INFRA-RED SPECTRA OF CHEMISORBED SPECIES

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ABSTRACT

Infra-red spectra for CO chemisorbed on various metals are reported. The metals Ti, Cr, W, Mo, Ta, Mn, Fe, Ni, Rh, Pd and Pt were studied and, in all cases, the sample was in the form of evaporated metal film. Bakeable infra-red cells were used in an attempt to obtain cleaner and more clearly defined surfaces than those used by previous workers. The cells which were used were of two types. Cells incorporating MgO windows enabled the spectral range from 4000 - 1200 cm^{-1} to be studied. The longer wavelength region was studied using a bakeable cell which incorporated AgCl windows. This cell was developed during the course of the study.

The films which were prepared were more highly dispersed than is usually the case in normal chemisorption studies. The following techniques were used to prepare them:-

(a) Deposition in the presence of A or Kr.

(b) Co-evaporation of metal and NaCl.

(c) Deposition in the presence of CO.

(d) Bombardment of the metal with Kr ions.

(e) Deposition in vacuo.

In most cases the substrate was cooled by liquid nitrogen during the evaporation to lessen sintering effects.

All the metals mentioned were studied by using at least one of the techniques labelled (a) to (d). Ti, Fe, Ni, Pd, Rh and Pt were also studied by technique (e).

No absorption bands were observed when Ti was investigated and the results with the high melting point metals W, Ta and Mo were disappointing in that such bands as were observed were small and the sample tended to sinter when the system was evacuated.

Where applicable, it was noted that spectra for CO adsorbed on the other metals were similar to those obtained by previous workers. Differences were noted, however, and it is shown that the spectra which are obtained depend very critically upon the mode of sample preparation.

Studies in the far infra-red were successful only in the case of the Fe/CO system. Similar results to previous workers were obtained in that one band at 570 cm^{-1} was observed. This is attributed to a bending mode of the chemisorbed CO.

When vacuum deposited films were studied the cell was designed so that the amount of CO adsorbed by the film deposited on the plate in the infra-red beam could be measured. Some estimate of the extinction coefficient and integrated absorption intensity of the chemisorbed CO could be made because CO was not allowed to make contact with film that was not deposited on the plate.

Just one band was obtained when Pt, Rh, Pd and Fe were studied and the position of this varied between 2090 cm^{-1} and 1960 cm^{-1} depending upon the metal. Band intensities varied from $4^{o}/o$ absorption for Pt/CO to $1^{o}/o$ absorption for Pd/CO. Ni/CO showed bands at 2060 cm^{-1} and approximately 1960 - 1940 cm^{-1}. Desorption studies were possible because the samples did not sinter when the system was evacuated. These studies indicated that the species adsorbed on Pt is not easily removed at $300^{o}K$. Some weakly held CO was present on Rh surfaces. This represented only a small fraction of the total amount of adsorbed CO but it contributed markedly to the band. For Fe/CO the band was entirely due to weakly held CO although strongly held CO was probably present on the surface in much greater concentration. Such experiments with the Pd/CO and Ni/CO systems were not completely satisfactory due to the smallness of the bands. In general, however, the results are inconsistent with previous theories for the bonding of CO on metal surfaces and some attempt is made to explain the discrepancies.

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INTRODUCTION

In 1912 Langmuir (1) published the first of a series of papers which were devoted to the chemical interaction of various gases with W filaments. Langmuir was the first person to study the chemisorption of gases on metals with any real success but since the time of his pioneer work there have been many contributions to this field of study. Much of the success which has been achieved is due to the development of new techniques and the last 15 - 20 years have been particularly fruitful in this respect. The Field Emission Microscope (F.E.M.), which was developed by Muller (2), is ideally suited for the study of chemisorption but some of the other techniques that have been used had been developed previously in other relatively unrelated branches of chemistry and physics. This does not, in the least, detract from the skill employed by the initiator. Chemisorption involves the study of very small quantities of material and any new mode of investigation must be geared to take this into account.

Such a technique is the application of infra-red spectroscopy to the study of chemisorbed species. This method was first successfully used by Eischens (3) and it has been adopted in this study. CO chemisorption on transition metals has been studied in this work and it seems appropriate at this point that the information obtained for CO chemisorption by other techniques be considered and compared with that which can be obtained by using the infrared technique.

Brennan and Hayes (4) have measured the heat of adsorption of CO on a variety of transition metal films. Such data gives useful information about the strength of the bond between the adsorbate and the adsorbent. They found that the initial heat ranged from 40 kcal. $mole^{-1}$ for Fe/CO to 153 kcal. $mole^{-1}$ for Ti/CO. These results are very strong evidence that CO is chemically bonded to the metal; a heat of not more than 6 kcal. $mole^{-1}$ would be expected if the CO was held to the surface by Van der Waals attractive forces.

For many of the systems studied, the heat remained invariant with surface coverage. This was explained by assuming that consecutive additions of gas fill completely equivalent patches of the surface. W/CO and Mo/CO exhibited peculiarities in that the heat decreased with coverage. Here, it was assumed that the bond strength of the CO decreases as the surface coverage increases. For W/CO this decrease is especially marked at low coverage. Studies with the F.E.M. (5) show that CO molecules are immobile on W surfaces at 0°C and it is therefore difficult to see why the sites with higher bonding energy are preferentially occupied as the results of Brennan and Hayes would tend to indicate.

The Flash Desorption work of Redhead (6) and Ehrlich (7) for CO chemisorbed on W wires has also produced some interesting information about the bond strength of the adsorbed CO. In this technique the temperature of the wire is increased at a constant rate and the rate of desorption of CO is followed with an ionization gauge. Redhead found that the evolution of gas takes place in distinct steps. Pressure peaks were noted at distinct filament temperatures and Redhead has associated these with different types of bonding. Four states termed α, β_1, β_2 and β_3 have been observed with activation energies of desorption (E_D) of 29, 61, 69 and 75 kcal. mole^{-1} respectively. Redhead's results show that the activation energy of adsorption (E_A) is very small. In such circumstances E_D is equal to the heat of chemisorption and comparison of Redhead's data with that of Brennan and Hayes (4) shows that they are in fairly good agreement except at low coverage.

Ehrlich (7) has obtained very similar results and as his heating cycle was of the order of 300 milliseconds compared with the 1 minute heating cycle in Redhead's experiments it is evident that diffusion of the CO does not play an important role. Gomer (5) has measured the activation energy for diffusion of CO on W surfaces using the F.E.M.

Two types of diffusion were noted with activation energies of 36 Kcal. mole^{-1} and 65 Kcal. mole^{-1} and Ehrlich (8) has associated these with the β_1 and β_3 states. In so doing he has shown by calculation that molecules in each of these states must migrate approximately 60Å before desorbing. Since the size of the peaks is little altered by the rate of heating, and the different binding states occupy a significant fraction of the surface, Ehrlich has postulated that the β states are a result of chemical bonding of a slightly different nature caused by adsorption on different crystal planes. He considers that the variation in the number of nearest neighbour metal atoms on the different crystal planes can account for the observed variation in bonding energy. The nature of the α state is rather more uncertain. Redhead considers that, as it is formed mostly at high coverages, the α state consists of CO molecules which are filling gaps in the surface not occupied by β CO.

When a gas is adsorbed on a metal surface the bond between the metal and the adsorbate is polarised. A surface potential (S.P.) is set up and its magnitude can be ascertained by measuring the resultant change in work function of the metal. From the results some idea of the magnitude of the surface dipole can be obtained. However, on a heterogeneous surface the dipole may vary from site to site and it is usually only possible to obtain a measure of the average value of the dipole moment. The results for CO chemisorption are further complicated by the fact that the contribution from both the C - O and metal - C dipoles is measured.

Culver et al (9) find that for the transition metals Fe, Ni and Co the S.P. is large and negative, ranging from -1.68 volts for Fe/CO to -1.38 volts for Ni/CO. For the sp metals Cu, Ag and Au they find that the S.P. change is smaller and positive. The results have been interpreted by postulating that for CO on the d metals the CO is chemically bonded to the surface via the C atom. The O atom is visualised as sticking outward from the surface and having excess negative charge. The explanation given for the results with the sp metals is that the CO is weakly held to the surface via the oxygen atom by some sort of no-bond charge transfer mechanism.

Recently Heyne and Tompkins (10) have obtained the peculiar result of a S.P. value of 0.0 ± .01 volts for Pt/CO even at near maximum coverage. From other work it seems likely that the CO is chemically bonded to the Pt in a similar manner to that found for Fe and other d metals. It is very difficult to explain this result but it may be that the negative charge on the metal counteracts that on the oxygen atom.

Somewhat indirect investigations into the nature of the chemisorption bond have been made from surface area measurements. There is no real certainty about the point at which monolayer saturation is reached and, consequently, some arbitrary guess must be made. Hickmott (11) and Ehrlich (8) have used the criterion that the chemisorbed layer can be regarded as saturated when the sticking coefficient has fallen to a value of 10^{-5} - 10^{-6}. Working on these lines it was deduced from the experimental data that $1cm^2$ of a W surface will chemisorb 6.8 10^{14} molecules of CO and 7.0 10^{14} molecules of H_2. Since it is generally thought that hydrogen chemisorption is dissociative Ehrlich (8) has concluded that the adsorbed CO occupies two surface sites. Brennan and Hayes (4) have assumed monolayer saturation when the pressure of CO above the metal surface has an approximately constant value of 10^{-5} torr. Kr monolayer values were also measured before and after CO chemisorption. The deduced Kr monolayer values of Brennan and Graham (12) were then applied in deducing the arrangement of CO molecules on the surface. Several possible arrangements of bridged and linear bonded CO were considered and the concentration/cm^2 of adsorbed CO which each model gave was compared with experiment. As a result of these calculations they claim that CO chemisorbed on the h.c.p. metals Zr and Ti is mainly bridge bonded. Similar conclusions were also drawn for the f.c.c. metals but with the b.c.c. metals the evidence was not conclusive.

The measurements just mentioned were concerned with fast, non-activated chemisorption. It is known that a slow activated process follows the initial fast reaction. Not much appears to be known about the bonding of the CO adsorbed during this process. However, it is possible to measure the extent of the slow adsorption. For CO chemisorbed on a Ni film Gundry and Tompkins (13) found that the ratio

$$\frac{\text{amount of slow adsorption } (X_S)}{\text{amount of fast adsorption } (X_F)}$$

depended upon the sintering temperature of the film. For films sintered below 305°K X_S/X_F was practically constant and of the order 0.15.

With the F.E.M. it is possible to observe the behaviour of adsorbate on the different crystal planes of the metal and in this way activation energies for diffusion have been obtained (5), as previously indicated. This is obviously a very direct and valuable method of approach. However, in order to obtain electron emission very high fields must be applied and these may affect the data obtained. This is even more the case in field ion microscopy where higher fields have to be applied. With both techniques the investigations are restricted to a small number of high melting point metals which are able to withstand the stresses involved. With the Field Ion Microscope events on the atomic scale can be observed but the results are somewhat complicated by the effect of the high field on the adsorbate.

The infra-red method has several advantages over all the techniques which have been mentioned and these will now be considered.

The Infra-red Technique

It seems clear from the work previously mentioned that the bonding of CO on metallic surface is heterogeneous in character. Infra-red spectroscopy offers the advantage that all the different bonding types can, in principle, be separately observed. It should be possible to observe, for example, the change in concentration of one particular species with surface coverage or whether the bonding of a certain species is affected by the presence of more admolecules on the surface. At the outset, moreover, there seems to be no reason why the range of metals that can be studied should be limited. This point will be discussed later, however.

In principle, chemisorbed molecules should produce two general types of infra-red absorption bands; one due to the chemisorbed radical itself and the other type due to the chemical bond between the radical and the metal surface. The bands which have been obtained have been interpreted by comparing them with the spectra of chemical compounds of known structure. This method appears to have been fairly sucessful and this could be regarded as somewhat surprising. One might expect that the force field experienced by a chemisorbed molecule would be sufficiently different from that in a simple chemical compound that the spectra could not be compared.

One of the main drawbacks with the infra-red technique is that samples have to be prepared in a special manner. Chemisorption results only in the formation of a monolayer and comparison with the liquid phase shows that the radiation must traverse 50 - 500 monolayers of chemisorbed material if a moderately intense absorption band is to be obtained. Moreover, the bulk metal does not transmit infra-red radiation; unless the metallic particle size is less than 200Å radiation losses due to scattering and absorption are severe. Eischens (14) is of the opinion that the infra-red radiation is transmitted through the particles when they are small and although he has given no theoretical explanation for this behaviour it is evident from experimental experience that small particles of metal must be used if spectra are to be obtained with the infra-red absorption technique.

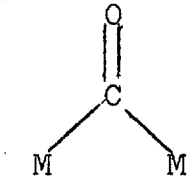
Sample preparation will be discussed later. The information that has been obtained will now be considered so that the aims of this particular work may be seen more clearly.

Most of the work that has been done has been concerned with the spectra due to the chemisorbed radical itself. The first successful studies were those of Eischens and co-workers (3, 15). They worked with the systems Pd/CO, Ni/CO, Pt/CO and Cu/CO. The metal was in the form of very small particles supported in Cabosil (non-porous silica).

The first point of immediate interest to come from this work was the occurrence of bands in the region of 2000 cm^{-1} which could be attributed to the fundamental C - O stretching frequency. This was the first piece of evidence to show that CO chemisorption is non-dissociative. All the systems gave rise to a band in the region 2040 - 2100cm^{-1} whilst for Pd/CO and Ni/CO a further band was noted in the region of 1900 cm^{-1}. By analogy with the spectra of metal carbonyls Eischens (3) has associated bands occurring in the region 1980 - 2100 cm^{-1} with the linear bonded species.

$$M = C = O \longleftrightarrow \overset{-}{M} \leftarrow C \equiv \overset{+}{O}$$

whilst bands around 1900 cm^{-1} have been interpreted in terms of the bridge structure



Thus Eischens et al claim that CO can be linearly and bridge bonded on Ni and Pd surfaces whereas the CO on Pt surfaces is mainly linearly bonded. For Cu/CO the band associated with C - O stretching frequency was found at 2100 cm^{-1}

compared with 2143 cm^{-1} for gas phase CO. This seems to denote weak chemical bonding for CO on Cu surfaces and this is in accordance with the S.P. data of Culver et al (9) who used Cu films. In fact, the study of the absorption bands of the adsorbed moleccule itself offers an ideal way in which to differentiate between physical adsorption and chemisorption. One would expect band shifts from the gas phase molecule to be small for physically adsorbed molecules compared with the shifts obtained for chemisorbed molecules.

At this junction just two more of the points which arise from Eischens' original work are considered; a fuller review is left until later.

It was noted that the bridged band for Pd/CO system alters with surface coverage, the band shifting to higher wave-number due to the formation of side bands as the surface concentration increased. This seems to indicate that new species are formed as the coverage increases and Eischens has interpreted this in terms of surface heterogeneity. He claims that the bands are a result of chemical bonding to metallic surface sites of differing energy. Although this surface heterogeneity had been predicted at a much earlier date,Eischens' results seem to be the first to give unequivocal experimental confirmation.

For Pt/CO the ratio of bridged to linear species alters with the type of support used. There appear to be very few bridge bonded CO molecules on silica-supported Pt whilst the bridge bonded species is quite noticeable on alumina-supported Pt surfaces. O'Neill and Yates (16) observed similar behaviour for the Ni/CO system. No complete theoretical explanation has been given for this and such behaviour makes comparison of spectroscopic results with those derived from other techniques using metallic films and filaments very difficult.

Blyholder (17) has noted that where there is a band in the near infra-red due to the so-called 'bridged' species there should also be a band in the region 700 - 1000 cm^{-1} due to the asymmetric metal-C stretching frequency. In his studies of the Ni/CO system he was unable to find this band and this has led him to doubt Eischens' original interpretation. Kraihanzel and Cotton (18) have shown that for a number of carbonyls which contain foreign ligands the C-O stretching frequency for linear metal-C-O bonding can occur even at wavenumbers of the order of 1800 cm^{-1}. Thus Blyholder (19) has claimed that all the bands in the region 2100 - 1800 cm^{-1} can be interpreted in terms of linearly bonded CO. His model is based on Molecular Orbital theories of bonding for gas phase CO and the metal carbonyls and these are therefore considered below.

The bonding in an isolated CO molecule can be simply and qualitatively descibed as follows (20):

There are three occupied σ orbitals which correspond to a σ bond between the two atoms, and the lone pairs of electrons on the C and O atoms. Only the first mentioned σ orbital contributes to the bond strength of the CO. In addition there are two π orbitals resulting from combination of the p_x and p_y orbitals of the C and O atoms. The result is a triple bond $(\sigma)^2$ $(\pi_y)^2$ $(\pi_x)^2$.

In metallic carbonyls, bonding is thought to be caused by two factors (21):

(a) The 3σ orbital, which consists almost entirely of a digonal hybrid C sp_z orbital, donates its electrons to a suitable, empty metal d orbital.

(b) A dative overlap of a filled $d\pi$ or hybrid $dp\pi$ metal orbital with an empty antibonding $p\pi$ orbital of the CO.

The drift of metal electrons into CO orbitals tends to make the CO as a whole negative; at the same time, drift of electrons to the metal from the 3σ orbital tends to make the CO positive, thus enhancing the acceptor strength of the π orbitals. Up to a point, the effects of the σ bond formation strengthen the π bonding and vice versa.

Now we refer again to the work of Kraihanzel and Cotton (18) on whose results the Blyholder theory is partially based. These workers noted that as CO in hexacarbonyls is replaced by ligands which do not π bond the C-O stretching frequency of the remaining linearly bonded CO ligands decreases down to 1800 cm^{-1}. For such compounds more electrons are available to go into the π anti-bonding orbitals of the CO. The CO bond strength will thus decrease and this will be reflected in the decrease of the C-O stretching frequency. Blyholder (19) uses a model where a metal atom on the surface is regarded as the central atom in a complex with the surrounding metal atoms and chemisorbed CO as ligands. He considers that the surrounding metal atoms compete with the adsorbed CO for electrons from the adsorbent atom since they have partially filled d orbitals which can π bond with this atom. Thus Blyholder is of the opinion that any bands detected in the region 2100 - 2000cm^{-1} are due to CO chemisorption on crystal planes where the adsorbent atom has a large number of nearest neighbours. In such a case, competition for electrons would be severe, resulting in only a small amount of electronic charge in the π anti-bonding orbitals of the CO. Likewise, he claims that bands in the region of 1900 cm^{-1} are due to chemisorption on lattice defects, edge atoms etc. where competition from surrounding metal atoms is considerably less.

As Eischens (22) points out, much of Blyholder's argument rests on his failure to observe any band due to the asymmetric metal - C stretching frequency expected for the bridged structure. This is scant evidence that bridged species do not exist but we shall discuss both theories in more detail at a later stage.

Bands due to the surface bond have not often been observed. The reason for this is not very clear; it may be that such bands will be very broad and that the extinction coefficient of the metal - admolecule bond is small.

The metal - C stretching frequency for CO chemisorption has been studied (17, 23, 24, 25) for several favourable systems where the fundamental C - O stretching band is intense. The bands obtained were found in the region 400 - 600 cm^{-1} as might be expected from metal carbonyl studies. Results are sometimes complicated by the presence of a bending mode of the chemisorbed CO but Blyholder (26) has used isotopes of CO in order to overcome this problem. For Fe/CO, which exhibits only one band in the near infrared, he has also calculated force constants for the Fe - C and C - O bonds.

The only other instance in which spectra due to a surface bond have been claimed is for the H_2/Pt system studied by Eischens et al (27). Isotopic work with D_2 would tend to indicate that some kind of Pt - H complex was observed but since a pressure of 400 torr of H_2 was required before the band could be observed it is not clear that these results have any bearing on the structure of chemisorbed hydrogen.

Much work has been done with adsorbates other than

CO. In practically all cases, spectra due to the chemisorbed radical itself have been observed. As can be seen from this review there is still ample controversy surrounding the interpretation of the bands due to chemisorbed CO and this applies, to some extent, to these other systems. Apart from this, a lot of doubt has been expressed regarding the quality of the surfaces which have been used. The preparation of these surfaces will now be considered, as it was one of the aims of this work to improve the method of sample preparation, and further points in favour of the use of CO as adsorbate will be raised.

Critical Review of Sample Preparation

As stated previously, if the chemisorbed state is to be studied by the infra-red absorption technique then the metal particles must be less than 200 Å and the infra-red radiation must pass through at least 50 chemisorbed monolayers. In 1954 Eischens et al overcame (3) these difficulties although Terenin (28) had previously obtained spectra for species adsorbed on an infra-red transparent material. Eischens et al prepared their samples (15) by impregnating a non-porous infra-red transmitting support, such as silica or alumina, with a metallic salt. The latter was then decomposed to the oxide, reduced to the metal at 300°C with H_2 and outgassed at the same temperature under a vacuum of 10^{-5} - 10^{-6} torr. In this way a large number of metallic particles, whose size was less than 200 Å, were obtained dispersed in the transmitting support. A 100 mg sample will transmit enough radiation for a commercial spectrometer to operate accurately and the particle size is so low that many more molecules adsorb on these samples than for a metallic wire or film. Thus, Heyne (10) has found that a 100 mg Aerosil-supported Pt sample containing 9 °/o Pt adsorbs 50.10^{16} molecules of CO/cm^2 of geometric area whilst a Pt film will chemisorb only 4.10^{15} molecules of CO/cm^2 of geometric area.

Eischens' technique has been modified by other workers but the basic idea remains unchanged. Much information has been obtained but many criticisms can be levelled at the mode of sample preparation.

First, there must be serious doubts about the cleanliness of the metallic particles produced. It is not known how effective the reduction of the metallic salt is. This is probably not serious for metals such as Pt whose oxides are unstable but Eischens (29) admits that it is not possible to effectively reduce Fe salts. Recently, Peri (30) has reduced NiO at higher temperatures than used by Eischens and he is of the opinion that it is very difficult to obtain completely reduced Ni. It seems to be generally agreed that the presence of the support makes reduction more difficult than might be supposed although no satisfactory explanation has been given for this. Plainly, it will be very difficult to study the metals W, Mo and Ti in this manner since they have very stable oxides.

The presence of the support also limits the power of the technique. The supports used transmit infra-red radiation in a limited region of the spectrum only. It is not possible to study the spectral region below 1300 cm^{-1}. Moreover, O'Neill and Yates (16) obtained different spectra for the Ni/CO system depending upon whether the support used was chromia, alumina or silica. The reason for this behaviour is not too clear; it could be that the support affects the electronic properties of the metal. However it is evident that the presence of the support can add an unwanted complication to the interpretation of the results.

There is one more criticism. Although an outgassing temperature of 500°C is desirable to ensure that the H_2 used for reduction is desorbed (31) it is probable that prolonged outgassing at 300°C is sufficient. However, the cell used by Eischens could not be baked and the final vacua obtained were probably of the order 10^{-5} - 10^{-6}torr. Simple kinetic theory shows that a vacuum of at least 10^{-8}torr is required in order that an uncontaminated surface be preserved for a reasonable length of time. It has been argued that the surface area of supported metal samples is so large that only a small fraction of the surface will become contaminated by residual impurities. This is certainly true if the impurities are present only in the gas phase. However, experience in this laboratory and elsewhere has shown that it is exceedingly difficult to evacuate an unbaked vacuum system to a vacuum less than 10^{-5}-10^{-6}torr as measured by an ionization gauge. Mass-spectrometric studies in unbaked vacuum systems (32) have shown that the residual impurities usually consist of H_2O, Hg, O_2, CO and CO_2. It is believed that these vapours are trapped in the glass walls of the system and that they can be removed efficiently only by heating the glass during evacuation. All these gases are active in chemisorption and, as the supply from the glass walls is very large, even the enormous surface areas encountered in the supported samples would be quickly contaminated in an unbaked system.

Thus, although the work of Eischens et al promoted the great stimulus it would appear that a better method of sample preparation is required. In an attempt to overcome these difficulties a lot of work has been done using metallic films. These have the advantage that the virgin metal is used and can be outgassed, usually in an efficient manner, at high temperature. As previously indicated, however, the roughness factor of films is usually much smaller than that of supported metals. Eischens (23) has obtained spectra for the Pt/CO system using an unsupported vacuum evaporated film but this is the only recorded instance for the transmission technique. Even in this case the vacuum conditions were poor. Evaporation took place in an unbaked vessel and the film was exposed to the atmosphere before CO was added.

Blyholder (33) has attacked this problem from a different angle. In his method metallic film is deposited on a salt plate coated in oil. Quite intense absorption bands have been obtained, presumably because the oil prevents growth of large particles of metal. Absorption by the oil itself prevents studies in the spectral regions near 3000 cm^{-1} and 1450 cm^{-1}, but, otherwise, the whole spectrum from 5000 - 350 cm^{-1} can be investigated. It may be noted however that the samples are, in a sense, supported by the oil and the nature of the metallic surface in the presence of oil and cracking products must be extremely complex.

Different methods of approach have been used by other workers. Pickering and Eckstrom (34) have used a multiple reflection cell where an infra-red beam undergoes 15 - 35 reflections from the surface of a metallic film on which gas is chemisorbed. Absorption by the chemisorbed molecules is very small and the spectral data has to be analysed by a computer to remove noise effects. Gardner and Petrucci (35) have deposited Ni film on the inside of a long cylinder. Infra-red radiation was then allowed to make multiple reflections with this film. Like Pickering and Eckstrom, these workers obtained very small bands. At the present stage it would seem that the advantages obtained by using bulk, unsupported metallic films are offset by the small amount of information obtainable.

Eischens (23) has obtained emission spectra for oleic acid adsorbed on highly polished aluminium rods. At temperatures greater than 200°C considerable desorption of most chemisorbed material occurs and since the emitted radiation is weak at such temperatures this technique has not been developed to any great extent. There is the added difficulty that, with the bulk metal, the amount of adsorbed material is small. This method will probably be developed much further using the now commercially available interferometer (36) which can operate at much lower levels of radiation intensity than the conventional infra-red spectrophotometer.

Sample Preparation adopted in this work and the aims of the study

There seems to be little doubt that the surfaces used for infra-red studies have been of a somewhat uncertain character and probably contaminated by gaseous impurities. In all chemisorption studies it is desirable that vacua very much less than 10^{-8} torr are achieved before samples are prepared and measurements are taken. The invention of the inverted ionization gauge by Alpert (37) made it possible to measure, and, thus, accurately produce, vacua less than 10^{-8} torr. Although Langmuir and other workers probably achieved vacua of the order of 10^{-9} torr their routine was by no means a common feature of that era. For the most part, therefore, it is only in the last 15 years that metallic surfaces have been produced which are substantially clean. Experimental results and, consequently, theoretical explanations of the chemisorption mechanism are now achievinging some clarity and much of the early work has been shown to be erroneous probably due to contamination effects. This motivated us to question the validity of the infra-red results because, as previously mentioned, the surfaces which have been used have been of poor quality.

In chemisorption studies clean metallic surfaces have been obtained mainly in the form of either evaporated metal films, wires or field emission tips. The use of wires and tips has the advantage that the surface structure is known to some extent. The metal surface area is very small and background vacua of the order of 10^{-10} torr are essential if the surface is to be maintained in an uncontaminated condition during the course of its preparation and the experiment. The range of metals that can be used is limited to those that can be outgassed at high temperatures (greater than 2000°C). To study the chemisorbed layer on wires by the infra-red technique an emission method has to be used. Consideration of these points therefore precluded the use of filaments in this study.

Evaporated metal films offer a number of advantages. A larger variety of metals can be used and their surface areas are much greater than those of filaments. During the evaporation new surface area is continually generated and residual impurities in the system are therefore 'gettered' during film formation. Ultra-high vacuum conditions are desirable but not completely essential.

It was therefore decided that metal films would be used in these studies. CO was used as adsorbate since there is good reason to believe that the extinction coefficients associated with both the C - O and metal - C stretching frequencies are large. Films have smaller surface areas than supported metals and it was hoped that by using CO this disadvantage would be offset to some extent. To combat contamination, bakeable infra-red cells were used and these are described in the next section. Techniques were developed so that metal films could be formed with higher surface areas than found for films used in other chemisorption studies. Most of the films were deposited on substrates cooled by a surrounding dewar full of liquid nitrogen since, in general, films with larger surface areas can be formed in this way. When vacuum evaporated films were studied CO was added to the film before it was warmed to room temperature in the hope that the resultant sintering would be lessened to some extent. In other instances films were thrown in the presence of a foreign medium in an attempt to prevent the growth of the metal particle size. The methods are referred to in more detail later but they will be briefly considered here.

(a) Film deposited in the presence of an inert gas.
It was expected that physical adsorption by the inert gas would limit particle size. CO was added later to displace the inert gas.

(b) Film deposited in the present of CO. CO should chemisorb on the surfaces of small aggregates of metal particles and thus prevent further growth.

(c) Films formed by co-evaporation of the metal and an infra-red transmitting material such as NaCl. The NaCl should prevent the growth of large particles of metal.

Other methods of preparation are noted in the text. Some of the methods described are similar to those published recently by Garland et al (24). A full comparison of their results and ours is given wherever this is applicable.

In most of this work the spectral region from 2500 - 1200 cm^{-1} was studied but evaporations carried out in the presence of CO were so successful that attempts were made to study the far infra-red region of the spectrum.

Full details of film preparation and experimental set-up are given in the next section.

EXPERIMENTAL

The Vacuum System

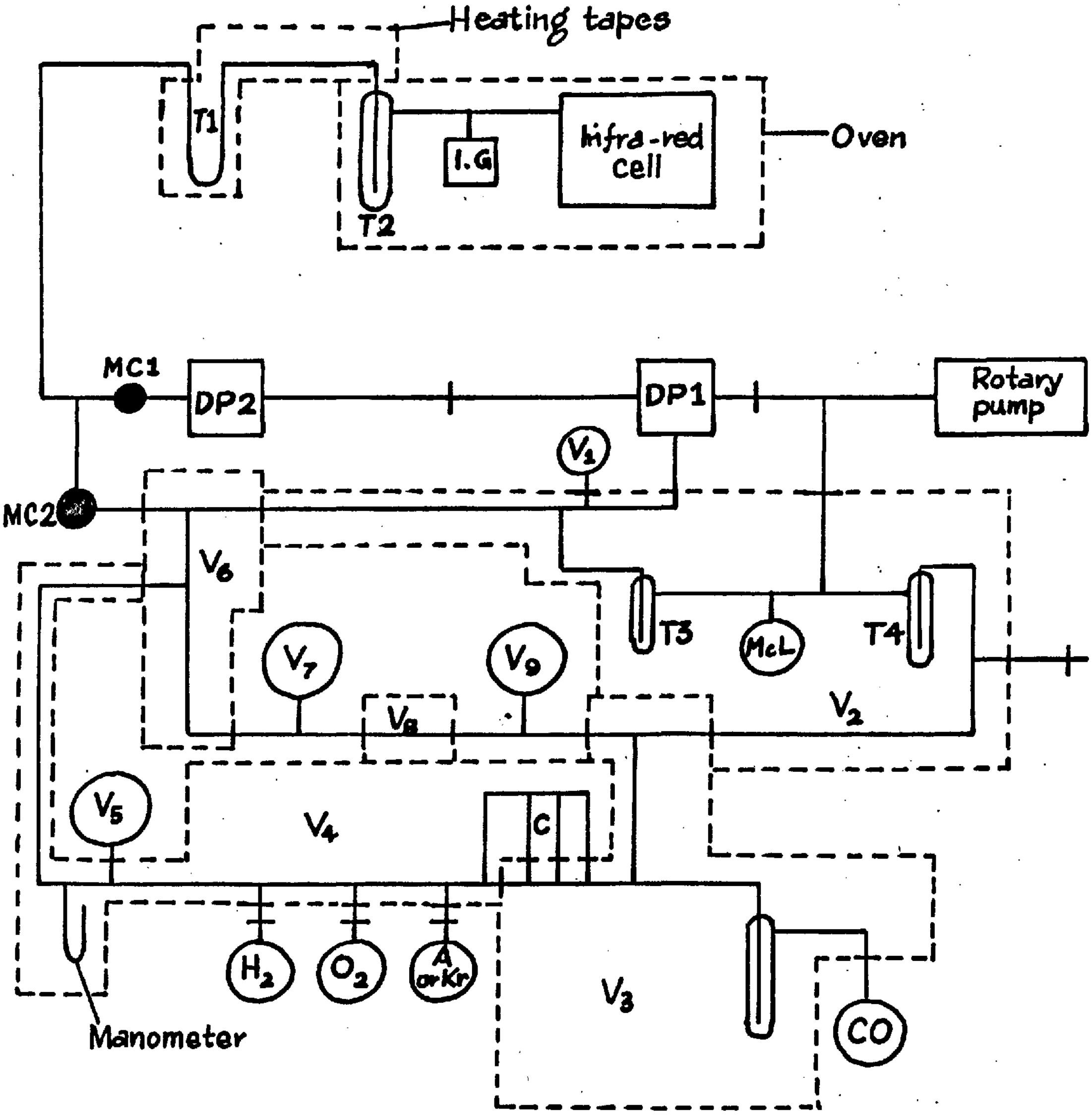
The vacuum system was mounted on a laboratory bench and supported by aluminium framework. It is shown schematically in Figure 1. Evacuation was carried out using an Edwards 'Speedi-Vac' rotary pump in series with two mercury diffusion pumps, DP1 (3-stage type) and DP2 (high speed, single stage). The main vacuum line leading to the cell was constructed from 25 mm diameter tubing and there were no grease stop-cocks in this section of the apparatus. The cell could be isolated from the pumps and the dosing system by the mercury cut-offs MC1 and MC2.

The McLeod gauge capillary was approximately 1 mm in diameter and the bulb volume was of the order of 250cc It was calibrated in the usual manner and pressures were determined by using the formula

$$P = (X(\text{cm}))^2 . 3.23 . 10^{-4} \text{torr.}$$

where X is the difference in height between the mercury levels in the two capillaries when the higher of the two was coincident with the top of the closed capillary stem.

FIGURE 1 — THE VACUUM SYSTEM.
SCALE EXAGGERATED FOR CLARITY.



MC = MERCURY CUT-OFF
DP = DIFFUSION PUMP
McL = McLEOD GAUGE
I.G = IONIZATION GAUGE
T = COLD TRAP
C = CAPILLARIES

$V_1 = 1150 \pm 10$ cc.
$V_2 = 550 \pm 20$ cc.
$V_3 = 165 \pm 10$ cc.
$V_4 = 105 \pm 5$ cc.
$V_5, V_7, V_9 = 3300 \pm 100$ cc.
$V_6 = 17{\cdot}6 \pm 0{\cdot}5$ cc.
$V_8 = 18{\cdot}5 \pm 0{\cdot}5$ cc.

The Dosing System

6 mm stop-cocks (supplied by Springhams, lubricated with Apiezon L or N grease) were used throughout the dosi system and were connected by 10 mm diameter tubing.

The volume V_1 in the dosing system was calibrated by filling it with water. All the other volumes were then calibrated by gas (argon) expansion at constant temperature. No cold traps were used during these determinations.

Accurate dosing procedure was used only in the work with vacuum evaporated metal films. It will, therefore, be discussed later in the chapter. When films were evaporated in the presence of gas, gas pressures of the order of 2-20 torr were generally used. In such experiments gas was added to the cell directly from the ampoules.

3 Capillary tubes, of diamter 0.6 mm, 0.2 mm and 0.06 mm and each 5 cm long, were attached to V_3 and V_4 so that it was possible to leak gas into the cell at a slow rate. No calibration of these capillaries was made.

The Bake-Out Oven

The oven used to bake out the cell, ionization gauge and T2 consisted of a double walled aluminium box (made from 1/16'' aluminium sheet), insulated by a $1\frac{1}{2}$'' thickness of Vermiculite. The top of the furnace was covered by a lid made from 1/16'' aluminium sheet. It was 2'' thick and packed with Vermiculite. Holes were made in it to allow passage of the pumping lead from the cell and the support which held the cell in position. Heat losses at these junctions were lessened by using Sindanio plugs. Heating was from two 1-Kilowatt finrod heaters (supplied by the Tetra Engineering Co.). The temperature of the oven was monitored by a chromel-alumel thermo-couple.

Ionization Gauges and the Control Circuit used

Edwards IG3 and Mullard IOG12 ionization gauges were used. The ionization gauge control circuit was similar to that described by Delchar (38) except for the outgassing circuit. The potentiometer controlling the outgassing current during electron bombardment cleaning was positioned in the primary circuit of the 11 volt 10 amp transformer which supplied outgassing current to the cathode. When Mullard IOG12 gauges were used with this ciruit it was found that emission currents of 1mA tended to be slightly unstable so that lower values (0.86 - 0.90 mA) were used. No attempts were made to calibrate the gauges as they were not used for measuring accurate, absolute values of pressure.

Bake-out and General Outgassing Procedure

The whole system was usually pumped to 10^{-2} torr with the rotary pump before the diffusion pumps were brought into operation. MC2 was raised and the system was baked up to the second trap T1 using the oven and heating tapes. Great care was taken in wrapping the heating tapes around the glass tubing, especially where this protruded from the top of the furnace. Here, the tape actually penetrated the inside of the oven and further heat losses were prevented by the Sindanio plug.

The maximum oven temperature was in the region 360 - 390°C when the MgO cell was used. The cell section was baked, usually overnight, for at least 12 hours. Heating tapes were then removed from T1 and a refrigerant (liquid nitrogen or cardice-acetone mixture) was placed round this whilst it was still hot. The level of the refrigerant was gradually increased over a period of 1 hour and then the power supplies to the other heating tapes and the oven were turned off. When the temperature inside the oven had decreased to 150°C the oven was removed and the pressure in the system was quickly monitored with the ionization gauge. If the reading indicated a vacuum less than 5.10^{-6} torr the gauge was outgassed and the metal filament in the cell was heated to very near its evaporation temperature whilst the glass was still hot. The power supply to the metal filament consisted of a 20 volt, 20 ampere step down transformer connected to the mains via a variac. An a.c. ammeter (0 - 13 A) was connected in series with one of the leads of the power supply from the out-put of the transformer.

In the cases of Fe and other metals which are difficult to outgas some film was deliberately thrown before an experiment was commenced. That it was possible to do this without invalidating the results will become apparent later. In this way residual impurities were gettered from the system and the filaments were outgassed more efficiently. Due to the inefficiency of the heating tapes it was sometimes necessary to place refrigerant round T2. However, with experience, it was found that this trap could be dispensed with and vacua in the region 2.10^{-9} - 5.10^{-8}torr were regularly achieved when T1 was cooled with liquid nitrogen. After this outgassing procedure the cell and traps were sometimes subjected to another bake-out but this was not done very often.

During this evacuation period it was usually possible to obtain a 'sticking' vacuum in the dosing section, although some difficulty was experienced when taps in this system had been newly greased. In this instance the taps had to be turned many times in their sockets and the dosing line was evacuated for periods up to 48 hours to remove CCl_4 vapour and air dissolved in the grease. Occasionally, liquid nitrogen traps were placed round T3 and T4 to assist the removal of condensible materials but this procedure was not usually required.

Materials used

CO, H_2, O_2, A and Kr were supplied by B.O.C. in break-seal ampoules and were used without further purification. Seals were broken after the system had been pumped for a long time (about 48 hours) and the McLeod gave a 'sticking' vacuum. The sections V_3 and V_4 in which these gases were kept were held in vacuo unless a gas bottle had to be replaced, and the taps were regularly examined for signs of leakage. Ni, Pd, Fe, Rh and Ti were supplied by Johnson-Matthey. The metals were spectroscopically standardised and films were usually deposited from 0.5 mm diameter wire.

Pt films were deposited from a filament made by winding 0.2 mm diameter spec-pure Pt wire (supplied by Johnson-Matthey) evenly around 0.3 mm diameter W wire. Some Ni films were deposited in a similar manner.

To deposite Mn films Mn chips (supplied by Johnson-Matthey) were heated in a Ta basket. Some Cr films were deposited from a W filament on which Cr had been electrodeposited.

Mo, W and Ta were used in the form of 0.3 mm diameter wire. The suppliers were Murex Ltd.

The Spectrophotometers

The early stages of this work were carried out using a Perkin-Elmer 137 spectrophotometer. For the most part, the wide slit programme was chosen and the slowest scanning speed of approximately 1µ per minute was used. The resolution of the instrument under these conditions is 15 - 16 cm^{-1} at 2000 cm^{-1}. For very sharp bands it is not possible to locate band heads with an accuracy greater than ± .03µ (± 13 cm^{-1} at 2000 cm^{-1}) and since a NaCl prism is used the spectral studies are limited to the region 4000 - 650 cm^{-1}.

However, most of the studies were carried out using a Perkin-Elmer 337 spectrophotometer and many of the earlier experiments were repeated with this instrument. Note is made in the text where spectra were recorded with the 137 model; spectra are represented in transmission-wavelength plots. With the 337 the slow scanning speed (100 cm^{-1} per minute) together with the '7' slit programme were mainly used and spectra could be recorded in the range 4000 - 400 cm^{-1}. At 2000 cm^{-1} band positions can be measured to a lower limit of ± 6 cm^{-1} and the resolution is 5 - 6 cm^{-1} when the conditions mentioned above are used. A gauze was placed in both reference and sample beams, reducing the transmission by a factor of 10. It was found that a polystyrene spectrum recorded under these conditions was practically the same as that obtained under normal conditions. Reproducibility was found to be quite good even when the sample transmitted only $5^{o}/o$ of the incident radiation. The superior performance of this instrument is due to the use of a diffraction grating in the monochromator allied with the slower scanning speed.

The instrument was mounted on a trolley so that it could be moved into the correct position around the infrared cell, which was fixed. During bake-outs the spectrophotometer was removed at least 1' away from the oven. The instrument was calibrated monthly with either polystyrene or liquid indene in a KBr cell. The indene calibration spectrum was compared with the results of R.N. Jones et al (39). These calibrations showed that the instrument's performance was unaffected by its movement on the trolley. Indeed, throughout the 2 years it was used, it met the maker's specifications.

During experiments, the transmitted radiation used was often of the order 5 - $10^{o}/o$ and under these conditions it was necessary to attenuate the reference beam. This was achieved by using wire gauze and the attenuator control built into the spectrophotometer.

The Infra-red Cells

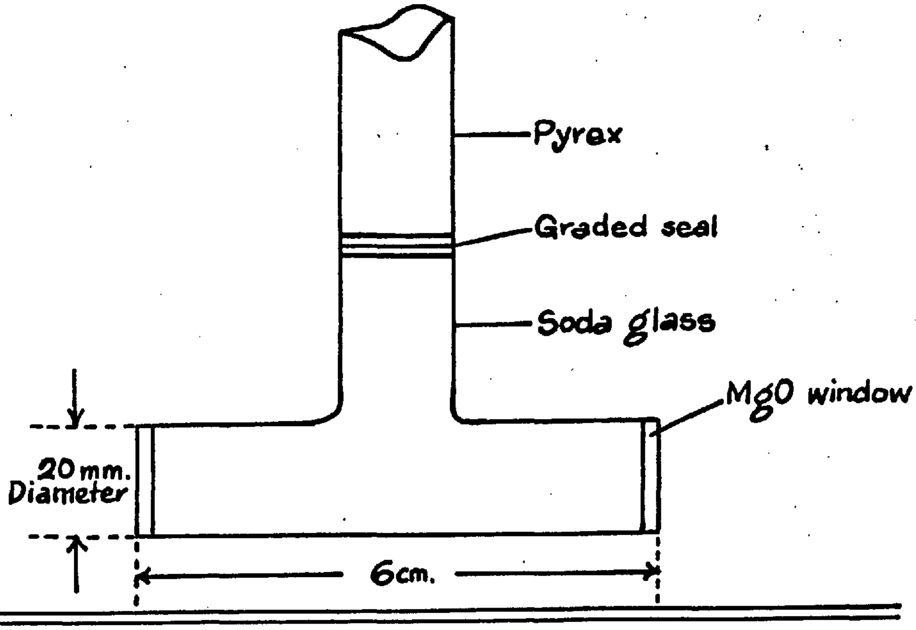
Most workers have used cells in which NaCl, CaF_2 or CsBr windows have been affixed to a ground glass surface by materials such as picein. With such window materials direct attachment to pyrex is not possible since the coefficients of expansion do not match. Moreover, such materials are very susceptible to thermal shock. In this work a small number of experiments were carried out in which cells with picein-affixed AgCl and NaCl windows were used. Mostly, however, bakeable cells were used and these were of two types:-

Cells using MgO windows affixed to Soda glass were most frequently used. These are similar to the type described by O'Neill and Yates (16) and were supplied by Manufacturer's Supply Co., Totton, Southampton. Due to difficulty in manufacture, the window diameters were limited to 20 mm. They were found to be exceedingly reliable. Bake-out temperatures were between 350° - 400°C and no leakage due to bake-out was ever experienced. Under favourable conditions vacua of 2.10^{-9} torr could be achieved and there was no evidence, at these vacua, that the cells were leaking. In fact, the ultimate vacuum produced was probably more a function of system design rather than the cell itself. The disadvantage of the cell is that the spectral region below 1200 - 1300 cm^{-1} cannot be studied as shown from Figure 2.

For work at long wavelength we counteracted this difficulty by designing a bakeable cell incorporating AgCl windows which transmit infra-red radiation quite well throughout the region 4000 - 400 cm^{-1}. Its preparation and transmission characteristics are shown schematically in Figure 3. The technique was to coat a ground glass flat with liquid-bright platinum (supplied by Johnson-Matthey). The coating was dried at 400°C. A cylindrical disc of AgCl, cut from 2 mm AgCl sheet (supplied by Johnson-Matthey) was placed on the flat and held in the coil of a 5 Kilowatt radio-frequency heater. The eddy-currents induced in the liquid-bright Pt coating were sufficient to heat the rim of the AgCl disc above its melting point. When the AgCl had melted all around the rim the heater was switched off and the cell was allowed to cool. It was found, by trial and error, that the most suitable diameter of AgCl window was 25 mm. The AgCl tended to crack on cooling when larger window diamters were used. The transmission of the AgCl sheet decreased during the preparation of the seal. The whole window was heated up during the process and this seemed to cause some fogging. No way was found to overcome this.

The seal obtained was not as good as that in the MgO-type cell. Bake-out temperatures below 300°C had to

FIGURE 2 _ THE MgO CELL AND ITS TRANSMISSION CHARACTERISTICS.



SPECTRUM WITH MgO PLATE IN CELL

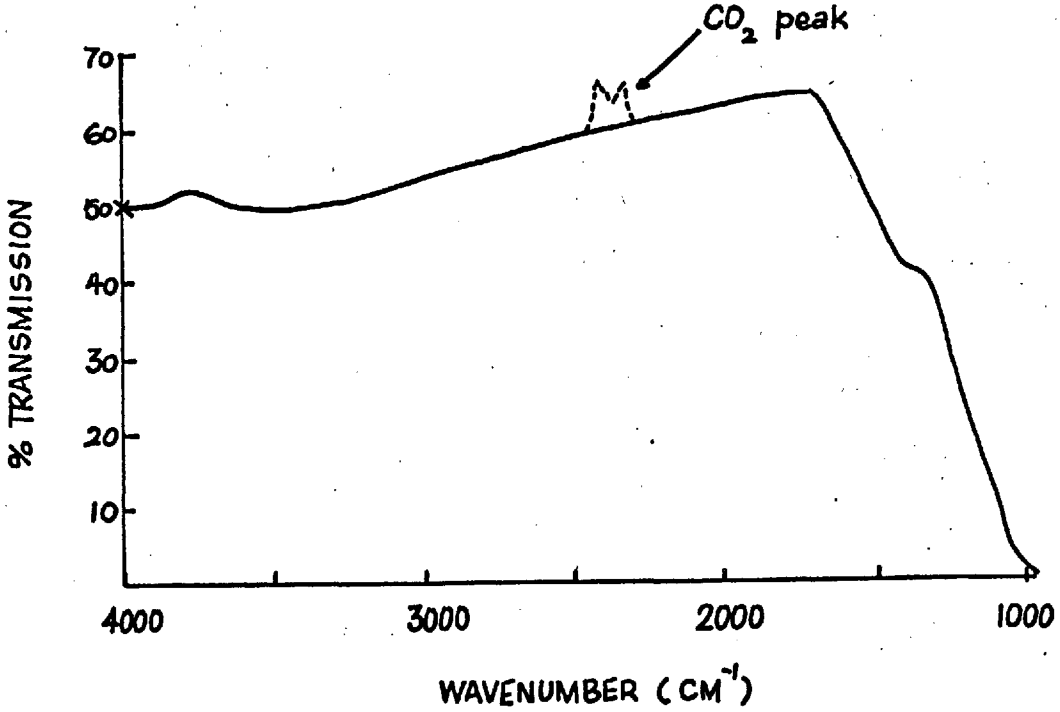
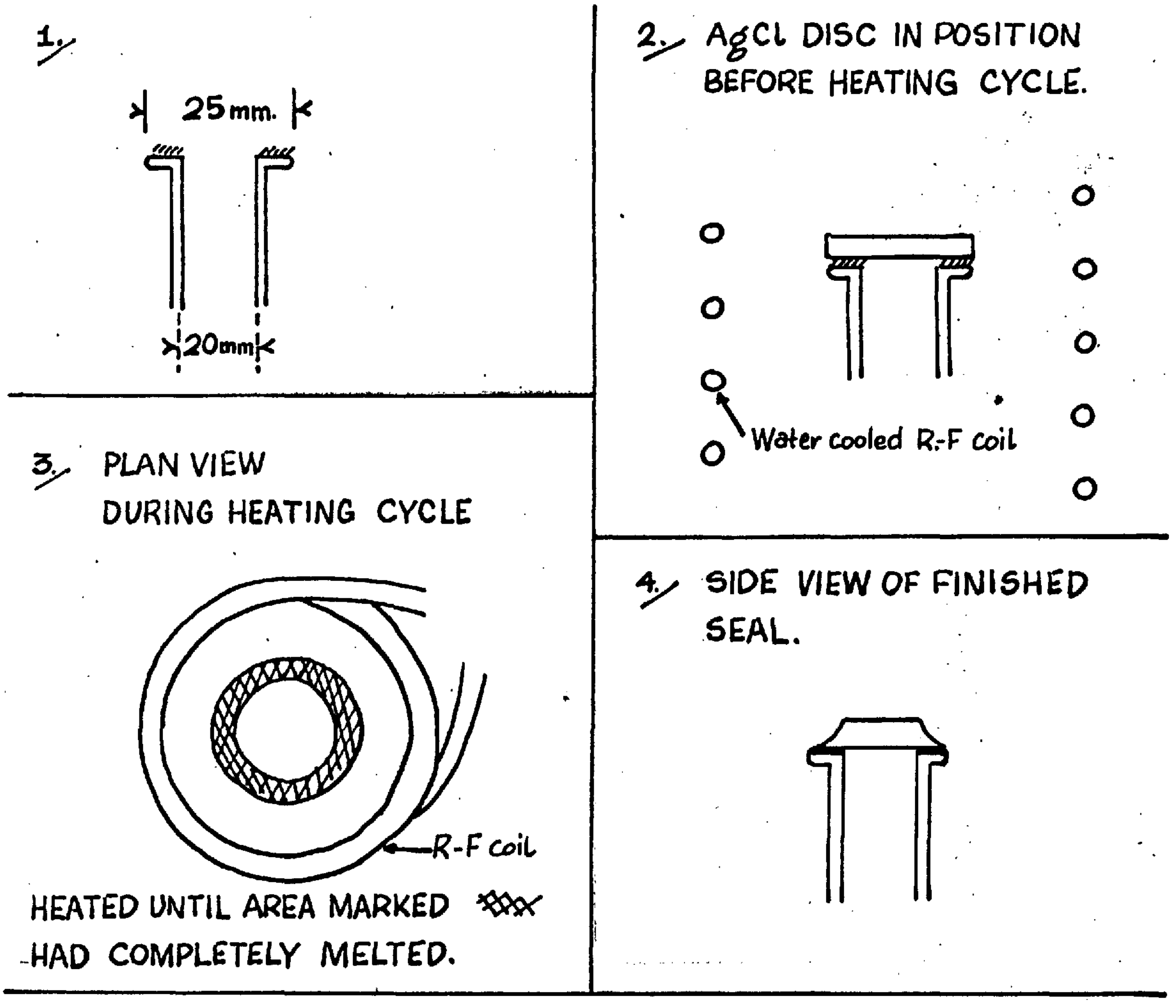


FIGURE 3 — PREPARATION OF THE AgCl CELL AND ITS TRANSMISSION CHARACTERISTICS



1.

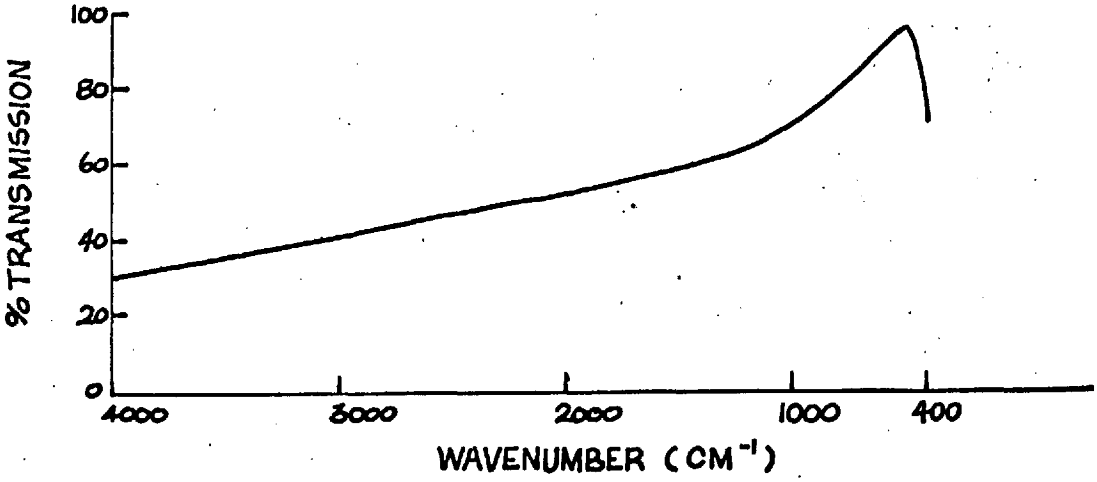
2. AgCl DISC IN POSITION BEFORE HEATING CYCLE.

3. PLAN VIEW DURING HEATING CYCLE

HEATED UNTIL AREA MARKED ▨ HAD COMPLETELY MELTED.

4. SIDE VIEW OF FINISHED SEAL.

TRANSMISSION CHARACTERISTICS



be employed or else the seal tended to leak. It was unfortunate that there was no ionization gauge attached when this cell was in operation but it was found that after several bake-outs the vacuum in the system was too low to be measured by the McLeod gauge even when the cell was at peak bake-out temperature and no traps were used. However, after several months use a leak was developed during bake-out. The strength of the seal under bake-out is probably due to the plastic nature of the AgCl sheet. Photolysis of AgCl results in the formation of particles of Ag. These cause Rayleigh scattering which is responsible for the form of the transmission curve in Figure 3. Also, it is probable that the Ag particles cause the AgCl to lose some of its elasticity with the result that weaknesses develop and leaks are produced.

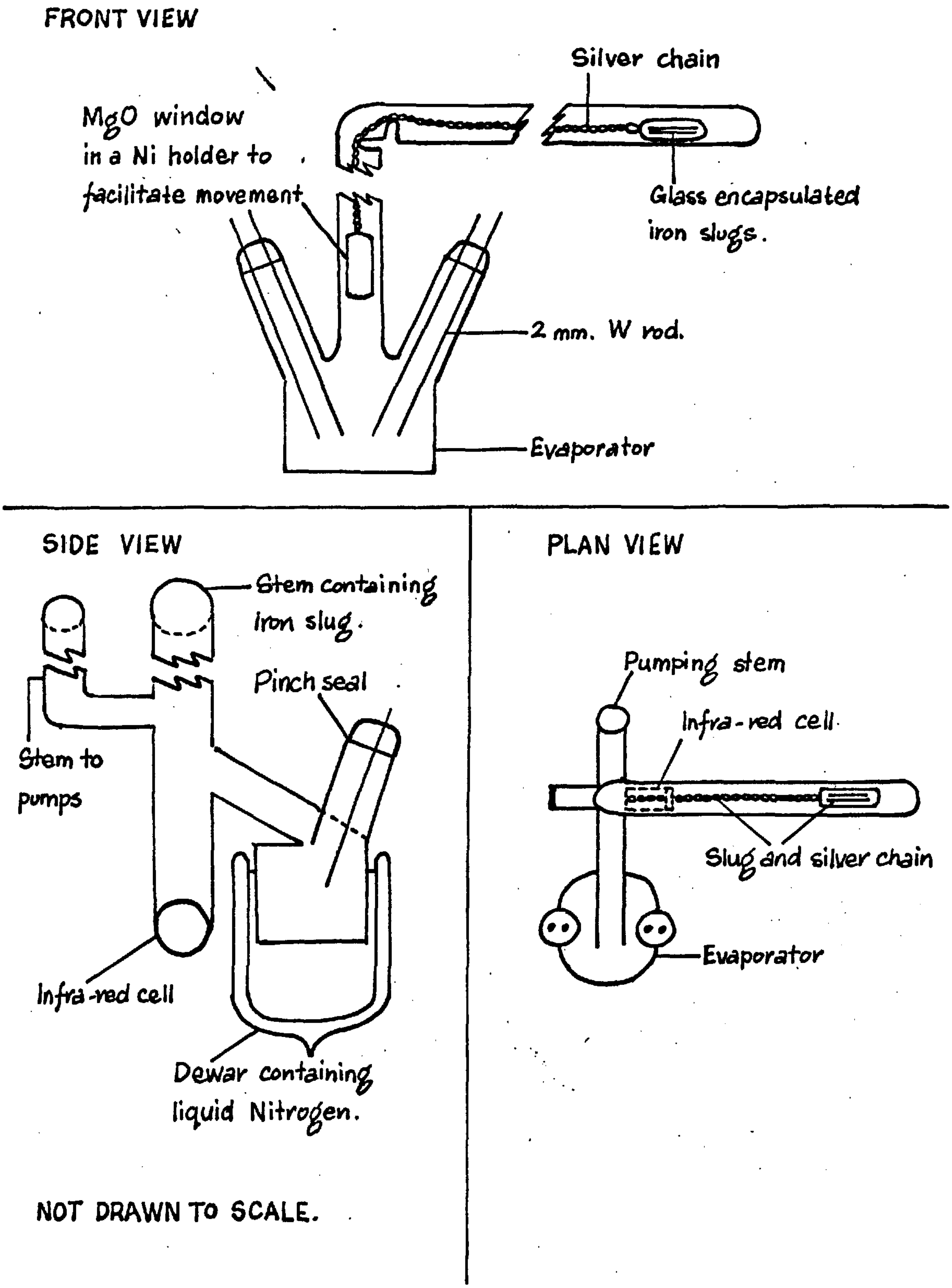
Preparation of Metallic Films

Basically, metal films were prepared in two different ways, and different cell designs and experimental technique were used in each case.

(a) Films prepared in the present of a foreign medium

The cell used in this work is shown in Figure 4 and will be hereafter referred to as Cell 1. Film was deposited onto either a MgO or AgCl plate which was attached by a silver chain to a glass encapsulated iron slug. AgCl

FIGURE 4 _ CELL 1



NOT DRAWN TO SCALE.

substrate was used only when the infra-red cell was of the AgCl-type. The design of Cell 1 had several advantages. Film could be deposited in the evaporator during the outgassing procedure since it was only the film which was formed on the window that was of interest. During the actual evaporation the evaporator was cooled with liquid nitrogen. This was done in an effort to overcome sintering effects, and the resultant loss in surface area, caused by the hot filament. Glass is a poor conductor and it is likely that the sample temperature was somewhat greater than that of the boiling nitrogen. The temperature of the latter must also be somewhat uncertain but, for convenience, such evaporations will be termed 'evaporation at $78^{o}K$'.

Since it was possible to move the window, gas phase spectra could also be studied. This was found to be especially valuable in the study of the Ni/CO system since $Ni(CO)_4$ vapour is easily formed under the conditions of many of the studies.

The types of film studied with Cell 1 can be further sub-divided into classes, and each type is considered separately.

(1) <u>Evaporation in Argon and Krypton</u>

For studies with argon, gas was added to the isolated, out-gassed cell until the pressure was 2 torr (such dosing is, in future, referred to as 'adding 2 torr of gas').

Evaporation was commenced with the cell cooled to $78^{\circ}K$. After evaporation the argon was pumped off for several minutes with the sample kept at $78^{\circ}K$. Then 2 - 3 torr of CO were added and allowed to make contact with the film for several minutes before the window was transferred to the infra-red cell.

Cardice-acetone traps were employed when the film was deposited in a Kr atmosphere. 20 - 50 torr of Kr were added to the cell, which was then cooled to $78^{\circ}K$. Cooling to $78^{\circ}K$ caused the Kr to condense in the evaporator since the vapour pressure of Kr at $78^{\circ}K$ is approximately 3 torr; patches of solid Kr were visible to the eye. Radiation from the filament prevented formation of Kr on the window. After evaporation the liquid nitrogen bath was removed and some of the Kr was transferred to V_1 by means of the trap T3, which was cooled to $78^{\circ}K$. The cell was then recooled to $78^{\circ}K$ and 2 - 3 torr of CO were added. After a contact time of several minutes the window was transferred to the infra-red cell and spectra were recorded.

(2) Evaporation in CO

The cell was usually baked before such evaporations were performed but exceptions to this are noted in the text. CO pressures between 10^{-2} - 12 torr were used. Evaporations were carried out at $78^{\circ}K$ and, in most instances, the filament was between 1 - 2 cm distant from the window. Unlike Garland et al (24), who used a flash evaporation technique, evaporations lasted for about 10 - 20 minutes and it was common practice to carry out several evaporations during the course of a single experiment. Even with an initial CO pressure of 2 torr some decrease in pressure was noted during the course of evaporation and, in certain instances, the supply was replenished from the doser.

(3) Co-Evaporation with NaCl

Broken pieces of crystalline NaCl (from infra-red windows; supplied by Hilger and Watts) were placed in a Ta basket and the NaCl was evaporated at the same time as the metal. The window was equidistant from both sources in an attempt to obtain a homogeneous frilm. Evaporations at room temperature and 78°K were carried out. It was difficult to outgas the NaCl completely. Pockets of gas were continuously evolved and the gas condensed on surfaces cooled by liquid nitrogen. Presumably, this behaviour was caused by water vapour desorbing from the interior of the crystal. However, after prolonged outgassing during which NaCl was evaporated, it was possible to reduce this effect to reasonable limits. CO was added to these films until the pressure in the cell was approximately 10^{-1}torr. Spectra were then recorded.

(4) Sputtering in Kr and Kr/CO mixtures

Sintering effects are likely to be severe when high melting point metals such as W or Mo are thermally evaporated, even when the substrate is cooled to 78°K. An alternative method of forming metal films is by ion bombardment of a metal filament and, under favourable conditions, the temperature of the wire can be kept quite low whilst maintaining a reasonable rate of deposition. During ion bombardment the metal particles ejected from the filament have high velocities and this effect may contribute to some sintering.

Two metal filaments were mounted in the evaporator and both were thermally outgassed until some film was formed. Cardice-acetone traps were used. Gas was then added to the cell. Usually, 20 torr of Kr were used but in some experiments 0.5 torr of CO was added to this. Sputtering was started by applying the out-put of a 1000 volt mains-powered transformer across the metal filaments. The potential was controlled by a variac which was used to vary the mains in-put to the transformer. When pure Kr was used some sputtering was allowed, before the window was transferred to the evaporator, to getter any impurities. The sputtering was carried out with the substrate cooled to 78°K and, although no accurate measurements were made, the wire temperature probably did not exceed 1000°C when

Mo was sputtered. CO was added to the film in the same way as described for films thermally evaporated in a Kr atmosphere. A contact time of 5 minutes was allowed with the film before spectra were recorded.

(b) Vacuum-evaporated Films

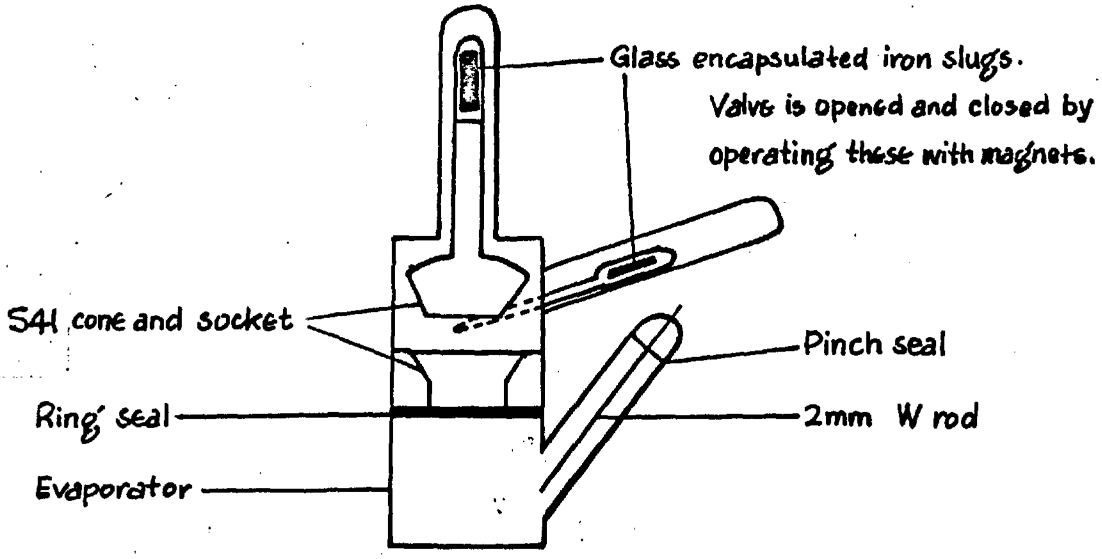
The cell used in these studies is shown in Figure 5 and is referred to as Cell 2. It was designed so that the number of CO molecules chemisorbed by the film on the window ONLY could be measured. This quantity was found to be small so that special experimental precautions had to be taken.

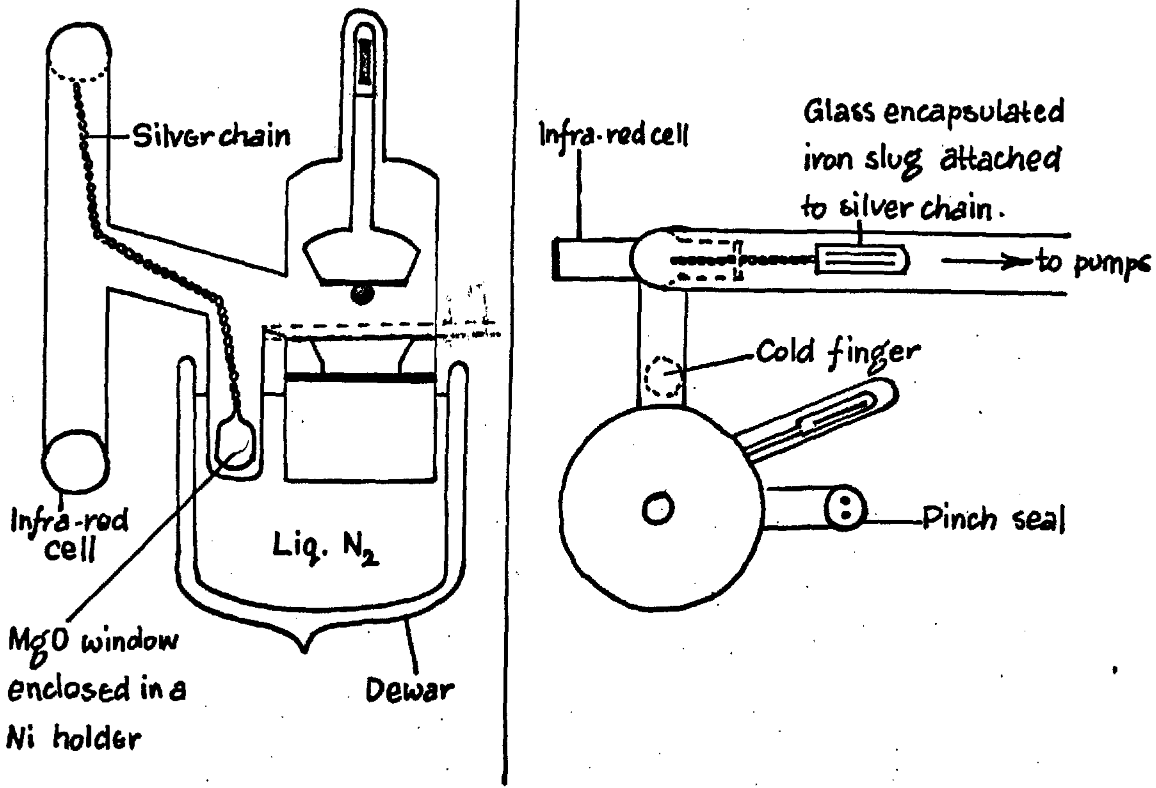
(1) The Dosing Procedure

The whole dosing system was always pumped to a 'sticking' vacuum before doses were prepared. There was only one instance when liquid nitrogen traps had to be placed round T3 and T4 in order to attain such a vacuum. Three taps were regreased during the whole of the period in which these experiments were performed. However, all the taps were outgassed by turning them in their sockets before doses were prepared. On the occasion when the newly greased taps were in the final stages of outgassing MC2 was lowered and the taps were turned whilst DP2 was evacuating the system. Pressure bursts of the order of 3.10^{-7} torr were noted initially but after some time these bursts decreased

FIGURE 5 _ CELL 2.

FRONT VIEW OF THE EVAPORATOR.




SIDE VIEW OF CELL

PLAN VIEW OF CELL

to 1.10^{-8} torr. Such effects due to the taps were never eliminated but they were minimised as much as possible by these outgassing procedures.

To prepare the doses the volumes in the dosing section were isolated. A quantity of CO was released from the ampoule into V_3 and V_4 and the pressure was measured with the manometer. This was expanded into V_9 which was then isolated. The gas was transferred from V_9 to V_8 and thence from V_8 to V_7. Doses were added to the cell from V_6 by extracting gas from the large reservoir V_7. Thus each dose is 0.995 times smaller than the one added before it. This decrease in dose size is quite important when a large number of doses is added to the cell and corrections were therefore made. Using the calibrated volumes given in Figure 1 the initial dose size, D, is given by the formula:

$$D = 2.35.10^{14}. \, Y \text{ molecules at } 300^{\circ}K.$$

and the initial pressure of gas, $P(V_6)$, in V_6 is calculated from the formula

$$P(V_6) = 4.16.10^{-4}. \, Y \text{ torr at } 300^{\circ}K.$$

Y is the pressure of gas in V_3 and V_4 measured (in torr) by the manometer. Values of Y between 20 - 40 torr were used.

Calibrations of the Cell

To determine the amount of CO adsorbed by the film on the window CO was dosed into the cell with the dekker valve closed and the window in the cold finger cooled to 78°K. Dosing was stopped when the pressure was of the order 4.10^{-4} - 8.10^{-4} torr and the sample was transferred to the infra-red cell. It was therefore necessary that calibrations be made of the number of CO molecules in the gas phase at a particular pressure so that the number of molecules on the film could be calculated. Corrections for the leakage of gas through the dekker valve during dosing were also carried out by measuring this leakage at different pressures.

To minimise dekker leakage effects an ionization gauge was used to measure pressures because readings can be taken quite quickly. The gauge was operated with emission currents in the range 0.86 - 0.90 mA and only intermittent readings were taken to minimise gauge pumping effects. Most of the readings were taken with the gauge operating on 0.86 mA emission but the ion currents in the calibration graphs are normalised for 1mA emission, assuming that the ion current is linearly dependent upon the emission current. It is felt that the error introduced here can be ignored since the range of emission currents used was small.

The gauge was not calibrated to obtain absolute pressure readings. Instead, the ion current was measured when a known number of CO molecules were added to the blank cell. The number of molecules in the gas phase could then be calculated from an ion current reading during an experiment. 6 separate calibration runs were performed and these runs were carried out on a newly baked system and also a system that had been flushed with approximately 10^{-3} torr of CO. No detectable differences were noted.

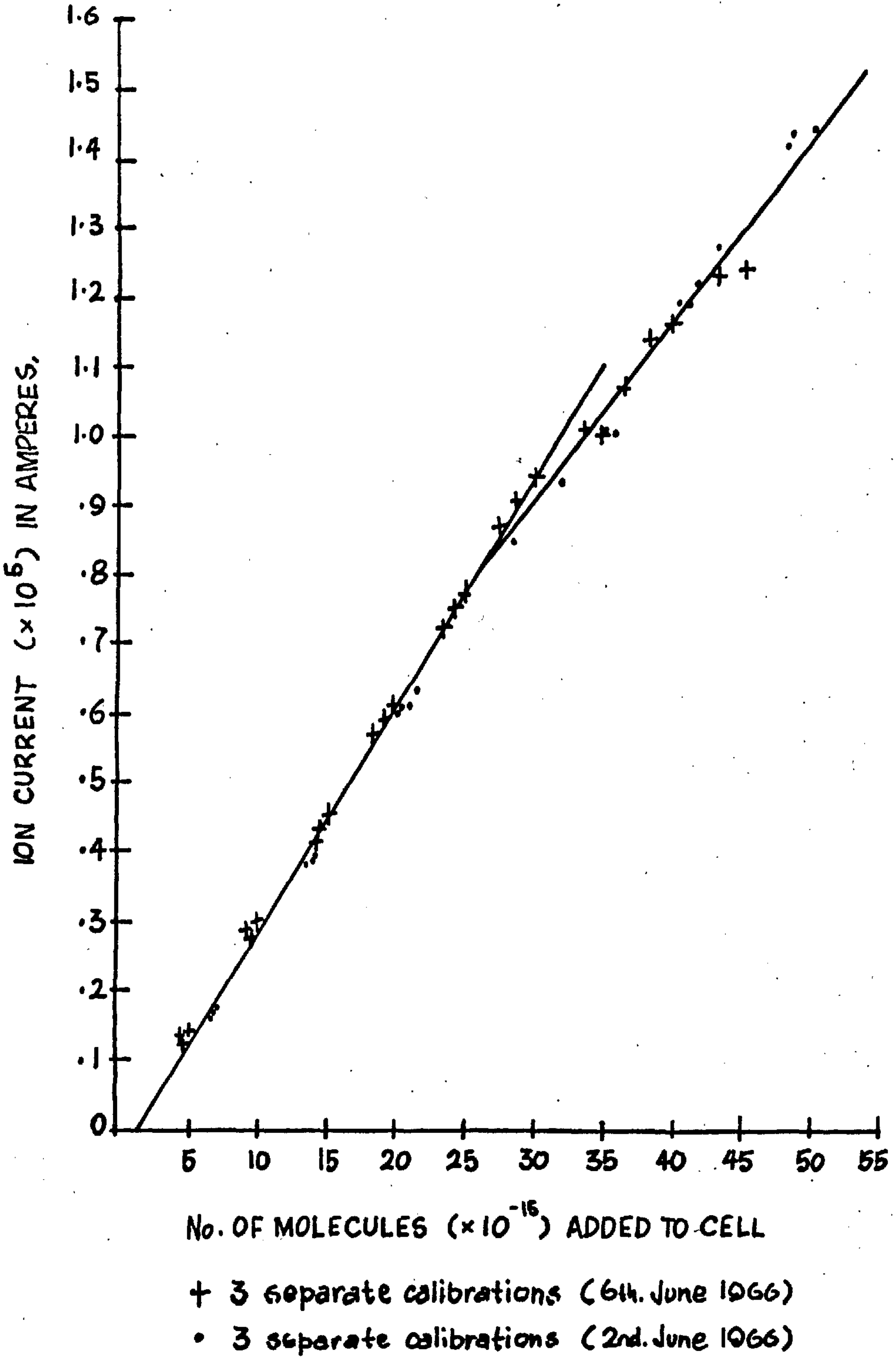
Early measurements showed that adsorption of CO by the liquid nitrogen cooled traps was greater than adsorption by the film deposited on the window even when the pressure in the cell was as low as 10^{-5} torr. Cardice-acetone traps were therefore used and, although the vacua produced were not as good, it was found that adsorption of CO by glass at 195°K could be ignored.

For all measurements trap T1 was cooled with cardice-acetone and the level of the bath was always brought to a fixed mark. Trap T2 was not cooled.

To calibrate the gauge the cell was isolated from the pumps by the cut-off MC1 and the dekker was closed. MC2 was then lowered. Both cut-offs were adjusted to fixed marks during this procedure. Known doses of CO were then added to the system. After each dose the ionization gauge was switched on for a maximum period of 5 seconds and the ion current was measured. The cell was held at $300^{o}K$ during these measurements. The calibration curve which was obtained from the data is given in Figure 6. The calibration curve seems to indicate that some of the CO is adsorbed by the cell. This adsorption is reversible because the addition of CO to a newly baked cell gives practically the same results as when CO is added to the flushed cell. A Knick electrometer was used to measure ion currents. The f.s.d. of this instrument is 8.10^{-n}A where n can range from 5 to 12. It is likely that the linearity of the scales varies and this probably accounts for the break in the calibration curve at an ion current corresponding to 8.10^{-6}A.

To test the dekker leakage rate some film was thrown in the evaporator. The dekker valve was then closed. Observing the same precautions as before, known quantities of CO were added to the cell until the pressure was approximately 10^{-3}torr. Intermittent readings were then taken with the ionization gauge at fixed intervals of time and the 'pressure' decrease with time was noted. In 50 minutes the ion current reading fell from $1.5.10^{-5}$A to $2.5.10^{-6}$A. On opening the dekker valve the pressure immediately fell to approximately 5.10^{-6}torr, showing that leakage was still occurring and that equilibrium had not been reached. A repeat with the dekker valve in a different position

FIGURE 6 _ CALIBRATION OF IONIZATION GAUGE BY DOSE-WISE ADDITION OF CO. CELL AT 300°K. DEKKER VALVE CLOSED.

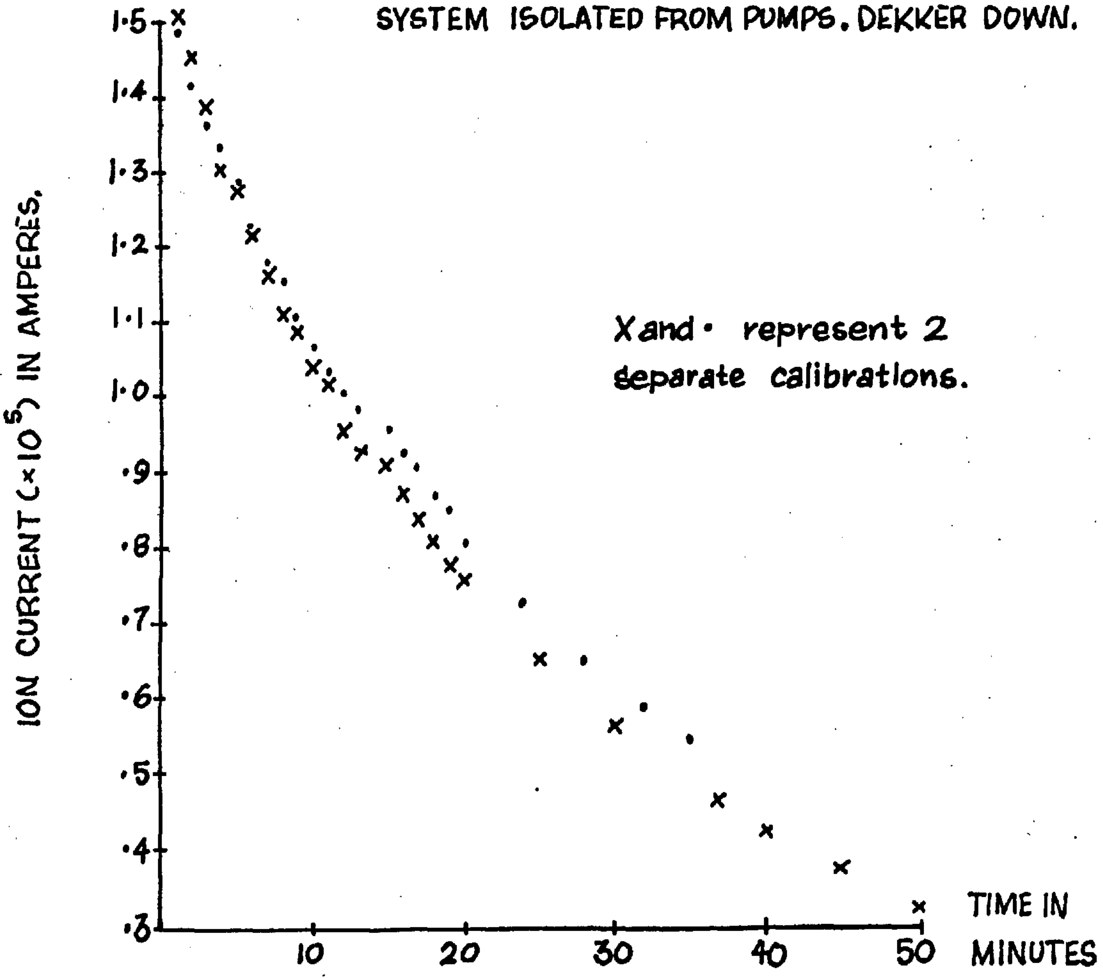


showed that the dekker leakage rate was slightly different but not sufficiently so that the experimental results would be seriously affected. The results are shown in Figures 7(a) and 7(b). In Figure 7(b) the number of CO molecules in the gas phase has been obtained by using the data from Figure 6 and some attempt has been made to express the dekker leakage in absolute terms. The method of this determination probably accounts for the scatter in Figure 7(b). The leakage through the dekker during the measurements to obtain Figure 6 makes the calibration uncertain for ion current readings greater than 1.10^{-5}A and, thus, the reliability of Figure 7(b) can only be taken to have significance for ion current readings lower than this value.

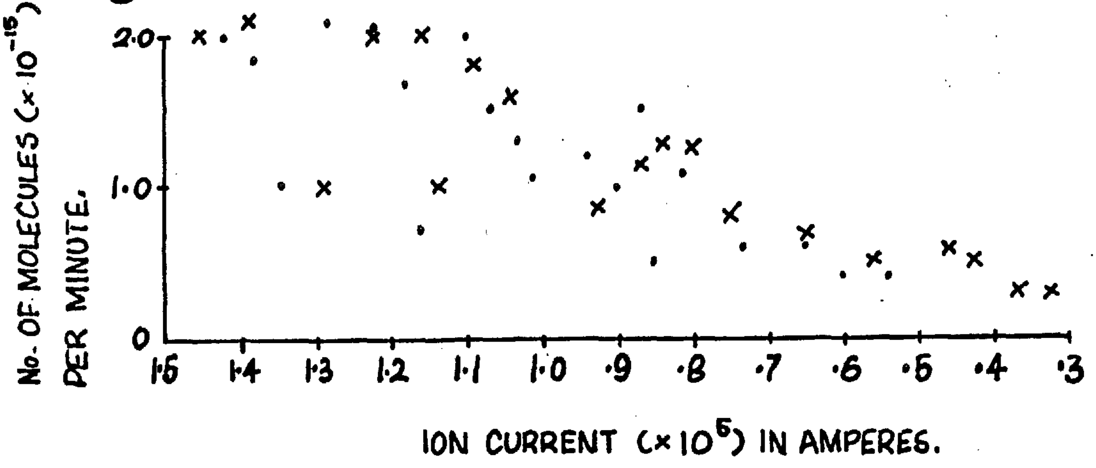
Before the calibrations for dekker leakage were carried out a fairly thick film (of Fe) was deposited. CO was dosed into the system with the dekker valve closed and all other precautions were observed before the leakage tests were commenced. It was found that more CO was adsorbed than was found in previous calibrations with the blank cell, indicating that some film was thrown outside the area contained by the dekker valve. However, the amount of CO adsorbed by this film was of the order of 2.10^{15} molecules and, as thinner films were formed during experiments, this effect was ignored.

FIGURE 7_ GRAPH TO ILLUSTRATE DEKKER LEAKAGE.

(a) DECREASE OF ION CURRENT READING WITH TIME.
SYSTEM ISOLATED FROM PUMPS. DEKKER DOWN.



(b) LEAKAGE RATE PLOTTED VS. ION CURRENT READING.



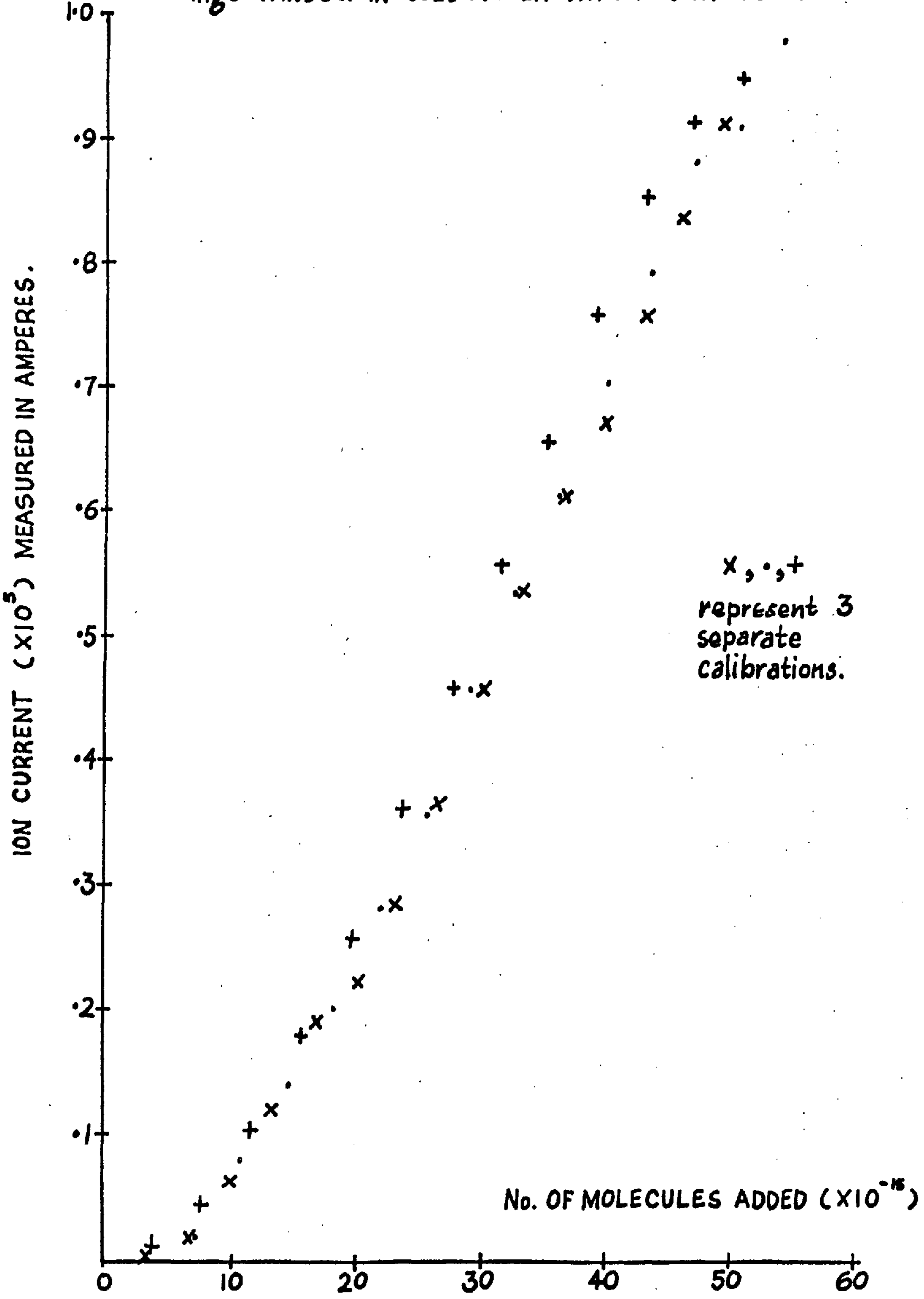
In the experiments, the film on the window was cooled to 78°K whilst gas was dosed into the cell. Calibrations were made in an attempt to calculate the extent of this adsorption at 78°K. The dekker valve was closed and the clean MgO window was placed in the cold finger. The cell was then cooled to 78°K and gas was dosed into the cell after the usual precautions had been observed. Figure 8 shows the calibration curve. It is difficult to maintain the liquid nitrogen at a constant level and it is likely that this is the cause of the experimental scatter. Calculations based on Figure 8 are not regarded with much confidence but the calibration serves as a useful guide to the extent of adsorption at a particular gas pressure.

In conclusion, it is believed that these calibrations show that dekker leakage is not usually serious and that the ionization gauge gives readings which are much easier to obtain, and also more accurate, than would be possible with a McLeod gauge.

Experimental Procedure

The bake-out procedure was as described earlier. The same ionization gauge (Mullard IOG12 model) was used for all calibrations and experiments. Care was taken to avoid contamination of the W grid structure by water vapour when the cell was cleaned. The gauge was outgassed by

FIGURE 8 _ CO ADDED TO THE CELL DOSE-WISE. DEKKER DOWN. MgO WINDOW IN COLD FINGER WHICH IS AT 78°K.



X, •, + represent 3 separate calibrations.

electron bombardment and suitable precautions were taken to prevent film deposition during this process. After a series of 41 experiments there was no sign of film formation.

3 - 4 experiments were done each week. Except for cleaning out unwanted film, the system was almost continually evacuated and it very quickly became a matter of routine to achieve very good background vacua, even with one cardice-acetone trap. The gauge sensitivity is given as 12 $torr^{-1}$ by the makers and, operating on 0.86 mA emission, ion currents of the order $1 - 2.10^{-10}$A were regularly obtained when measuring the background vacuum. Taking these facts into account, it seems likely that the major contaminant in the system was Hg vapour since the vapour pressure of Hg is $2 - 3.10^{-9}$torr at 195^{o}K (40).

Outgassing of the metals is considered in detail when each system is mentioned in the text. During the period in which the filament was outgassed the power was gradually increased until the filament was evaporating to a noticeable extent over a period of 10 minutes and the variac reading was noted. When film was deposited on the window the variac was set to this reading or slightly above it but during the outgas period a slightly lower power supply was used. Fe was usually outgassed for a short while at power ratings greater than used for depositing film on the window.

After outgassing, the MgO plate was transferred to the evaporator and positioned so that it was approximately 1 - 2 cm distant from the filament. The evaporator and cold finger were then surrounded by liquid nitrogen held in a transparent, glass dewar and evaporation was commenced. Evaporation usually lasted about 10 minutes. Its course was followed by eye and it was sometimes necessary to increase the pre-determined power serving the filament. The cell was evacuated throughout this period by DP2 and the cut-off MC2 was closed. When the evaporation was finished the window was quickly transferred from the evaporator to the cold finger without removing the coolant. As quickly as possible, the dekker valve was closed and the cut-offs were adjusted to the required positions. MC2 was usually lowered just before the addition of gas from the doser. Gas was then dosed into the cell as described previously and the ion current was noted after each dose. Approximately 20 seconds were required to add a dose and take a reading. The greatest number of doses ever added was ten and, as it is only in the final stages of the dosing that the pressure in the cell rises above 10^{-4} torr, leakage through the dekker valve during the time that doses were added was considered to be an unimportant source of error.

Comparison with the calibration curve in Figure 8 showed that most of the adsorption was complete when the pressure in the cell was approximately 1 - 2.10^{-4}torr but gas was usually dosed into the cell until the pressure was of the order 4.10^{-4} - 1.10^{-3}torr. Previous data had indicated that the ionization gauge saturated when the ion current reading was 6.10^{-5}A with 0.86mA emission current. The dewar was then removed, a stop watch started, and the sample was quickly transferred to the infra-red cell. The ion current reading was noted at fixed periods of time and spectra were recorded. In this way it was possible to make an estimate of the amount of gas that desorbed from the film on warm-up and thus calculate the amount of gas adsorbed on the film when spectra were actually recorded. The accuracy of the determination depended, to some extent, on the degree of sintering of the metal on warm-up. In some instances the pressure in the cell remained fairly constant for longer than would be expected from the dekker leakage tests. This behaviour was undoubtedly caused by sintering since the pressure fell rapidly on opening the dekker valve. Sintering problems, evacuation of the system and redosing with CO are considered in more detail when the results are discussed.

RESULTS AND DISCUSSION

No metal has been studied by all of the techniques developed. Each of the metal/CO systems that has been studied will be considered in turn.

It was found that the mode of evaporation influenced the spectra which were obtained. To compensate for this complication a discussion follows the results obtained by one particular technique and all the results are then compared at the end of the section.

General discussion, in which spectra obtained for all the metals are compared will be given in a separate section.

Platinum/CO

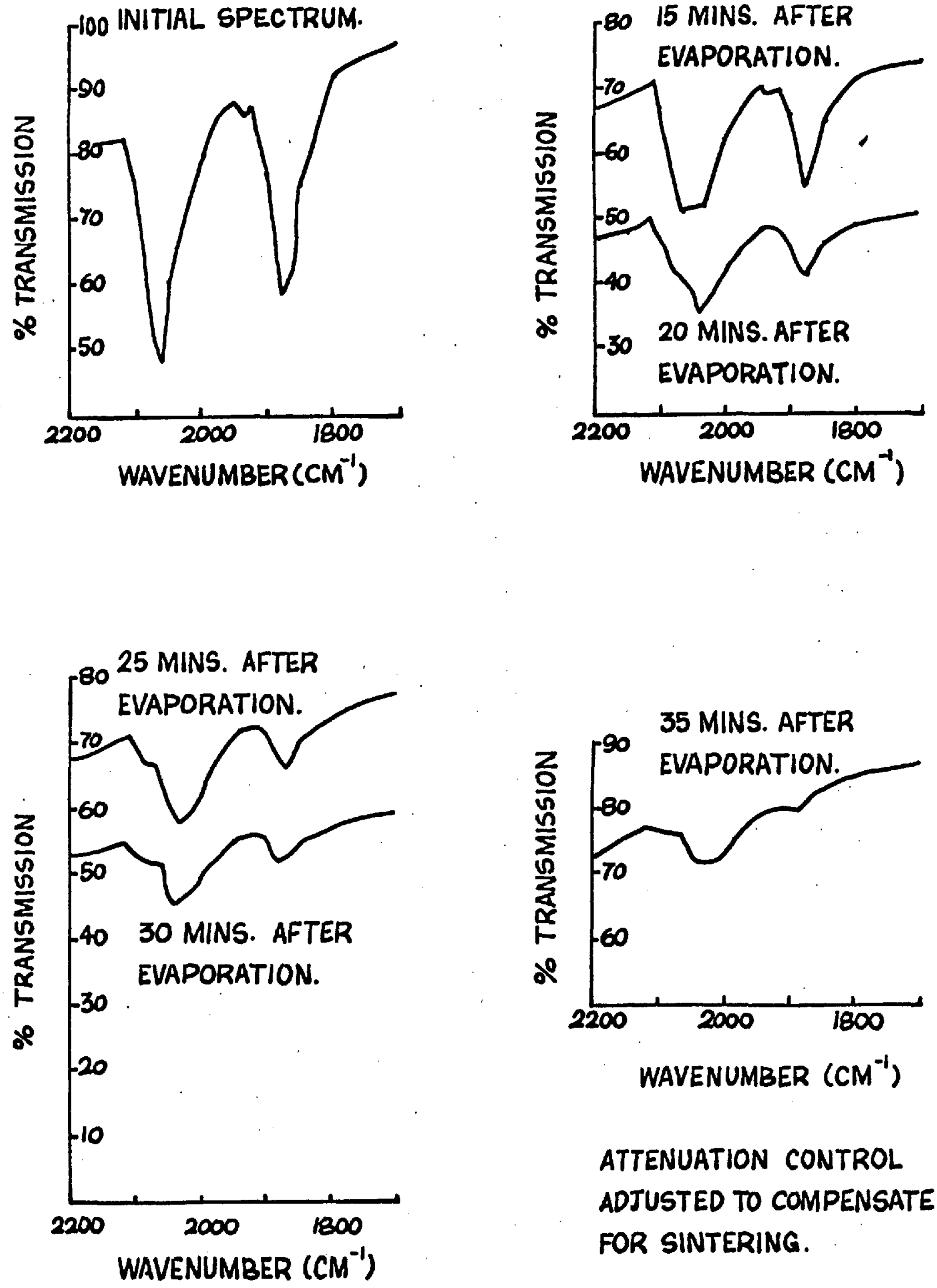
All Pt films were deposited from filaments consisting of 0.2 mm Pt wire wound evenly round 0.3 mm W wire. In general it was found that the filaments could be outgassed fairly easily but some care had to be taken when films were deposited. The Pt tended to melt and 'short' the filament if the heating current was too high.

Evaporation in CO

Pressures of CO between 9.10^{-2} - 12 torr were used. The cell was baked out only when CO pressures in the lower range were to be used.

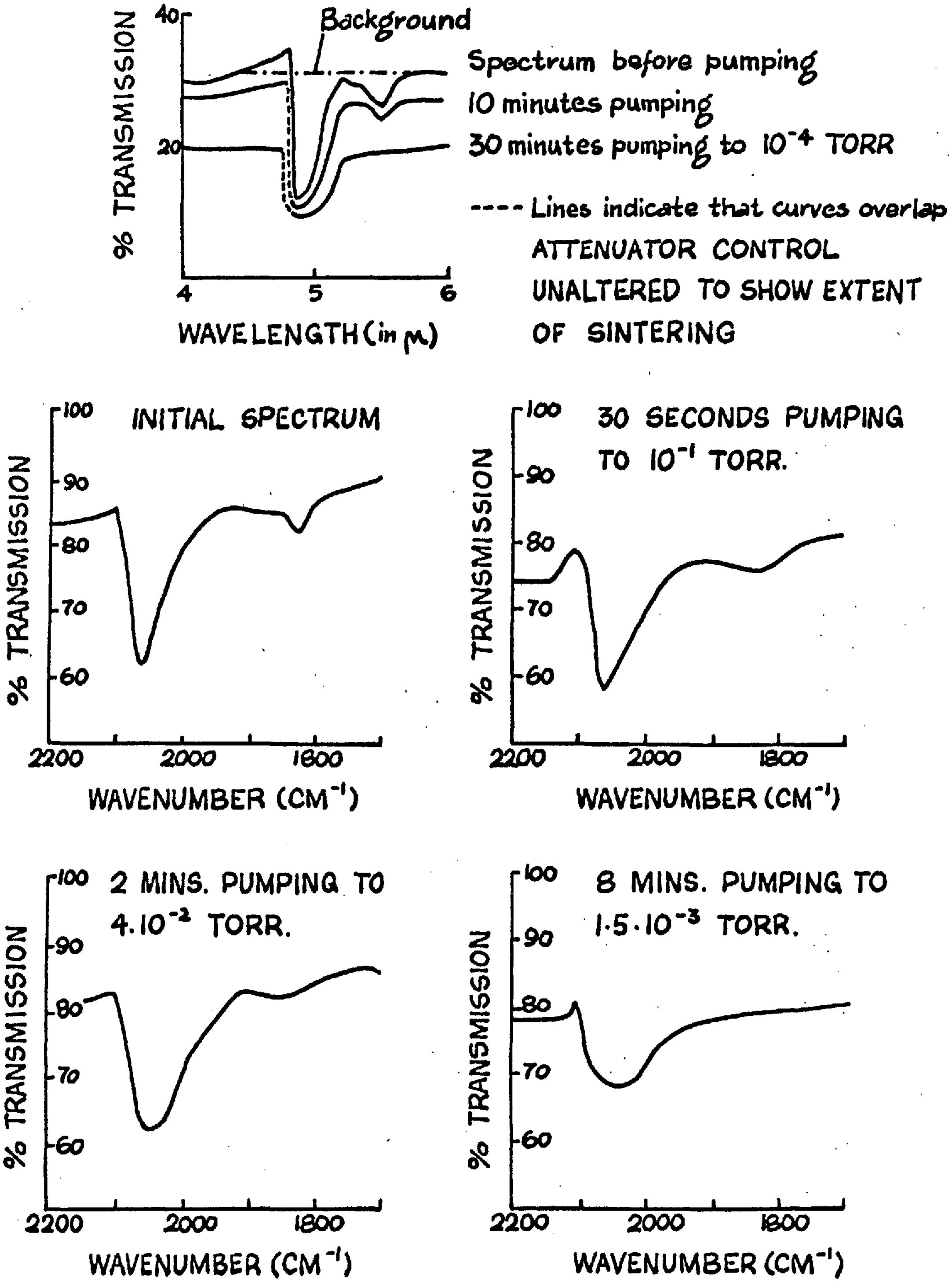
When Pt was evaporated in 2 - 12 torr of CO two bands were obtained. One was in the region 2065-2050cm^{-1} (Band A) whilst the position of the other varied between 1820 - 1880 cm^{-1}. This latter band is referred to as Band B. A general discussion of these results now follows but Figures 9 and 10 show some of the spectra that were obtained. The ratio of the peak intensity of Band B to that of Band A (referred to as R) varied from 0.3 to 0.84 with no apparent dependence on the pressure of CO used provided that this was greater than 10^{-1} torr. These effects are considered in more detail later. In all cases it was found that Band B decreased quite noticeably on pumping to 10^{-1} torr. It was completely removed on pumping to 10^{-3} torr. The intensity and shape of Band A did not change to such an extent during this time but it was noted that the transmission through the film decreased. Presumably, this was caused by sintering effects which increased the particle size. Band B could not be restored by addition of CO. Also it was found that Band A could never be completely removed by pumping although its intensity and shape altered distinctly. Sintering also occurred during the period that Band A decreased and, again, it was found that Band A could not be restored to its full intensity by addition of CO. It was found that the behaviour observed depended upon the rate of evaporation of Pt and two experiments are considered to illustrate this

FIGURE 9 _ Pt FILM EVAPORATED IN 2 TORR CO AT A SLOW RATE.



ATTENUATION CONTROL ADJUSTED TO COMPENSATE FOR SINTERING.

FIGURE 10 _ Pt FILMS EVAPORATED IN 2 TORR CO AT A FAST RATE



ATTENUATOR CONTROL UNALTERED TO SHOW EXTENT OF SINTERING

INITIAL SPECTRUM

30 SECONDS PUMPING TO 10^{-1} TORR.

2 MINS. PUMPING TO 4.10^{-2} TORR.

8 MINS. PUMPING TO $1.5 \cdot 10^{-3}$ TORR.

ATTENUATION CONTROL ALTERED TO COMPENSATE FOR SINTERING.

point.

Figure 9 shows the spectra obtained after a Pt film had been slowly deposited in the presence of 2 torr of CO. The metal particle size must have been very small because, initially, no film could be seen on the window. The small band at 1940 cm^{-1} is a genuine absorption band. Its presence was noted only when Band B was intense. The film was allowed to stand in 2 torr of CO at 300°K for 1 hour. During this time the film sintered and the band intensities and positions varied as shown. In the final stages the film was grey and metallic. The appearance of the sideband at 2070 - 2080 cm^{-1} was noted in all such runs but its relative intensity varied. In some cases it was almost as intense as the band at 2040 cm^{-1}.

Figure 10 shows the spectra obtained when the film was deposited quickly in the presence of 2 torr CO. In such cases the film had a brownish colour initially. The band head of B was shifted to 1820 cm^{-1}, although there was definite evidence of a side band at 1880 cm^{-1}. Also, R values were much smaller for such films. The behaviour of the bands on pumping is shown in Fig. 10. During this process there was never any evidence of the formation of a side-band at 2080 cm^{-1} although the band was very broad.

The increase in transmission at the high frequency side of Band A as shown in Figure 10 is due to the

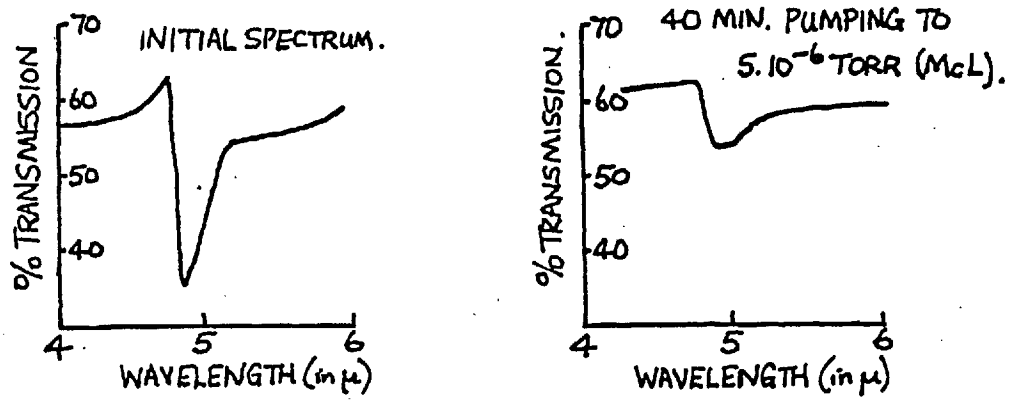
Christiansen Filter Effect (C.F.E.) which is found in many systems where radiation scattering losses are severe (41). The variation in refractive index associated with the absorption band alters the amount of radiation that is scattered by the metallic particles. Scatter tends to be increased on the low frequency side of the band so that it appears to be broader than it is; the transmission is increased on the high frequency side of the band due to a lessening of scattering. The spectra in Figure 9 show little evidence of the C.F.E. Scattering in these samples must, therefore, have been small and it is postulated that this is further evidence that in such samples the particle sizes are small.

Figure 11(a) shows the spectra obtained when film was evaporated in the presence of 9.10^{-2} torr of CO. Evaporation was carried out at a fast rate. Only one band, at 2050 cm^{-1}, was observed and the behaviour of this on evacuation was very similar to its counterpart in Figure 10 in that some sintering was observed during this process and the band became less intense and broader. Addition of CO did not restore the band to its original state.

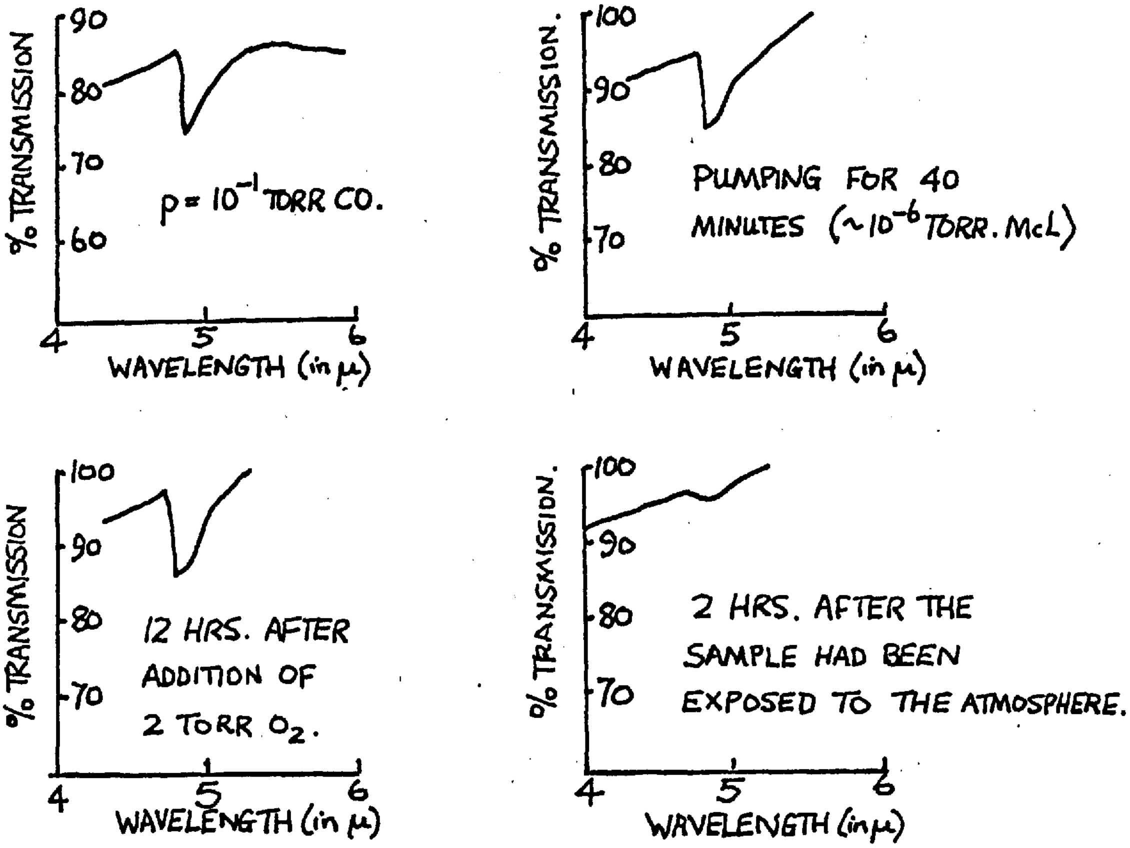
In all cases it was found that addition of 1 torr of O_2 caused the bands to disappear rapidly. This process was accompanied by an initial increase in transmission.

FIGURE 11 — Pt/CO

(a) EVAPORATION IN 9.10^{-1} TORR CO



(b) Pt/NaCl FILM DEPOSITED IN VACUO.



It was not possible to cause the return of the band by addition of CO.

Discussion

It is evident, from these results, that the size of the metallic particles influences the spectra that are obtained. This is a useful pointer towards the interpretation of the results but to give a full explanation would require that the actual structure of the particles be known. No such studies were undertaken. Unfortunately, in studies where the structure of the film has been examined by electron microscopy, the sample is first exposed to the atmosphere. The present results show that the structure of the sample undergoes an irreversible change during such a process. We therefore disagree with Garland et al (42) that useful information can be obtained from such studies.

Since the structure of these films is unknown, much of this discussion must be tentative. However, it seems likely that they consist, initially, of a large number of metallic particles which are prevented from coalescing by the CO molecules which are attached to the surface. Sintering is probably initiated by the desorption of some weakly held CO. If sites on neighbouring particles are free then the particles should be able to weld together.

It seems tempting to associate Band B with the weakly held CO whose desorption leads to sintering. Band B is most intense when the samples are unstable and it decreases rapidly during the initial pumping process. Moreover, it is not restored when CO is added to the evacuated sample. As seen from the Introduction, C - O stretching frequencies in the region 1800 - 1970 cm^{-1} are the subject of some controversy. Working on the Eischens model it could be that Band B represents a species in which a CO molecule is 'bridging' two separate particles of metal. If such a species desorbed the particles would be free to weld together and this would explain the observed behaviour. In the event that it represented a linear bonded Pt - CO species then the CO molecule would be attached to a Pt atom which has very few nearest neighbours. Although both structures are easy to visualise it might be thought that, in each case, the CO would be strongly bonded to the metal.

Another possibility is that weakly held CO could be positioned at a site in close proximity to the species accounting for Band B. Sintering of the sample could cause drastic alteration of the structure of the sample at this point with the result that the effects causing Band B would disappear. This would mean that the weakly held CO is not observed or that it is a composite part of Band A. The former is unlikely and, although some alteration is observed in Band A during the initial sintering this is not to any large extent. There is only one instance in the literature with which these data might be usefully compared. For CO adsorbed on Pt supported on γ-alumina Eischens (23) observed a band similar to the Band B obtained in these studies. It is known that the structure of γ-alumina supported Pt samples is much more complex than those of Pt supported by Cabosil. However the comparison must rest here since Eischens has not stated how the band behaves when the cell is evacuated and it is concluded that the nature of the weakly bonding CO and the species causing Band B must remain uncertain.

Even after Band B has completely disappeared the sample still sinters slightly and the shape of Band A alters. In such cases the band becomes much broader although there is no evidence for side bands. Side bands were only noted when the sample was unstable. A possible explanation for this behaviour is that in all cases Band A is composite with contributions from CO linearly bonded on different crystal planes. This model would predict that, for the stable films, crystal planes are distributed in such a manner that it is not possible to distinguish between the different species; the unstable films would show a preference for certain crystal planes during the sintering process. Again, the model is speculative but further evidence in its favour will be considered later when the results for vacuum evaporated Pt films are considered.

Co-evaporation of Pt and NaCl in vacuo

Figure 11(b) shows the spectra obtained for CO adsorbed on a Pt/NaCl film which was deposited in vacuo. The film was deposited at room temperature and the vacuum was fairly constant at 5.10^{-7} torr during deposition. CO was added to the film to give a pressure in the cell of 10^{-1} - 1 torr. After this the cell was evacuated for 40 minutes to 10^{-6} torr and this had little effect; the band intensity decreased slightly and the band-head became broader. This change was irreversible as the band could not be restored to its original intensity by addition of CO. Addition of 4 torr of O_2 had little effect on the band. The band disappeared after the vacuum system had been let down to air for 3 hrs. However, on re-evacuation and addition of 5 torr of CO it reappeared once more to almost the same intensity. Band B was not observed at any stage during this experiment.

Discussion

The sample exhibits unusual behaviour in that the band cannot be removed by the addition of 1 torr of O_2. With all other Pt samples the adsorbed CO was rapidly removed when oxygen was added. Since it does not seem likely that diffusion of oxygen through the sample is the rate determining factor it must be concluded that the CO is more strongly bonded to the Pt in this case. No sound reason can be given for this but Eischens (23) has noted that it is difficult to remove all the adsorbed CO from alumina-supported Pt surfaces; it may be that the support does, in fact, influence the chemistry of Pt in these particular cases.

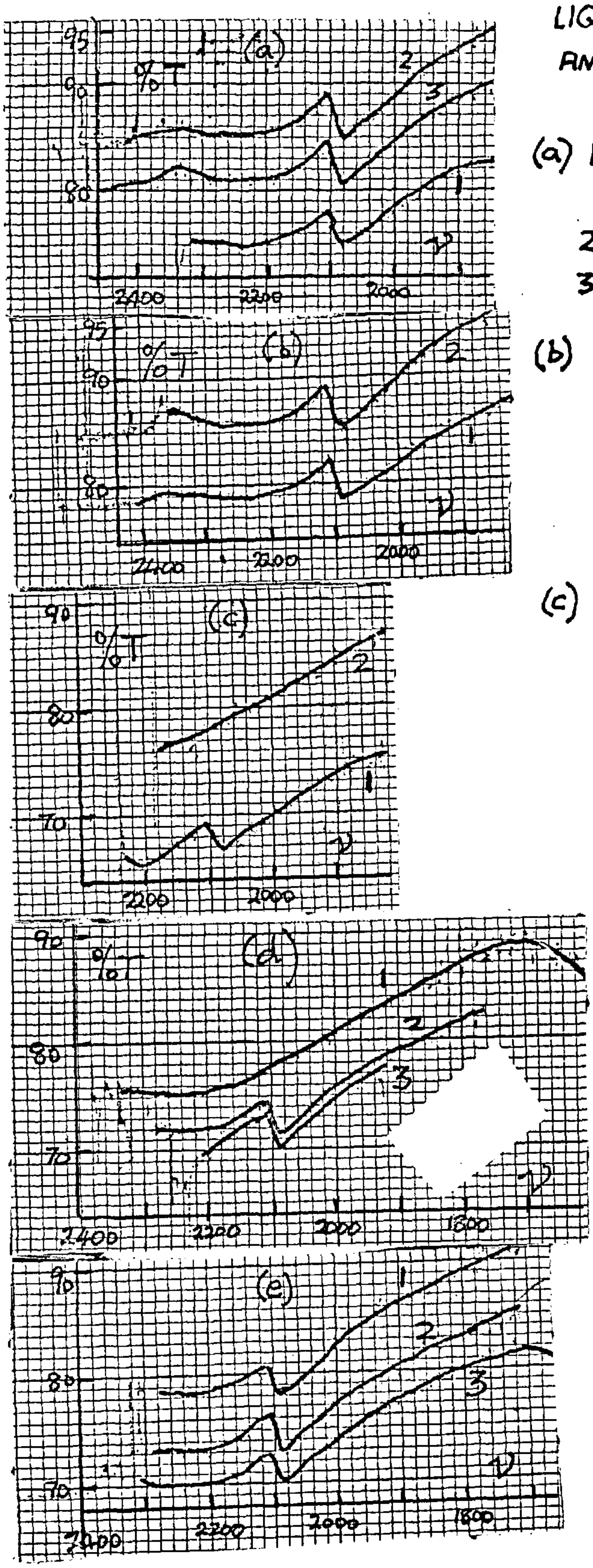
Vacuum Evaporated Films

Runs were carried out using liquid nitrogen traps or cardice-acetone baths. Where liquid nitrogen traps were used it was not possible to determine the amount of CO chemisorbed by the film due to adsorption in the traps. Better vacua could be obtained when liquid nitrogen traps were used but it was found that the spectra obtained were independent of the vacuum conditions; films were deposited in vacua ranging from $1.5.10^{-7}$ - 2.10^{-9} torr and all the experiments gave similar behaviour within the accuracy of the measurements. Five separate determinations showed that the band centred at 2085 ± 5 cm^{-1}.

Figure 12 shows reproductions of the actual spectra obtained for a film deposited at 2.10^{-9} torr. The spectra were recorded in green ink and, unfortunately, the Rank

FIGURE 12

Pt/CO.



LIQUID NITROGEN TRAP USED.
AMOUNT OF CO ADSORBED NOT KNOWN.

(a) 1 – 5 MINUTES AFTER WARM-UP TO 300°K.
2 – REPEAT. ATTENUATION CONTROL ALTERED.
3 – REPEAT. ——"——

(b) 1 – REPEAT OF (a)3.

2 – ADDITION OF 0·5 TORR OF CO. ATTENUATION CONTROL ALTERED.

(c) 1 – AFTER 15 MINUTES EVACUATION. ($p \sim 2.10^{-6}$ TORR)

2 – 2 MINUTES AFTER ADDITION OF 1 TORR OF O_2. ATTENUATION CONTROL WAS ADJUSTED BUT TRANSMISSION THROUGH SAMPLE DID INCREASE.

(d) 1 – REPEAT OF (c)2

2 – 2 MINUTES AFTER ADDITION OF 2 TORR OF CO. ATTENUATION CONTROL ADJUSTED.
3 – REPEAT. ATTENUATION CONTROL ADJUSTED.

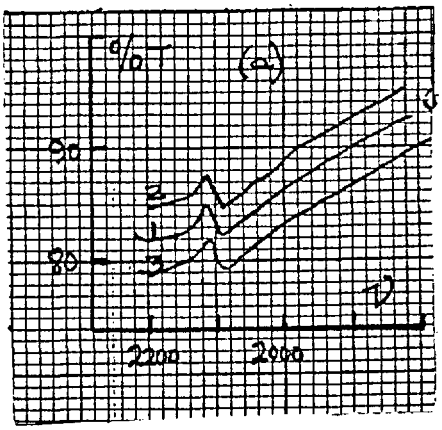
(e) 1 – REPEAT. ATTENUATION CONTROL ADJUSTED.
2 – AFTER 30 MINUTES EVACUATION. ATTENUATION CONTROL ADJUSTED.
3 – AFTER 35 MINUTES EVACUATION. ATTENUATION CONTROL ADJUSTED.

Xerox photocopying machine is not sensitive to this colour. The reproductions tend to give a false impression in that a line was drawn in black ink, to give the average response; signal to noise effects were ignored for clarity. In most cases the signal to noise ratio was of the order 100 : 1 but the reproducibility of the spectra was found to be very good. There is no doubt that the representations give a true picture of the spectra recorded by the instrument. To obtain the spectra shown in Figure 12 film was deposited on both sides of the window and this accounts for the size of the band compared with that shown in Figure 13. CO was added to the film until the pressure in the cell was approximately 10^{-3} torr. Pumping for 60 minutes to 2.10^{-7} torr had little effect on the band. Likewise, increasing the CO pressure to 0.5 torr made little difference. The band disappeared immediately when O_2 was added to the evacuated sample to a pressure of 1 torr but it was restored to approximately its original intensity and position when the O_2 was removed and 2 torr of CO was added. After this process it was found that the band was unaffected by 30 minute pumping. This behaviour was always found but the band could not be restored at CO pressures of the order of 10^{-3} torr.

The amount of CO adsorbed by the film was determined in two separate experiments. The spectra obtained during

FIGURE 13 – Pt/CO.

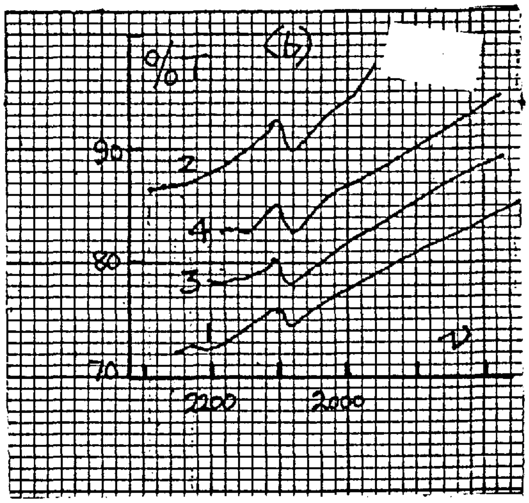
5.10^{15} MOLECULES OF CO ADSORBED BY FILM.



(a). 1 – 5 MINUTES AFTER WARM-UP TO 300°K.

2 – 10.5 MINUTES AFTER WARM-UP.

3 – 16.25 MINUTES AFTER WARM-UP.

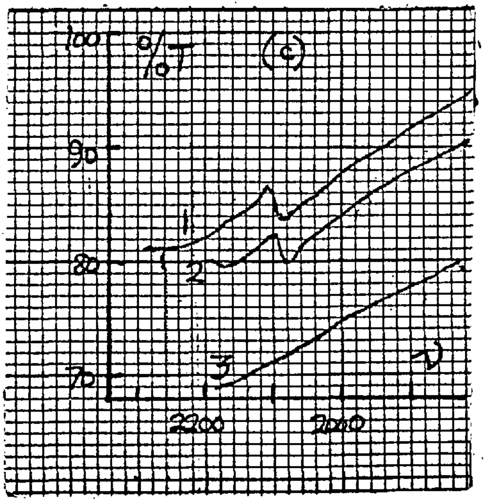


(b) 1 – 16 MINUTES EVACUATION
($p \sim 6.10^{-7}$ TORR).

2 – 23 MINUTES EVACUATION
($p \sim 5.10^{-7}$ TORR; ATTENUATION CONTROL ADJUSTED)

3 – CO ADDED TO CELL DOSE-WISE.
$P \sim 7.10^{-4}$ TORR.

4 – REPEAT. ATTENUATION CONTROL ADJUSTED. $p \sim 5.3.10^{-4}$ TORR.



(c) 1 – REPEAT OF (b)4.

2 – EVACUATION FOR 5.25 MINUTES.
$p \sim 9.10^{-7}$ TORR.

3 – ~20 SECONDS (AT $2100 cm^{-1}$)
AFTER ADDITION OF 1 TORR OF O_2.

N.B. <u>FOR ALL EXPERIMENTS INVOLVING VACUUM EVAPORATED FILMS. UNLESS STATED OTHERWISE:</u>

1. NO ALTERATION IN TRANSMISSION WITH TIME WAS OBSERVED.
2. ALL TIMES REFER TO WHEN SCAN IS AT ~$2100 cm^{-1}$

one such determination are shown in Figure 13. The quantity of gas adsorbed by the film depended upon its thickness. A film that transmitted 80°/o of the radiation incident upon it at 2100 cm^{-1} chemisorbed 5.10^{15} molecules of CO. A thicker film which transmitted 35°/o of the incident radiation chemisorbed $13.5.10^{15}$ molecules. In both cases, any sintering that occurred as a result of the film warming to room temperature was negligible as far as the accuracy of the dosing measurements is concerned; the pressure in the cell decreased as expected from the dekker leakage tests. The spectra remained unaltered, in one case for 93 minutes, prior to evacuation. Evacuation of the cell appeared to have little effect on the spectra and addition of CO to the evacuated system (with the dekker valve closed) showed that if any CO was adsorbed the quantity was less than 5.10^{14} molecules which is the limit of experimental accuracy.

Attempts were made with this and other systems to calculate extinction coefficients and integrated absorption intensities. However in all cases the C.F.E. was noticed and, as shown previously, this distorts the intensity and shape of the band. Efforts were made to compensate for this on the high frequency side of the band but, since all the bands are small, the effect is likely to be very important. Thus, all calculations based on intensity measurements are regarded as useful from a semi-quantitative point of view only.

Corrections were made in the calculations for the fact that radiation passes through 1 cm^2 of window whilst the total surface area of this was 2 cm^2. In all cases, calculations are the mean result of several values for different spectra. Extinction coefficients (K) were determined by using the formula

$$\log_{10}\left(\frac{I_o}{I}\right) = Kc$$

where $\log_{10}\left(\frac{I_o}{I}\right)$ is the absorbance at the band head and c is the concentration of CO/cm^2 of geometric surface area. Values of K of 4.10^{-18} cm^2 molecule^{-1} and 2.10^{-18} cm^2.molecule^{-1} were found from two separate experiments. These compare with the values of 3.10^{-18} cm^2.molecule^{-1} (Eischens et al (23)) and 2.10^{-18} cm^2.molecule^{-1} (Heyne and Tompkins (10)) found in the literature.

The apparent integrated absorption intensity, B, is given by the formula

$$B = \frac{1}{c} \int_{\nu_1}^{\nu_2} \log_e\left(\frac{I_o}{I}\right)_\nu d\nu$$

where

$\nu_2 - \nu_1$ is the band width in cm^{-1}

c is the concentration of CO/cm^2 of geometric surface area and

$$\log_e\left(\frac{I_o}{I}\right)_\nu = (\text{Absorbance}).\ 2.303 \text{ at } \nu \text{ cm}^{-1}.$$

B was found to be 340.10^3 litre. cm^{-2}.$mole^{-1}$ compared with Heyne's value (43) of 120.10^3 litre.cm^{-2} $mole^{-1}$. It was determined by plotting $\log_e(^{I_o}/I)$ versus ν at 10 cm^{-1} intervals, followed by a graphical determination of the area under the curve.

<u>Discussion</u>

The species obtained with vacuum evaporated films behaves, in every respect, like those observed by Heyne and Tompkins in their S.P. measurements (10); the CO is easily removed by O_2 and can also replace oxygen from a Pt surface. Moreover, the CO is not easily removable by pumping for periods of up to one hour and this indicates that E_D must be greater than 25 kcal.$mole^{-1}$. This would be expected from the results of Brennan and Hayes (4) who find that the heat of chemisorption is 50 kcal.$mole^{-1}$ for CO chemisorbed on Pt. Contamination effects are not considered to be serious for the Pt/CO system. CO_2 and N_2 are not chemisorbed by Pt (43, 44) andHeyne and Tompkins' work indicates that chemisorbed oxygen is easily removed by CO. It seems reasonable, therefore, to claim that the species observed in this work are of the same type as those observed by Heyne and Tompkins and Brennan and Hayes.

Comparison with the results of Eischens et al (23, 14) for vacuum evaporated Pt films is interesting. When the film was deposited on a NaCl substrate they found that the band centred at 2050 cm^{-1} whereas on a CaF_2 substrate the band centred at 2040 cm^{-1}. In this work the film was deposited on MgO and the band was found at 2085 cm^{-1}. Eischens considers that band shifts of this type are due to some inductive effect of the substrate or the support which affects the actual chemistry of the metal concerned. An equally attractive argument is that the support or substrate can influence the crystal structure of the metal particle. Investigations of the formation of metal films show that the structure of these is dependent upon the nature and temperature of the substrate and the rate of deposition. Unfortunately most work has been performed using very poor vacuum conditions and it is not altogether clear whether this affects the results. However, according to Bruck (45) Pt films deposited on NaCl held at 250°C are formed with the 100 plane preferentially oriented and, although little other work has been done for Pt, studies with other metals show that the nature of the substrate strongly influences the crystal structure. The films used in this work were slowly deposited on MgO which was cooled by liquid nitrogen. Eischens' films were deposited with the substrate held at room temperature. Taking into consideration the information given in the reviews by Pashley et al (46) and Brenner (47) it is considered that the films used in this work probably consisted of small crystallites which were less well formed than those prepared by Eischens. However it does not seem likely that any highly energetic configurations were formed because the film did not appear to sinter to a great extent on warming to room temperature. It is therefore postulated that it is the different physical structures of the films which account for the spectra obtained. The work of Ehrlich and Gomer indicates that the bond strength of CO is different on the crystal planes of W and there seems to be no reason why this should not be a general effect. One would expect any changes in the bond strength to be reflected in the C - O stretching frequency. Therefore the observed difference in the spectra obtained in this work and that of Eischens is thought to be caused by the different crystal structures of the sample.

A further point of interest is that the band centre did not seem to shift when the system was evacuated or when 0.5 torr of CO was added. It is possible, of course, that such a shift does occur but that it is too small to be observed by the spectrophotometer. However, Heyne and Tompkins found that for CO on aerosil-supported Pt the band shifted from 2090 cm^{-1} to 2070 cm^{-1} after 1 hour of evacuation. It can only be concluded that in this instance the support or the highly compressed sample gave rise to weak CO chemisorption. Further discussion on this point is deferred until later because other systems show interesting differences.

General Discussion

In the literature there seems to be general agreement that any bands obtained in the region 1970 - 2100 cm^{-1} can be interpreted in terms of a CO molecule linearly bonded through the C atom to a surface metal atom. Arguing on this basis it would appear that most of the CO on stable Pt surfaces is linearly bonded. From the work with vacuum evaporated films there is no evidence that bridge bonded CO exists on such surfaces. The spectra obtained are certainly not good proof of this. However since our value of K is in fairly good agreement with that of other workers it would seem that most of the CO on the surface is contributing towards the observed band. Otherwise one would have to postulate that either (1) the CO contributing to band A in our samples had a much higher extinction coefficient than that on the cabosil supported samples. It is interesting to note that the B value obtained in this work is higher than that obtained by Heyne even if it is assumed that all the CO on the surface is contributing to the band.

However, judgement must be rather reserved as it is difficult to say how reliable the B values obtained in our work are.

or

(2) that in the cases of Eischens et al, Heyne and Tompkins and this work there is the same fraction of adsorbed CO on all the samples which is not observed. Since the other workers observed a very intense band at approximately 2070 cm^{-1}, this seems unlikely. The conclusion that CO is linearly bonded is in direct contradiction to that of Brennan and Hayes (4) who claim that CO on Pt surfaces is bridge bonded. The infra-red technique is a much more direct approach than that used by Brennan and Hayes and, further, it is possible that the models used in their argument are too simplified. However, final judgement is left until all the metals have been considered.

Together with other workers it has been observed that the centre of Band A can vary over a range of 40 cm^{-1} even when the coverage is high. The deciding factor is the method of sample preparation and it is postulated that this behaviour is caused by the exposure of different crystal planes on the various samples. In this work it was found that the species which gives rise to a band at 2085 cm^{-1} is most predominant for vacuum evaporated films For films evaporated in CO a similar species seems to exist in certain circumstances but, in general, the band centres around 2040 cm^{-1}. This compares with the result for a vacuum evaporated film supported by CaF_2. It is true that, in this work, all films were deposited on MgO but it does not seem impossible that the force fields which influence particle growth vary with the method of preparation.

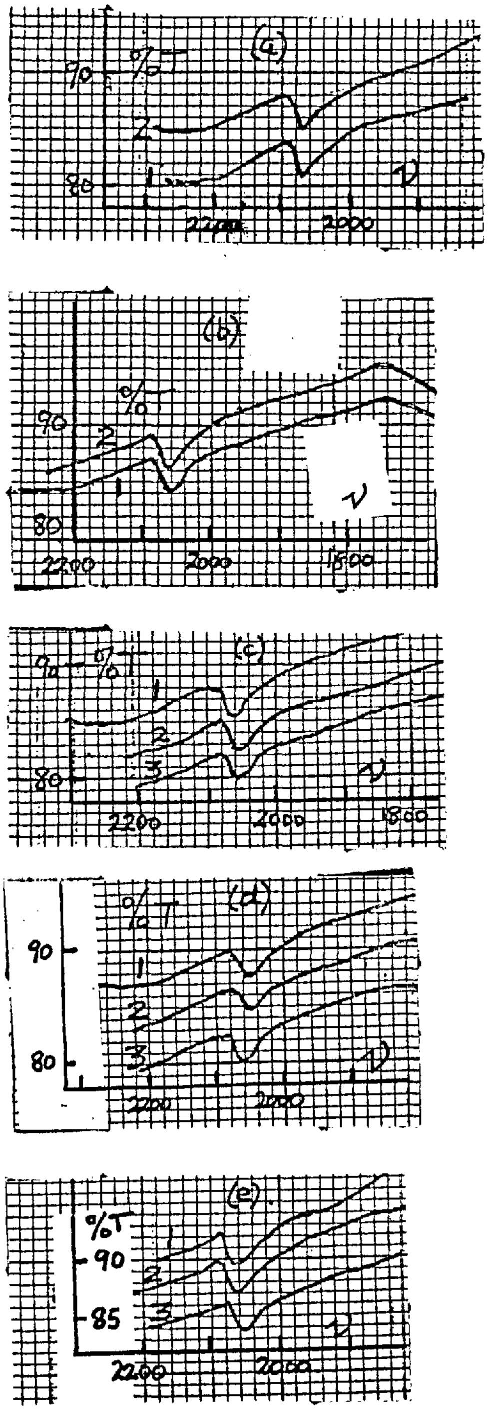
The above explanation for the variation of the C - O stretching frequency requires that the cabosil-supported samples have a similar polycrystalline nature to the vacuum evaporated films on a MgO substrate. For alumina-supported samples Band B is found (23) and, on the basis of this work, it would be required that alumina-supported samples give rise to unusual sites not usually found on well formed crystal surfaces. The work of Lewis (49) indicates that well defined crystallites are not formed when alumina is used as a support so it would appear that the argument used to explain these results is fairly satisfactory.

RHODIUM/CO

Vacuum evaporated films

Films were deposited from 0.5 mm Rh wire. To obtain the spectra in Figures 14 and 15 the system was baked and outgassed so that the background ion current was 1.10^{-10}A (0.86 mA emission). In future, such background ion currents will be referred to as being equivalent to approximately 1.10^{-8}torr pressure although it is probable that the true pressure is somewhat less than this. The filament was outgassed until the pressure was approximately 4.10^{-8}torr. Before evaporation was commenced the mercury cut-off MC2 was lowered and the background pressure increased to 6.10^{-8}torr. Evaporation was carried out at a steady pressure of 5.10^{-8}torr. It was found that the film adsorbed 28.10^{15} molecules CO and from this it is calculated that $K = 1.1.10^{-18}$ cm^2.molecule^{-1}. The film did not appear to sinter on warming to room temperature. During a period of 58 minutes the pressure in the system decreased as expected from the dekker leakage tests. As can be seen from Figure 14(c), 3 minutes pumping to approximately $1.5.10^{-6}$torr caused the band centre to shift from approximately 2065 cm^{-1} to 2055 cm^{-1}. There is no doubt that this is a genuine effect. All spectra were taken on the same chart paper to eliminate errors caused by the mal-

FIGURE 14 — Rh/CO.



28.10^{15} MOLECULES OF CO ADSORBED BY FILM.

(a) 1 — 5 MINUTES AFTER WARM-UP TO 300°K.

2 — 9 MINUTES AFTER WARM-UP.

(b) 1 — 38 MINUTES AFTER WARM-UP.

2 — 45 MINUTES AFTER WARM-UP.

(c) 1 — 53 MINUTES AFTER WARM-UP.

2 — 3 MINUTES EVACUATION.
($p \sim 1.5.10^{-6}$ TORR).

3 — 9 MINUTES EVACUATION.
($p \sim 7.10^{-7}$ TORR).

(d). 1 — 16 MINUTES EVACUATION.
($p \sim 5.10^{-7}$ TORR).

2 — 29 MINUTES EVACUATION.
($p \sim 4.10^{-7}$ TORR).

3 — CO ADDED TO CELL DOSE-WISE.
($p \sim 8.10^{-4}$ TORR; $\sim 1.10^{15}$ MOLECULES OF CO ADSORBED BY FILM.)

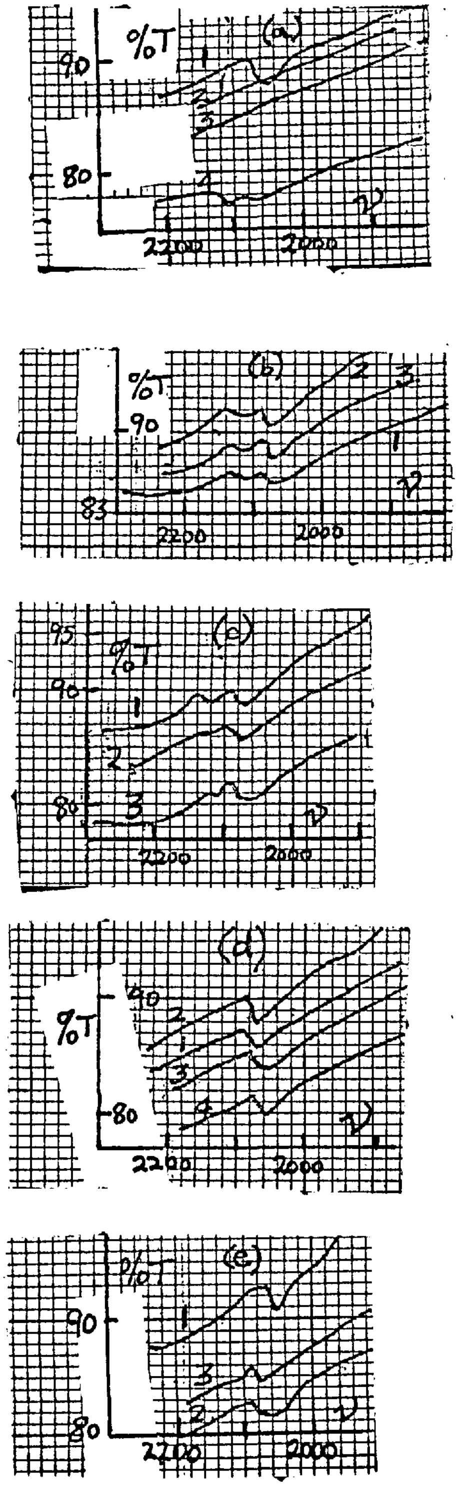
(e) 1 — ATTENUATION CONTROL ADJUSTED.
($p \sim 6.6.10^{-4}$ TORR).

2 — ATTENUATION CONTROL ADJUSTED

3 — 1.5 MINUTES EVACUATION
($p \sim 2.10^{-6}$ TORR)

FIGURE 15 — Rh/CO

CONTINUATION OF EXPERIMENT DESCRIBED IN FIGURE 14.



(a) 1 – 8 MINUTES EVACUATION TO ~7.10^{-7} TORR.

2 – ~ 1 MINUTE AFTER THE ADDITION OF 2 TORR O_2.

3 – 5 MINUTES EVACUATION. (p ~ 1.10^{-5} TORR)

4 – 80 SECONDS AFTER ADDITION OF 1 TORR CO.

(b) 1 – 5 MINUTES LATER.

2 – 19.5 MINUTES LATER.

3 – 60 MINUTES LATER.

(c) 1 – 67 MINUTES LATER.

2 – 30 SECONDS EVACUATION, USING DP1 AND ROTARY PUMP. (p ~ $1.2.10^{-1}$ TORR).

3 – FURTHER EVACUATION FOR 1 MINUTE (p ~ 6.10^{-2} TORR).

4 –

(d) 1 – REPEAT OF (c)-3.

2 – FURTHER EVACUATION FOR 2 MINUTES. (p ~ $1.9.10^{-3}$ TORR).

3 – FURTHER EVACUATION FOR 5 MINUTES. (p ~ $7.5.10^{-4}$ TORR).

4 – FURTHER EVACUATION FOR 11 MINUTES. (p ~ $1.2.10^{-5}$ TORR).

(e). 1 – EVACUATION FOR 8 MINUTES WITH DP2. (p ~ 4.10^{-6} TORR).

2 – 4 TORR OF CO ADDED.

3 – REPEAT. ATTENUATION CONTROL ADJUSTED.

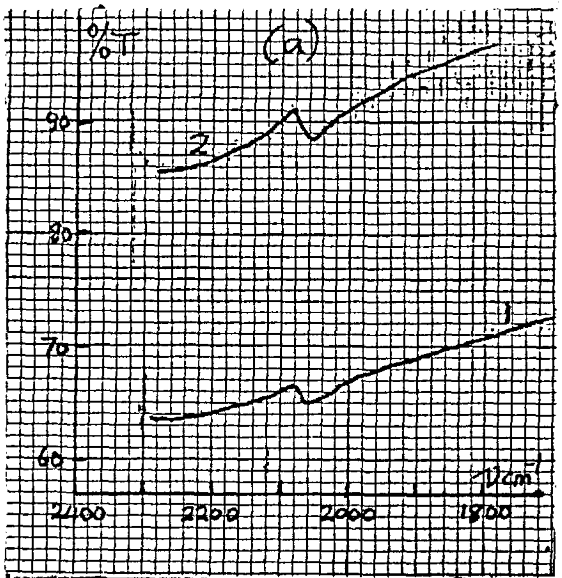
alignment of the paper on the drum and the behaviour was repeated in a separate run. Moreover, as Figure 14(d) shows, addition of CO to the evacuated sample causes the band to return to its original position. In this process CO was added to the sample in small doses with the dekker valve closed. An initial dose of $5.4.10^{15}$ molecules gave an ion current reading of $8.5.10^{-7}$A (0.86 mA emission). From the calibration graph this correspondsto approximately 1.10^{15} molecules of CO adsorbed by the film. Subsequent doses of gas to a pressure of approximately 8.10^{-4}torr indicate that no more than an extra 5 - 7.10^{14} molecules of gas were adsorbed. Not much confidence is held in the absolute values that are quoted above but it seems evident that most of the desorbed gas is re-adsorbed by addition of the first dose of gas; furthermore, the adsorbed gas which causes the shift in the band frequency is only a very small fraction of the total amount of CO adsorbed by the Rh. Although intensity measurements are not exceedingly reliable it seems that the band intensity decreases on pumping but that on addition of CO the intensity appears to increase again to its original value. Re-evacuation of the system after the second set of dosing experiments produced the same band shift as noted initially. Addition of 2 torr of O_2 caused the transmission through the sample to increase slightly and, after 1 minute, no bands could be observed in the region 2200 - 1800 cm^{-1}. Evacuation of the system to 10^{-5} torr followed by the addition of 1 torr of CO resulted in the immediate formation of two bands at approximately 2120 cm^{-1} and 2080 cm^{-1} (see Figure 15(a)). Approximately 20 minutes was required for the bands to reach full intensity. The band at 2120 cm^{-1} was easily removed by pumping to 10^{-1} torr and it was found that the centre of the other band shifted to 2050 cm^{-1} after about 19 minutes pumping. The band centre shifted to 2080 cm^{-1} on addition of 4 torr of CO but the band at 2120 cm^{-1} did not reappear.

Figures 16 and 17 show the spectra obtained in a similar experiment. In this case the background pressure was approximately 1.10^{-8} torr and the filament was outgassed until the pressure in the system was approximately 2.10^{-8} torr. Film was deposited at 9.10^{-8} torr with MC2 lowered. The film was very thin. It transmitted 80°/o of the incident radiation at 2100 cm^{-1} and adsorbed $17.5.10^{15}$ molecules of CO. From this, K was calculated to be $1.3.10^{-18}$ cm^2 $molecule^{-1}$. Similar effects to those noted previously were observed when the system was evacuated and, also, when O_2 was added.

Towards the end of the experiment represented by the spectra in Figures 14 and 15 the system was evacuated to approximately 4.10^{-6} torr and 4 torr of CO was added.

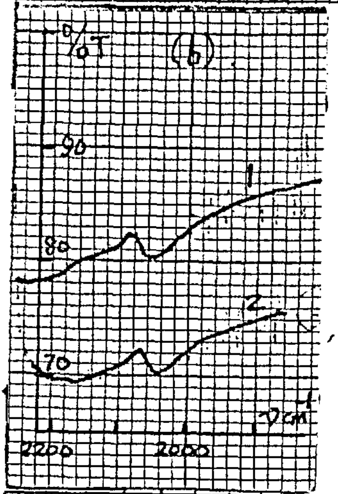
FIGURE 16. Rh/CO.

$17{\cdot}5.10^{15}$ MOLECULES OF CO ADSORBED BY THE FILM.



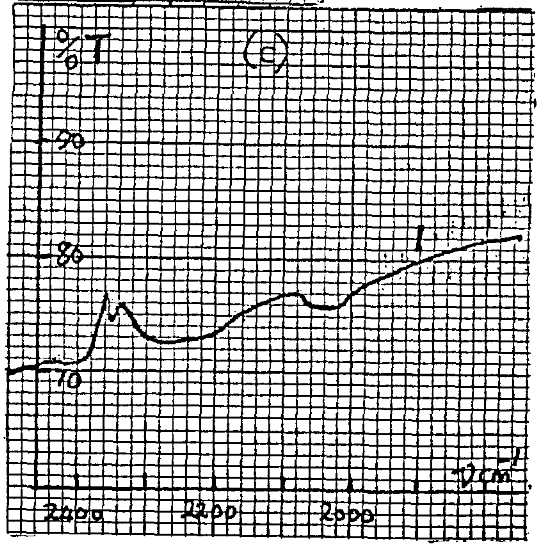
(a) 1- 5 MINUTES AFTER WARM-UP TO 300°K.

2- 10 MINUTES AFTER WARM-UP TO 300°K. ATTENUATION CONTROL ADJUSTED.



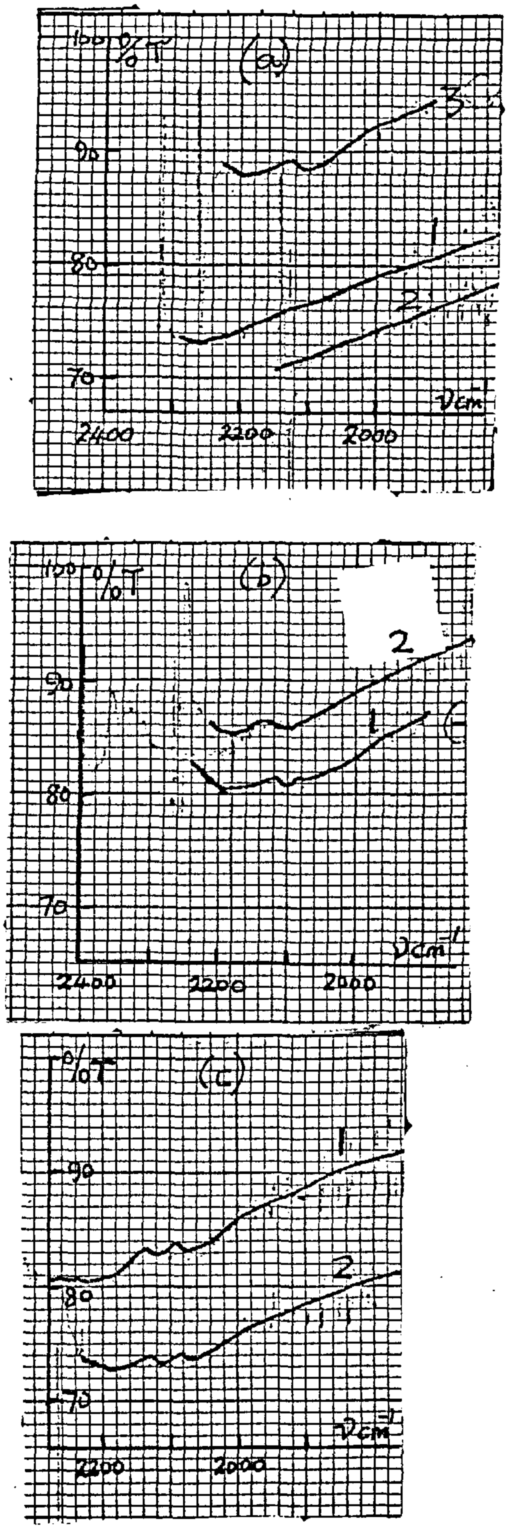
(b) 1- 25 MINUTES AFTER WARM-UP.

2- 3·5 MINUTES EVACUATION. ($p \sim 2.10^{-6}$ TORR).



(c) 1- AFTER 4 HOURS OF EVACUATION.

FIGURE 17 — Rh/CO.



CONTINUATION OF EXPERIMENT DESCRIBED IN FIGURE 16.

(a) 1 — AFTER THE ADDITION OF 2 TORR O_2.

2 — AFTER 10 MINUTES EVACUATION.

3 — AFTER THE ADDITION OF 5 TORR CO.

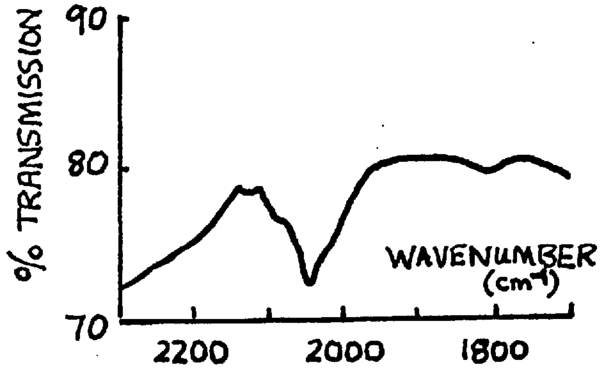
(b). 1 — REPEAT OF (a) — 3.

2 — REPEAT. ATTENUATION CONTROL ADJUSTED.

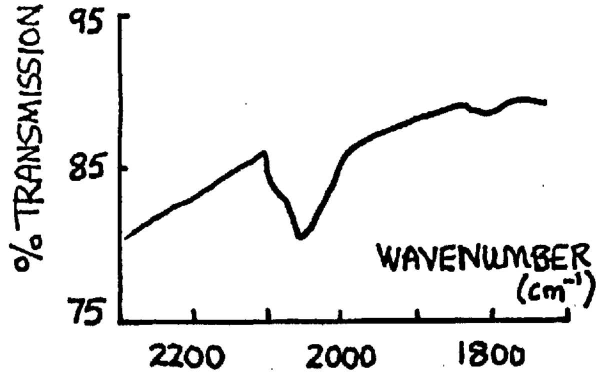
(c) FURTHER REPEATS.

FIGURE 18 — Rh/CO.

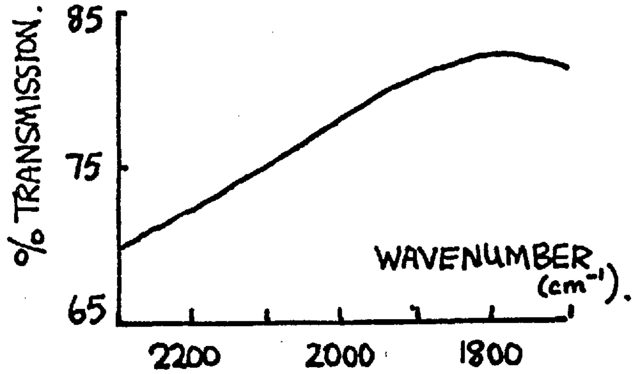
FILM DEPOSITED IN THE PRESENCE OF 4 TORR OF CO.



INITIAL SPECTRUM.



AFTER 5 MINUTES EVACUATION.



IMMEDIATELY AFTER THE ADMISSION OF AIR INTO THE APPARATUS.

Rh was then evaporated, in the presence of CO, onto the MgO plate which was cooled by liquid nitrogen. Film was deposited on the side of the window which was covered with vacuum evaporated film. The spectra which were obtained are shown in Figure 18. In the initial spectra one main band at 2055 cm^{-1} and two very small bands at 2120 cm^{-1} and 1820 cm^{-1} were noted. On pumping, the band at 2120 cm^{-1} rapidly disappeared whilst the band at 1820 cm^{-1} remained unchanged. The centre of the main band remained unaltered after 5 minutes pumping but a side band developed at 2080 cm^{-1}. Addition of O_2 removed the bands immediately.

Discussion

The spectra that were obtained for vacuum evaporated films can be compared with those of Pickering and Eckstrom (34). These workers used a multiple reflection cell. The films they prepared were deposited on a glass substrate whose temperature varied between 80 - 100°C. Thus, it is very likely that the films prepared in our work were much less sintered than those of Pickering and Eckstrom. They observed a band at 2060 cm^{-1} which shifted to 2040 cm^{-1} on pumping from the initial CO pressure of 0.9 torr to 10^{-4} torr. It is evident from our work that the band centre depends very critically upon the pressure of CO above the film and this makes comparison very difficult.

However, with a pressure of approximately 2.10^{-4} torr of CO in the cell the band observed in our spectrum was cent at approximately 2065 cm^{-1} which is at a higher frequency than that observed by Pickering and Eckstrom. It is interesting to note a similar shift in band centre between our results for Pt/CO and those of Eischens. The explanation that was given there is adopted for the Rh/CO system; i.e. that different crystal planes are present in the unsintered samples and this is reflected by a variation of the C - O stretching frequency caused by CO species of different bonding energies. It is possible that there may be some significance in the fact that the C - O stretching frequency is highest for unsintered films. Nothing definite can be expressed because the structure of the films is not known. However, it is interesting to observe that the Blyholder model of CO chemisorption requires that the CO is bonded to atomically smoother crystal planes on th unsintered films than is the case for the sintered films. In fact, one might have expected the predominance of smoother crystal planes in the films prepared by Pickering and Eckstrom since the substrate was held at a high temperature and the films were very thick and highly reflecting. Although the films prepared by Eischens probably consisted of small crystallites a similar argument does not seem inappropriate.

It is interesting to note that the intensity of the band decreases and the band centre shifts to lower frequencies when the system is pumped for only a very short time. This indicates that some of the CO is weakly bound to the Rh, having a value of E_D less than 25 kcal.mole^{-1}. The dosing measurements indicate that the weakly bound CO occupies only a very small fraction of the surface. These results are not at variance with those of Brennan and Hayes (4). They found that the initial heat for the Rh/CO system is 44 kcal. mole^{-1} and remains constant until high coverage where it decreases rapidly. In our experiments only a small fraction of the CO could be rapidly removed and the remainder was quite strongly bonded as prolonged pumping had little effect and so it is concluded that the chemisorbed CO observed in our experiments is probably of the same nature as that observed by Brennan and Hayes.

Other workers (23) have noted that the band centre shifts to lower frequencies as the coverage decreases and there are two separate theories to explain this behaviour.

The Blyholder model predicts a shift on the basis that as the coverage decreases the competition for electrons to go into the π anti-bonding orbitals of the CO decreases. Thus the C - O bond strength decreases and the net effect is that the C - O stretching frequency shifts to lower values. However it is difficult to reconcile our results with this theory. Jones (50) has observed that as the degree of π bonding increases in metal cyanide complexes the extinction coefficient associated with the C - N group increases. Blyholder has incorporated this result in his theory and claims that the extinction coefficient of the C - O group should decrease as coverage increases. This is in direct contradiction with our results. A rough calculation shows that before evacuation the average extinction coefficient is $1.1.10^{-18}$ cm^2 molecule if it is assumed that all the adsorbed CO contributes to the band. After evacuation the extinction coefficient is determined to be $7.4.10^{-19}$ cm^2.molecule^{-1} and from this data it is calculated that the extinction coefficient of the weakly held CO is 5.10^{-18} cm^2.molecule. The apparent integrated absorption intensity also decreases by a factor of 0.85 as the coverage decreases. The important point is that these changes are caused by a very small (approximately 1/30) fraction of the total amount of adsorbed CO, and, whilst it is agreed that the above calculations are very crude, it is felt that they show that the Blyholder model is incorrect in this instance. Using his theory one would not expect such large alterations in the band intensity to be caused by such a small fraction of the total adsorbe

CO. Moreover the changes are in the opposite direction to those predicted by the Blyholder theory.

Eischens et al (23) claim that band shifts to higher frequencies as the coverage increases are due to dipole - dipole interactions. They are of the opinion that such interactions weaken the metal - C bond; if the orders of the metal - C and C - O bonds are roughly complementary this will result in the C - O band shifting to higher frequency. In other branches of infra-red spectroscopy, band shifts and changes in integrated absorption intensities have been noted (51) during phase changes (usually gas to liquid) but no deep theoretical understanding has been reached as to how intermolecular forces affect these quantities. It is noted, however, that, if the C - O bond strength is increased, a decrease of the C - O dipole would be expected and, consequently, a marked increase in the band intensity which we have observed would not be expected.

It is apparent that the behaviour is, in some way, connected with the nature of the bonding of weakly adsorbed CO. Little is known about this so that any explanation of the spectral data must be rather speculative. It is rather odd that Pt does not exhibit such behaviour but, as will be seen later, Fe does follow the same pattern only in a more marked form. Attempts to give a unified picture are therefore left until all the systems which have been studied are discussed.

Comparison with the results of Garland et al (52, 24) who studied CO on alumina-supported Rh and CO on Rh films which had been deposited in an atmosphere of CO, are interesting. In our studies, evidence for a band below 2000 cm^{-1} was obtained only when Rh was evaporated in the presence of CO. Even then, only one band was observed at 1820 cm^{-1}. In Garland's studies, bands were found at 1900 cm^{-1}, 1850 cm^{-1} and 1820 cm^{-1}. There is agreement only in that in both cases bands are observed at approximately 2060 cm^{-1} as found with vacuum evaporated films. When Garland et al studied supported Rh samples they found that in addition to the band at 2060 cm^{-1} bands were also present at approximately 2100 cm^{-1}, 2030 cm^{-1} and 1920cm^{-1}. In some instances the bands at 2100 cm^{-1} and 2030 cm^{-1} were quite intense but it was found that the spectra obtained were very dependent on sample preparation. We conclude that in all cases the band at 2060 cm^{-1} is probably due to linear bonded CO. The assignment of the other bands is somewhat uncertain. From the data that has been considered so far there is not enough evidence to disagree with Garland's original interpretation. It would seem however that these species correspond to CO chemisorbed on Rh sites of unusual encironment which are not usually found on the surfaces of vacuum evaporated Rh films.

Apart from this, it would appear that the alumina support does, in some ways, effect the chemistry of the Rh. Garland found that the sample had to be heated to 170°C in 190 torr of O_2 for a very long period before the band at 2060 cm^{-1} could be removed. In this work the corresponding band was removed in less than a minute when 1 torr of O_2 was added with the sample kept at 25°C.

We found that addition of CO to the oxygenated Rh surface gave rise to two bands, one at 2120 cm^{-1} and the other at 2080 cm^{-1}. This is in marked contrast to the results for the addition of CO to oxygenated Pt surfaces where only one band was observed. From the desorption data it seems likely that the species at 2080 cm^{-1} is very similar to that observed when CO is added to an initially clean surface. We postulate that the band at 2120 cm^{-1} is associated with some species in which the CO is associated with adsorbed oxygen. It is visualised that on evacuation this desorbs as CO_2. This explains why the band at 2120 cm^{-1} does not return when CO is later added to the evacuated system and it is known (44) that CO_2 is not adsorbed on Rh surfaces. The exact structure of the species at 2120 cm^{-1} must be a matter of conjecture. In the past, bands have been obtained in the region of 2170 cm^{-1} for CO on various oxide surfaces which have been attributed (23) to the structure $O{\equiv}C{=}O$--- metal.

However the results of Brennan et al (53) show that the bonding of oxygen on Rh is likely to be somewhat different from that in oxides because chemisorption virtually ceases after monolayer formation. Heyne (43) has recently observed a band at 2120 cm^{-1} for CO adsorbed on a Pt surface which had been treated with 20 torr of O_2 at 300°C for 1 hour. This, he has attributed to CO chemisorbed on a Pt^{2+} ion. However, the species was very strongly bound and so it is not thought likely that it is of the same nature as that observed in this work. The differences which we have observed when CO is added to oxygenated Rh and Pt surfaces are not difficult to rationalise. Brennan et al (53) have found that oxygen is bound to Rh surfaces more strongly than to Pt. It does not seem unlikely, therefore, that CO will react more slowly with oxygen on Rh surfaces, especially when the binding energies of CO/Rh and CO/Pt surface complexes are so similar (4).

IRON/CO

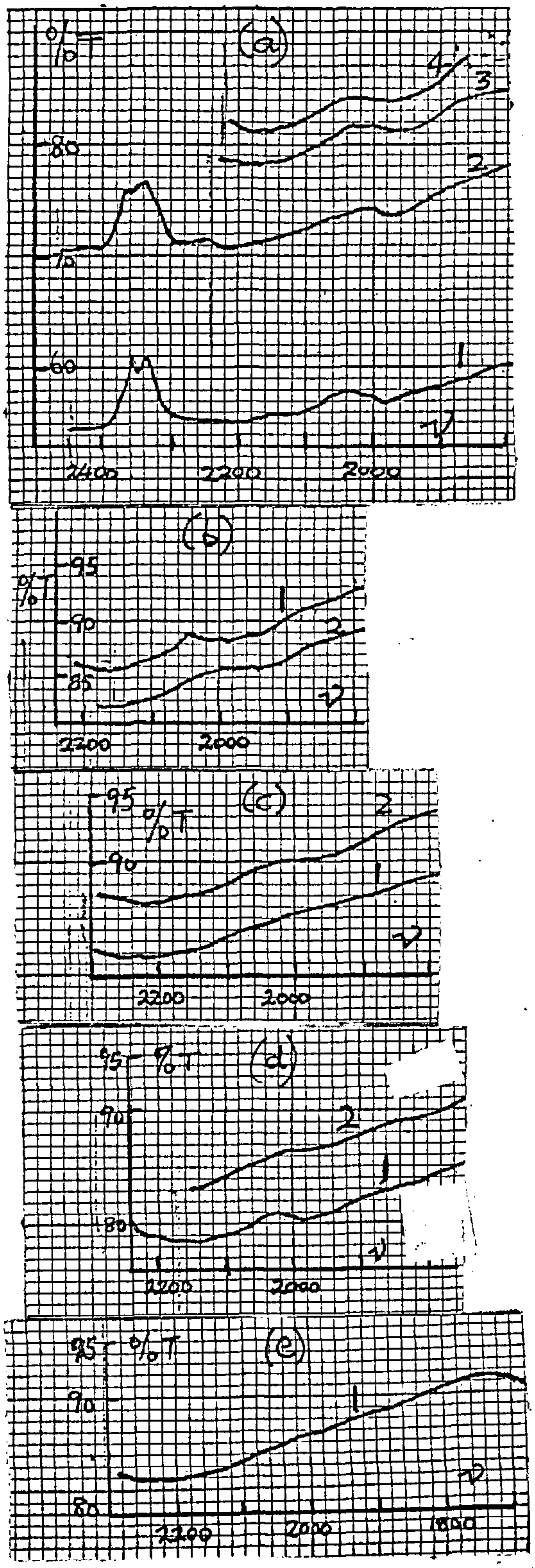
Fe films were deposited from 0.5 mm diameter Fe wire. Great difficulty was experienced in outgassing the wire. Usually, it was outgassed for about 1 hour in vacuo. Then 2 torr of H_2 were added to the system and the filament was heated near its evaporating temperature for 6 - 8 hours. The H_2 was evacuated and the filament was then outgassed for another 30 minutes. After this procedure the system was baked once more for 12 hours and the filament was again outgassed in vacuo. In this way it was possible to obtain vacua of the order of $4 - 6.10^{-8}$ torr when the system was evacuated and the filament was outgassing at its evaporating temperature. The volatile impurities were trapped by liquid nitrogen-cooled glass which suggests that the major constituent was either CO or O_2 or, possibly, both of these. It was not possible to completely outgas the filament. In some cases, the same filament was used in three consecutive runs and, yet, vacua less than 4.10^{-8} torr could not be obtained when the filament was outgassing.

Vacuum evaporated films

When CO was added to vacuum evaporated Fe films so that the pressure in the cell was of the order $1 - 8.10^{-4}$ torr a single band at approximately 1980 - 1990 cm^{-1} was observed. The bands were always small and of the order of 1 - $1\frac{1}{2}$°/o absorption but there is no doubt that they were genuine because all the experiments showed a band at this frequency. In all cases the band became broader on standing and the band centre seemed to shift to lower frequencies of the order of 1960 cm^{-1}; this is probably caused by sintering. There was no alteration in transmission during this period but sintering would not be expected to have such a drastic effect as observed for films deposited in the presence of CO. Further evidence that the film sintered during this period was provided by the fact that the pressure in the cell did not decrease as rapidly as would be expected from the dekker leakage tests. When the spectral evidence and pressure measurements indicated that sintering had ceased, the system was evacuated and it was noted that in some experiments a band, which was very similar to that observed before the evacuation process, formed; in other experiments it was difficult to judge whether this was so since the spectral reproducibility and noise was of the same order as the intensity of any possible band that was present. Several runs are now considered so that more detail can be brought to bear on the general points mentioned above.

Figure 19 shows the spectra obtained during an experiment when the system was baked and outgassed to

FIGURE 19 — Fe/CO.



18.10^{15} MOLECULES OF CO ADSORBED BY THE FILM.

(a) 1 — 5 MINUTES AFTER WARM-UP.

2,3,4 — REPEATS WITH ATTENUATION CONTROL ADJUSTED.

(b) 1 — FURTHER REPEAT.

2 — 3 MINUTES EVACUATION. ($p \sim 4.10^{-6}$ TORR).

(c). 1 — 10 MINUTES EVACUATION. ($p \sim 1.10^{-6}$ TORR).

2 — DOSEWISE ADDITION OF CO. ($p \sim 8.10^{-4}$; NOT POSSIBLE TO CALCULATE AMOUNT OF CO ADSORBED BECAUSE THE QUANTITY WAS $< 1.10^{15}$ MOLECULES)

(d). 1 — AFTER 30 MINUTES.

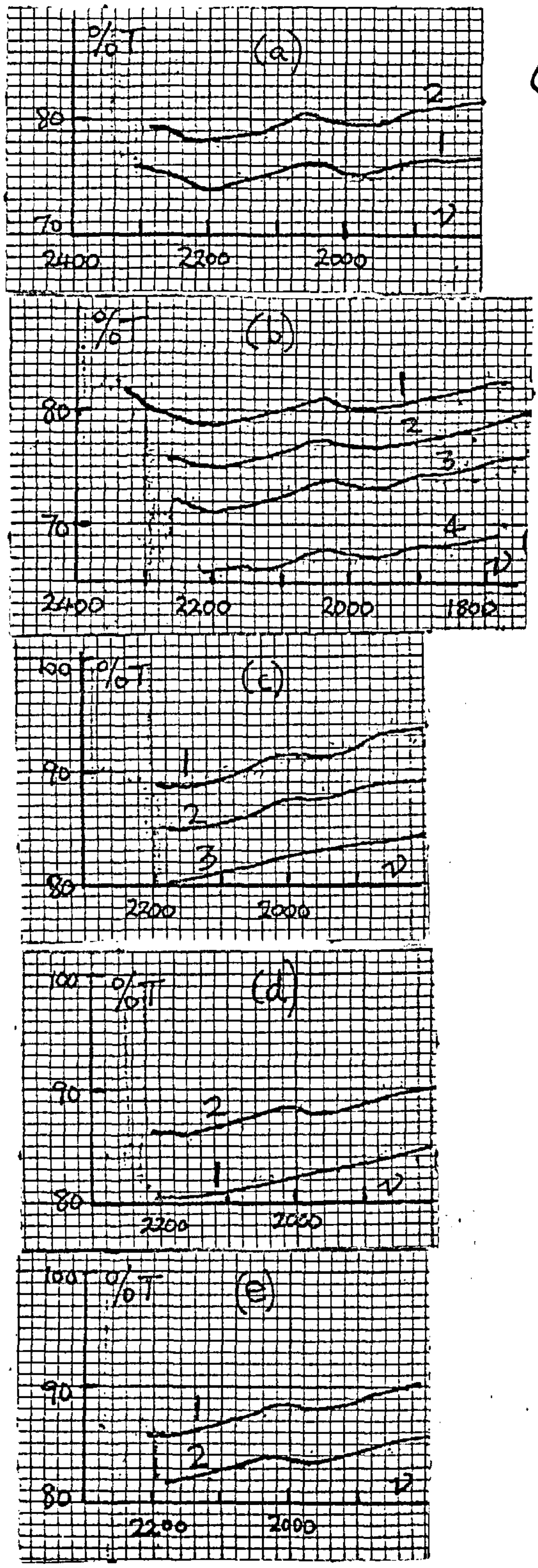
2 — 10 MINUTES EVACUATION ($p \sim 1.5.10^{-6}$ TORR).

(e) 1 — REPEAT.

approximately 3.10^{-8} torr and the filament was outgassed to a final pressure of approximately 9.10^{-8} torr. Film was deposited with the pressure in the system steady at approximately 1.10^{-8} torr. The film transmitted 41°/o of the incident radiation at 2100 cm^{-1} and, initially, 18.10^{15} molecules of CO were adsorbed when CO was added to a pressure of approximately 9.10^{-4} torr. From this it is calculated that $K = 1.10^{-18}$ cm^2 $molecule^{-1}$. In these spectra there seems to be a band at 2020 cm^{-1} in the initial stages. Although it is not evident from the diagrams, a low signal-to-noise ratio was employed during this experiment and it could be that this accounts for the behaviour; it was never observed in other experiments where a higher signal-to-noise ratio was used. There were definite signs that the silm sintered on warming to room temperature but, unfortunately, no measurements were taken which could give an indication of the extent of this effect. The band was removed by evacuating the system for 10 minutes to give a pressure of approximately 1.10^{-6} torr. Addition of CO to a pressure of approximately 8.10^{-4} torr resulted in the return of the band. It was, once more, removed by evacuating the system to 1.10^{-6} torr.

Figure 20 shows spectra which were obtained in an experiment where the background pressure was approximately 1.10^{-8} torr and the filament was outgassed to approximately

FIGURE 20 — Fe/CO.



17. 10^{15} MOLECULES OF CO ADSORBED BY FILM. INITIALLY, $i_+ = 1{\cdot}18 \times 10^{-5}$A.

(a) 1— 5 MINUTES AFTER WARM-UP TO 300°K.

2— 10 MINUTES AFTER WARM-UP. $i_+ = 1.10^{-5}$A

(b) 1— REPEAT OF (a)-2.

2— 10 SECONDS PUMPING WITH DP1 AND ROTARY PUMP. $i_+ = 7.7.10^{-6}$A.

3— FURTHER 5 SECONDS PUMPING. $i_+ = 5.10^{-6}$A.

4— FURTHER 10 SECONDS PUMPING. $i_+ = 3.3.10^{-6}$A.

(c) 1— AFTER 9 MINUTES EVACUATION WITH DP1, FOLLOWED BY 5 MINUTES EVACUATION WITH DP2. $p \sim 4.10^{-7}$ TORR.

2— 5 MINUTES EVACUATION.

3— A FURTHER 5 MINUTES EVACUATION.

(d) 1— REPEAT OF (c)-3.

2— DOSE-WISE ADDITION OF CO. FINAL PRESSURE $\sim 1.10^{-3}$ TORR. APPROXIMATELY 1.10^{15} MOLECULES OF CO ADSORBED BY FILM.

(e). 1— REPEAT.

2— REPEAT WITH ATTENUATION CONTROL ADJUSTED.

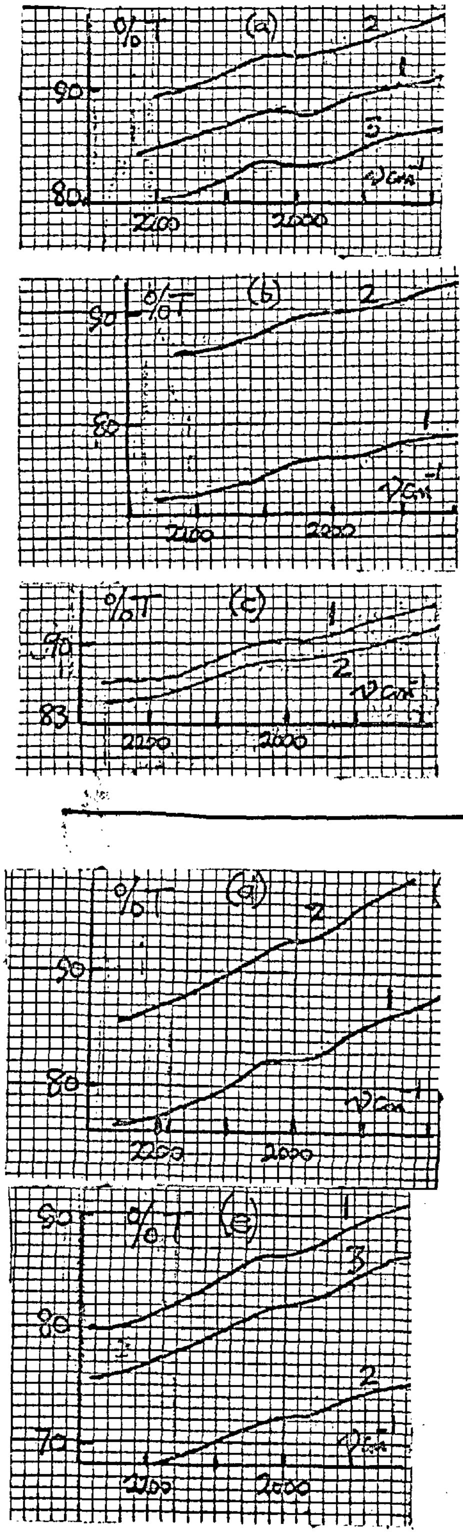
6.10^{-8} torr. On dosing CO into the cell, after film preparation, until the pressure was approximately 9.10^{-4} torr, calculations showed that 17.10^{15} molecules were adsorbed. From this, K = 1.10^{-18} cm^2 molecule^{-1} and the apparent integrated absorption intensity, B, is equal to 53.10^3 mole^{-1}. litre.cm^{-2}. The film sintered but it is estimated that no more than 4 - 5.10^{15} molecules of CO were desorbed during this process. CO was evacuated from the system very slowly, in bursts, by the 3-stage diffusion pump. 11.5 minutes of pumping to a pressure of approximately 3.10^{-6} torr had a negligible effect upon the band. No evidence for the presence of the band could be found after a further 10 minutes evacuation with the high speed diffusion pump to 3.10^{-7} torr. CO was then dosed into the system with the dekker valve closed and it was found that approximately $1.5.10^{15}$ molecules were adsorbed when the pressure in the cell had been increased to approximately 7.10^{-4} torr. From this data K = 12.10^{-18} cm^2 molecule^{-1} and B = 480.10^3 mole^{-1}.litre.cm^{-2} for this weakly bound CO.

In general, it was found that dosing experiments to evacuated Fe samples were not as clean-cut as for the Rh/CO system. For example, in the experiment discussed above it was found that the weakly held CO was not taken up when the first dose was added. Instead, the extent of the adsorption was dependent upon the number of doses added up to a pressure of approximately 5.10^{-4} torr.

In an attempt to solve this problem two separate experiments were carried out in which CO was dosed to the clean sample to lower final pressures. The final pressure in one case was approximately 3.10^{-4} torr and in the other case it was 1.10^{-4} torr. In both instances practically the same spectra as observed in previous experiments were obtained as can be seen from Figure 21. Again, sintering occurred and it was found that the film did not adsorb any CO when this was dosed into the cell to give a final pressure of approximately 8.10^{-4} torr. In both cases the final band was small although the dekker leakage rate showed that the amount of CO that desorbed from the film during the sintering process was probably no more than $2 - 3.10^{15}$ molecules. The band definitely disappeared on pumping but, in these experiments, it was difficult to judge whether it reappeared on the addition of more CO to a pressure of 10^{-3} torr. Some spectra showed a band whilst others did not and where a band was observed it was of the order of $0.5^{\circ}/o$ absorption. To be absolutely certain about this point would have necessitated about 20 scans and, since the slow scanning speed was used, there was not time to do this in these particular experiments. However, in a similar experiment where the same circumstances were

FIGURE 21.

Fe|CO.



16.10^{15} MOLECULES OF CO ADSORBED INITIALLY.

(a) 1- FIRST SPECTRUM; $i_+ = 3.10^{-6}$A.

2- REPEAT. ATTENUATION CONTROL ADJUSTED.

3- AFTER FURTHER DOSING; $i_+ = 8.10^{-6}$A.

(b) 1- REPEAT OF (a)3. ATTENUATION CONTROL ADJUSTED.

2- FURTHER REPEAT; AT THIS TIME $i_+ = 6{\cdot}1.10^{-6}$A.

(c) 1- FURTHER REPEAT; $i_+ = 5.10^{-6}$A.

2- 30 SECONDS EVACUATION WITH 3-STAGE PUMP. $i_+ = 2{\cdot}4.10^{-6}$A.

SEPARATE EXPERIMENT: 12·5.10^{15} MOLECULES OF CO ADSORBED INITIALLY.

(d) 1- FIRST SPECTRUM; $i_+ = 1{\cdot}2.10^{-6}$A.

2- REPEAT. ATTENUATION CONTROL ADJUSTED.

(e) 1- REPEAT OF (d)2. ATTENUATION CONTROL ADJUSTED.

2- AFTER FURTHER DOSING; $i_+ = 8.10^{-6}$A

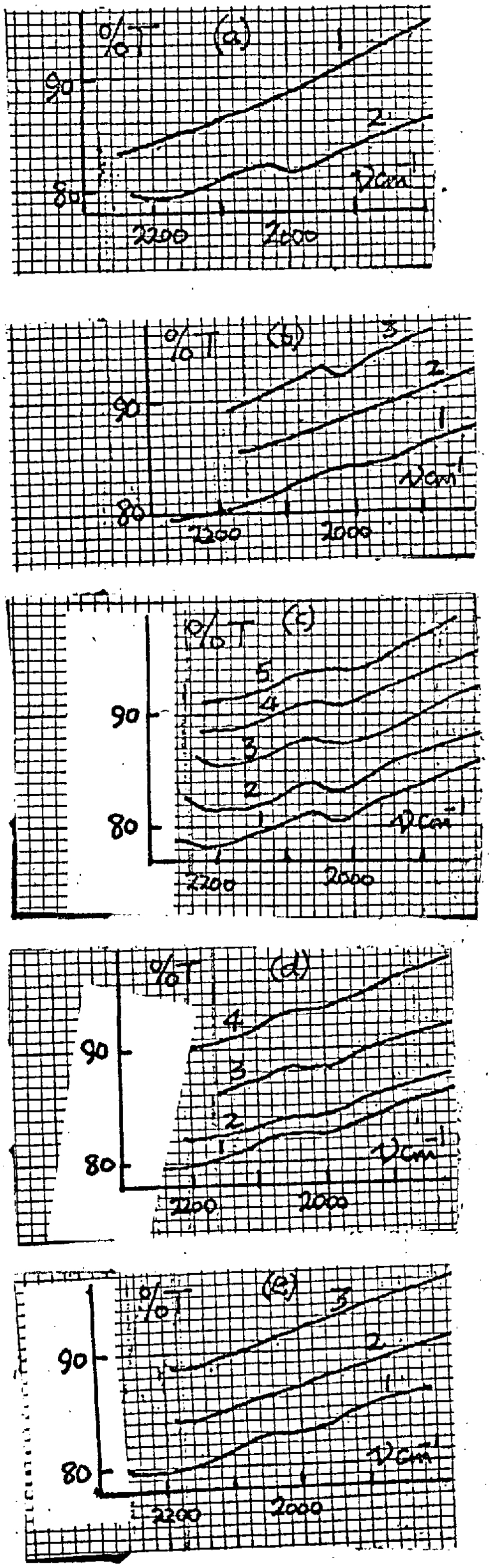
3- REPEAT. ATTENUATION CONTROL ADJUSTED.

met, a band definitely did appear when the pressure of CO in the cell was increased to 2 torr. As can be seen from Figure 22 the band was centred at 2020 cm^{-1} and it seems very likely that it was mainly due to $Fe(CO)_5$. In this particular case the film was allowed to make contact with 2 torr of CO for 12 hours, although the band at 2020 cm^{-1} formed immediately on the addition of the CO. On evacuation, the band intensity definitely decreased quite markedly as the pressure decreased to 10^{-2} torr and the band centre moved to 1980 - 2000 cm^{-1}. This behaviour is probably caused by the removal of $Fe(CO)_5$ but the interesting point is that a band was left which resembled that obtained when CO was added in small doses to the evacuated Fe sample in the experiments represented in Figures 19 and 20; prior to the addition of the 2 torr of CO it had not been possible to ascertain whether any absorption band was present. The band at 1980 - 2000 cm^{-1} could be removed by pumping for 1 hour with the 3-stage pump.

Discussion

Both Blyholder (54) and Eischens (23, 29) have observed one single band in the region of 1980 cm^{-1} which could be attributed to CO chemisorbed on silica-supported Fe. This is in good agreement with our work. However,

FIGURE 22



Fe/CO.

30.10^{15} MOLECULES OF CO ADSORBED INITIALLY.

(a) 1- BACKGROUND SPECTRUM.

2- IMMEDIATELY AFTER DOSING WHEN THE SAMPLE HAD BEEN TRANSFERRED TO THE INFRA-RED CELL.

THERE WERE, THEN, SOME EVACUATION AND REDOSING EXPERIMENTS.

(b) 1- AFTER DOSE-WISE ADDITION OF CO TO THE EVACUATED SYSTEM. NO BAND COULD BE OBSERVED IN THE SCAN PREVIOUS TO b(1).

2- REPEAT.

3- 2 TORR OF CO ADDED.

(c) 1- AFTER 12 HOURS.

THE CELL WAS THEN EVACUATED IN BURSTS WITH THE 3-STAGE DIFFUSION PUMP.

2- AFTER 15 SECONDS EVACUATION.

3- AFTER 30 SECONDS EVACUATION.

4- AFTER 1 MINUTE EVACUATION.

5- AFTER 1 MINUTE EVACUATION ($p \sim 1{\cdot}3.10^{-2}$ TORR).

(d) 1- 1 MINUTE EVACUATION; $p \sim 3{\cdot}6.10^{-3}$ TORR

2- 1 MINUTE EVACUATION; $p \sim 1.10^{-3}$ TORR.

3- 1·5 MINUTE EVACUATION; $p \sim 2{\cdot}6.10^{-4}$ TORR.

4- 1·5 MINUTE EVACUATION; $p \sim 1.10^{-4}$ TORR.

(e) 1- 5. MINUTE EVACUATION; $p \sim 1.10^{-5}$ TORR.

2- 60 MINUTE EVACUATION; $p \sim 10^{-6}$ TORR.

3- 90 MINUTE EVACUATION.

although the data given by the aforementioned workers is scanty, it would appear that the species observed in their studies was bound more strongly to the Fe. Our results show that practically all of the observable band is due to weakly bound CO and that this weakly bound CO occupies approximately 5 - 10°/o of the surface sites. The sample does sinter for an appreciable time after it has been allowed to warm to 300°K but all the evidence points to the fact that only about 25°/o of the initial amount of CO is desorbed during this process. The band which is observed after this time can be completely removed by pumping and, in favourable cases, it is evident that the band is restored to almost its original intensity by addition of only a small quantity of CO. It seems inconceivable, therefore, that a large amount of CO could have been removed during the time that the system was evacuated and it is concluded that the extinction coefficient of the strongly held CO must be very small. It is interesting that if it is considered that all the adsorbed CO contributes equally to the band the calculated extinction coefficient of 1.10^{-8} $cm^2.molecule^{-1}$ agrees well with the value obtained recently by Eischens and Poling (29). Not much can be made of this, however, since their desorption data is scant and our value of K is probably very inaccurate. Our results compare favourably with the heat data of

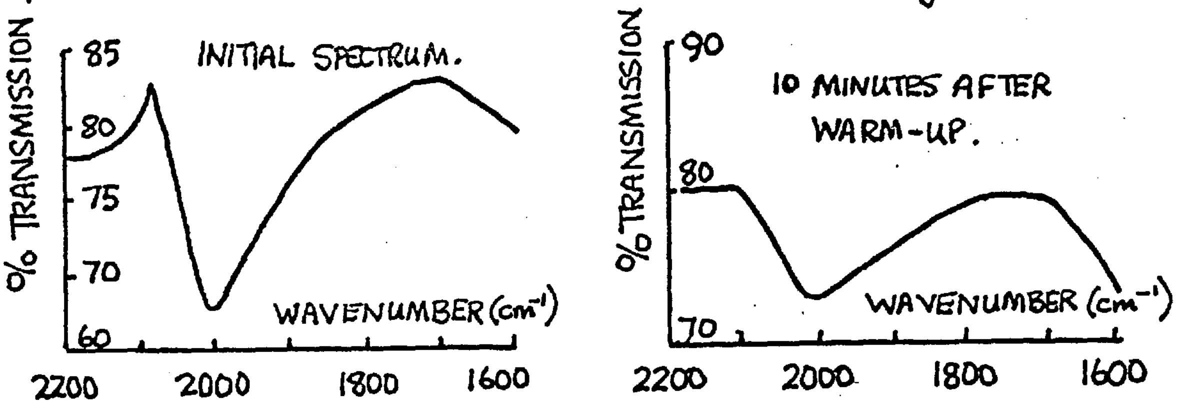
Brennan and Hayes (4). They found that the heat of chemisorption for the Fe/CO system fell, at high coverage, to approximately 27 Kcal. mole^{-1}. Since their dosing experiments were stopped when the pressure in the system was approximately 10^{-5} torr it seems likely that the same species were obtained in each case. The formation of the weakly held CO which gives rise to the band at 1980 - 1960 cm^{-1} appears to be pressure dependent. Addition of 2 torr of CO causes the formation of $Fe(CO)_5$ and the weakly bound species. This leads to some interesting speculations about the nature of the weakly held CO. Chemisorption must be one of the initial steps in the formation of $Fe(CO)_5$ and it is tempting to suppose that the weakly bound CO observed in these spectra is due to a species in which two CO molecules are attached to one Fe atom.

Evaporation in 2 torr of CO

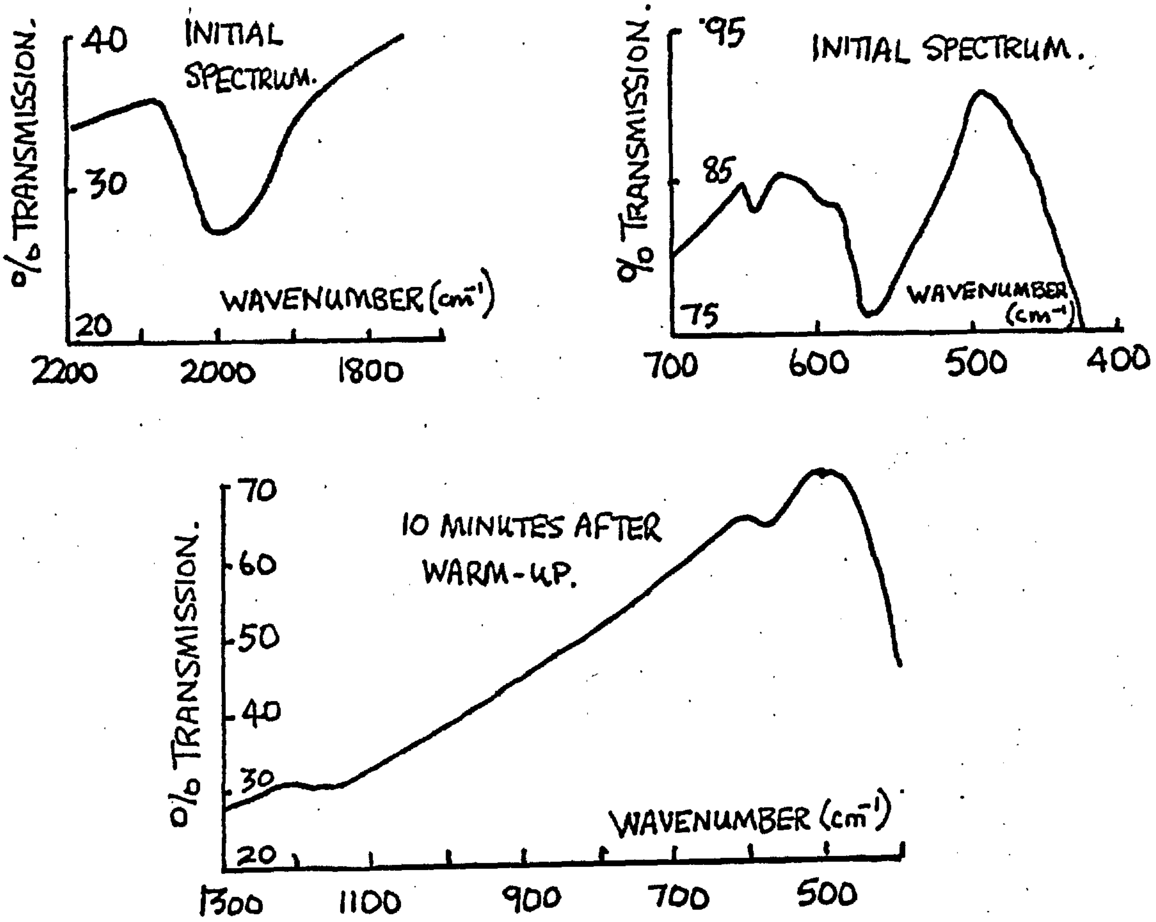
Figure 23(a) shows spectra which were obtained when Fe was evaporated onto a MgO plate in the presence of 2 torr of CO after the system had been baked and the filament outgassed until the pressure was approximately 5.10^{-7} torr. One very broad band, centred around 1990 - 2010 cm^{-1}, was obtained. The film sintered rapidly on warming up during which time the band intensity merely decreased and the

FIGURE 23. Fe/CO.

a/ EVAPORATION IN THE PRESENCE OF 2 TORR OF CO. MgO SUBSTRATE.



b/ EVAPORATION IN THE PRESENCE OF 2 TORR OF CO. AgCl SUBSTRATE. BAKEABLE AgCl CELL USED.



band centre became slightly broader, extending from 1980 - 2020 cm^{-1}. The band was easily removed by 5 minutes pumping to 10^{-3} torr.

Figure 23(b) shows spectra that were obtained when Fe was evaporated onto a AgCl plate in the presence of 2 torr of CO. The bakeable AgCl cell was used in these experiments. Very similar behaviour to that observed when the substrate was MgO was noted. In the near infra-red region a broad band, centred around 2000 cm^{-1}, was obtained. In the far infra-red at least two bands were observed initially. One broad band at 570 cm^{-1} and a small band at 642 cm^{-1} were noted and there is a possibility that a weak band at 600 cm^{-1} was present. The film sintered on standing and the band at 642 cm^{-1} quickly disappeared; the intensity of the bands at 2000 cm^{-1} and 570 cm^{-1} also decreased but the band centres did not shift appreciably. Unfortunately, it was not possible to obtain an accurate measure of the relative intensity of the band at 2000 cm^{-1} to that at 570 cm^{-1} because it is necessary to use separate diffraction gratings on the 337 spectrophotometer to record the different spectral ranges; this necessitates the use of a fresh chart paper and instrument setting. However, the band intensity at 2000 cm^{-1} was approximately 3 times greater than that at 570 cm^{-1}.

Discussion

The presence of the band at 642 cm^{-1} shows that some $Fe(CO)_5$ is formed during the preparation of the sample because Edgell and co-workers (55) have shown that a very intense band due to one of the Fe - C - O bending modes of $Fe(CO)_5$ occurs at 646 cm^{-1}. However the band quickly disappears on standing, probably due to collection by the liquid nitrogen trap, and so it does not seem likely that $Fe(CO)_5$ contributes significantly to the spectra. Once more, the spectra are very similar to those observed by previous workers who have used silica-supported Fe samples. The spectra obtained in the far infra-red region also compare well with those of Blyholder (26) whose sample consisted of a dispersion of Fe in oil. Unlike him it was not possible to distinguish any side-bands in the main absorption band at 570 cm^{-1} but this is probably due to the fact that the band at 570 cm^{-1} was not so intense in our studies. Since the results of Blyholder and of this work are so similar we ascribe the 570 cm^{-1} band to the bending mode of the chemisorbed CO as he has done on the basis of isotope studies.

Like the Pt/CO system, the sample probably sinters because of desorption of weakly held CO. The spectra for vacuum deposited Fe films and Fe films deposited in the presence of CO are similar and it may well be that the same species are observed in both cases. If this were so it would not be expected that the films deposited in CO would be stable since the metallic particles are in much more intimate contact than is the case for the vacuum deposited films; desorption of any weakly held CO should give rise to sintering.

General Discussion

It has already been postulated that the weakly held species which gives rise to the band at 1980 - 2000 cm^{-1} may be due to two CO molecules adsorbed on one Fe atom. This assignment is somewhat speculative but will be discussed later. Taking the band on its face value, however, it seems very likely that it is due to some linearly bonded CO species since the strain incurred in a bridged structure is very great for stretching frequencies above 1940 - 1950 cm^{-1}.

PALLADIUM/CO

Pd films were deposited from 0.5 mm Pd wire. Not much difficulty was experienced in outgassing the wire. Only 4 - 5 hours outgassing was required to reach the background pressure with the wire near its evaporating temperature and it was not necessary to evaporate much metal during this time.

Vacuum evaporated films

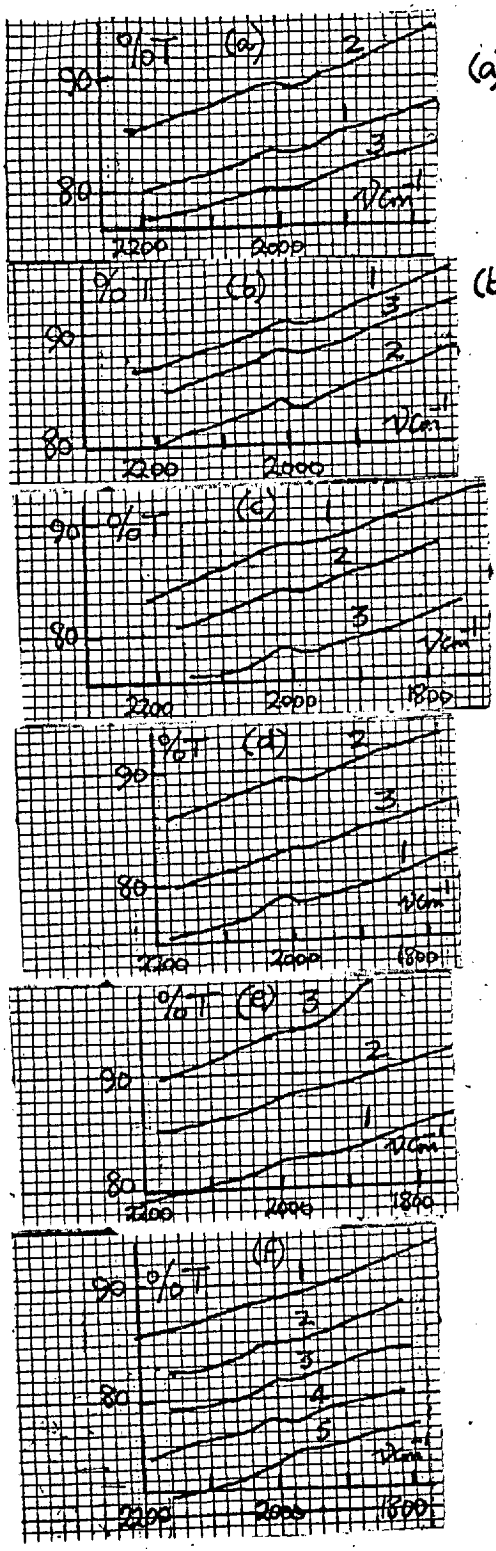
All the samples that were prepared sintered on warming to 300°K. Initially, a single band centred at 1980cm^{-1} was obtained but after some time this definitely broadened. The initial band that was observed was always small and, consequently, inferences from the spectra were rather difficult.

Figure 24 shows the spectra that were obtained in an experiment where the system and the Pd wire were outgassed to approximately $1.5.10^{-8}$ torr. A single band centred around 1980 cm^{-1} was obtained initially. It was very small even though the film adsorbed $33.5.10^{15}$ molecules of CO; the film transmitted 50°/o of the incident radiation at 2100 cm^{-1} and the final pressure of CO was approximately 6.10^{-4} torr. Over a period of 20 minutes the band became broader and pressure measurements during this time indicated that approximately 8 - 10.10^{15} molecules

FIGURE 24.

Pd/CO.

$33{\cdot}5.10^{15}$ MOLECULES OF CO ADSORBED INITIALLY.



(a) 1 – 2·5 MINUTES AFTER WARM-UP. $i_+ = 5{\cdot}6.10^{-6}$A.

2 – 8 MINUTES AFTER WARM-UP.

3 – 14 MINUTES AFTER WARM-UP. $i_+ = 5{\cdot}5.10^{-6}$A.

(b) 1 – 19 MINUTES AFTER WARM-UP

2 – AFTER THE ADDITION OF CO TO A PRESSURE OF 1 TORR.

3 – REPEAT.

(c) 1 – REPEAT.

2 – REPEAT.

3 – REPEAT.

(d) 1 – REPEAT.

AFTER d(1) THE CELL WAS EVACUATED CONTINUOUSLY.

2 – AFTER 1 MINUTE; $p \sim 1.10^{-5}$ TORR.

3 – AFTER 6·25 MINUTES; $p \sim 6.10^{-6}$ TORR.

(e) 1 – AFTER 11·5 MINUTES; $p \sim 3{\cdot}5.10^{-6}$ TORR.

2 – AFTER 18 MINUTES; $p \sim 2{\cdot}5.10^{-6}$ TORR.

3 – AFTER 24·5 MINUTES; $p \sim 2.10^{-6}$ TORR.

(f) 1 – AFTER 29 MINUTES; $p \sim 1{\cdot}5.10^{-6}$ TORR.

2 – EVACUATION CEASED. CO ADDED TO THE CELL DOSE-WISE; $\sim 2.10^{15}$ MOLECULES ADSORBED.

3,4 – REPEATS.

5 – AIR ALLOWED TO ENTER CELL.

of CO desorbed, presumably, due to sintering. Addition of 1 torr of CO seemed to cause an increase in the band intensity but it is difficult to be certain about this point since the band was of the order 0.75 - 1°/o absorption. On evacuating the system the band definitely seemed to disappear when the pressure in the system was below 10^{-5} torr and, moreover, it seemed to reappear when CO was added to the cell dose-wise. 2.10^{15} molecules of CO were adsorbed during this dosing and the amount of CO adsorbed depended upon the number of doses added. 4 doses, of approximately $4.5.10^{15}$ molecules, were added and after each addition approximately 5.10^{14} molecules of CO were adsorbed. Because the bands obtained were so small it is not possible to place complete reliability on the spectral evidence. All it is possible to say is that the spectra obtained during the evacuation and re-dosing experiments were very reproducible; it seems to be easier to distinguish whether a band is present or not, rather than whether a band intensity has increased, when absorption of such small magnitude is studied.

Discussion

It is difficult to make absolute pronouncements on the results mentioned above because of the small bands encountered. However, the experiment described tends to indicate that the Pd/CO system is very similar to the Fe/CO system. The absorption band that is obtained seems to be due only to weakly bonded CO and this occupies about 10°/o of the surface sites. Again, the results are not at variance with those of Brennan and Hayes (4) who found that the heat of chemisorption for the Pd/CO system fell below 30 K cal. mole^{-1} at high coverage.

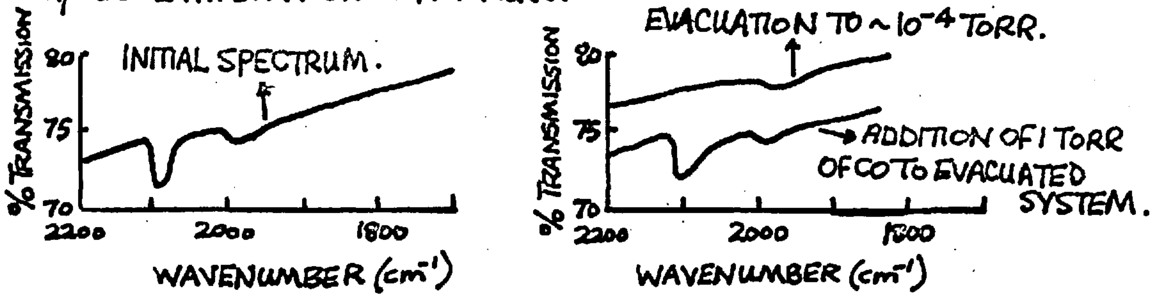
It is interesting to note that addition of 1 torr of CO appears to cause an increase in band intensity. As yet it has not been possible to prepare a Pd complex containing CO ligands only. However, work with Fe and Ni shows that addition of such high pressures of CO leads to carbonyl formation and it could be that the band obtained for the Pd/CO system corresponds to a surface complex in which two CO molecules are attached to one Pd atom.

Co-evaporation with NaCl

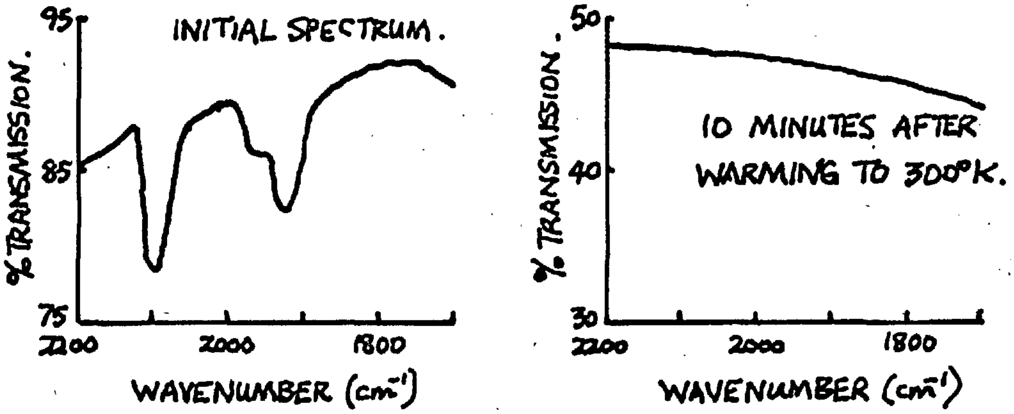
The intensity of bands for CO on Pd/NaCl films varied from sample to sample and was probably dependent upon the rate of evaporation of the Pd and NaCl. In all cases a small band was observed at 2090 - 2100 cm^{-1}. When samples were prepared in which this band corresponded to about 2 - 4°/o absorption the presence of another band at 1980cm^{-1} was apparent. Figure 25(a) shows the spectra obtained in

FIGURE 25 Pd/CO.

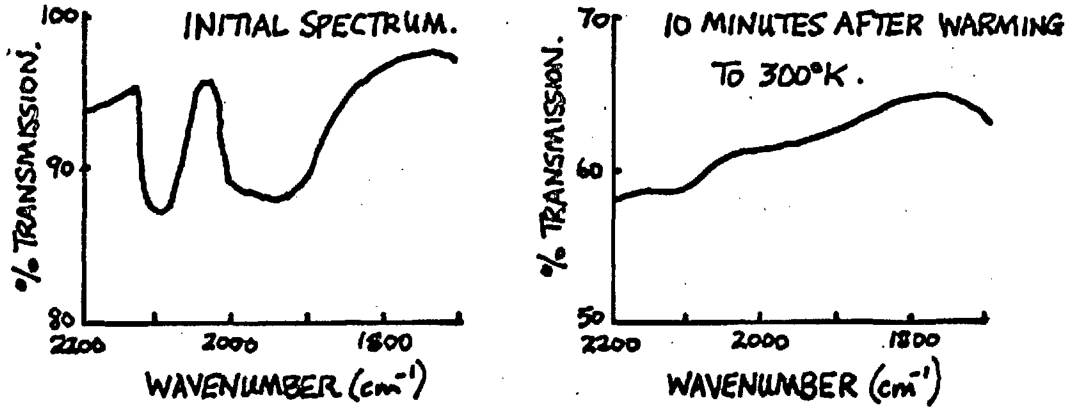
a/ CO-EVAPORATION WITH NaCl.



b/ EVAPORATION IN THE PRESENCE OF 2 TORR OF CO.



c/ SEPARATE EXPERIMENT: EVAPORATION IN THE PRESENCE OF 2 TORR OF CO.



an experiment where the bands were most intense. In this experiment both the Pd and NaCl were outgassed to a final pressure of 4.10^{-9} torr and the film was deposited onto a MgO plate cooled to 78°K whilst the pressure was steady at $1.5.10^{-9}$ torr. CO was then added to the sample, which was cooled to 78°K, to give a final pressure of approximately 10^{-5} torr in the cell. On warming to 300°K the pressure rose to approximately 10^{-2} torr. This desorption of CO was found to be reversible. The band at 2090 cm^{-1} could be removed by pumping to 10^{-4} torr but that at 1980 cm^{-1} did not seem to be greatly affected during this time. Addition of CO to a final pressure of 1 torr resulted in the return of the band at 2090 cm^{-1}.

Discussion

The weakly held species which gives a band at 2090cm^{-1} is not observed on vacuum evaporated films and it is concluded that this is due either to some inductive effect of the NaCl on the Pd particles or to some difference in structure between the two samples. It seems likely that the species corresponding to the band at 1980 cm^{-1} is similar to that obtained with vacuum evaporated films but, unfortunately, no extensive desorption studies were made.

Films deposited in the presence of 2 torr of CO

Such studies were difficult because it was found that the sample sintered very rapidly on warming to 300°K.

Figure 25(b) shows the spectra obtained when the Pd wire was outgassed to a final pressure of approximately 2.10^{-7} torr and the film was deposited on a MgO plate cooled to 78°K. Two bands were obtained. One centred at 1925 cm^{-1} and had a shoulder at 1970 cm^{-1}. The other centred at 2100 cm^{-1}. The sample was very unstable and sintered so quickly that 10 minutes after warming to 300°K no bands could be observed. Figure 25(c) shows spectra for a similar experiment which gave slightly different results in that no structure could be observed in the lower frequency band; it was very broad and extended from 2000 - 1925 cm^{-1}. Once more, this sample sintered very quickly on warming to 300°K.

Discussion

The above results can be compared with the similar studies of Garland et al (24). Differences in the two results arise in that we observed no band at 1840 cm^{-1} and also that the band at 2100 cm^{-1} obtained in our studies was more intense. However, the major difference was that the samples of Garland et al were much more stable. Explanations for these differences are difficult because the structures of the films are not known. Garland et al state that scattering losses were severe with their samples and that the film transmitted less radiation than was the case in their other studies. It seems possible, therefore, that the differences can be rationalised in terms of metallic particle size. Comparison with the results for Pd/NaCl films would indicate that the species at 2100 cm^{-1} is weakly bonded. Since the band obtained at 2100 cm^{-1} in our work was relatively more intense than that obtained by Garland et al it would appear that a greater quantity of weakly bonded CO was formed on our samples. Desorption of this species could thus lead to sintering. On this basis it would appear that the weakly held species which gives the band at 2100 cm^{-1} is held only on very small metallic particles. It is not really possible to take the argument any further until the structure of the samples is known.

General Discussion

Eischens et al (15) and Lygin et al (56) have studied the spectra due to CO adsorbed on silica-supported Pd samples. Their data is not consistent and this makes comparison with our results somewhat complicated. Eischens et al found two bands. One, corresponding to a very weakly held species, centred at 2075 cm^{-1}. The position of the other varied with coverage. When the pressure of CO in the cell was 10^{-4} torr the band was weak and centred at 1825 cm^{-1}. As the pressure was increased to 10^{-1} torr the band centre shifted to 1930 cm^{-1} and there was some sign of side-band formation. Lygin et al also observed two bands. These were more intense than those observed by Eischens et al and they centred at 2085 cm^{-1} and 1960cm^{-1}. The latter band was not removed by pumping to 10^{-4} torr and there was no evidence of side-bands. Heyne (43) has shown that addition of H_2, N_2, CO_2 or A to a silica-supported Pt sample gives rise to a band in the region of 1850 cm^{-1}. He claims that this is due to some interaction effect with the silica which causes an enhancement in one of the Si - O combination bands. Thus he concludes that any bands obtained in the region 1850 - 1875 cm^{-1}, when silica-supported samples are used, must be viewed with caution. It does not, therefore, seem impossible that the low frequency band obtained by Eischens and Lygin is of a composite nature, consisting of contributions from adsorbed CO and the Si - O combination frequency. If this were the case only the high frequency side of the band would correspond to adsorbed CO and this would bring their results in line with ours. Lygin's desorption data is scant but it is tentatively suggested that the same type of weakly bonded CO is observed in all three samples.

Further, we suggest that strongly bound CO has a low extinction coefficient and is not observed to any great extent.

NICKEL/CO

Ni films were deposited from either 0.5 mm Ni wire or a filament made by evenly winding 0.2 mm Ni wire around 0.3 mm W wire. The Ni wire was easily outgassed to the background pressure but some difficulty was experienced in outgassing the supported filament. Supported filaments were used only when films were deposited in the presence of CO.

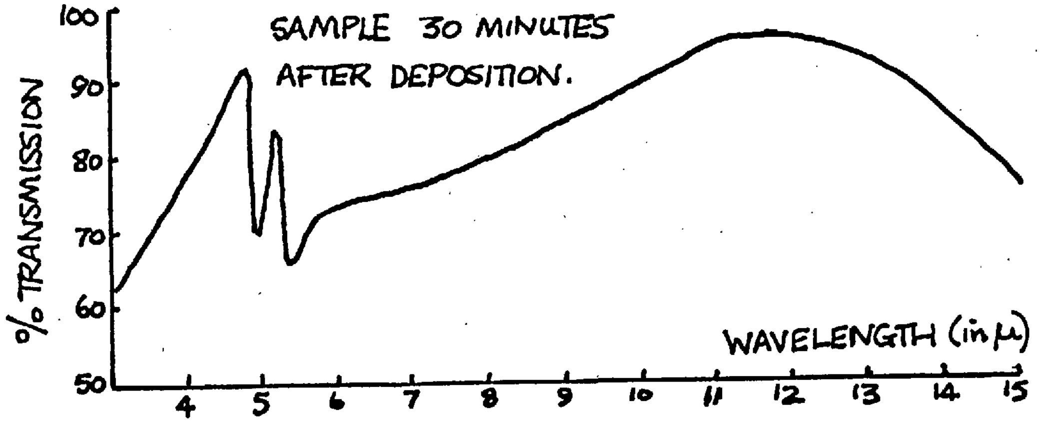
Films deposited in the presence of 2 torr of CO

The spectra that were obtained with this technique depended very critically upon the rate of deposition of metal and the distance of the substrate from the filament during deposition. If the filament was positioned greater than 0.5 cm from the substrate when Ni was evaporated in the presence of 2 torr of CO only $Ni(CO)_4$ was formed. Like the Pt/CO system, it was found that when deposition was quick the sample was stable. When the Ni was slowly deposited the sample sintered on warming to $300^{\circ}K$.

Figure 26(a) shows spectra that were obtained when Ni was quickly deposited onto a NaCl plate in the presence of 2 torr of CO. An infra-red cell with picein-affixed NaCl windows was used and the substrate was not cooled during the deposition. Two bands at $4.9 \pm .03\mu$ ($2040 \pm 10\ cm^{-1}$) and $5.3 \pm .05\mu$ ($1890 \pm 15\ cm^{-1}$) were observed in

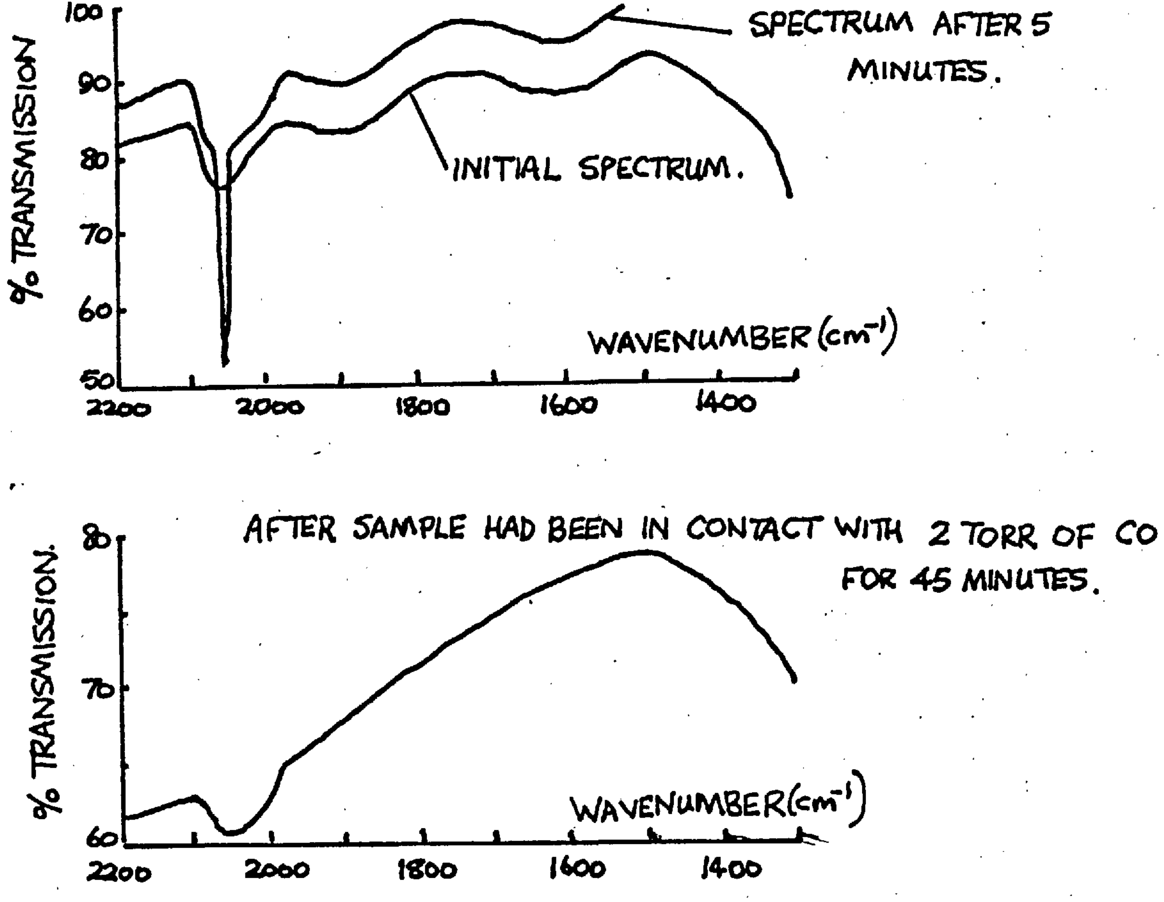
FIGURE 26 Ni/CO.

a/ FILM DEPOSITED IN 2 TORR OF CO AT A FAST RATE. NaCl SUBSTRATE.



SAMPLE 30 MINUTES AFTER DEPOSITION.

b/ FILM DEPOSITED IN 2 TORR OF CO AT A SLOW RATE. MgO SUBSTRATE.



SPECTRUM AFTER 5 MINUTES.

INITIAL SPECTRUM.

AFTER SAMPLE HAD BEEN IN CONTACT WITH 2 TORR OF CO FOR 45 MINUTES.

the spectral region 4000 - 650 cm^{-1}. The bands were of approximately the same intensity and the sample did not sinter. No evidence was found for the presence of $Ni(CO)_4$. This is probably due to the fact that the cell was not cooled during the evaporation; any $Ni(CO)_4$ that was formed would probably be collected very quickly by the liquid nitrogen trap. A similar experiment gave practically the same results except that the lower frequency band was less intense (by a factor of approximately 0.75) than that at 4.9μ. Factors such as the deposition rate and the distance of the filament from the substrate need to be controlled very carefully if completely reproducible results are to be obtained.

In the experiments where MgO substrate was used this was cooled to 78°K during the evaporation and film was deposited at a slow rate over a period of 20 - 45 minutes. As figure 26(b) shows, spectra recorded immediately after the transference of the MgO plate from the evaporator showed three bands; one centred at 2060 cm^{-1} whilst the others were rather broad but centred at approximately 1900 cm^{-1} and 1620 cm^{-1}. As the evaporator warmed to 300°K $Ni(CO)_4$ evaporated and the presence of this is shown by the very sharp band which is superimposed on the original high frequency band at 2060 cm^{-1}. The whole sample sintered so that only a small band at 2060 cm^{-1} was observed after

45 minutes although the pressure in the cell was not reduced. It was shown that this band was not due to gas phase $Ni(CO)_4$. After this time the bands at 1900 cm^{-1} and 1620 cm^{-1} could not be observed but the spectra indicated that all the band intensities decreased at approximately the same rate; since the low frequency bands were the less intense in the first spectrum it is possible that the species contributing to the bands were present, in smaller concentration, on the sintered sample.

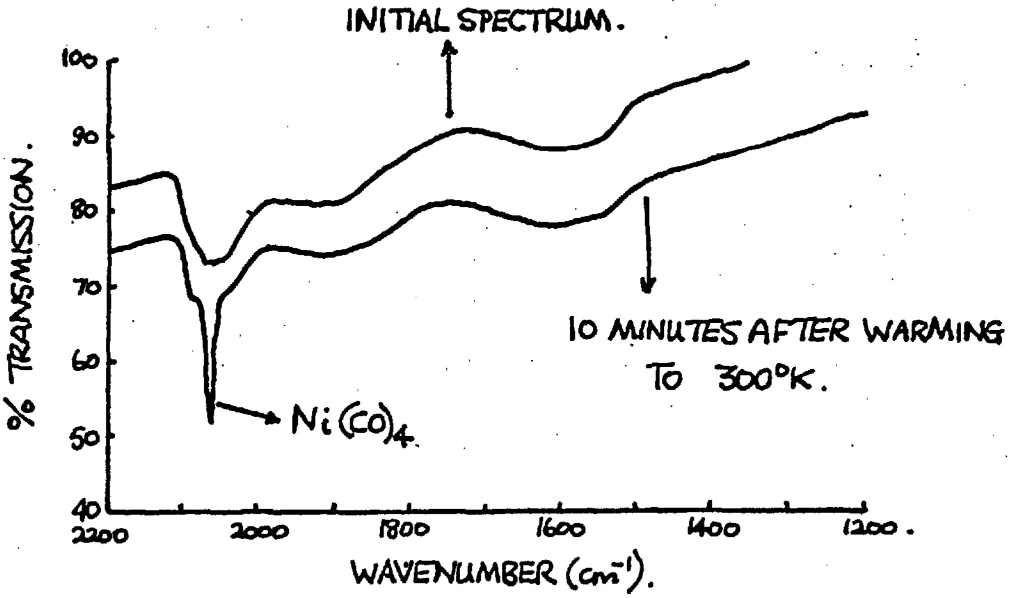
The Ni/CO system was also studied in the far infra-red region using the bakeable AgCl cell and AgCl substrate. These studies were unsuccessful, probably as a result that the band in the near infra-red region was not very intense. Spectra in the near infra-red were similar to those described above using a MgO substrate. (See Figure 27(a)).

Discussion

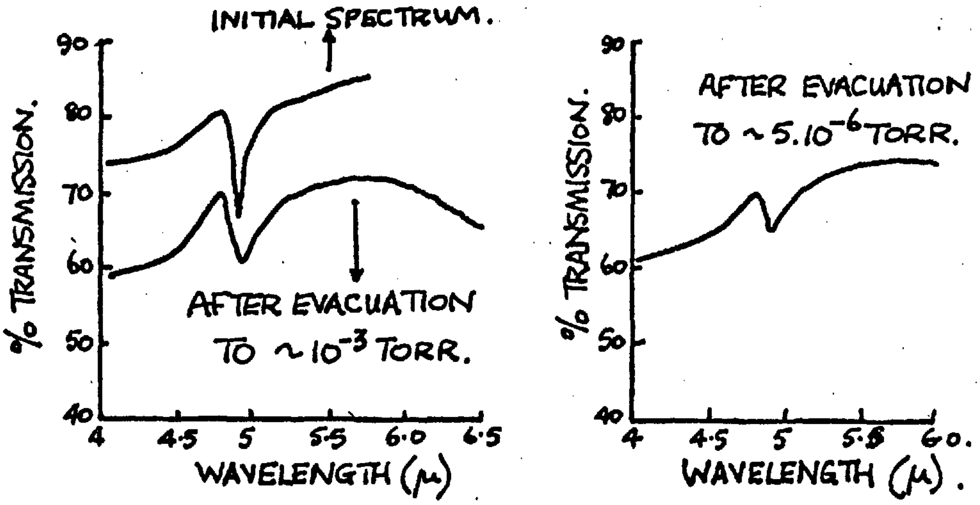
Differences in the stability of the samples are difficult to rationalise since the nature of the weakly bound species whose desorption leads to sintering is very uncertain. The band at 2040 - 2060 cm^{-1} is more predominant in the unstable samples but the structure of this is masked by $Ni(CO)_4$ during the sintering process so that it is not possible to say whether any weakly held species contribute to it. It is unlikely that the species

FIGURE 27. Ni/CO.

a/ DEPOSITION IN THE PRESENCE OF 2 TORR OF CO. AgCl SUBSTRATE.



b/ FILM DEPOSITED BY ION BOMBARDMENT USING A Kr/CO MIXTURE CONTAINING 0·5% CO.



represented by the band at 1620 cm^{-1} plays an important role in the sintering process because Garland et al (42) noted a similar band in their samples which were stable. It can be stated, however, that, once more, differences in stability are probably a result of the fact that smaller metal particles are likely to be present in the unstable samples. It may be that in these samples there are very small aggregations of perhaps 4 - 5 Ni atoms to which CO molecules are bonded and it might be expected that these would decompose to give $Ni(CO)_4$ and larger clusters of Ni as the sample warmed to room temperature. In larger particles, the greater attraction between the Ni atoms could prevent this. Garland et al (42) claim that the band at 1620 cm^{-1} is due to a bridge-bonded CO molecule in which the C - O bond is weakened via association of the oxygen atom with another Ni atom. They dispel the idea that it is due to some carboxylate-type complex arising from oxygen contamination and their argument is convincing. If the band was due to some such complex the presence of another band near 1400 cm^{-1} would be expected. Such a band was not observed in our studies so it seems likely that the band at 1620 is due to some species which is in a peculiar environment as visualised by Garland et al. The band at 1620 cm^{-1} was not observed when the metal particle size was bigger but it seems likely that some other effect is responsible for the sintering.

Film prepared by Ion Bombardment

Figure 27(b) shows the spectra that were obtained after Ni had been sputtered onto a MgO plate cooled to 78°K and CO had been added to the sample. Kr containing a small percentage (0.5°/o) of CO was used to ion-bombard the Ni wire and the gas pressure was 2 torr. 10 torr of CO were added to the sample which was cooled to 78°K with the Kr still present in the cell. Initially, some $Ni(CO)_4$ vapour could be observed together with some CO species which gave a band at $4.9 \pm .03\mu$ (2040 ± 15 cm^{-1}). $Ni(CO)_4$ was quickly collected by the cold trap (liquid nitrogen was used) but the other species were bonded to the Ni fairly strongly. As figure 27(b) shows, the band intensity was decreased by a factor of 50°/o after evacuation of the cell for 1 hour to approximately 5.10^{-6} torr. No bands were observed in the region 2000 - 1600 cm^{-1} at any stage.

Discussion

The species corresponding to the band at 2040-2050cm^{-1} can be likened to those observed by Eischens et al (15) at 2040 cm^{-1} on silica-supported Ni and those at 2035 cm^{-1} and 2060 cm^{-1} observed by Yates and Garland (57) on alumina-supported Ni. However, these other workers also observed strongly held species which gave bands in the region 1940 - 1850 cm^{-1} of almost the same intensity. It is possible that oxygen or carbon is formed by decomposition of CO during the sputtering process. The spectral evidence shows no sign of oxygen contamination but it could be that the species which give rise to the low frequency band are precluded by impurities. Equally, of course, the structure of the sample may be such that these species are not present and the argument must rest here since the structure of the sample is not known.

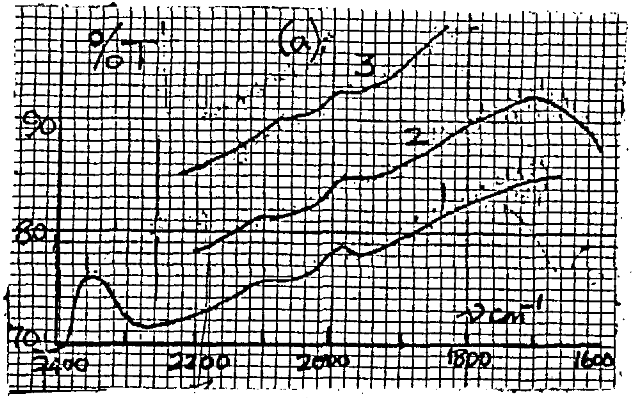
Vacuum Evaporated Films

These studies showed that two small bands centred at approximately 2060 cm^{-1} and 1950 cm^{-1} are obtained for CO adsorbed on Ni.

Figure 28 shows the spectra obtained in two separate experiments. The spectra obtained in Figure 28(a) were obtained in an experiment where the filament was outgassed to a final pressure of approximately 4.10^{-8} torr; the film adsorbed $25.5.10^{15}$ molecules of CO and the final pressure in the cell was approximately 9.10^{-4} torr. The spectral evidence indicated that the film sintered on warming to room temperature but no estimate was made of any possible desorption of CO during this time. More film was deposited onto the plate, after the system had

FIGURE 28. Ni/CO.

$25\cdot5.10^{15}$ MOLECULES OF CO ADSORBED INITIALLY.

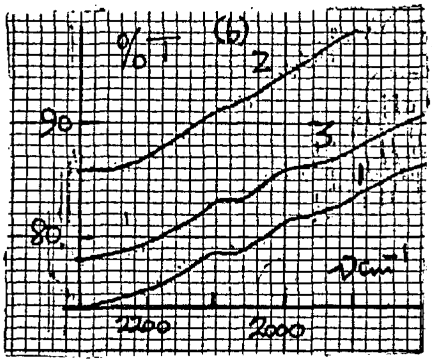


(a) 1 - IMMEDIATELY AFTER WARM-UP.

2- REPEAT. ATTENUATION CONTROL ALTERED.

3 - REPEAT. ———— " ————

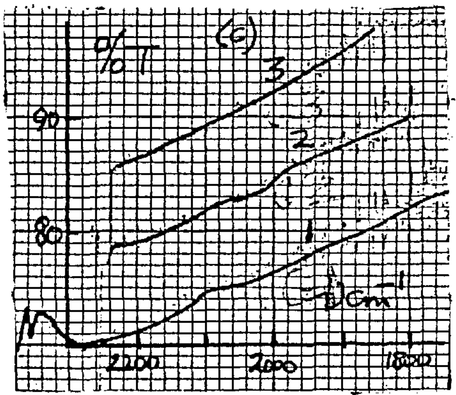
SEPARATE EXPERIMENT. 15.10^{15} MOLECULES OF CO ADSORBED INITIALLY.



(b) 1- IMMEDIATELY AFTER WARM-UP.

2 - REPEAT. ATTENUATION CONTROL ALTERED.

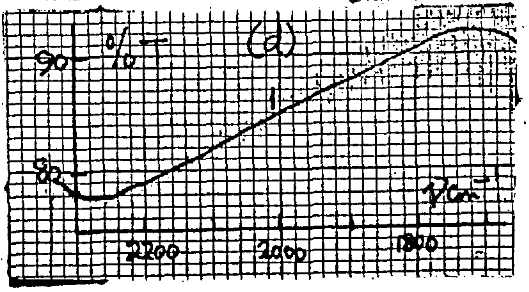
3 - ———— " ————



(c) 1 - ~30 MINUTES AFTER WARM-UP.

2 - 65 MINUTES AFTER (c)-1.

3 - 3 MINUTES EVACUATION; $p \sim 1\cdot5.10^{-6}$ TORR.



4 - 10 MINUTES EVACUATION; $p \sim 4.10^{-7}$ TORR.

been evacuated, in an attempt to obtain larger bands. However, the sample was then so opaque that reproducible spectra could not be recorded.

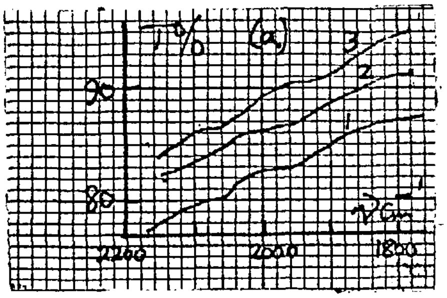
Figure 28(b) - (d) shows the spectra obtained in an experiment where the filament was outgassed to the background pressure of approximately 2.10^{-8} torr; the film adsorbed 15.10^{15} molecules of CO and the final pressure in the cell was approximately 1.10^{-3} torr. In this experiment the low frequency band was not so predominant. Over a period of 30 minutes the sample sintered and the band intensities decreased so much that it was difficult to tell whether the low frequency band was present. Several minutes pumping seemed to remove the band but judgement must be reserved owing to the facts that the bands were so small and no re-dosing experiments were carried out. Unfortunately, the transmission characteristics of the sample were ruined when more film was deposited in an attempt to obtain bigger bands.

The spectra in figure 29 were obtained in an experiment where the filament was outgassed to the background pressure of approximately 2.10^{-8} torr; the film adsorbed $19.5.10^{15}$ molecules of CO and the final pressure in the cell was approximately $6.5.10^{-4}$ torr. Pressure measurements over a period of 40 minutes showed that as the sample warmed to 300°K some sintering did occur but no more than

FIGURE 29

Ni/CO.

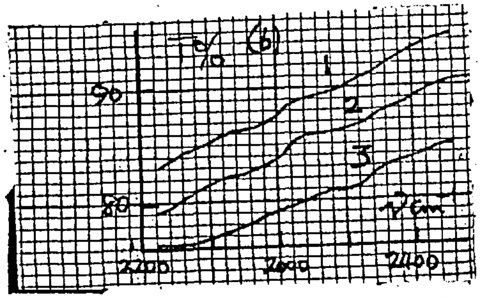
19.5. 10^{15} MOLECULES OF CO ADSORBED INITIALLY.



(a) 1 - 13.5 MINUTES AFTER WARM-UP.

2 - 18.5 MINUTES AFTER WARM-UP.

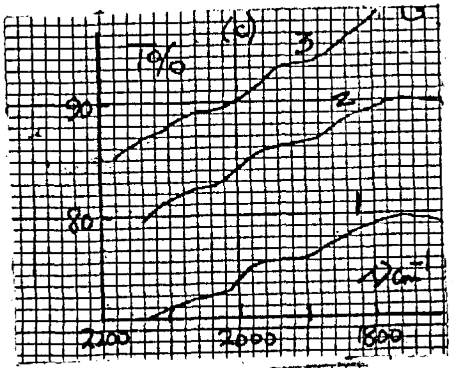
3 - 22.5 MINUTES AFTER WARM-UP.



(b) 1 - 29 MINUTES AFTER WARM-UP.

2 - 39 MINUTES AFTER WARM-UP.

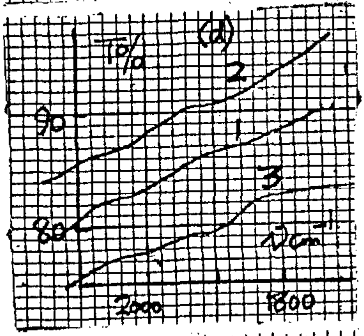
3 - 1.5 MINUTES EVACUATION; $p \sim 2.3 . 10^{-6}$ TORR.



(c) 1 - 7 MINUTES EVACUATION; $p \sim 7.5 . 10^{-7}$ TORR.

2 - 15.5 MINUTES EVACUATION; $p \sim 5 . 10^{-7}$ TORR.

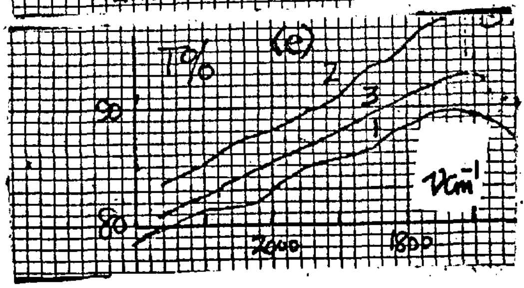
3 - 28.5 MINUTES EVACUATION; $p \sim 4 . 10^{-7}$ TORR.



(d) 1 - 33.5 MINUTES EVACUATION.

2 - 35 MINUTES EVACUATION.

3. DOSE-WISE ADDITION OF CO TO ISOLATED CELL; $\sim 4 . 10^{15}$ MOLECULES ADSORBED.



(e) 1 - REPEAT.

2 - 2 TORR OF O_2 ADDED. TRANSMISSION INCREASED BY ~ 4% T UNITS.

3 - REPEAT.

2 - 3.10^{15} molecules of CO were desorbed during this time. Spectral reproducibility was not very good in this run but the evidence showed that two small bands at approximately 2060 cm^{-1} and 1960 cm^{-1} were obtained after sintering effects appeared to have died away. Desorption studies were unsatisfactory due to the smallness of the bands. The evidence tends to indicate that the bands were not completely removed by pumping but it is difficult to be certain about this point as Figure 29(d) still seems to show a trace of bands after 35 minutes pumping. Re-dosing experiments were also inconclusive from a spectral point of view. However it was found that when the CO was dosed into the evacuated cell to a final pressure of about 7.10^{-4} torr approximately 4.10^{15} molecules of CO were re-adsorbed. Like the Fe/CO system, the amount taken up by the sample depended upon the pressure of CO in the cell. After each of 5 doses of CO (each consisting of approximately $5.5.10^{15}$ molecules) approximately 0.75 - 1.10^{15} molecules were adsorbed.

Discussion

The spectral evidence definitely shows that two bands are formed as a result of adding CO to an initially clean film. In this respect the Ni/CO system differs from the other systems studied by this technique. There is no evidence to show that the bands obtained with the Ni/CO system are due to interference fringes; no other absorption maxima and minima were found in the spectral region 2300 - 1600 cm^{-1}. When Pickering and Eckstrom (34) studied the Ni/CO system using a multiple reflectance cell they observed one band in the region of 2060 cm^{-1}. However, this band was obtained only at CO pressures greater than 10^{-3} torr and it could be that they were observing $Ni(CO)_4$. It is interesting to note that where our results and theirs compare in the Rh/CO system our band was approximately three times more intense. For the Ni/CO system our bands were of the order of 1°/o absorption and it therefore seems likely that the device used by Pickering and Eckstrom was not sensitive enough to detect similar bands.

General Discussion

Except where sputtered films were studied, the results are similar to other workers in that bands in the region 2040 - 2060 cm^{-1} and 1900 - 1950 cm^{-1} were obtained even though the method of sample preparation varied. It is interesting to note that Yates and Garland (57) have measured so-called adsorption isotherms which indicate that a large amount of CO is adsorbed at pressures greater than 10^{-3} torr. Moreover, the first charge of gas gives an 'equilibrium' pressure between 10^{-3} - 10^{-4} torr. These effects could be caused by a contaminated surface; they are certainly in disagreement with our results and those of Gundry and Tompkins (13). Also, their desorption studies showed that much of the high and low frequency bands disappeared on evacuation, in disagreement with the heat data of Brennan and Hayes (4). On this point it is possible that our studies agree with those of Yates and Garland and, in spite of the above criticisms, the spectra obtained for vacuum evaporated films are similar. There seems to be a distinct possibility that in the spectra obtained to date the contribution of strongly adsorbed CO to the high and low frequency bands is small. Sample preparation plays an important role in the spectra that are obtained. O'Neill and Yates found that the bands they observed disappeared to quite a large extent on pumping from 1.3 torr to 0.1 torr and yet the spectra were similar to those obtained by us and other workers. Furthermore we note that, for our results for films deposited in the presence of CO are similar to those obtained for vacuum evaporated films. We conclude that it is possible that the spectra obtained are due to some CO species which are bonded to Ni atoms which have few nearest neighbours; differences in the position of the low frequency band would, on this model, arise from differences in exact environment but, in all cases, it is postulated that the Ni atoms which provide the sites are not close packed. However, a more thorough treatment of all the possibilities is given later when all the systems are compared.

MANGANESE/CO

Mn films were deposited from Mn chips held in an electrically heated Ta basket. The Mn was difficult to outgas but, by depositing some film before the experiment commenced, it was possible to obtain vacua in the region 3.10^{-8} - 3.10^{-7} torr with the Mn just below its evaporating temperature.

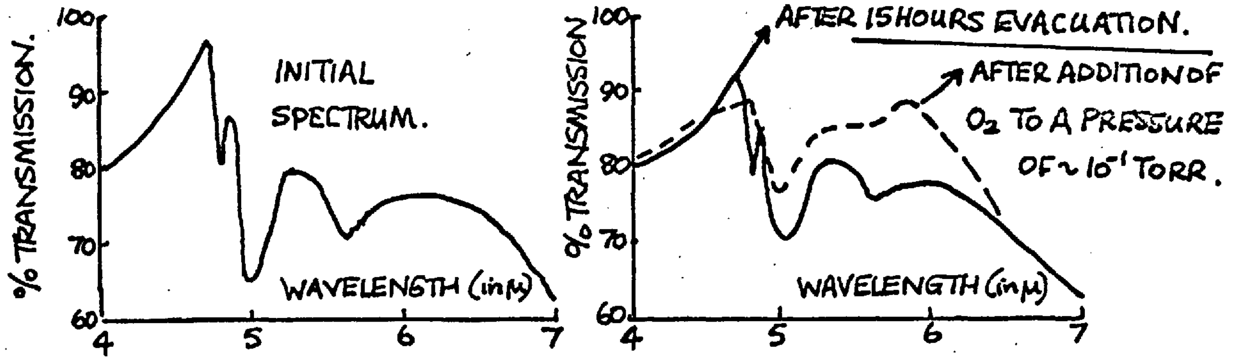
Films deposited in the presence of 2 torr of CO

In all such studies the cell was baked and outgassed to give background vacua less than 10^{-7} torr. The results that were obtained in three separate experiments were quite consistent. Three bands were always obtained. One was quite sharp and centred at 2080 cm^{-1} whilst the others were broad and centred at 2000 cm^{-1} and 1760 - 1780 cm^{-1}. The relative intensities of the bands varied slightly from run to run but the band positions were unaltered within the limits of experimental accuracy.

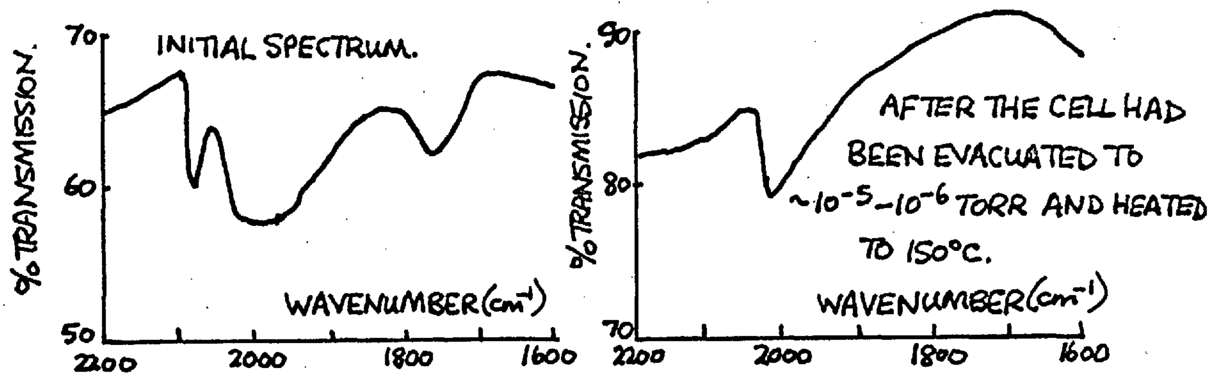
Figure 30(a) shows the spectra obtained in an experiment where the filament was outgassed to approximately 3.10^{-7} torr. After 15 hours evacuation the band intensities were slightly decreased but the spectra showed no sign that a particular band decreased more than the others. There was little evidence for sintering during this time

FIGURE 30. Mn/CO

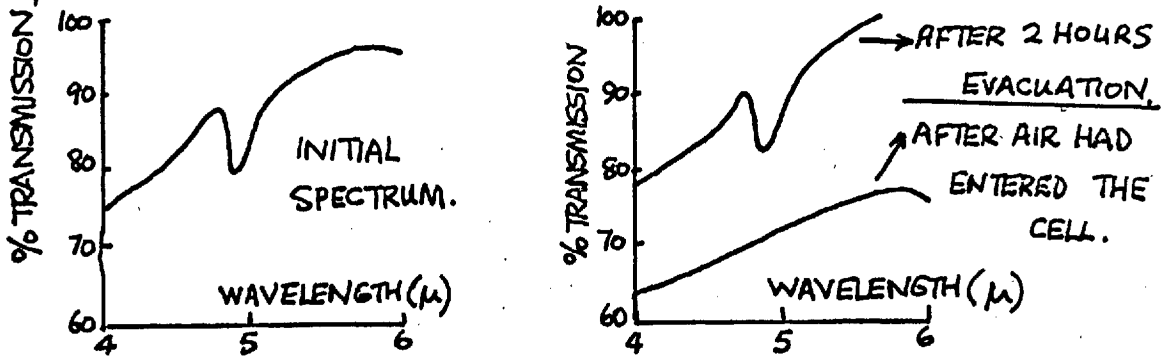
a/ EVAPORATION IN THE PRESENCE OF 2 TORR OF CO.



b/ SEPARATE EXPERIMENT: EVAPORATION IN PRESENCE OF 2 TORR OF CO.



c/ EVAPORATION IN PRESENCE OF 1 TORR OF H₂ FOLLOWED BY THE ADDITION OF CO.



but addition of 2 torr of CO did not result in the restoration of the band intensities to their original values. The band at 2080 cm^{-1} disappeared and those at 2000 cm^{-1} and 1760 - 1780 cm^{-1} decreased in intensity when O_2 was added to a pressure of 10^{-1} torr.

Figure 30(b) shows the spectra obtained in a separate experiment. The sample was heated by a furnace at the same time as spectra were recorded. This was achieved by placing the furnace, which had two diametrically opposed holes drilled through its walls, around the infra-red cell. It was found that the bands at 2080 cm^{-1} and 1760 cm^{-1} disappeared on evacuating the system and heating the cell to approximately 150°C. The band head intensity of the other band did not decrease much duringthis time but its centre shifted to 2020 cm^{-1} and it became less broad. The resulting band was removed only by allowing air to enter the cell.

Discussion

The band at 2080 cm^{-1} and part of the band at 2000 cm^{-1} are probably due to the presence of $Mn_2(CO)_{10}$ in the sample. $Mn_2(CO)_{10}$ is a quite stable solid with a melting point of 154°C (58). Cotton et al (59) obtained bands at 2060 cm^{-1}, 2014 cm^{-1} and 1989 cm^{-1} for particles of solid $Mn_2(CO)_{10}$ held in a KI matrix. Whilst the position of the higher frequency band is not in agreement with these latter workers, the desorption data is consistent with the removal of $Mn_2(CO)_{10}$ from the sample since the band at 2080 cm^{-1} is removed by evacuation at approximately 150°C and the band at 2000 cm^{-1} appears to be of a composite nature. However, not all of the band at 2000 cm^{-1} can be due to $Mn_2(CO)_{10}$ and it is possible that the most stable species represents CO linearly bonded to a Mn surface atom. The band at 1760 cm^{-1} is in the region of the spectrum where assignment is uncertain. However, for the C - O stretching frequency to occur at such a low frequency the C - O bond must be weakened to a great extent. This weakening could be caused by a neighbouring Mn atom but, also, bridge-bonding or bonding to a Mn atom with few nearest neighbours cannot be totally excluded.

Deposition in the presence of H_2

It is known (60) that hydrogen is not strongly adsorbed by Mn and it was, therefore, decided to deposit film in the presence of this gas, followed by the addition of CO, in the hope that the CO would displace the hydrogen.

Figure 30(c) shows the spectra obtained in one such experiment. The filament was outgassed to 4.10^{-8} torr and the film was deposited in the presence of 1 torr of H_2. After the deposition was finished the H_2 was pumped away for 30 seconds with the sample cooled to 78°K and then 2 torr of CO were added. One band, centred at 4.85 ± .03μ (2060 ± 15 cm^{-1}), was obtained. The band was not affected by 2 hours evacuation but was quickly removed when air was allowed to enter the system.

Discussion

It is likely that the observed band represents species similar to those which gave rise to the band at 2020 cm^{-1} in the heated Mn sample. Certainly, it is unlikely to be due to $HMn(CO)_5$ since this is a liquid at S.T.P.

General Discussion

In view of previous results mentioned it is dangerous to associate any of the observed bands with a species resembling chemisorbed CO on Mn surfaces. CO species have been observed which are quite strongly bonded to the Mn but Brennan and Hayes (4) have shown that the heat of chemisorption for the Mn/CO system is 75 $kcal.mole^{-1}$. Since our desorption studies did not encompass the temperature range above 150°C it is not possible to conclude that the same species were studied. However, it is likely that the species observed were due to CO linearly bonded to Mn. The change in band-head frequency of the strongly held species cannot be rationalised in absolute terms but it is known that Mn has a very complex crystal structure

(61) so it is possible that the bands represent species bonded to Mn atoms which have different numbers of nearest neighbours.

CHROMIUM/CO

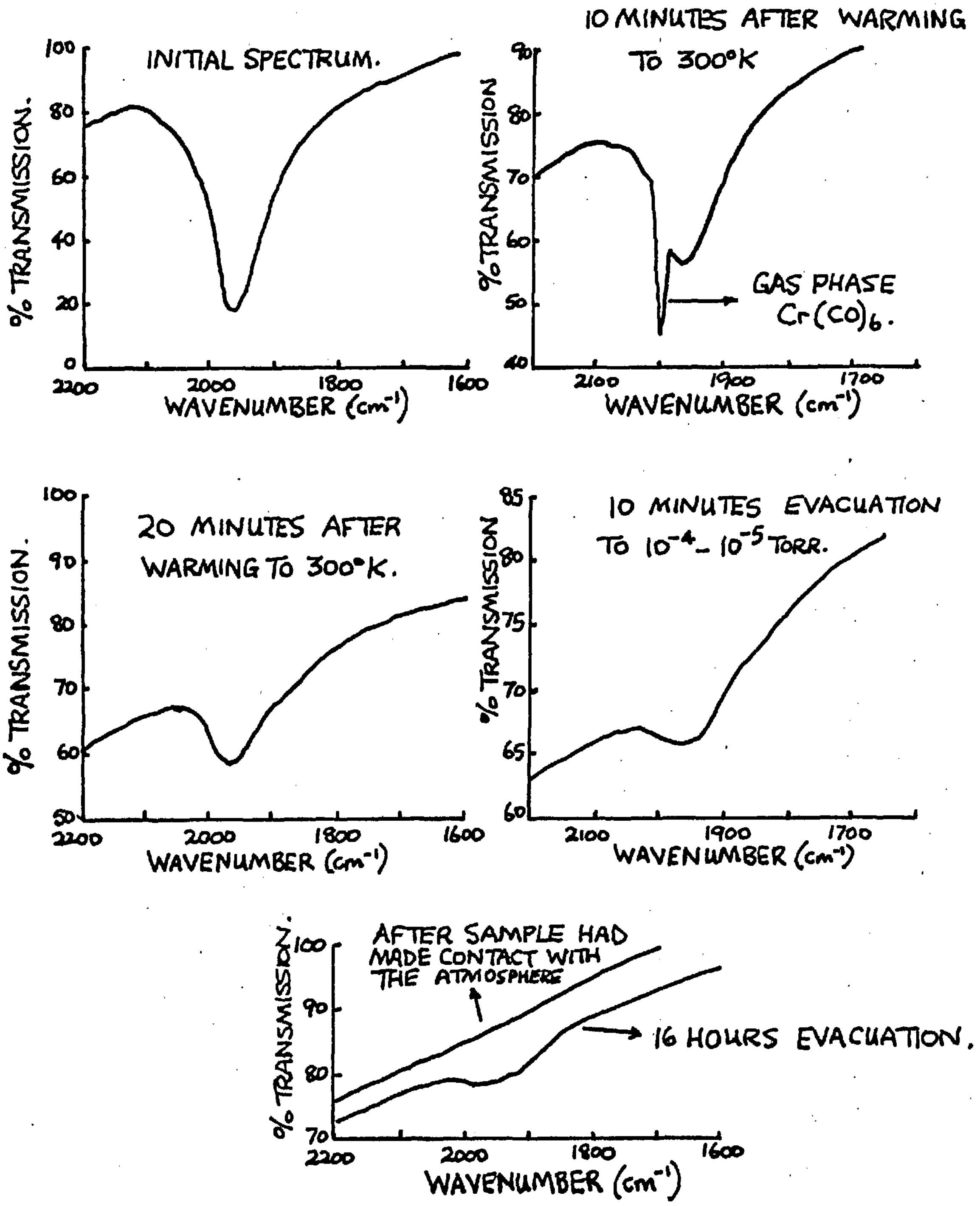
Cr films were deposited from a W filament onto which Cr had been electro-plated. Cr was electro-deposited from an aqueous solution (heated to 40°C) of CrO_3(250 gms/litre) and $Cr_2(So_4)_3$ (3 - 5 gms/litre) with the W wire as the cathode and Pb sheet as the anode. The filaments were outgassed for periods of 7 - 18 hours and film was deposited during this period.

Deposition in the presence of 2 torr of CO

The cell was not baked in these experiments. All the experiments gave consistent results. As figure 31 shows, a broad band, centred at 1960 - 1980 cm^{-1} was obtained when a spectrum was recorded immediately after the sample had been transferred to the infra-red cell. As the sample and the evaporator warmed to 300°K a very sharp band, centred at 2000 cm^{-1}, appeared in the spectrum. This was shown to be due to gas phase $Cr(CO)_6$. During the time that the sample was allowed to make contact with 2 torr of CO at 300°K the band at 1960 - 1980 cm^{-1} decreased in intensity and the $Cr(CO)_6$ disappeared, presumably by collection in the cold trap. The band due to $Cr(CO)_6$ could not be observed 20 minutes after the sample had warmed up to 300°K but the intensity of that at 1960 - 1980 cm^{-1} ceased to decrease after 2 hours. The transmission

FIGURE 31. Cr/CO.

DEPOSITION IN THE PRESENCE OF 2 TORR OF CO.



did decrease over this whole period but not by more than 10°/o. After this period, 10 minutes evacuation to 10^{-4} - 10^{-5} torr resulted in a decrease in the band intensity by a factor of approximately 0.5 but the intensity did not alter to any noticeable extent after a further 16 hours evacuation. The band was removed immediately upon contact with the atmosphere.

Discussion

The possibility that the observed band is due to solid $Cr(CO)_6$ is not considered to be likely. Unfortunately, it does not appear that anyone has measured the infra-red spectrum of this. However the data of Rezukhina and Shvyrev (62) indicates that the vapour pressure of $Cr(CO)_6$ is approximately 0.25 torr at 300°K and, so, $Cr(CO)_6$ should be quickly collected by the cold trap under the conditions of our experiment. Moreover, physically adsorbed $Cr(CO)_6$ should be removed by evacuation to 10^{-6} torr. It is not possible to convincingly equate the band that remains after evacuation with chemisorbed CO because of much the same reasons given when similar studies were considered for the Mn/CO system. It seems likely that it is due to some CO species which is linearly bonded to the Cr but whether this is in the form of some complex carbonyl or chemisorbed CO must remain undecided.

TITANIUM/CO

Ti films were deposited from 0.5 mm Ti wire. Of all the metals studied, Ti was the easiest to outgas. Very good background vacua were also obtained because Ti film deposited during outgas acted as a strong 'getter' of residual impurities.

No absorption bands were observed when the Ti/CO system was studied by the technique involving deposition in the presence of A followed by addition of CO. Likewise, depositions in the presence of CO gave no absorption bands.

Studies with vacuum-deposited Ti films were also unsuccessful. In an experiment where the Ti was outgassed to the background pressure of approximately 1.10^{-8} torr it was found that the sample, which transmitted 90°/o of the incident radiation at 2100 cm^{-1}, adsorbed only $6.5.10^{15}$ molecules of CO when this was added, dose-wise, to a final pressure of approximately 7.10^{-4} torr. The sample sintered slightly as it warmed to 300°K and approximately $1 - 2.10^{15}$ molecules of CO were desorbed. No bands were observed at any stage of the experiment. A different sample, which transmitted 40°/o of the incident radiation at 2100 cm^{-1}, adsorbed approximately 15.10^{15} molecules of CO whilst it was cooled to 78°K. Pressure measurements were not taken when the sample was warmed to $300^{\circ}K$ but, again, no absorption bands were observed.

Discussion

Failures to observe bands when film is deposited in the presence of A or CO do not, in themselves, mean very much. In the former case it could be that the metal particles which are produced are not small enough whilst in the case where film is deposited in the presence of CO, the CO could decompose as it makes contact with the hot Ti filament. However, the results obtained for vacuum evaporated films would indicate that the chemisorbed CO on Ti surfaces has a low extinction coefficient. The roughness factors for Ti films are not very high but they compare well with those obtained for Pt films and where these were studied a quite noticeable band was obtained.

THE HIGH MELTING POINT METALS (TANTALUM, MOLYBDENUM AND TUNGSTEN/CO

All these metals were deposited from the appropriate 0.3 mm wire. Unfortunately, no ionization gauge was attached to the cell during the course of these experiments but, in all cases, the cell was baked and film was deposited during the outgassing of the filament.

Deposition in the presence of CO

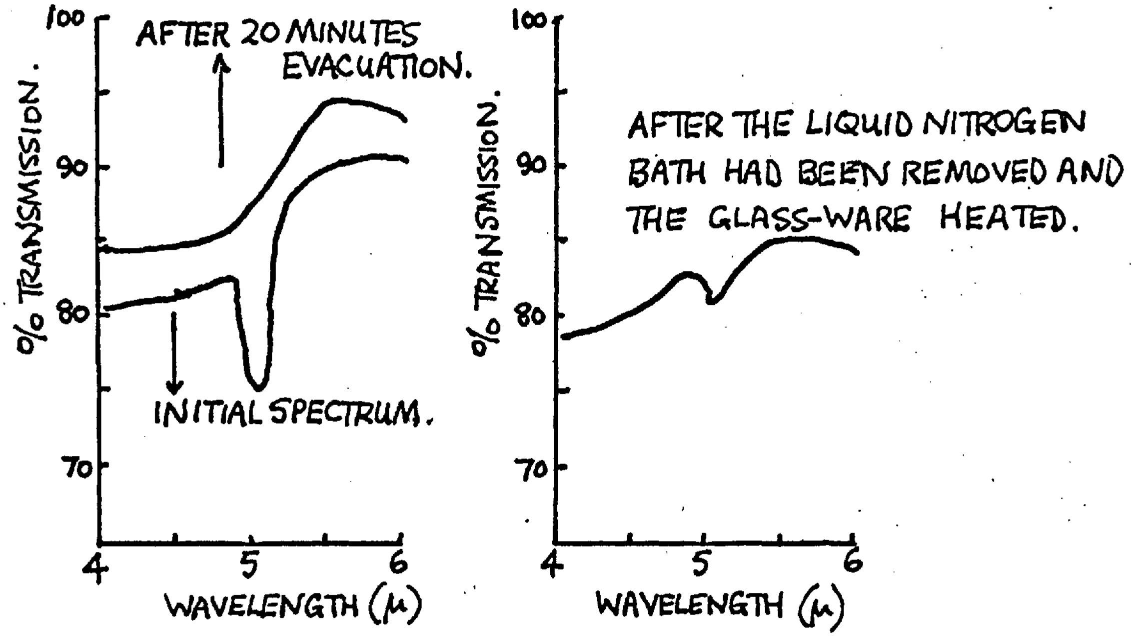
Experiments with Ta were unsuccessful. As Figure 32(a) shows, when W was deposited in the presence of 10^{-1} torr of CO one single band at 5.05 ± .03μ (1980 ± 10 cm^{-1}) was obtained. No gas phase absorption bands were found. The band at 5.05μ was not observed after 20 minutes evacuation and addition of 8 torr of CO did not lead to its return. However, when the liquid nitrogen trap was removed and the glass-ware heated it was observed, in diminished intensity, once more.

Discussion

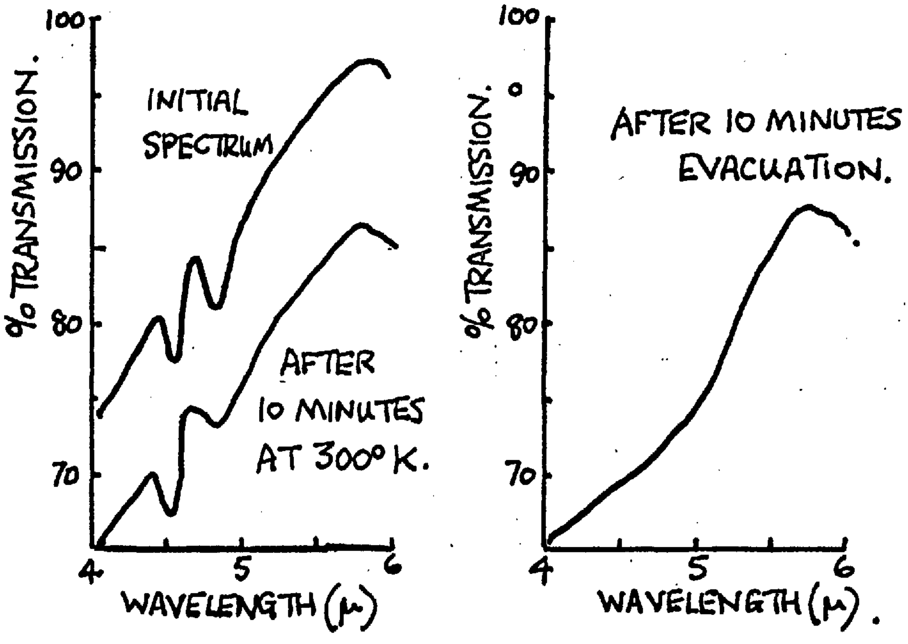
Using the F.E.M., Klein and Leder(63) have shown that chemisorbed CO decomposes on Ta surfaces when these are heated above 1300°K. It is possible, therefore, that CO decomposition leads to oxygen contamination which prevents the formation of chemisorbed CO on Ta.

FIGURE 32.

a/ W/CO. FILM DEPOSITED IN THE PRESENCE OF 10^{-1} TORR OF CO.



b/ Mo/CO. FILM DEPOSITED BY ION BOMBARDMENT. Kr/CO MIXTURE CONTAINING 1% CO WAS USED.



The band observed when the W/CO system is studied is undoubtedly due to solid $W(CO)_6$. The data of Rezukhina and Shvyrev (62) indicates that the vapour pressure of $W(CO)_6$ is approximately 6.10^{-3} torr at 300°K and, so, evacuation would be required to remove it from the MgO plate. Moreover, the spectrum in the region of 2000 cm^{-1} for solid $W(CO)_6$ is almost identical (64) to that obtained in this work. Failure to obtain a band due to adsorbed CO could be due to the inability to obtain small enough particles of metal; however, like the Ta/CO system, decomposition of the CO may play an important role.

Deposition in the presence of Kr and A

Such studies were carried out for the Ta/CO system only. Spectra were not very reproducible but it is probable that a very small band (approximately 1°/o absorption) was observed in the region of 4.8μ when Ta was deposited in the presence of 2 torr of Kr and 2 torr of CO was added to the film which was cooled to 78°K. No absorption bands could be observed after 20 minutes evacuation.

Discussion

The spectra obtained in these experiments were of poor quality but it is unlikely that chemisorbed CO was observed since Brennan and Hayes (4) have found that the heat of adsorption for CO on Ta films is 135 $kcal.mole^{-1}$.

Ion Bombardment by Kr and Kr/CO mixtures

Only the Mo/CO system was studied by this technique. No bands were observed when samples were prepared by ion bombardment with Kr. When samples were prepared with Kr/CO mixtures (containing about 1°/o CO) two absorption bands, centred at 4.55 ± .03μ (2200 ± 15 cm^{-1}) and 4.8 ± .03μ (2080 ± 15 cm^{-1}) were obtained (see Figure 32(b)). After deposition it was noted that the Mo filament was coated with carbon. Over a period of 10 minutes, as the sample warmed to 300°K, the intensity of the band at 4.8μ decreased and the band became broader. Both bands were removed by evacuating the system for 10 minutes.

Discussion

The band at 4.55μ is probably due to CO adsorbed on some type of oxide site since Eischens et al (23) have observed a similar band for CO on oxidised Ni surfaces. The oxygen contamination is likely to be due to decomposition of CO during the ion bombardment process. The nature of the species giving the band at 4.8μ is uncertain. Since the species are weakly bonded they cannot be related to chemisorbed CO.

General Discussion

The results are similar to those obtained for the Ti/CO system. It is likely that the surface area of the samples in these experiments is very small and this could account for the failure to obtain bands attributable to chemisorbed CO. Room must also be made for the possibility that the extinction coefficient for CO on Ta, Mo and W is small.

GENERAL DISCUSSION AND CONCLUSION

Sample Preparation adopted in this work

The results obtained when film was deposited in the presence of inert gas are disappointing in that the observed bands were small and, in most cases, the sample sintered on warming to room temperature and also when the system was evacuated. Even when the filament deposition temperature was reduced by using the ion bombardment technique the bands were still not very large. In the case of the sputtered samples it may be that the high velocities with which metal atoms are ejected from the filament play an important role in the eventual size of metal crystallite obtained. However, it seems likely that, in general, the inert gas is not bonded with sufficient strength, even at 78°K, to prevent the growth of large crystallites.

Usually, medium - large absorption bands are obtained when the sample is prepared by deposition in the presence of CO and, in appropriate cases, comparison with the results of other workers, who have used supported metal samples, shows that the initial spectra are similar. This is not definite proof that the same species are observed but it is a good indication. Unfortunately, desorption studies are not usually possible because, unlike supported samples, the films prepared in this manner sinter when the sample is evacuated. We note other shortcomings of the technique. Firstly, it is limited to those systems in which the gas does not decompose as it makes contact with the hot metal filament. Also, it would seem likely that, in limiting the particle size by deposition in CO, a sample is obtained in which the CO molecules are bonded to a particle containing only a very small number of metal atoms. If the number of metal atoms in a particle is less than 20 - 30 it is possible that the CO bonded to the metal will not have the same characteristics as that adsorbed on the surface of a film or filament. Since the spectra are so similar to those obtained with supported samples it seems possible that a good deal of the CO observed in these studies is held to very small metal particles.

Co-evaporation of metal and NaCl does not yield completely satisfactory results but these do provide useful information. CO bonded to metal in these samples does not have the same characteristics as CO bonded to metal films. This is possibly due to some inductive effect of the NaCl which alters the chemistry of the metal. It is not possible to give an exact mechanism for this. It has been found (10, 23) that CO species adsorbed on silica-supported Pt surfaces are very similar to those adsorbed on the surfaces of Pt films whereas CO species adsorbed on alumina-supported Rh (52) have been shown by us not to have the same properties as those adsorbed on Rh films. Experiments therefore indicate that the inductive effect varies, depending upon the type of support used.

The studies with vacuum evaporated films are potentially the most useful as far as elucidating the structure of CO species is concerned since the surfaces and the crystallites formed are more clearly defined. The major drawback is that the observed bands are small but this is off-set to some extent by the associated adsorption - desorption studies. The prepared films were very thin and it is in such cases that contamination risks are most serious. It is not felt that contamination was a very serious problem when the Rh/CO and Pt/CO systems were studied because it is very likely that CO displaces all likely contaminants from the surface. The problem is more serious for the other metals. However, apart from the Fe/CO system, it appears that the major contaminant in the system was Hg vapour. Thus, the surface should not be badly contaminated before CO is added and, since this is strongly bound, it probably displaces Hg from the surface. For the Fe/CO system the most prevalent impurity is either Co or O_2. However, in view of the adsorptive capacity of the samples it does not seem as though oxygen contamination can have been very serious.

The results obtained indicate that the substrate does not influence the chemistry of the metal to any great extent; CO on Rh and Pt films behaves as would be expected from other studies in which thick films have been deposited on glass. It is possible that inductive effects are important only when all of the metal particle is in close contact with the support and, even in this instance, the effect does not appear to be great when silica is used.

The Assignment of the bands

Assignments have been made, in the past, by comparing the spectra with those of metal carbonyls. This is a very tricky procedure because absorption bands for metal carbonyls in the region below 1960 cm^{-1} can arise from different mechanisms which are difficult to differentiate unless the structure of the compound is known. From the literature there is little doubt that bands obtained in the region 1970 - 2100 cm^{-1} for metal carbonyls are due to CO which is linearly bonded to a metal atom. It is the conviction of many workers (65, 66) that bands due to bridge bonded CO species are found in the region 1900 - 1750 cm^{-1}. However, complications arise in that Cotton and Kraihanzel (18) have found that, in certain circumstances, linear bonded CO species can give bands as low as 1800 cm^{-1}. The matter is made more complex by the recent finding (67) that the compound $Rh_6(CO)_{16}$ contains a grouping with three Rh atoms in contact with one CO molecule. It is believed (65) that the C - O stretching mode of this type of species gives a band in the region 1800 - 1700 cm^{-1}. Furthermore, Cotton et al (59) have found that, for a range of cyclopentadienyl carbonyl complexes, two bands in the region 2000 - 2050 cm^{-1} and 1920 - 1960cm^{-1} are found. They consider that these bands are due to the coupling of two CO molecules bonded to the same metal atom. These are only some of the factors which can influence the spectra; the problems are even more multiplied for surface species since other work cannot give a complete picture of the structure of the complex.

In most instances, data for surface CO complexes is available for the C - O stretching vibration only. In cases where the metal - C stretching frequency has been studied (26) surfaces of very doubtful quality have been used but these indicate that the metal - C bond is somewhat different from that in carbonyls. We feel that the assumption that the metal - C bond in surface complexes is similar to that in carbonyls is dubious. All it is possible to say from our data is that the electron distribution in the C - O bond is affected in some way which MAY be similar to that in carbonyls. In the case of the low frequency band there are then several choices as to how this may occur.

The problem would seem, at the outset, to be easiest when bands in the region 2100 - 1980 cm^{-1} are obtained. By comparison with carbonyl spectra CO species on Pt surfaces should be linearly bonded to a surface Pt atom. However, other chemisorption studies conflict with this view. The surface area studies of Brennan and Hayes (4) indicate that CO molecules on Pt surfaces are each associated with two Pt atoms and the electron diffraction studies of Tucker (68) show a similar conclusion. Objections can be made to both these techniques and, so, no definite judgement can be made. The spectroscopic evidence certainly indicates that a conventional bridge-type bond as found in carbonyls is not possible but there may be some kind of multi-centre bond involving two Pt atoms and the CO.

We do not believe it possible to present a complete picture on the variation of bond strength with band position. Obviously, this will arise but the very fact that strongly held Pt - CO complexes give a band at 2085 cm^{-1} whilst weakly held Pd - CO complexes give a band at 2100cm^{-1} means that it is not possible to get an accurate picture on this basis. The observation of a band at 2120 cm^{-1} (43) corresponding to strongly held CO on oxidised Pt surfaces further exemplifies this point.

In the few instances where absorption bands below 1980 cm^{-1} indicate a strongly bound species care must be exercised in the interpretation. Allowing that bridge bonding involving localised bonds can exist it is seriously doubted that a C - O stretching frequency greater than 1900 cm^{-1} could be obtained. In $Fe_2(CO)_9$ the metal - C - metal bond angle of the bridge bonded CO is 87° (69) and the band due to this group centres at 1829 cm^{-1} (59). More strain could be tolerated in the bond angle on metal surfaces but it is doubtful whether frequencies greater than 1900 cm^{-1} could be obtained, especially as the model calculations of Halford (70) predict a high frequency shift of approximately 50 cm^{-1} in changing the bond angle from 90° to 60°. Bands between 1900 - 1980 cm^{-1} which are associated with strongly held species could be similar in nature to those at higher frequencies as is visualised in the Blyholder model. It may be that his model gives a too simplified picture of the part that surface metal orbitals play but since heat data (4) shows that CO is strongly bonded to metal surfaces it seems likely that some type of back donation into the π anti-bonding orbitals of the CO occurs. It does not seem unreasonable to suppose that the type and extent of back donation could alter from metal to metal and, also, with surface coverage. Bands at frequencies less than 1900 cm^{-1}, which correspond to strongly bound species, could arise from a similar mechanism but, here, interpretation is exceedingly difficult as bridge bonded CO species are also possible. Furthermore, with silica-supported samples, possible enhancement of the Si - O combination mode complicates matters.

The exact nature of weakly held species which give bands below 1960 - 1970 cm^{-1} must remain uncertain. The possibility that such bands in the region above 1900 cm^{-1} could be due to bridge bonded CO species which are under a great deal of strain cannot be totally excluded but, in view of other spectroscopic evidence, this seems remote. It may be that such bands are caused by the coupling of two CO molecules attached to one metal atom. Such species would be found only on atomically rough regions of the surface.

A comparison of the results for all the metal/CO systems

One of the immediate points to come from the results is that the extinction coefficient of the C - O bond varies quite markedly from metal to metal. Since the extinction coefficient is a function of the dipole moment change with vibrational coordinate this would indicate that the bonding of CO does vary from metal to metal. As the heat data of Brennan and Hayes (4) shows, this is not a surprising conclusion when the Ti/CO and Pt/CO systems are compared.

However, their data would indicate that the bonding of CO on the metals Fe, Ni, Pd, Pt and Rh is not much altered whereas our results show that the latter two metals give marked differences.

It is difficult to rationalise the results obtained with Fe, Ni, Pd, Pt and Rh in this work. From the heat data it would seem unjustified to suggest that CO chemisorption on Fe, Ni and Pd is mainly dissociative; the same objection is applied to the theory that both the C and O atoms are held to the metal.

It is thought (8) that the bonding energy of adsorbed CO depends upon the crystal plane on which it is held. If such circumstances hold true then the heat value obtained will depend upon the structure of the film because adsorbed CO is immobile and each addition of gas probably fills an equivalent patch of the surface. It is tempting, therefore, to try to analyse the differences in our results in terms of sample structure. A greater difference would, perhaps, be expected from metal to metal in our samples because the films are thin.

Our experimental evidence shows that Pd, Fe and Ni films sinter on warming from 78°K to 300°K whereas Rh films sinter to only a slight degree. Thus, the possibility is entertained that the CO on atomically rough regions of the surface has the highest extinction coefficient. However, this model cannot be taken so seriously as there are numerous objections. Firstly, although Fe, Ni and Pd samples sinter, the experiments show that the stable films at 300°K are quite rough. There should still be a fair amount of 'hill and valley' structure in these samples at 300°K. Furthermore, Pt films of low roughness factor show quite noticeable bands. On this model, one would have to assume that some of the CO on the surface has a low extinction coefficient. Our calculated value of integrated absorption intensity is 340 litre.cm^{-2}.mole^{-1} when it is assumed that all the CO is contributing equally to the band. This value is probably not very accurate but we compare it with the value of 199.10^{3} litre.cm^{-2} mole^{-1} for $Cr(CO)_6$ obtained by Jones (50). Even when all the CO molecules are considered, the B value is high; very little data for B values of carbonyls is available but it may be that a bigger value than that obtained would be unrealistic.

The only other conclusion we can reach is that, despite the heat data, the bonding of CO on Rh and Pt surfaces is different from that on Fe, Pd and Ni surfaces. There is little to back up this idea. However, the maximum surface potential (S.P.) for the Pd/CO system is -0.84 volts (43) and for the Fe/CO and Ni/CO systems it is -1.68 volts and -1.38 volts respectively (9). For

Pt/CO the maximum S.P. is 0.0 ± .01 volts. Even though polycrystalline films were used in all the studies these results would indicate that the metal - C and C - O dipoles in the Pt - CO complex are quite different from those of the other systems. It is not possible to give values for the C - O dipole moment in these complexes but it may be that they are such as to account for the differences in the B and K values for the various systems. It is not clear why Rh and Pt should behave so differently. It is known that the Rh/O_2 and Pt/O_2 systems show differences from the Ni/O_2 and Fe/O_2 systems but Pd/O_2 is very similar to the two first mentioned. However, it would appear that there is some intricate change in the chemistry of Rh and Pt, compared with that of Fe, Ni and Pd, which accounts for the observed behaviour when CO is the adsorbate.

The nature of the bands observed with the Fe/CO, Ni/CO and Pd/CO systems is now considered. The fact that these bands broaden as the sample warms to 300°K would indicate that they are associated with some species adsorbed on atomically rough regions of the surface. The evidence shows that the band observed with the Fe/CO system is due to weakly held species and this may be so for the Pd/CO and Ni/CO systems. Thus, in the text, the possibility has been mentioned that these bands could be caused by two CO molecules attached to one metal atom. With such a species, coupling is possible and two bands should be obtained. This is observed for the Ni/CO system but not for the others. It could be that the shift produced in these other systems is small and that, since the bands are broad, resolution is not possible. However, we consider another model in which the weakly held CO is held in the 'gaps' between strongly held CO. Once more, coupling could occur but, since the molecules in this structure would be parallel to one another, only the in-phase vibration would be observed. A similar model, applied to the Rh/CO system, would explain the decrease in intensity of the band when the weakly held species is removed. For Pt/CO the surface area of the sample is small and this could account for the failure to observe similar behaviour. Such weakly held CO should bond on crystal planes where the repulsive forces between adjoining CO molecules are least and this could account for the broadening of the band. In view of the poor nature of the spectra for the Ni/CO and Pd/CO systems the assignment cannot be cleared up. However, the latter argument gives a more general picture.

Final Conclusion

It is disappointing that we cannot be more dogmatic in our explanation of the results. Some of the arguments given in the text are speculative with little evidence to back them up but, to the author, they seem the best available since alternative models are poor. It is felt that uncertainty will continue to exist in this type of study until:

1. It is possible to obtain larger absorption bands with reasonably well-defined samples such as vacuum evaporated films. We believe it is possible that other workers have obtained bands attributable to strongly bound CO on Fe, Pd and Ni surfaces. However, it is aubdantly clear that much weakly held CO is also held on these samples. Owing to their preparation, it is probable that supported samples do not bear as much resemblance in structure to films and filaments as would be desired.
2. The structure of any sample studied is known in more detail.
3. The spectral data is backed up with other chemisorption studies which indicate the true environment of the chemisorbed molecule.
4. General theoretical understanding of the part that metal orbitals play in the bonding of surface complexes is improved.

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