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THE ADSORPTION OF CARBON MONOXIDE ON EVAPORATED METAL FILMS

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CONTENTS

Calorimetric measurements at 0 °C. have been made of the heats of adsorption of carbon monoxide on evaporated films of iron, cobalt, nickel, manganese, titanium, molybdenum, tungsten, tantalum, niobium, zirconium, platinum, palladium and rhodium. The variation of the heat of adsorption with coverage is considered in terms of a precursor state whose energy determines the form of the variation. For the adsorption on tungsten, the present results and heat values calculated from data derived from flash filament desorption studies show encouraging similarities, but comparison with results from field emission microscopy is disappointing. Theoretical calculations of heats of adsorption have been criticized with special reference to carbon monoxide adsorption. Attention is again drawn to the linear dependence of heat of adsorption on metallic radius.

Saturation coverages of carbon monoxide and monolayer values for krypton before and after chemisorption are reported. In an attempt to interpret these values, possible configurations of adsorbed carbon monoxide are considered for all the metals. Simple restrictions relating to (i) the form of bonding, namely linear or bridge, (ii) the M—C bond length and the M—C—M

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bond angle, (iii) the number of bonds in which any one metal atom can participate, (iv) the form of the potential energy of interaction energy between neighbours, and (v) the krypton monolayer concentrations as deduced in the preceding paper, are applied in arriving at maximum coverages for the various regular arrangements of admolecules which are conceivable. For titanium and zirconium, the experimental coverages are readily accounted for by these means, with the conclusion that carbon monoxide is held by a bridge bond with each metal surface atom able to participate in only one bridge. For the face-centred cubic metals, similar conclusions are compatible with the experimental results, although they are not so well founded as for the hexagonal, close packed metals. The difficulties of applying the discussion to the body-centred cubic metals are also considered.

Arguments are presented which cast doubt on the view that the reduction in the adsorption of krypton after chemisorption is the result of sintering of the metal film owing to the liberation of the heat of adsorption. An alternative explanation in terms of a redistribution of sites for the adsorption of krypton due to the presence of the chemisorbed layer is examined and found to be inadequate in the simple form used.

INTRODUCTION

The adsorption of carbon monoxide on metals has been the subject of a large number of investigations and, in particular, there is now some measure of agreement on the salient features of the adsorbed state on tungsten. Flash filament studies and field emission microscopy both provide evidence for the existence of a number of states of adsorption, and infra-red spectroscopy of the adsorbed state further suggests the existence of different states of binding of the adsorbate. The properties and distribution of these various states depend on the adsorbent and its history, and there remains also the problem of whether different techniques examine the same states of the adsorbate so as to permit direct comparison of the various findings. Additionally, there is the problem of describing these states in chemical terms. Carbon monoxide has been postulated to be held on the surface either by a bridge bond involving two surface metal atoms, or by a linear bond involving only one surface metal atom. More complex configurations involving both types of bonding at a metal atom have also been suggested. Again, different states of binding have been associated with adsorption on different crystal faces. The object of the present investigation has been to obtain reliable data for the energetics of the adsorbed state and for the surface concentration of the adsorbate for several metals with a view to correlating behaviour in the knowledge of recent work and discerning patterns of behaviour which may themselves throw fresh light on these problems.

EXPERIMENTAL

The Beeck type calorimeter, its mode of operation and general experimental procedures are as already described (Brennan & Hayes 1964).

Carbon monoxide was obtained from the National Chemical Laboratory in break-seal ampoules, and was 99·9 % pure.

RESULTS

The calorimetric results are presented in figures 1 and 2; each point corresponds on the coverage scale to the mean coverage due to a gas increment. The parameter p is defined by the relation

$$p = N(\mathrm{CO})/N(\mathrm{Kr}),$$

where $N(\mathrm{CO})$ is the number of carbon monoxide molecules adsorbed by the clean surface at 0 °C, and $N(\mathrm{Kr})$ is the number of krypton atoms in a monolayer adsorbed on the clean surface at 77 °K. For several of the metals, measurements have been made on very small doses to ascertain whether the heat of adsorption is different at low coverage. The high initial heat for tungsten is in marked contrast to the findings for the other metals, on which carbon monoxide is adsorbed initially with a heat which is not significantly different from that at 10% coverage. Two sets of measurements on small doses were made with tungsten and both gave this distinctive result. It would seem that the profile of the graph of heat

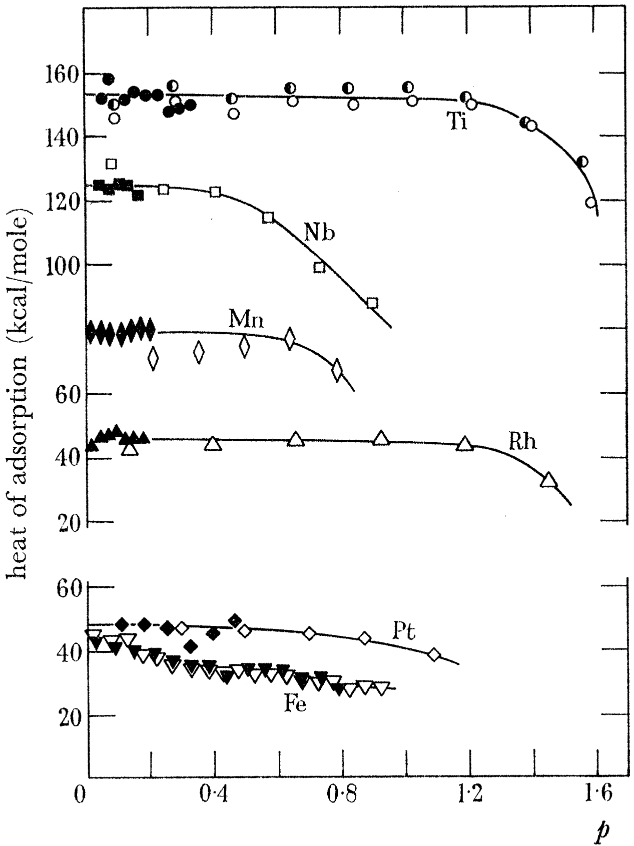

FIGURE 1

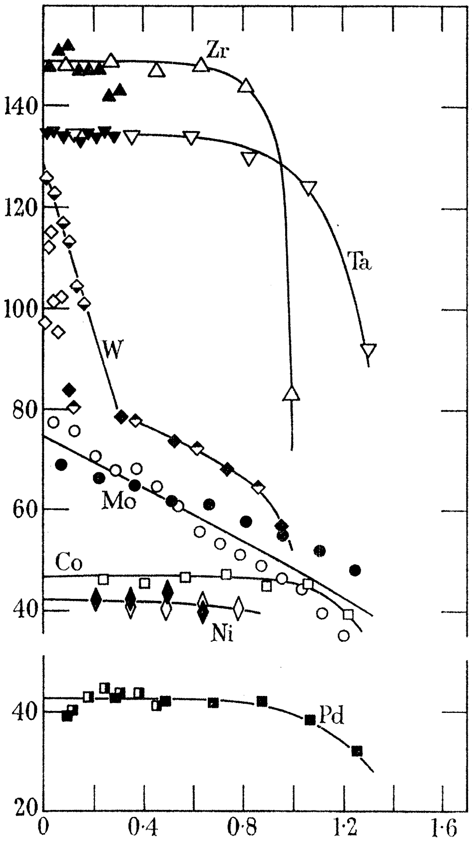

FIGURE 2

FIGURE 1. The variation of the heat of adsorption of carbon monoxide with surface coverage for titanium (○, 36·3 mg; ◐, 31·8 mg; ●, 29·9 mg; 150 kcal/mole), niobium (■, 17·5 mg; □, 11·3 mg; 116 kcal/mole), manganese (⧫, 26·4 mg; ◊, 31·6 mg; 76 kcal/mole), rhodium (▲, 36·0 mg; △, 16·6 mg; 44 kcal/mole), platinum (◆, 26·3 mg; ◇, 32·3 mg; 44 kcal/mole) and iron (▽, 37·9 mg; ▼, 18·7 mg; 35 kcal/mole).

The numbers in parenthesis are the film weights and the average integral heats of adsorption, respectively.

Manganese films were prepared from thoroughly outgassed chips indirectly heated by tungsten and were believed to be clean. A value of $N(\mathrm{Kr})$ is not available for this surface and the points in the figure have been derived from the data of Brennan *et al.* (1960).

FIGURE 2. The variation of the heat of adsorption of carbon monoxide with surface coverage for zirconium (▲, 16·0 mg; △, 10·8 mg; 148 kcal/mole), tantalum (▼, 25·1 mg; ▽, 21·2 mg; 128 kcal/mole), tungsten (◇, 34·5 mg; ⬙, 26·4 mg; ⬘, 30·4 mg; ◆, 28·3 mg; 80 kcal/mole), molybdenum (●, 38·5 mg; ○, 28·5 mg; 60 kcal/mole), cobalt (□, 18·7 mg; 46 kcal/mole), nickel (⧫, 39·7 mg; ◊, 39·0 mg; 40 kcal/mole) and palladium (■, 45·4 mg; ◧, 48·2 mg; 40 kcal/mole).

against coverage for tungsten is initially dependent on the dose size and this could be related to the distribution of adsorbate within the film being a function of dose size. This problem will be a referred to again, but it is noted here that, in general, there will be a non-uniform distribution of adsorbate over the available surface. Consequently, the coverage axes in figures 1 and 2 represent arbitrary scales and do not provide a valid measure of surface concentration except at saturation. In table 1 are summarized the saturation capacities of the various surfaces for carbon monoxide and the influence of adsorbed carbon monoxide in reducing the monolayer capacity of the surface for krypton. The parameter q is defined by the relation

$$q = N(\mathrm{Kr/CO})/N(\mathrm{Kr}),$$

where $N(\mathrm{Kr/CO})$ is the number of krypton atoms adsorbed in the monolayer at 77 °K on the surface saturated with carbon monoxide at 0 °C.

TABLE 1. SATURATION COVERAGES* FOR CARBON MONOXIDE ON THE METALS AND THE EFFECT OF ADSORBED CARBON MONOXIDE ON THE MONOLAYER CAPACITY OF THE SURFACES FOR KRYPTON

metal	weight of film (mg)	monolayer value for krypton; carbon monoxide adsorption (10^{-5} mole) before	after	carbon monoxide adsorbed at saturation (10^{-5} mole)	p	q
Co	37·1	0·144	0·072	0·183	1·27	0·50
Ni	32·1	0·139	0·072	0·138	0·99	0·52
Pt	29·7	0·094	—	0·139	1·48	—
Rh	17·4	0·274	0·153	0·402	1·47	0·56
Pd	48·9	0·112	0·067	0·141	1·27	0·60
Fe	27·6	0·421	0·344	0·508	1·21	0·182
Mo	36·7	1·50	1·13	2·02	1·34	0·75
W	22·6	0·57	0·46	0·64	1·13	0·81
Ta	7·8	0·144	0·144	0·215	1·49	1·00
Nb	9·8	0·191	0·154	0·246	1·29	0·81
Ti	22·4	0·344	0·232	0·609	1·77	0·68
Zr	16·6	0·192	0·159	0·900	1·05	0·83

DISCUSSION

Variation of the heat of adsorption with coverage

The graphs of figures 1 and 2 exhibit three distinct kinds of dependence of heat of adsorption on coverage:

(1) The heat of adsorption remains quite constant, within the limits of experimental error, until a critical coverage is reached, when the heat falls sharply.

(2) The heat falls initially, or at a very low coverage, and continues to do so steadily until the saturation coverage is reached, when it falls sharply.

(3) The heat falls rapidly initially, and thereafter falls continuously but less rapidly with increasing coverage until the cut-off value is reached. Tungsten is the only metal which exhibits this behaviour.

The shape of the curve of heat against coverage for these systems is influenced by a variety of factors, none of which can as yet be discussed in quantitative terms. However,

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* The term 'saturation coverage' here denotes the adsorption after exposure of the film for 5 min to a pressure of carbon monoxide of about 10^{-5} torr.

some useful deductions can be made by consideration of limiting cases. The first point which can be clearly established is that these adsorbed layers are in a metastable condition. There is no possibility of equilibrium being established by transport of adsorbate via the gas phase. The possibility that adsorbate molecules might minimize the free energy of the system by exploration of the available sites through surface diffusion can also be discounted. Field emission microscopy (Gomer 1959) has shown that the activation energy for surface diffusion of carbon monoxide on tungsten is about 0·7 of the energy of desorption, and a general discussion of the relation between activation energies of diffusion and desorption indicates that this factor will very probably apply also to other metals. Hence, even for the metals which adsorb carbon monoxide least strongly, the activation energy for diffusion of adsorbed molecules is too great to permit appreciable mobility at 0 °C. Again, there is no evidence from the present work that the dependence of heat of adsorption on coverage can be related to the strength of adsorption. The distribution of adsorbate in all these cases, therefore, is determined by kinetic, not thermodynamic, considerations.

Unfortunately, most of the experimental work available on the kinetics of the adsorption step relates to surfaces directly exposed to the gas phase, whereas for films, the adsorption process is dominated by the interior as opposed to the exterior surface. Thus, for the high area films, for example tungsten, molybdenum and zirconium, the roughness factor is of the order of 100 for films of the weight employed in this work, while even for the low area films, for example, platinum, palladium and nickel, it is greater than 10. It has been shown recently (Brennan & Jackson 1963), that, for a given geometry of reaction vessel and mode of gas admission, the form of the distribution of adsorbate within the film can vary between two limiting cases, depending on the metal. The adsorption of oxygen on a tungsten film was found to take place initially with a concentration distribution which decayed along the axis of the cylindrical adsorption vessel in the direction away from the gas inlet; this type of adsorption is referred to as ‘banding’. In contrast, oxygen adsorbed on nickel, in the same apparatus, gave a constant concentration along the entire length of the tube, apart from the very first stages of the adsorption. In this case, it is believed that, for successive doses, the adsorbate is located in annular sections of the film of constant thickness; this type of behaviour is referred to as ‘layering’. While it is useful to have this direct confirmation of earlier indirect deductions (Brennan, Hayward & Trapnell 1960) that both banding and layering of the adsorbate can occur, there is as yet no experimental evidence available for carbon monoxide adsorptions, though presumably a similar range of behaviour will be exhibited by these systems also. Having concluded that each increment of gas is adsorbed on a restricted portion of the available surface, we will now consider each of the special cases listed above.

1. *Invariant heat of adsorption*

Ehrlich (1962) has considered, with reference to the adsorption of nitrogen on tungsten, the special requirements for the heat of adsorption to be independent of coverage; these are as follows:

(i) The adsorbing surface is entirely uniform and there are no lateral interactions within the adsorbed layer.

(ii) Interactions between adsorbed species are negligible and the adsorption process occurs at the same rate on all available sites; these sites may, however, differ in binding energy.

(iii) Consecutive additions of gas to the surface completely fill equivalent patches of the surface.

(iv) Adsorption occurs preferentially at certain sites, but the binding energy does not vary from site to site.

(v) The rate of adsorption, the energy of interaction within the adsorbed layer, as well as the strength of binding to the lattice, vary from site to site, but in such a fashion as to compensate.

Condition (i) can be rejected on the grounds that these surfaces are certainly not uniform and condition (ii) is discounted because of the experimental observations that the different adsorption states of carbon monoxide on a tungsten filament are formed at different rates and that, in general, the distribution of adsorbate within a film will not be uniform. Condition (v) is rejected on the grounds that, as a special case, it could scarcely be met with so often as the frequency of this kind of behaviour would require. Ehrlich preferred condition (iv) to account for the constancy of the heat of adsorption of nitrogen both on tungsten filaments and films, and his arguments for doing so might well be tenable in that case. However, we do not regard this description of the adsorption as being generally valid, although it has to be admitted that, even for carbon monoxide, there is some evidence (Redhead 1961) that although the different states of adsorption have different energies, the energy of any one state is independent of coverage. Only condition (iii), which was first proposed by Beeck (1950*a*, *b*) to account for an invariant heat of adsorption, seems applicable to the wide variety of systems which exhibit this behaviour; examples, besides the adsorption of carbon monoxide, include carbon dioxide and oxygen adsorbed on a variety of metals at room temperature and hydrogen on metals at sufficiently low temperatures. Hydrogen adsorption (Brennan & Hayes 1964) is particularly instructive. At room temperature, the heat of adsorption of hydrogen on tungsten and nickel falls with increasing coverage and this is readily explained in terms of a mobile adsorbed layer. For adsorption on both these metals at −183 °C, the heat is independent of coverage. This observation is explicable in terms of a mobile precursor state transforming to the final chemisorbed state when it meets the edge of the previously chemisorbed layer, which is immobile at the lower temperature. In this way, the chemisorbed layer, as it extends across the metal surface, is always maintained at a coverage the same as or near to, the saturation coverage, and the heat observed is in fact the integral heat. These examples are important because they clearly demonstrate the ability of an adsorbed layer, known to be subject to substantial internal interactions, to be formed with an energy independent of coverage. Objection has been made to this description of the adsorption (Ehrlich 1962) on the grounds that Beeck (1950*a*, *b*) reported a heat of adsorption of hydrogen on nickel at −183 °C which fell with increasing coverage; the correction of this result (Brennan & Hayes 1964) removes this objection. We believe that this description can be applied to all those adsorptions which exhibit an constant heat over a wide range of coverage. There is much evidence for the existence of weakly held chemisorbed states at high coverages (Mignolet 1950, 1957; Sachtler & Dorgelo 1958), but it is not immediately obvious why the whole of a species held in such a state should become bound at the edge of the chemisorbed layer, regardless of the natures of the chemisorbed states which it enters. Any differentiation between states at this step would still lead to a heat which was a function of coverage. However, an analogous process has been observed with the field emission microscope. (Gomer & Hulm 1957; Gomer, Wortman & Lundy 1957; Gomer 1958) when physically held adsorbate precipitates at the boundary of the clean surface with the chemisorbed layer, which consequently maintains a sharp front as it increases in area. The mobile precursor states for the various adsorptions which are the subject of this discussion cannot, of course, be identified with a physisorbed state of the kind observed in the field emission experiments, but it is not difficult to imagine weakly chemisorbed precursor states having similar properties in respect of precipitation at the boundary of the chemisorbed layer.

2. *Diminishing heat of adsorption with increasing coverage*

If the precursor state is only very weakly held, its concentration and the period of residence of an adsorbate molecule in such a state prior to re-evaporation will both be small. In these circumstances, chemisorption on the internal area of the film will not be restricted to the boundary of the chemisorbed layer with the clean surface, but will occur also from the gas phase in a manner similar to the adsorption on the outer surface of the film. Even so, the gas will not be able to penetrate far into the film before re-adsorption, either into a precursor state or into a chemisorbed state, because the sticking efficiencies for both processes are high. However, adsorption will no longer result in a saturated chemisorbed layer with a sharp boundary. Succeeding increments of adsorbate will be adsorbed partly in filling some of the sites of relatively low sticking coefficient available in the existing chemisorbed layer and partly on fresh metal both in the vicinity of the boundary of the chemisorbed layer and at some distance from the boundary. The heat of adsorption will be greater, initially, than the integral heat, provided the higher sticking efficiencies can be associated with the sites of higher energy. The difference between the two quantities and the rate of decrease in the heat of adsorption will thus depend on the energy of the precursor state, which is the parameter determining the diffuseness of the boundary between the adsorbed layer and the clean surface. This hypothesis is capable therefore, of accounting for the varying degrees of slope of the heat versus coverage plots of figures of this paper, and similar plots in other publications.

3. *Tungsten*

The adsorption of carbon monoxide has been studied by Gomer (1959) and Klein (1959), using field emission microscopy, and by Ehrlich (1961) and Redhead (1961) who followed the kinetics of the desorption from filaments. There is considerable agreement between these complimentary studies. All agree that carbon monoxide exists on tungsten in a weakly bound α state and more strongly held β states, of which there are three distinct kinds. The energies variously reported for these states are summarized in table 2. The long desorption times used by Redhead prevented his determining the populations of each kind of state owing to transfer between states during desorption. The much shorter desorption times employed by Ehrlich minimized this difficulty and in table 3 are given the populations estimated by Ehrlich at the various stages of the adsorption on the polycrystalline filament employed. These figures cannot be very accurate, but they are probably good enough to permit a realistic calculation of the integral and differential heats of adsorption for this surface as a function of coverage. The results of these calculations are given in table 3 and figure 3 as derived from the energies of the various states given in table 2.

TABLE 2. COMPARISON OF THE REPORTED ENERGIES FOR THE ADSORBED STATES OF CARBON MONOXIDE ON TUNGSTEN

	desorption energies of the various states (kcal/mole)			
source	α	β_1	β_2	β_3
Ehrlich (1961)	20	53	75	100
Redhead (1961)	29	59	70	76
Gomer (1959)	—	52	—	90
Klein (1959)	12	53	—	—
values used for table 3 and figure 3	20	50	75	100

TABLE 3. INTEGRAL AND DIFFERENTIAL HEATS OF ADSORPTION OF CARBON MONOXIDE ON A POLYCRYSTALLINE FILAMENT CALCULATED FROM THE STATE POPULATION AT 336 °K DERIVED FROM THE DATA OF EHRLICH (1961) AND THE ENERGIES GIVEN IN TABLE 2

total number of adsorbed molecules ($10^{12}/cm^2$)	state populations (10^{12} molecules cm^{-2})				heat of adsorption (kcal/mole)	
	α	β_1	β_2	β_3	integral	differential
50			25	25	88	85
100			55	45	86	80
150			95	55	84	78
200			140	60	83	69
250		18	170	62	79	58
300		57	180	63	76	51
362	15	90	190	67	71	50
440	35	135	200	70	67	36
530	80	180	200	70	62	

In figure 3, the number of carbon monoxide molecules adsorbed per unit of available area of film has been calculated from a value of 18·5 Å^2 for the effective cross-sectional area of krypton on tungsten, derived from the assumption of equal areas of 100, 110 and 211 planes and configurations of krypton adsorbed thereon as detailed in figure 8*A*, *B*, and *D*, and table 4 of the preceding paper. Setting aside, for the moment, the very high heats obtained in this work for the smallest gas increments, it is gratifying that the results of Ehrlich, and those of Swanson & Gomer (1961, 1963) obtained with the field emission microscope, agree well with the present results at low coverages. Strictly, according to the discussion under §2 above, the present plot of heat of adsorption versus coverage and the plot of integral heat derived from Ehrlich's data should cross, but their failure to do so cannot be regarded too seriously in view of the difficulties inherent in this kind of comparison. The fact that the two plots remain in the same vicinity over the full coverage range is remarkable enough, remembering the very different origins of the two sets of data. However, it is very difficult to understand why the points of Swanson & Gomer should also so clearly follow the profile of these plots. Swanson & Gomer obtained their energies from the kinetics of desorption of carbon monoxide from a tungsten point at decreasing coverage, and, therefore, a differential heat comparable to the differential heat derived from Ehrlich's data might have been expected from their investigation. Apart from the technical difficulties and limitations involved, the desorption experiment carried out in this way could yield results which appear anomalous because it is essentially a different kind of experiment to the coverage experiments reported here and by Ehrlich. It is notable that similar measurements with the field emission microscope to determine the energetics of adsorbed hydrogen on tungsten also give unexpected results (Brennan & Hayes 1964).

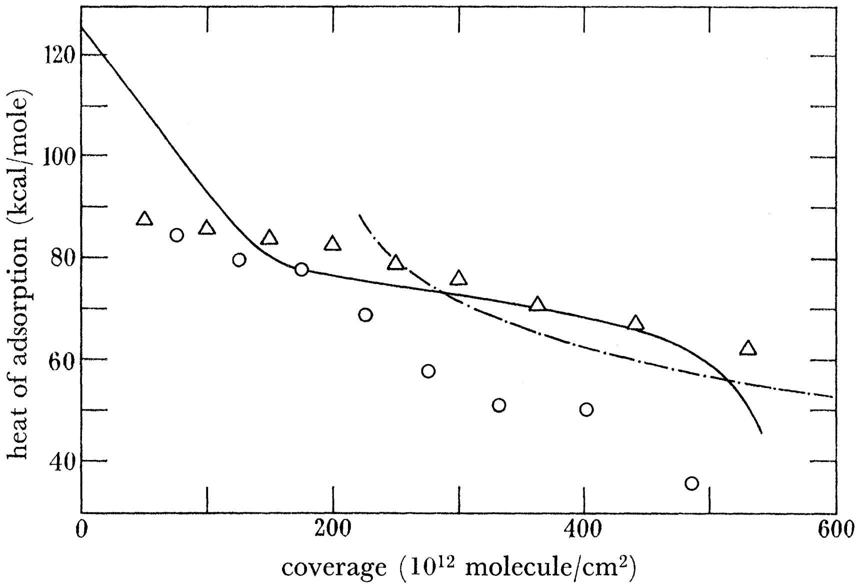

FIGURE 3. Comparison of the heats of adsorption of carbon monoxide on tungsten, as a function of coverage (see text), derived from different experimental methods; —— the present results; △, ○, the integral and differential heats from flash filament desorption studies (Ehrlich 1961); ·—·—, the differential heats from field emission microscopy (Gomer & Swanson 1961).

The very high heats obtained with tungsten when carbon monoxide is admitted to the film in small doses are exceptional and difficult to account for. There can be little doubt that these results are real and do not arise from an artefact. The possibility that part of each dose is being held in the cold traps can be eliminated on the grounds of the calibration experiments and the fact that such an effect would lead to anomalously low heats. Further, the possibility that some systematic error of calorimetric origin is present can also be disregarded because it would manifest itself in the case of the other metals, which, however, do not exhibit this behaviour. Exceptionally high heats are obtained at coverages which imply considerable penetration of adsorbate into the interstices of the film and the ability to select sites of high energy preferentially would seem to be a function of dose size. Why tungsten should be so exceptional in this respect and differ so markedly from such a close congener as molybdenum is not understood.

Correlations of heats of adsorption

1. *Calculations based on the properties of related bonds*

Two common methods of calculating heats of adsorption from atomic properties and the properties of the bulk metal are those due to Eley (1950) and Higuchi, Ree & Eyring

(1957). Because both these methods have been applied to carbon monoxide adsorbed on metals, and because the methods are frequently referred to in adsorption literature, it seems desirable to consider how the approximations implicit in them restrict the usefulness of their application.

Eley sought to apply the Pauling concept of electronegativity (Pauling 1940) to the adsorbed state by writing

$$E(M\text{—}A) = \tfrac{1}{2}[E(M\text{—}M)+E(A\text{—}A)]+23\cdot06\,(x_m-x_a)^2,$$

with the term involving electronegativities (x_a, x_m) evaluated by means of the Malone (1933) relation

$$\mu = x_m - x_a,$$

where μ is the dipole moment of the surface bond, and m and a represent surface and adsorbate atoms, respectively. If this equation has any value, it is limited to the case of adsorbed hydrogen, for which it yields calculated heats in fair agreement with the experimental values. Even in this case, however, the procedure is open to the charge of empiricism on the grounds that the assumptions involved lack any real theoretical foundation. Thus, it is usual to write $E(M\text{—}M) = fS$, where S is the heat of sublimation of the metal and $f = 1/6$ for all metals, or for only the face-centred cubic metal, and $f = 1/4$ for the body-centred cubic metals. An attempt to allow for a weakening of the bonding of the surface atom to its neighbours in the presence of an adsorbate molecule has been made by Schuit, van Reijen & Sachtler (1961), though not with any marked success, and it is customary to neglect the contribution of this effect to the heat of adsorption. It is also the practice to write $\mu = \Delta V \times 10^{18}/2\pi\ 300n$, where ΔV (volts) is the change in surface potential corresponding to the adsorption of n particles per square centimetre. Apart from the fact that the value of n generally employed corresponds to saturation coverage, but this expression for μ refers only to very sparsely populated surfaces, it seems a gross over-simplification to equate the surface dipole moment per molecule calculated in this way with the moment of the surface bond. These objections are especially severe when the procedure is applied to the adsorption of a molecule like carbon monoxide. The result of the calculation depends very much on how the adsorbed state is represented. There are three limiting possibilities (i) M—CO, (ii) M=C=O, and (iii) $\begin{matrix}M\\M\end{matrix}\!\!>\!\text{C=O}$. To evaluate $E(M\text{=}M)$ for the purposes of (ii), it is necessary to write $E(M\text{=}M) = 2E(M\text{—}M)$. For the purposes of (i) and (iii), it is presumably necessary to evaluate $E(C\text{—}C)$ by reference to the energy of the C—C bond in saturated hydrocarbons, a crude approximation which even fails to make allowance for the difference between the M—C bonds in the two cases. For E(C=C), the comparison is with the C=C bond in olefins. In evaluating μ, it is customary to use the measured surface potential, without regard to the large dipole moment and the polarizability of the CO bond. In the case of hydrogen, the term involving μ is small, and this is possibly the reason why the equation conforms to experiment moderately successfully; for carbon monoxide, this term makes a major contribution.

The equation of Higuchi *et al.* (1957) is also derived from a quantum mechanical argument; according to these authors:

$$E(M\text{—}A) = \frac{H_{\text{cc}}-C_i^2(H_{\text{cc}}+H_{\text{ii}})}{1-2C_i^2},$$

where H_{ii} and H_{cc} are the energies of the ideal ionic and covalent bonds respectively and the constant C_i^2 determines the relative contribution of each of these limiting bond types. The dipole moment of the surface bond is used to evaluate C_i^2, thus $C_i^2 = \mu/er_{MA}$, where r_{MA} is the length of the surface bond and e the charge on the electron. H_{cc} is equivocal for the reasons given above, because it involves the quantities $E(M—M)$, $E(M{=}M)$, $E(\mathrm{C—C})$ and $E(\mathrm{C{=}C})$ depending on how the surface bond is formulated. For the evaluation of H_{ii}, it is supposed that:

$$H_{\mathrm{ii}} = A-I+W_e,$$

where A is the electron affinity, I the ionization potential and W_e the energy of the positive and negative ions at their equilibrium separation such that

$$W_e = \tfrac{8}{9}e^2/r'_{MA}.$$

Several difficulties arise with this equation. First, it is not clear in the case of carbon monoxide adsorption to which species A and I should refer, although Higuchi *et al.* assume the polarity is in the sense $\overset{+}{M}—\overset{-}{A}$. Nor is it certain that I (or A, as the case may be) should refer to the isolated atom rather than to the metal surface. The expression for W_e involves the quantity r'_{MA}, which is different from r_{MA}, but which, nonetheless, is assigned the same value as r_{MA}. In assessing the energy of surface bonds of the type $M{=}A$, Higuchi *et al.* consider the ionic bond to have the form $\overset{+}{M}—\overset{-}{A}$ and calculate $E(M—A)$ as a mean of $E(M—M)$ and $E(A—A)$; to this is added W_e calculated in the normal way. Such a procedure cannot be expected to give values accurate to better than an order of magnitude. Finally, the evaluation of C_i^2 is dependent on a correct interpretation of the change in the surface potential and, as indicated previously, this is difficult especially for a molecule like carbon monoxide which involves a polar bond. The use of an entirely empirical relation to evaluate C_i^2 (Manes & Molinari 1963) would seem to add an additional strain to a structure ill fitted to bear it.

Because of the number and severity of these assumptions, we consider that no useful purpose would be served by our adding to existing computations based on these methods.

2. *Comparison with metal carbonyls*

In the case of oxygen adsorption on metals, it has been shown (Brennan *et al.* 1960) that the heat of adsorption is closely related to the heat of formation of the corresponding oxide. Sachtler & van Reijen (1962) have commented more generally on this kind of relation. It is interesting to examine whether such a relationship exists for carbon monoxide adsorbed on metals. Unfortunately there are few data for the heats of formation of metal carbonyls; the relevant ones are listed in table 4. The table shows that there is no real correspondence between the energy of the gaseous carbonyl and carbon monoxide in the adsorbed state. Corrections for excitation of the metal atom to a different valency state (Abel 1963), or for the sublimation energy of the metal, could not bring the two groups of data closer together for both molybdenum and tungsten, and iron and cobalt simultaneously. Arguments for a bridge type surface bond for adsorbed carbon monoxide will be presented below and the energy of such a molecule would not be expected to be similar to that of a molecule which is one of a number of molecules bonded linearly to a common metal atom.

TABLE 4. COMPARISON OF THE ENTHALPY (ΔH°_{298}) OF THE GASEOUS REACTION $1/n\,M(\mathrm{CO})_n = 1/nM + \mathrm{CO}$ WITH THE CORRESPONDING HEAT OF ADSORPTION; ALL ENERGIES ARE IN KCAL

M	n	ΔH°_{298}	heat of adsorption per mole CO	
			initial	integral
Mo	6	35·9*	74	60
W	6	42·1*	82,(120)	80
Fe	5	27·7‡	46	35
Ni	4	35·2†	42	40

* Cotton, Fischer & Wilkinson (1956).
† Cotton, Fischer & Wilkinson (1957)
‡ Cotton, Fischer & Wilkinson (1959).

3. *Heat of adsorption as a function of metallic radius*

In figure 4, the initial heat of adsorption of carbon monoxide is plotted as a function of metallic radius. As for the adsorption of oxygen (Brennan *et al.* 1960), there are two branches, one almost parallel to the metallic radius axis for the group VIII metals and the other with an appreciable gradient for the remaining metals. Reference will again be made to this behaviour in the succeeding paper.

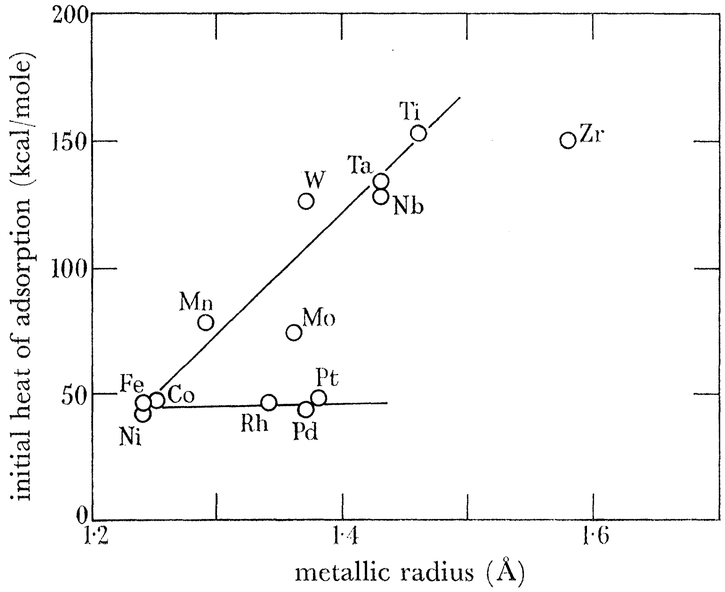

FIGURE 4. The initial heat of adsorption of carbon monoxide on the various metals as a function of the metallic radius.

An attempt to account for a heat of adsorption which diminishes with metallic radius in terms of intermolecular repulsion between adsorbed molecules can be dismissed in the light of arguments presented in the next section. Configurations which would involve

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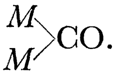
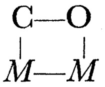
adequate repulsive energies would require values of p greater than observed, as well as an energy of activation for their formation. Additionally, a much more powerful dependence of heat of adsorption on metallic radius than observed would be required.

The configuration of adsorbed carbon monoxide

In table 1 are listed the experimental values of the parameters p and q. The parameter p is determined by the configurations both of krypton atoms and carbon monoxide molecules on the surface. For the former, the arguments developed in the preceding paper will be used and, for the latter, similar arguments will be developed below. The meaning of q is more difficult because there are at least two important contributory effects. The diminished monolayer capacity consequent upon chemisorption has generally been attributed to thermal sintering of the film due to the rapid liberation of the heat of chemisorption. However, the presence of a chemisorbed layer is likely to bring about a redistribution of sites available for the inert gas atoms to occupy and should this happen q could differ from p even if there were no diminution in surface area. An attempt will be made to estimate q for the different metals on the assumption that this parameter is entirely determined by the redistribution of sites available for occupation by krypton atoms.

Theoretical estimates of p

Configurations of adsorbed carbon monoxide molecules (figures 5, 6, and 7) have been constructed on the following principles:

(i) Carbon monoxide may be bonded to the surface either as a linear grouping, M—CO, or as a bridge grouping  $\begin{matrix}M\\M\end{matrix}\!\!>\!\mathrm{CO}$. The grouping  $\begin{matrix}\mathrm{C}\text{—}\mathrm{O}\\|\quad\;\;|\\M\text{—}M\end{matrix}$ and dissociative adsorption are not considered, there being no evidence to support their inclusion.

(ii) In assessing the maximum and minimum M—M spacings over which bridge bonding can occur (table 5), it is assumed that the M—C—M angle must lie between 80

TABLE 5. PERMISSIBLE M—M SPACINGS [$d(M$—$M)$] AS A FUNCTION OF METALLIC RADIUS r, (PAULING 1960) FOR BRIDGE-BONDING OF ADSORBED CARBON MONOXIDE, AND THE M—CO BOND LENGTHS FROM WHICH THEY HAVE BEEN DERIVED

	$d(M$–CO) (Å)	$d(M$–$M)$
	hexagonal close packed metals	
Ti, Zr	2·1*	$2r$
	face-centred cubic metals	
Co	1·83	$2r$
Ni	1·84	($a = 2\sqrt{2}r$
Pt	2·0*	prohibited)
	body-centred cubic metals	
Fe	1·84	
Cr	1·92	$2r$ and
Mo	1·98	$a = \frac{4}{\sqrt{3}}r$
W	2·06	
Nb, Ta	2·1*	

* These values are extrapolated values; the other values are those given by Sutton (1958) for the corresponding carbonyls.

and 110°. The use for this purpose of M—CO bond lengths derived from metal carbonyls might seem objectionable. However, it is probable that the M—C distance for a bridge bond will not be too different from that for the linear bond; thus, for $Fe_2(CO)_9$, the M—C lengths for the linear and bridge bonds are 1·90 and 1·80 Å, respectively. Again, the differences in bridge angle for the spacings under consideration are sufficiently great for a decision to be made between them which is not sensitive to the value of $d(M$—CO$)$.

(iii) An adsorbed carbon monoxide molecule, in either state of bonding, is spherical and has the same effective diameter for van der Waals interaction as it does in the solid, namely 4·08 Å² (Mason & Rice 1954).

(iv) The potential energy of interaction of a pair of neighbouring carbon monoxide molecules on the surface varies with their separation (d) according to the expression:

$$\mathscr{E}_{\text{pair}} = \frac{\epsilon\alpha}{\alpha-6}\left\{\frac{6}{\alpha}\exp\alpha\left(\frac{d_m-d}{d_m}\right)-\left(\frac{d_m}{d}\right)^6\right\}$$

with $d_m = 3{\cdot}937$ Å, $\alpha = 17{\cdot}0$ and $\epsilon/k = 119{\cdot}1°$ (Mason & Rice 1954).

The main difficulty in assigning a reasonable upper limit to the repulsive energy for a configuration lies in deciding when repulsion has become so great as to result in an activation energy of adsorption. The adsorption of carbon monoxide on these metals is virtually unactivated and any configuration adopted must satisfy that requirement. From the point of view of the energetic stability of a configuration, quite large repulsive energies can be tolerated without seriously diminishing the heat of adsorption, but we will suppose that $\mathscr{E}_{\text{pair}}$ must not exceed 10 kcal for fear of introducing an activation energy of adsorption.

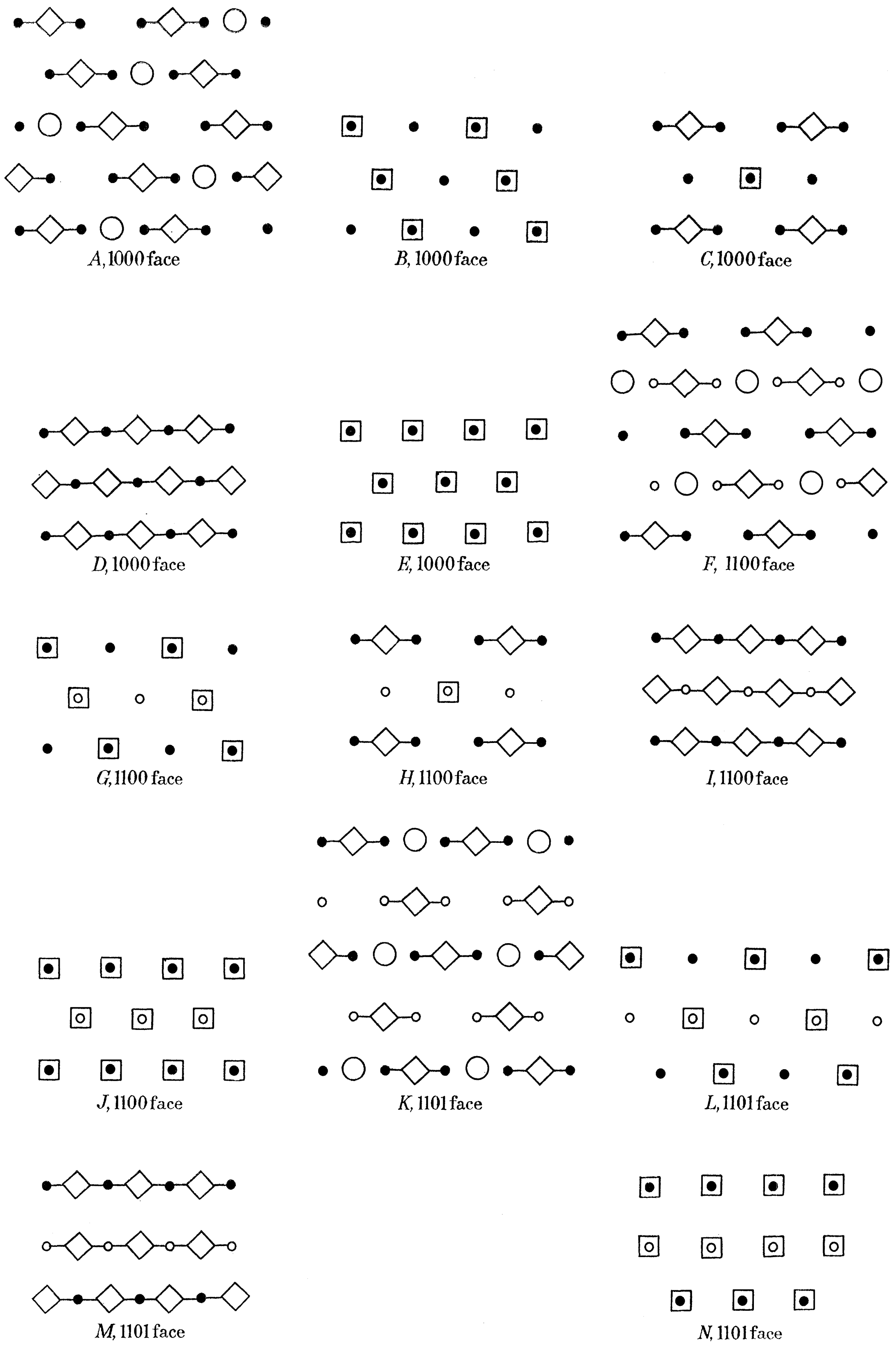
(v) The main crystal planes exposed in films are as follows. Hexagonal close packed metals: 0001, 1100 and 1101; face-centred cubic metals: 100, 110, and 111; body-centred cubic metals: 100, 110 and 211.

(vi) Ordered arrays of adsorbed molecules are permissible. Having in mind that the adsorbed molecules are immobile, the supposition that they form ordered arrays presents some difficulty. It must mean that the molecule immediately before adsorption has a knowledge of the availability of adsorption sites in the strongly chemisorbed layer. This knowledge could conceivably be acquired during the molecules sojourn in a precursor state. However, despite difficulties of interpretation, there is clear evidence (Schlier & Farnsworth 1957; Germer, Scheibner & Hartman 1960; Germer 1962) that ordered arrays of immobile adsorbed species do in fact form in a variety of cases, including that of carbon monoxide.

Hexagonal close packed metals

The various configurations are given in figure 5, A to N, and the associated coverages are as detailed in table 6.

1000 *plane*. Figure 5A has been constructed on the assumption that carbon monoxide is bridge-bonded and that each metal atom can participate in only one bond per adsorbed molecule. The configuration of admolecules represented in figure 5B is superimposable upon that of figure 5A and has been drawn for linearly bonded adsorbed carbon monoxide. In both these structures, the nearest approach of neighbouring admolecules is $a = 2r$ for which $\delta(\text{Ti}) = 1{\cdot}13$ Å and $\delta(\text{Zr}) = 0{\cdot}85$ Å; δ is the extent of the overlap of the van der



A, 1000 face *B*, 1000 face *C*, 1000 face

D, 1000 face *E*, 1000 face *F*, 1100 face

G, 1100 face *H*, 1100 face *I*, 1100 face

J, 1100 face *K*, 1101 face *L*, 1101 face

M, 1101 face *N*, 1101 face

FIGURE 5. Configurations of carbon monoxide adsorbed on the hexagonal close packed metals. ●, the centres of metal atoms in the plane; ○, the centres of metal atoms 0·577 r below the 1100 plane or 0·255 r above the 1101 plane; -◇-, □, the centre of bridge- and linear-bonded adsorbed carbon monoxide, respectively; ○, the centres of krypton atoms adsorbed on the chemisorbed carbon monoxide.

Waals envelopes of admolecules. The corresponding interaction energy between neighbours is 7 and 1·8 kcal/mole of molecules interacting as isolated pairs, which is acceptable. Thus, for configurations *A* and *B*, the total interaction energies are 14 and 3·6 kcal/mole, corresponding to negligible repulsion relative to the great strength of the surface bond. Configuration *A* represents the maximum coverage attainable subject to the valency restriction governing its construction. For configuration *B*, however, it is possible to add still more carbon monoxide molecules to the surface, provided the interaction energy between admolecules is not excessively increased as a result. Figure 5*E* shows every surface atom linearly bonded to one carbon monoxide molecule. The smallest separation is again *a*, but now each molecule has six neighbours and the total energy of interaction between admolecules is 42 and 11 kcal/mole for titanium and zirconium, respectively. Both these energies are considered feasible. For configuration *E*, $p = 2$ for both titanium and zirconium, whereas the experimental values are 1·77 and 1·05, respectively. Thus, for zirconium, configuration *E* can be rejected because its *p* value is too large. If this configuration is not possible for zirconium, it is unlikely that it will be for titanium. These conclusions are reinforced by the fact that the existence of the corresponding configurations for the 1100 and 1101 planes would also give excessively high values for *p* and the mean values of *p* would then be greatly in excess of the experimental values. These arguments lead to the rejection of linear-bonding of carbon monoxide adsorbed on this plane. Figure 5*D* shows the result of allowing each surface atom to participate in two bridge bonds and the resulting configuration is superimposable upon configuration *E*. Thus, configuration *D* also has $p = 2$ for both metals and is therefore rejected.

TABLE 6. NUMBERS OF CARBON MONOXIDE MOLECULES [N(CO)] ADSORBED PER UNIT AREA OF THE HEXAGONAL CLOSE PACKED METALS FOR THE VARIOUS CONFIGURATIONS (FIGURE 5), AND THE CORRESPONDING VALUES OF $p = N(\mathrm{CO})/N(\mathrm{Kr})$ BASED ON TABLE 4 OF THE PRECEDING PAPER

		p	
configuration	N(CO)	Ti	Zr
1000 *A*, *B*, *C*	$1/\sqrt{3}a^2$	1	1
1000 *D*, *E*	$2/\sqrt{3}a^2$	2	2
1100 *F*, *G*, *H*	$1/ac$	1·5	1
1100 *I*, *J*	$2/ac$	3	2
1101 *K*, *L*	$2/a\sqrt{(3a^2+4c^2)}$	2	1
1101 *M*, *N*	$4/a\sqrt{(3a^2+4c^2)}$	4	2

Figure 5*C* shows a mixed type of configuration in which both bridge-bonded and linear-bonded carbon monoxide molecules are present. Its surface concentration is the same as for *A* and *B*, and it is free of repulsions. This configuration is not in conflict with the experimental results, but *a priori* it seems improbable. We conclude that, on the 1000 plane of titanium and zirconium, carbon monoxide is held by a bridge bond and that each surface atom has available only one orbital to contribute to the bonding.

1100 *plane*. Configuration *F* has been constructed with the restriction that carbon monoxide is bridge-bonded and that each metal atom interacts with only one admolecule. Configuration *G* is identical to that of *F*, except that it involves linearly held carbon monoxide. The energy of interaction between admolecules for both these structures is the same as for configurations A and B, but there is an important difference in the values of p. As previously, $p(\mathrm{Zr}) = 1$, but now $p(\mathrm{Ti}) = 1{\cdot}5$. This is a step towards accounting for the higher experimental value of $p(\mathrm{Ti}) = 1{\cdot}77$. Configuration J is energetically equivalent to configuration D as far as intermolecular interaction is concerned, but it can be rejected because of its very high p values (see table 6). Likewise, configuration I can be rejected with the conclusion, as before, that carbon monoxide is held by a bridge bond, with each metal atom interacting with only one admolecule. Configuration H is the counterpart of configuration C and is also considered improbable, though there is no direct evidence against it.

1101 *plane.* For configurations K and L, $p(\mathrm{Ti}) = 2$ and $p(\mathrm{Zr}) = 1$ and a contribution from this plane and the 1100 plane accounts for the higher value of p observed for titanium. The intermolecular energy of these configurations is the same as for configurations A, B, F and G and presents no difficulty. Again, there is no reason energetically why the coverage should stop at configuration L, if carbon monoxide is held by a linear bond, because a molecule in configuration N has five neighbours at a distance a, corresponding to an interaction energy of only 35 and 9 kcal/mole for titanium and zirconium, respectively. The fact that configuration N requires $p(\mathrm{Ti}) = 4$ and $p(\mathrm{Zr}) = 2$ means that this configuration can be rejected, as can configuration M.

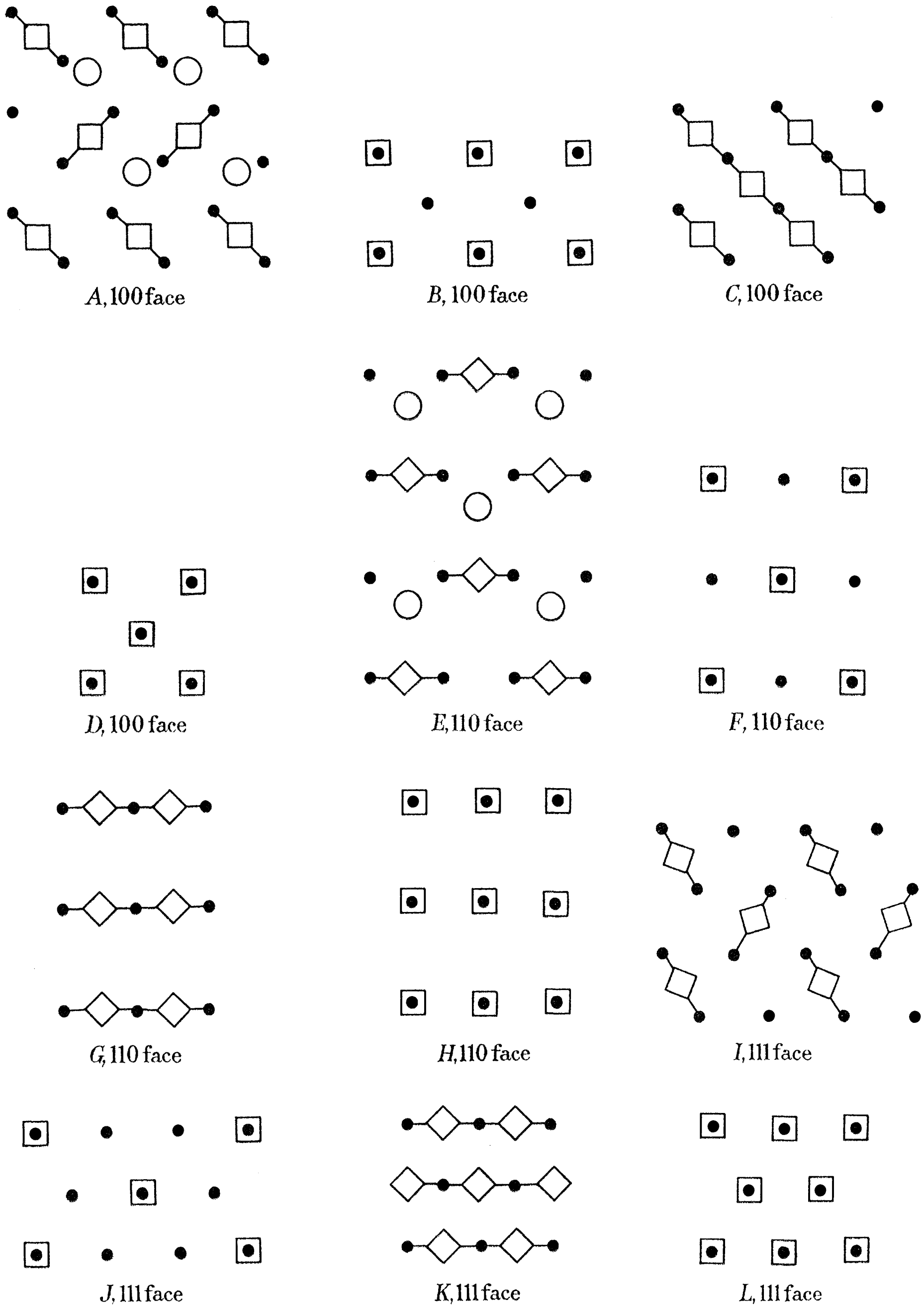
Thus, from the consideration of these three planes, we come uniformly to the conclusion that carbon monoxide is bridge-bonded and that each surface metal atom has available one orbital for interaction with admolecules. Further, the experimental values of p can be interpreted in terms of a contribution from each of the three planes. The usual assumption of an equal contribution from each of the planes requires $p(\mathrm{Ti}) = 1{\cdot}5$, which is too low, so a heavier weighting of the 1100 and 1101 planes is necessary.

Face-centred cubic metals

The configurations are shown in figure 6 and the corresponding coverages in table 7.

100 *plane.* Figure 6A represents one of the possible ways of covering the surface with carbon monoxide adsorbed by a bridge bond spanning a M—M spacing of $2r$, subject to the restriction that no one surface atom shall be associated with more than one admolecule. The smallest separation between admolecules is a which involves negligible repulsion. Configuration figure 6B is the equivalent structure for linearly held carbon monoxide, and, although it is not superimposable on configuration A, the concentration of admolecules is the same (table 7) and the smallest separation is again a.

To test whether or not configuration B represents saturation, the energetics of configuration D must be examined. Each admolecule in configuration D has four neighbours at a distance $2r$ and reference to table 8 shows that this means a repulsion energy which is prohibitive for all the metals, both because of its absolute value relative to the energy of the surface bond and because it would very probably mean an activation energy of adsorption. Hence, the denser configuration D, and the corresponding configuration C, must both be rejected on energetic grounds alone. With $p = 1$, configurations A and B must be regarded as equally acceptable, as far as this analysis is concerned, and it is not possible to distinguish between bridge-bonded and linear-bonded carbon monoxide as it was for the hexagonal close packed metals.



A, 100 face *B*, 100 face *C*, 100 face

D, 100 face *E*, 110 face *F*, 110 face

G, 110 face *H*, 110 face *I*, 111 face

J, 111 face *K*, 111 face *L*, 111 face

FIGURE 6. Configuration of carbon monoxide adsorbed on the face-centred cubic metals. ●, the centres of metal atoms in the plane; -◇-, □, the centres of bridge- and linear-bonded adsorbed carbon monoxide, respectively; ○, the centres of krypton atoms adsorbed on the chemisorbed carbon monoxide.

TABLE 7. NUMBERS OF CARBON MONOXIDE MOLECULES [N(CO)] ADSORBED PER UNIT AREA OF THE FACE-CENTRED CUBIC METALS FOR THE VARIOUS CONFIGURATIONS (FIGURE 6) AND THE CORRESPONDING VALUES OF $p = N(\mathrm{CO})/N(\mathrm{Kr})$ BASED ON TABLE 4 OF THE PRECEDING PAPER

configuration	N(CO)	p	configuration	N(CO)	p
100 *A*, *B*	$1/a^2$	1	111 *I*	$2/\sqrt{3}\,a^2$	1·5
100 *C*, *D*	$2/a^2$	2	111 *J*	$4/3\sqrt{3}\,a^2$	1
110 *E*, *F*	$1/\sqrt{2}\,a^2$	1	111 *K*, *L*	$4/\sqrt{3}\,a^2$	3
110 *G*, *H*	$\sqrt{2}/a^2$	2			

110 *plane*. As for the 100 face, carbon monoxide can be held on the 110 plane either by bridge bonds (configuration E) or linear bonds (configuration F) without repulsion between neighbours. The next most dense configuration is either figure 6 G (bridge bonds) or figure 6 H (linear bonds). Both these configurations require each admolecule to have two nearest neighbours at a distance of only $2r$ away and so can be eliminated on energetic grounds (table 8). Once again, the fact that configurations of the type G and H are not permissible for energetic reasons alone prevents a choice being made between linear- and bridge-bonding.

TABLE 8. THE INTERACTION ENERGY ($\mathscr{E}_{\text{pair}}$ KCAL/MOLE OF MOLECULES INTERACTING AS ISOLATED PAIRS) FOR CARBON MONOXIDE MOLECULES SEPARATED BY VARIOUS DISTANCES

	face-centred cubic metals			
metal	Co, Ni	Rh	Pd	Pt
$\mathscr{E}_{\text{pair}}$, separation $2r$	53	22	20	17
	body-centred cubic metals			
metal	Fe	Mo	W	Nb, Ta
$\mathscr{E}_{\text{pair}}$, separation $4/\sqrt{3}\,r$	11	2·8	2·5	1·2
$\mathscr{E}_{\text{pair}}$, separation $2r$	60	20	18	11

111 *face*. This face is notable for its ability to adsorb more bridge-bonded carbon monoxide molecules (see figure 6 I), than linear-bonded molecules (see figure 6 J). The denser configurations K and L involve each admolecule with six neighbours at a distance of only $2r$ and can be disregarded because of the very high energy involved. For the bridge-bonded configuration I, $p = 1{\cdot}5$, while for the linear-bonded configuration J, $p = 1$. The experimental values of p (table 1) are greater than unity, except for nickel and a contribution from configuration I provides a means of accounting for this observation; indeed, for platinum and rhodium, the 111 face covered by bridge-bonded carbon monoxide must be present practically to the exclusion of the other two faces. This is an argument in favour of bridge-bonded molecules, but it is not so strong as the argument applied to the hexagonal close packed metals.

Body-centred cubic metals

The configurations are shown in figure 7 and the corresponding coverages in table 9.

100 *face*. Configurations A and B do not involve any repulsive interaction between admolecules. In the more dense configurations C and D, which are superimposable, each admolecule has four nearest neighbours at a distance of $a = \dfrac{4}{\sqrt{(3)}}r$. Hence, configurations C and D are energetically unobjectionable (table 8), excepting iron for which the repulsive energy of 44 kcal/mole seems prohibitive. The value of $p = 2$ for these structures is not necessarily too large, since a contribution from configurations of lower p values would give conformity with the experimental values. Hence, it is not possible to eliminate configurations C and D (except for iron) by considering them in isolation.

110 *face*. Configuration E is free of repulsion between molecules, while configurations F, G and H involve two nearest neighbour separations of a per molecule. The density of coverage is the same for configurations E, F, G and H. Configuration E seems preferable

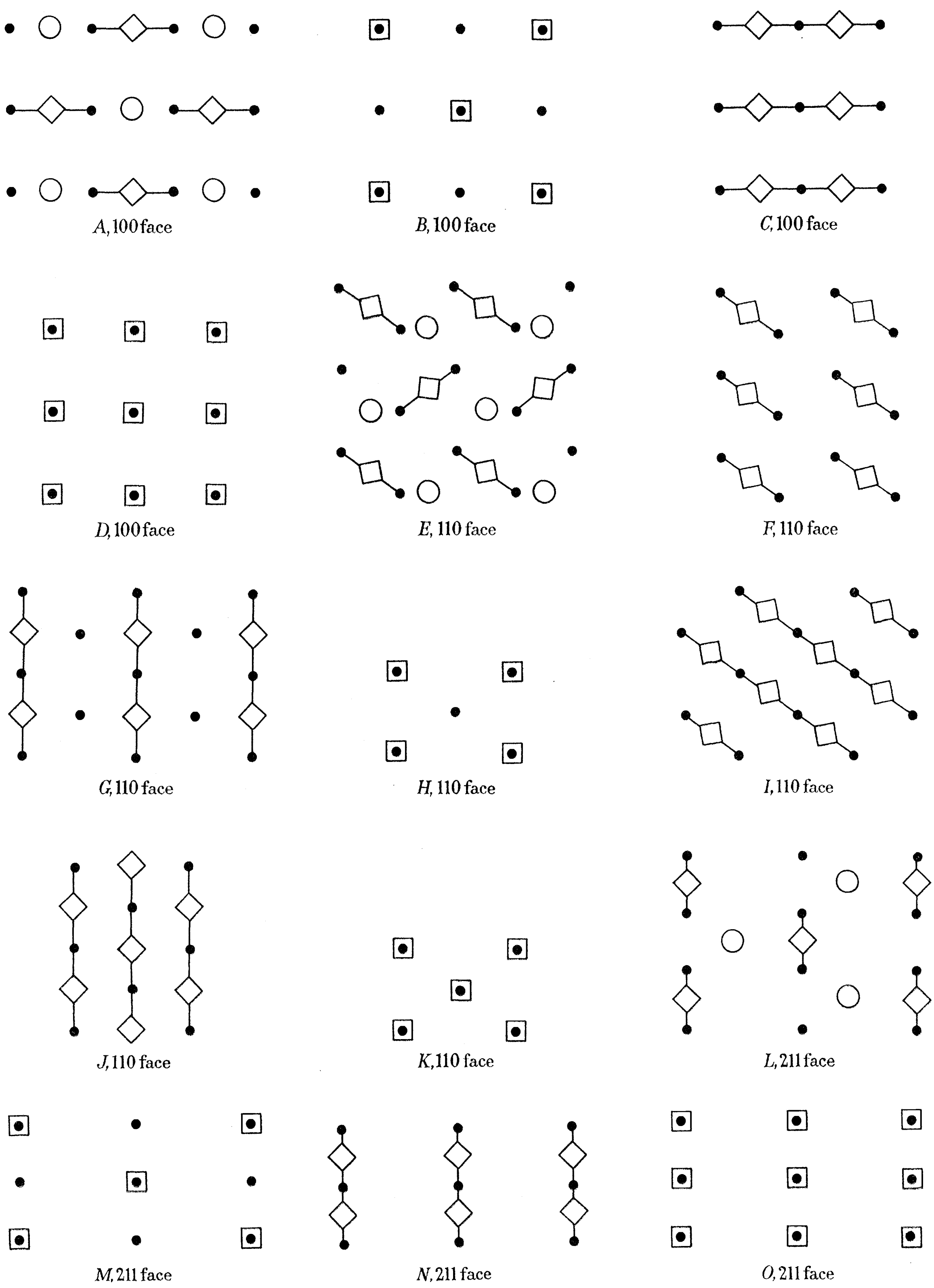


FIGURE 7. Configurations of carbon monoxide adsorbed on the body-centred cubic metals. ●, the centres of metal atoms in the plane; -◇-, □, the centres of bridge- and linear-bonded adsorbed carbon monoxide, respectively; ○, the centres of krypton atoms adsorbed on the chemisorbed carbon monoxide.

TABLE 9. NUMBERS OF CARBON MONOXIDE MOLECULES [N(CO)] ADSORBED PER UNIT AREA OF THE BODY-CENTRED CUBIC METALS FOR THE VARIOUS CONFIGURATIONS (FIGURE 7) AND THE CORRESPONDING VALUES OF $p = N(\mathrm{CO})/N(\mathrm{Kr})$ BASED ON TABLE 4 OF THE PRECEDING PAPER

configuration	N(CO)	p
100 *A*, *B*	$1/2a^2$	1
100 *C*, *D*	$1/a^2$ (except Fe)	2
110 *E*, *F*, *G*, *H*	$1/\sqrt{2}a^2$	1 (Fe, 1·5) see text
110 *I*, *J*, *K*	$\sqrt{2}/a^2$	2 (Fe, 3)
211 *L*, *M*	$1/\sqrt{6}a^2$	1
211 *N*, *O*	$\sqrt{2}/\sqrt{3}a^2$	2

to the equivalent structures *F* and *G*, in that it is free from repulsive interactions, but it is not possible to achieve this density for linearly bonded carbon monoxide (configuration *H*) without some repulsive interaction and, for iron, this is probably excessive. Configuration *E*, which is applicable to all the metals has $p(\mathrm{Fe}) = 1{\cdot}5$ and $p(\mathrm{Mo, W, Nb, Ta}) = 1$. Configurations *I*, *J* and *K* can be eliminated unequivocably, on energetic grounds, since each admolecule has four neighbours at only $2r$ and two neighbours at $\frac{4}{\sqrt{(3)}}r$, and reference to table 8 shows the consequent repulsions are very large. No help can be obtained from valency considerations in deciding between configurations *E*, *F*, *G* and *H*, since dense configurations involving surface atoms bonded to two carbon monoxide molecules, and the equivalent linearly bonded structures, have no probability of existing due to repulsion between neighbours alone.

211 *face*. Configuration *L* and the superimposable configuration *M* are free from repulsive interactions, while configurations *N* and *O* involve each molecule in two nearest neighbour separations of only $2r$ and their repulsive energies are excessive. The prediction is therefore, $p = 1$, with either bridge bonding or linear bonding of carbon monoxide molecules.

For iron, it is possible to account for the experimental value $p = 1{\cdot}21$ by including a contribution from configuration $E(p = 1{\cdot}5)$. For possible configurations on all the other metals, $p = 1$, except for configurations *C* and *D* with $p = 2$. Hence, unless configurations *C* and *D* are admitted, it is not possible to account for experimental values of $p > 1$ for these other metals using the arguments so far presented. It might be that these metals are capable of adsorbing carbon monoxide, either in the bridge form, with each surface atom participating in two bonds, or in a linear form, with each surface atom associated with one admolecule, but this description is contrary to the pattern of behaviour established earlier in this section. The body-centred cubic metals present difficulties because the interaction energies involved both for the inert gas and carbon monoxide adsorptions are of intermediate values and depend too sensitively on the potential energy function used to compute them. We will therefore re-examine the N(Kr) values upon which these p values are based. Xenon adsorbed on the 110 plane of molybdenum and tungsten (see figure 7*B* and *C* of the preceding paper) probably has a monolayer concentration of $\sqrt{2}/3a^2$, although a value of $1/\sqrt{2}a^2$ is also a possibility. The corresponding coverage for krypton would appear to be $1/\sqrt{2}a^2$ with less uncertainty. However, the capacity of these surfaces for krypton and xenon is found to be the same, so a configuration which is assigned to one ought to be assigned to the other. For molybdenum and tungsten, it is not difficult to believe that a more precise calculation would show that the energy of configuration B, figure 7, table 3 of the preceding paper was too large and that these metals had the same monolayer capacity as for iron, namely $\sqrt{2/3}\,a^2$, in which case configuration E of figure 7 of this paper would have $p = 1{\cdot}5$. It is more difficult to extend this argument to niobium and tantalum, but its acceptance provides a means of accounting for p (experimental) > 1 without disturbing the regularity of the conclusions reached previously. However, the arguments relating to these metals cannot be regarded as other than very tentative.

Relation to deductions from infra-red spectroscopy and flash filament desorption

Several investigations of the infra-red absorption of adsorbed carbon monoxide point to the existence of both the bridge and linear forms of bonding. Interpretational difficulties arise from a variety of causes. The state of the surface in these investigations is questionable. The fact that carbon monoxide adsorbed on a dispersion of iron in pump oil (Blyholder 1962) can give absorption spectra of the same form as when adsorbed on more conventional surfaces suggests that none of these surfaces is comparable to that presented by an evaporated metal film. For palladium, the reversibility of the absorption bonds as a function of carbon monoxide pressure points to the same inference. Apart from the issue of surface cleanness, it is known that the nature of the support employed is important in determining the positions and relative intensities of the absorption bands (O'Neill & Yates 1961; Eischens & Plisken 1958). The presence of residual hydrogen in reduced metals has a similar effect (Eischens 1960). There is also the fundamental difficulty that the extinction coefficients of the absorptions attributed to bridge and linear carbon monoxide are unknown, although there are grounds for thinking that the linear form has the larger extinction coefficients. Hence little can be said from infra-red absorption studies about the relative concentrations of the two species on the surface and none of these findings is necessarily incompatible with the present conclusions.

The nature of the α- and β-states elucidated by flash filament desorption is not clear, but the β-states cannot refer simply to distinctions of bonding between neighbouring admolecules. At the high temperatures necessary for desorption, rapid interchange between neighbouring states of different bonding would occur and such states, therefore, would not be resolved. It is more likely that these states correspond to adsorption on well separated regions of the surface having different adsorption properties and probably identifiable with different crystal faces.

The influence of the chemisorbed layer on the adsorption of krypton

It is frequently observed that the monolayer capacity of a surface is diminished by the presence of a chemisorbed layer. The explanation generally given is that there has been a real loss of area due to thermal sintering of the adsorbent resulting from the liberation of the heat of chemisorption. Because of the difficulties attending this hypothesis, as reviewed below, an explanation in terms of a reduction of sites available for krypton adsorption, due to the presence of the chemisorbed layer, seemed attractive. This alternative hypothesis is examined in the final section and found also to be inadequate.

Changes in the adsorbent temperature during chemisorption

If it is assumed that none of the heat of chemisorption is lost by the adsorbent, then very substantial temperature rises are possible, even for adsorption on films. For example, saturation of a typical nickel film with oxygen could in principle result in a temperature rise of about 300 °C, which could bring about a substantial degree of sintering. Indeed, in the case of nickel powders, there is evidence (Dell, Klemperer & Stone 1956) that poor heat dissipation during adsorption does lead to large increases in temperature, during interaction with oxygen, with the result that oxidation rather than just adsorption can occur. Similar effects might conceivably occur with nickel films. Chemisorption on films can initally be very rapid but, as adsorption proceeds, the rate falls because the adsorbate needs longer to find the interior surface of the film. Films are in very intimate contact with their support and heat transfer thereto must be rapid. If the heat capacity of the support is included, then the temperature increase due to chemisorption is negligible. Again, the rate of adsorption of oxygen on nickel has fallen to a slow rate (greater than 15 s required for the adsorption of a gas increment) when the film is only half saturated (Brennan *et al.* 1960) and presumably a fraction of the earlier coverage, while proceeding rather faster, will still be relatively slow. Therefore, a substantial part of the adsorption proceeds at a rate which would allow ample time for heat transfer to the film support and should not involve high temperatures within the film. The same arguments apply to a number of other metals. Thus, if there is to be thermal sintering, it must be associated almost exclusively with the initial stages of adsorption. It is doubtful whether these films are sufficiently porous to admit of this as a possible explanation, remembering the large decreases in V_M which are often involved. The hypothesis can now be definitely rejected because recent work (Brennan & Lees 1964) have shown for a number of metal films that V_m diminishes linearly with successive doses of oxygen, despite the falling rate of adsorption. Finally, it may be noted that gross oxidation does not generally result when oxygen is adsorbed on metal films, in keeping with the view that high temperatures are not experienced by the bulk of the film during chemisorption.

While there seem firm grounds, therefore, for doubting that macroscopic heating during chemisorption is responsible for the reduction in V_m there, remains the possibility that film sintering could arise because of intense heating within a few atomic diameters of the site of adsorption. It is very difficult to discuss this possibility in the absence of precise information concerning events immediately following the act of chemisorption. Such evidence as there is suggests that the heat of adsorption is liberated to the substrate, not in one quantum, but rather during the course of several jumps from site to site (Ehrlich 1962) and that the energy received by the substrate lattice is very rapidly accommodated among its vibrational modes. Thus, it would seem that the opportunities for serious local rises in temperature are not good. There is the additional consideration that sintering by processes of this kind does not seem very probable because it is difficult to imagine how they could result in the movement of the substantial mass of metal which is necessary. Support for this last point comes from the field ion work of Müller (1959), who found that the disorder of the tungsten lattice consequent upon the adsorption of oxygen did not extend beyond four or five lattice spacings below the surface.

Correlation with the melting-point of the metal

The melting-point of a metal provides a measure of the firmness with which its atoms are located in the lattice and accordingly, if thermal sintering were the cause of the reduction of V_m following chemisorption, then a correlation between the value of $q = N(\text{Kr}/\text{chemisorbed layer})/N(\text{Kr}/\text{clean surface})$ and the melting point of the metal would be expected. Figures 8, 9 and 10 show that there is in fact a rough correlation of this kind for oxygen, carbon monoxide and carbon dioxide adsorptions. Closer inspection, however, reveals some important inconsistencies. Thus, the heat of adsorption of carbon monoxide

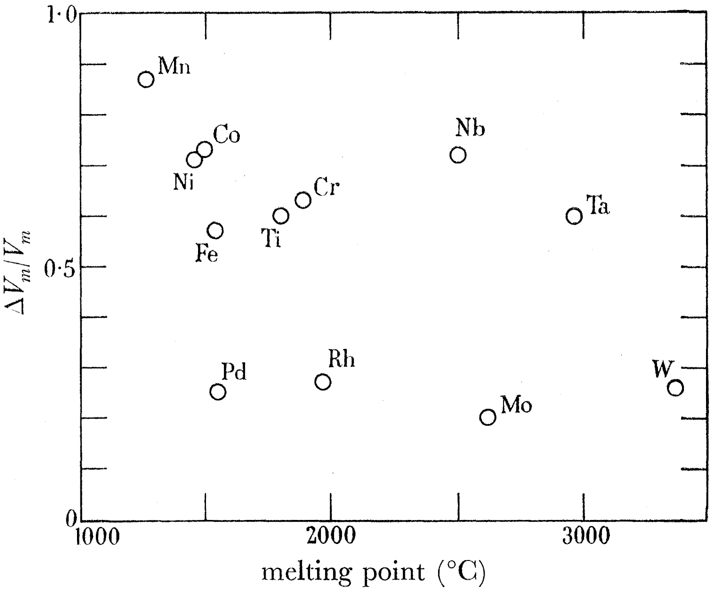


FIGURE 8. The fractional change in the krypton monolayer capacity of a metal film following chemisorption of oxygen as a function of the melting point of the metal.

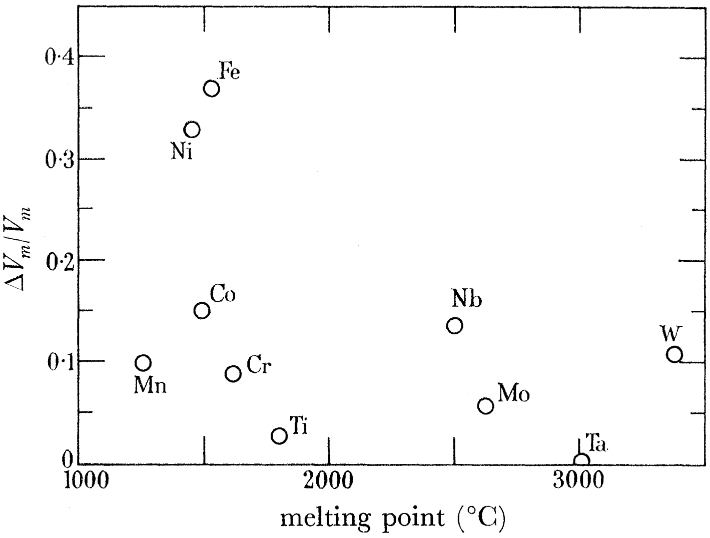


FIGURE 9. The fractional change in the krypton monolayer capacity of a metal film following chemisorption of carbon dioxide as a function of the melting point of the metal.

is about 70 kcal/mole on molybdenum, and on niobium it is about 130 kcal/mole; both these metals have similar melting points (Mo, 2620° C; Nb, 2500 °C and yet, notwithstanding the very different heats of adsorption involved, the degree of sintering in each case is about the same. Again, zirconium and tungsten, which have about the same initial heat of adsorption for carbon monoxide, have degrees of sintering which are also about the same, despite the fact that their melting points differ by about 1500 °C.

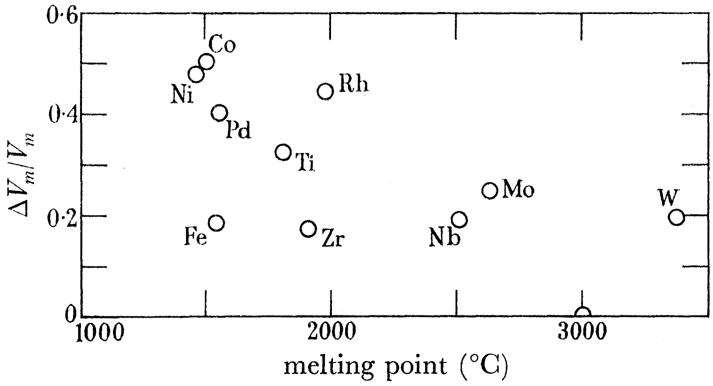


FIGURE 10. The fractional change in the krypton monolayer capacity of a metal film following chemisorption of carbon monoxide as a function of the melting point of the metal.

Correlation with the adsorbate

The heat of adsorption of hydrogen on nickel is very similar to that for the adsorption of carbon monoxide, and yet the value of V_m is scarcely affected by the presence of chemisorbed hydrogen ($q \sim 1$), while chemisorbed carbon monoxide reduces it considerably ($q = 0{\cdot}52$). The insensitivity of V_m to the presence of hydrogen (in the case of hydrogen on tungsten, $q = 0{\cdot}94$) can readily be interpreted in terms of site adsorption of the krypton atoms. There is evidence (Culver, Pritchard & Tompkins 1959), that the strongly bound hydrogen atoms are held in, or somewhat below, the plane of the surface. Further, the work function of the surface is not appreciably affected by the adsorption of hydrogen. In these circumstances, the relatively large krypton atom will experience much the same potential field on the hydrogen covered surface as on the clean surface, and the monolayer coverage of krypton would not be expected, therefore, to be altered significantly by the presence of hydrogen. On the other hand, the presence of large polar molecules, like carbon monoxide, held proud of the plane of the surface, will greatly alter the potential field experienced by a krypton atom compared to that due to the surface atoms alone, and *prima facie*, substantial changes in the krypton monolayer value might be expected. The failure of the attempt, presented below, to show such an effect, in terms of a change of sites presented by the chemisorbed layer does not admit thermal sintering as the cause of the decrease in $q(\mathrm{CO})$ in this case, because the problem posed by $q(\mathrm{CO}) < q(\mathrm{H_2})$ remains.

Manganese

The ability of a manganese film saturated with oxygen to regenerate a substantial fraction of its original adsorptive capacity for both krypton and oxygen on standing (Brennan *et al.* 1960) would seem to point again, not to a real loss of area, which could

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scarcely be regenerated in this way, but to a change in the adsorptive properties of the the presence of oxygen. Diffusion of adsorbed oxygen to a region below the surface would account for both the apparent regeneration of surface area, and the renewed capacity to adsorb oxygen.

Adsorption of krypton on chemisorbed carbon monoxide

The principles for deciding permissible configurations of krypton on chemisorbed carbon monoxide are the same as described in the preceding paper. The configurations of carbon monoxide employed for the present purpose, together with the associated q values are given in table 10. All the krypton configurations referred to in this table are free of nearest neighbour repulsions except for the 111 face of cobalt and nickel (see figure 6*I*). For this case, there is a total interaction energy of 1400 cal/mole due to four nearest neighbours at $\sqrt{7}\,r$ and this is considered permissible.

TABLE 10. THEORETICAL ESTIMATES OF THE MONOLAYER COVERAGES FOR KRYPTON ADSORBED ON UNSINTERED METAL SURFACES SATURATED WITH CARBON MONOXIDE, AND THE ASSOCIATED q VALUES

plane	CO configuration	N(Kr/CO)	q
		hexagonal close packed metals	
1000	figure 5*A*	$1/2\sqrt{3}\,a^2$	0·5
1100	*F*	$1/2ac$	Ti, 0·75; Zr, 0·5
1101	*K*	$1/a\sqrt{(3a^2+4c^2)}$	Ti, 1; Zr, 0·5
		face-centred cubic metals	
100	figure 6*A*	$1/a^2$	1
110	*E*	$1/\sqrt{2}\,a^2$	1
111	*I*	$2/\sqrt{3}\,a^2$	1·5
		body-centred cubic metals	
100	figure 7*A*	$1/2a^2$	1
110	*E*	$1/\sqrt{2}\,a^2$	1 (Fe, 1·5)
211	*L*	$1/\sqrt{6}\,a^2$	1

Apart from the values for titanium and zirconium, q in table 10 is either unity or greater, whereas, in practice, values as low as 0·5 are observed (table 1). Thus, this model fails to explain the reduction in the adsorption of krypton due to adsorbed carbon monoxide. However, the difficulties associated with the supposition of thermal sintering remain undiminished, but if an explanation of the low values of q is to be found in a site model of the adsorption, then clearly a more sophisticated treatment than tried here is necessary.

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