°K and has an activation energy for diffusion of c.a. 2 Kcal while the other, the δ state, does not diffuse at 77°K. The positive transient can therefore be ascribed to physically bound molecules diffusing over the tungsten surface. The small size of the transient suggests a small dipole for the 2nd layer species, even though the nitrogen molecule is more polarisable than the hydrogen or oxygen.

The change in S.P. value occurring with increase of temperature shows a maximum negative value at 190°K, at which temperature the pressure over the film also reached a maximum. This corresponds to the desorption of the nitrogen δ state, which Ehrlich (2) has shown is complete at 190°K, accompanied by freezing of the 110 planes of the tungsten crystal. From flash filament studies Ehrlich quotes a
value of $6 \times 10^{14}$ molecules cm$^{-2}$ for the $\gamma$ state concentration. This is more than the amount released from the tungsten films during warm up, but a strict comparison is of doubtful value. The agreement between this data and that of Ehrlich is very good; it is still not clear what meaning the points of inflexion (a) and (b) should have. The presence of the $\gamma$ state on top of a chemisorbed nitrogen layer apparently makes the S.P. less negative, suggesting that the $\gamma$ state itself has a positive dipole outwards, which is not unreasonable. The reason for the depression in S.P. over the range $190 - 300^0K$ is difficult to explain, though it seems to vary with the time taken during the warm up over this range.

The change in S.P. to a less negative value shows a rough proportionality to the time of warm up from $190^0K$ to $300^0K$; thus $0.14V$ in 20 min; $0.37V$ in 47 min, and $0.46V$ in 80 min. The last value shows signs of a tailing off from linearity. During the warm up from $190 - 300^0K$ the gas desorbed at lower temperatures, being readorsbed with an accompanying redistribution of surface states. As the temperature rises the concentration of both the $\beta$ and $\gamma$ states is increasing. The concentration of the $\alpha$ state is dependent on the concentration of the $\beta$ state, but for increasing adsorption times at temperatures, for example around $243^0K$, the amount of $\alpha$ state formed will increase and then decrease slightly as the $\beta$ concentration increases. Ehrlich (3)
The higher the temperature at which adsorption is allowed to occur the less the \( \alpha \) state will be formed in comparison with the \( \beta \) state. This would suggest that the change in S.P. over the temperature range 190 - 300°K results from the formation of the molecular \( \alpha \) state. The \( \alpha \) state must have a positive dipole outwards, in order to effect the S.P. in the way it does. The occurrence of a positive dipole on a molecular adsorbed species is in accordance with observations of other systems, and it is not inconceivable that the di-pole might be of similar, or even greater magnitude, than that of the atomic \( \beta \) state.

The adsorption of nitrogen on tungsten at room temperature after previous saturation at low temperature, is accompanied by no S.P. change, although the gas is adsorbed. The equilibrium pressure over the film under these conditions is left virtually unaltered by the condition of gas. This type of behaviour is only conceivable if all the gas added is adsorbed on the internal surfaces of the film, or the adsorbed species has no dipole; both seem improbable. Certainly if the tungsten film is cooled to 77°K before the addition of gas there is a most marked change in S.P., presumably due to the reoccupation of the \( \alpha \) state. It is noticeable though that much more gas, \( 4 - 5 \times 10^{17} \) mols, must be added to the film to depress the S.P. to a small negative value than the amount desorbed during the initial warm up. The addition of CO leading to a small positive
S.P. is unusual. It is probably adsorbed on the 110 planes and prevents the adsorption of nitrogen on these planes. Although some nitrogen is adsorbed the change in S.P. is small.

To summarise, the value of the $N_2$-$W$ surface potential is strongly dependent on the temperature at which gas is added to the film. If the addition is carried out at room temperature, the S.P. will not vary with temperature, while if the addition is carried out at 77°K then the value will vary with temperature and warm up time. The $\gamma$ and $\alpha$ states of nitrogen appear to have positive dipoles outwards from the surface, while the atomic $\beta$ state has a negative dipole.
Appendix 1.

The Kramer Effect.

The high apparent S.P. values found during the addition of large doses of oxygen to nickel and copper films were attributed to the Kramer Effect, or electron emission. An independent check of this hypothesis was carried out using a specially designed cell, in which S.P. changes during oxygen adsorption had negligible effect. The cell (fig. 42) comprised a glass tube of some 5cm. diameter, one end of which was closed by a pinch seal carrying an evaporation source, while the other end was formed into a re-entrant seal. Through the re-entrant seal passed a single 2mm tungsten rod carrying a circular section platinum wire cage of 4cm diameter one end, the other being terminated 1cm below the top of the seal. The evaporation source was sited symmetrically inside the wire cage. A side arm slightly above the cage carried a tungsten seal to which was spot welded a narrow strip of platinum foil. The other end of the strip was fused onto the glass surface, this arrangement provided a pick up point for the evaporated films. Films were evaporated out through the platinum wire cage onto the glass wall of the cell. To prevent an evaporated film shortcircuited the cell, a glass shadowing umbrella was mounted just above the cage. Once evaporated, the metal film screened the cage. Further screening was applied by a coating of "liquid"
FIG 42

D.C. AMP

"LIQUID" BRIGHT PLATINUM SHIELDING

VACUUM LINE

NICKEL FILAMENT.

FIG 43

CELL

D.C. AMP.

PEN RECORDER
bright platinum on the upper, outer half of the cell, continued over into the re-entrant seal.

A high insulation coaxial cable, type PT11GM was used to connect the central tungsten rod to a D.C. amplifier EKCO type N616A. The coaxial cable was bared back 3cm and the central conductor soldered to a small metal clip which fitted over the tungsten rod, while the braid was smoothed back and made contact with the "liquid" bright platinum shielding. The whole arrangement being rather like a plug and socket.

After evaporation of a film the bottom pinch seal was fastened to the film pick up point, and both were earthed to the amplifier earth. (fig. 43) With the amplifier operating on $10^{12}$ ohms input resistance, oxygen was admitted and the amplifier output recorded on a pen recorder.

The significant features are the very low yield of electrons, 1.2 electrons / $10^{10}$ molecules of oxygen at 90°K rising to 4.4 electrons / $10^{10}$ molecules at 273°K. (fig. 45) The biggest burst of electrons occurs during the warm up from 90°K to 273°K, during which time most oxygen incorporation is taking place. Addition of oxygen at room temperature shows different behaviour from the low temperature results. (fig. 44) After a peak on the first dose the emission tails off to practically zero on the fourth dose, then increases again. At this stage the electron yield is time dependent, that is, the yield is increased if the interval between oxygen doses is increased. How-
FIG 4.4

EX 129
Number of electrons
X 10^-5

EX 130
298°K
Number of electrons
X 10^-5

DOSE NUMBER

90°K

273°K

334°K

Warm-up emission
ever, beyond a certain interval (3 min.) there is no corresponding increase in emission.

Calculation shows that emission currents of the order recorded in these experiments would certainly be registered as a potential by the static capacitor during surface potential measurements. Instead, only during the addition of large amounts of gas, \((10^{18} \text{ molecules})\) was a potential change recorded. The reason for this is revealed by the work of Wright (1) who has shown that emission depends on the applied electric field above the metal surface according to the equation \(N = \alpha(V - V_o)^2\), where \(\alpha\) is a constant, \(V_o\) is the threshold voltage; whether it is effected by the surface field is not clear.

Provided the servomechanism maintains the zero field condition precisely, there will be no contribution to the S.P. measurements from the electron emission. However, if a large number of electrons are emitted during the response time of the servomechanism, they will be incorporated in the S.P. data. This is most probable if an extremely large dose of gas is added to the metal.

The nature of the source of exo electrons is not clear, although they have been said to originate from F\(^1\) centres (2) in this work the incorporation of oxygen into the nickel lattice has been shown to be of significance. The yield per molecule is an order of magnitude less than the value quoted by Klemperer and Anderson (3), of 1 in
$10^9$ molecules. This may be due to collector efficiency. The variation in the yield at $298^0K$ strongly suggests that two mechanisms are responsible for the emission especially in view of the time dependence of the second peak, though this may just be due to increasing difficulty of oxygen incorporation. The work on this subject is reviewed by Grunberg. (4)
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\[ \text{Ni-O}_2-\text{H}_2 \]


\[ \text{Ni-O}_2-\text{CO} \]

Tungsten-Nitrogen.

Kramer Effect.