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THE ADSORPTION OF CARBON DIOXIDE ON EVAPORATED METAL FILMS

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CONTENTS

Calorimetric measurements at room temperature have been made of the heats of adsorption of carbon dioxide on evaporated films of iron, cobalt, nickel, titanium, molybdenum, tungsten, tantalum and niobium. These new data, considered along with similar data obtained previously for oxygen and carbon monoxide, provide strong evidence for dissociative adsorption of carbon dioxide into CO and O, except possibly on iron, cobalt and nickel. The saturation coverages for the adsorption of carbon dioxide on all the metals are distinguished by their smallness. Despite this, the adsorptive capacity for hydrogen of surfaces saturated with carbon dioxide is very small, except for nickel and to a lesser degree for iron. These observations have also been accounted for in terms of dissociative adsorption of carbon dioxide and the concentrations of krypton atoms in the monolayer deduced previously. For nickel and cobalt (and to some extent iron), adsorption of carbon dioxide in an undissociated form is a distinct possibility, but a clear conclusion cannot be reached. The linear dependence of heat of adsorption on metallic radius is discussed.

The adsorbed state of carbon dioxide on metals exhibits some exceptional and interesting aspects (Collins & Trapnell 1957). In the present work, the energetics of the adsorption are studied and related to the conclusions of the previous paper.

Experimental

The calorimetric and general experimental procedures were as described by Brennan, Hayward & Trapnell (1960), except that carbon dioxide had to be admitted to the film via a trap at −78 °C rather than at −196 °C.

Carbon dioxide was prepared from A.R. lead carbonate, which was outgassed at 200 °C for 3 h and decomposed at 350 °C. A considerable volume of gas was pumped

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away before a sample was finally collected. The gas prepared in this way contained water and non-condensable components. The latter were removed by repeated cycles of pumping on the solid at −196 °C, followed by warming to room temperature. Condensable impurity was reduced to an acceptable level by passing the gas several times through a trap at −78 °C.

Cylinder hydrogen was purified by thermal diffusion of the gas through a palladium thimble.

Film surface areas were obtained by the B.E.T. method from the −196 °C isotherm of krypton. Calorimetric and surface area measurements were made, in some instances, on the same film and, in others, on separate films deposited in the calorimeter.

Results

Adsorption of carbon dioxide alone

The main calorimetric results are presented in figures 1 and 2. Each increment of carbon dioxide gives an average heat over a small range of the adsorption and the points are plotted to correspond to the centre of each such increment. Where measurements have been made on more than one film, the heat curves have been brought into accurate alinement by normalizing each set of data to the same average value for the limiting coverage. One set of points for titanium (figure 2) refers to heat measurements made with a film of unknown weight. The parameter p is defined by the relation $p = N(CO_2)/N(Kr)$, where $N(Kr)$ is the number of krypton atoms in the monolayer adsorbed on the clean surface and $N(CO_2)$ is the number of molecules of carbon dioxide adsorbed at saturation at room temperature. Saturation for these purposes refers to the coverage after the surface has been exposed to a pressure of about 10^{-5} torr for 5 min. The coverage data are given in table 1; the parameter q is defined by the relation $q = N(Kr/CO_2)/N(Kr)$, where $N(Kr/CO_2)$ is the number of krypton atoms in the monolayer adsorbed by the surface saturated with carbon dioxide.

Table 1. Saturation coverages for the adsorption of carbon dioxide on evaporated metal films, the monolayer volumes for krypton before and after the adsorption and the values of $p = V(CO_2)/V(Kr)$ and $q = V(Kr/CO_2)/V(Kr)$; the volumes are in millilitres at s.t.p.

metal	film weight (mg)	$V(CO_2)$	$V(Kr)$	$V(Kr/CO_2)$	p	q
Ti	—	0·164	0·152	0·148	1·08	0·97
Cr	45·6	0·431	0·782	0·714	0·55	0·91
Mn	43·1	0·132	0·192	0·173	0·69	0·90
Fe	65·3	0·0905	0·300	0·189	0·30	0·63
Co	30·5	0·0277	0·100	0·085	0·28	0·85
Ni	39·2	0·0480	0·149	0·100	0·32	0·67
Nb	8·2	0·0316	0·059	0·051	0·54	0·86
Mo	22·0	0·145	0·300	0·283	0·48	0·94
Ta	23·3	0·093	0·139	0·139	0·67	1·00
W	27·3	0·123	0·250	0·217	0·49	0·87

With the exception of chromium and molybdenum, it is possible to draw a smooth curve through the experimental points of figures 1 and 2. For chromium, the rate of

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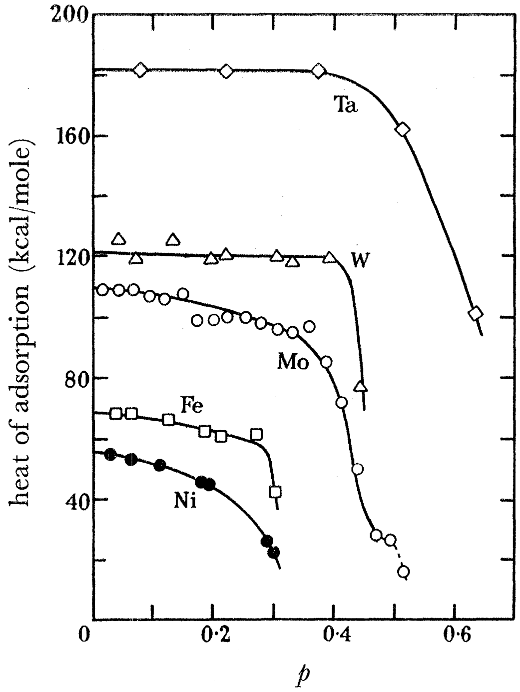


FIGURE 1. The variation of the heat of adsorption of carbon dioxide with surface coverage for tantalum (32·7 mg; 168 kcal/mole), tungsten (25·0 and 31·7 mg; 109 kcal/mole), molybdenum (47·5 mg; 89 kcal/mole), iron (64·3 and 61·8 mg; 61·5 kcal/mole), nickel (35·8, 37·6 and 33·0 mg; 44 kcal/mole). The numbers in parenthesis are the film weights and the average integral heats of adsorption, respectively.

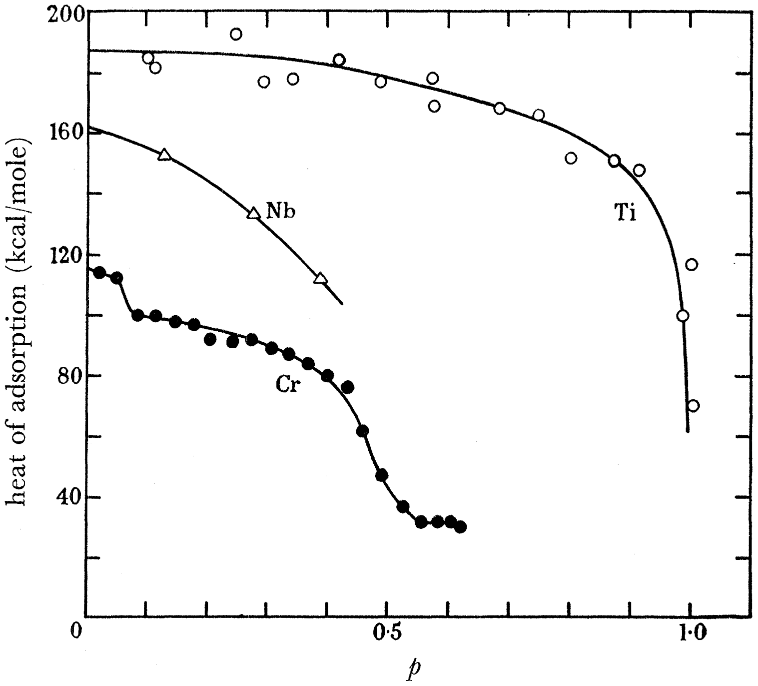


FIGURE 2. The variation of the heat of adsorption of carbon dioxide with surface coverage for titanium (12·7 and 9·8 mg; 163 kcal/mole) niobium (8·2 and 11·6 mg; 132 kcal/mole), chromium (45·6 mg; 81 kcal/mole). The numbers in parenthesis are the film weights and the average integral heats of adsorption, respectively.

uptake of doses subsequent to the admission of the fifteenth dose decreased steadily and the last four increments were adsorbed with a constant heat of 31 kcal/mole. For molybdenum, the last two doses were adsorbed at a much reduced rate and the heat was the same for each at 28 kcal/mole. The isolated point on the molybdenum curve at 16 kcal/mole corresponds to the small, but rapid uptake which was observed after the film had stood overnight. It is possible that other metals might exhibit shelves in the heat versus coverage curves at nearly full coverage, but that these are not apparent because the dose size has not been small enough.

Measurements of the heat of adsorption of carbon dioxide on manganese were also made, but the results have not been plotted because there is some doubt as to the cleanness of these films, which were prepared by evaporation from a tungsten filament onto which a deposit of manganese had been electroplated. Data relating to a film which had been prepared after vigorous outgassing, in which evaporation occurred to a considerable extent, are given in table 2; after each increment, the pressure fell to less than 10^{-6} torr until the limiting coverage was reached. For other manganese films, residual pressures were recorded during the course of the adsorptions and the heats of adsorption measured in these cases were rather lower than those reported in table 2. The data in table 2 refer to the cleanest manganese film prepared in this investigation, but the film may still not have been free of contamination. In table 2 are also reported the heats for the adsorption of carbon dioxide on cobalt for which the smallness of the coverage limited the number of increments to two.

TABLE 2. THE VARIATION WITH COVERAGE OF THE HEAT OF ADSORPTION OF CARBON DIOXIDE ON EVAPORATED FILMS OF MANGANESE (43·1 MG) AND COBALT (43·3 MG)

	manganese					cobalt	
$p = \dfrac{N(CO_2)}{N(Kr)}$	0·074	0·224	0·374	0·524	0·666	0·126	0·262
heat of adsorption (kcal/mole)	62	60	54	47	29	37	18

Collins and Trapnell (1957) have reported that very little chemisorption of carbon dioxide occurs on rhodium, platinum and palladium. We confirm their finding for platinum; such adsorption as did occur failed to produce any detectable calorimetric response.

The initial rates of adsorption were all extremely fast. The time taken to peak calorimeter deflexion was limited by the time taken for the gas dose to diffuse through the apparatus. For example, in the case of one molybdenum film, for which twenty doses of gas were required for saturation, the rate of uptake remained immeasurably fast until the sixteenth increment; thereafter the rate diminished with coverage. Similar behaviour was exhibited by the other metals, though the stage at which the rate of adsorption began to decrease depended on the metal.

The limiting coverages found here are smaller than those reported by Collins & Trapnell (1957), who used the extent of the adsorption of hydrogen to obtain a value for the number of available surface atoms. This procedure is unreliable (Porter & Tompkins 1953; Klemperer & Stone 1957) and probably accounts for the discrepancy. It is notable that despite the fall in rate of adsorption as saturation is approached, $p_{\max.}$ is a well defined parameter. Even after pumping for 30 min on saturated films of iron, cobalt and nickel, no fast adsorption of carbon dioxide could be detected subsequently; for molybdenum, tantalum and tungsten, after such treatment, there was a small rapid uptake of carbon dioxide, but the heat of adsorption was immeasurably small.

TABLE 3. CARBON MONOXIDE IN THE GAS PHASE OVER SURFACES SATURATED WITH CARBONDIOXIDE

metal	carbon monoxide present as a molar percentage of the adsorbed carbon dioxide
Ti	2·7
Nb	0·6
Ta	0·3
Cr	0·07

In some cases, tests were made for the presence of carbon monoxide over the saturated film. This was done by freezing out the carbon dioxide at −196 °C and ascribing any pressure of non-condensable gas remaining entirely to carbon monoxide. Data relating to these cases in which carbon monoxide was detected are given in table 3. The amount of carbon monoxide formed evidently increases rapidly as the heat of adsorption increases.

Adsorption of hydrogen after saturation of the surface by carbon dioxide

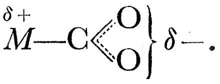
Collins & Trapnell (1957) noted that while films saturated with carbon dioxide would take up appreciable amounts of oxygen, their capacity for hydrogen was very small. We have examined the influence of chemisorbed carbon dioxide on the heat of adsorption of hydrogen; the results are shown in table 4. The admissions of hydrogen were made after pumping on the films to remove any unadsorbed carbon dioxide. Heat measurements were handicapped by the smallness of the adsorption. Apart from chromium, for which the heat observed here is considerably smaller than the value of 44 kcal/mole reported by Beeck (1950) for the initial heat of adsorption of hydrogen on clean chromium, the initial heats of adsorption of hydrogen in the presence of carbon dioxide are very similar to those reported for adsorption on the uncontaminated surfaces.

TABLE 4. THE EXTENT AND HEAT OF ADSORPTION OF MOLECULAR HYDROGEN ON SURFACES SATURATED WITH CARBON DIOXIDE

metal	pressure (torr × 10^3)	$V(H_2/CO_2)$ (ml at s.t.p.)	$p(H_2/CO_2) = \frac{V(H_2/CO_2)}{V(Kr)}$	heat of adsorption (kcal/mole)
Cr	—	0·0015	0·0019	26
Fe	0·4	0·0154	0·051	34
	5·4	0·0244	0·081	30
	13·1	0·0299	0·099	27
Ni	0·1	0·0210	0·142	36
	0·6	0·0407	0·275	27
	2·0	0·0565	0·382	19
	12·8	0·0594	0·402	13
Mo	—	0·0068	0·023	—
W	10·1	0·0050	0·020	38

Discussion

Infra-red absorption studies of carbon dioxide adsorbed on nickel (Eischens & Pliskin 1957) are interpreted in terms of the pseudo carboxylate ion



$$\overset{\delta+}{M}\text{—C}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\delta-.$$

This species may indeed be responsible for the absorption bands observed, but there can be little doubt that, for the majority of the metals studied in this investigation, the major part of the carbon dioxide adsorbed on metal films is not in this form. Indeed, under some conditions, infra-red spectroscopy also provides evidence for the dissociative adsorption of carbon dioxide on nickel (Eischens & Pliskin 1961). Direct evidence for dissociative adsorption of carbon dioxide comes from the work of Hayward & Gomer (1959) who found that carbon dioxide adsorbed on a tungsten field emitter was present as CO and O, in the temperature range 400 to 600 °K. They also found that when tips fully covered with carbon dioxide are heated above 400 °K a slight amount of reversible desorption occurs, leading to the conclusion that a small amount of undissociated, loosely chemisorbed carbon dioxide existed at high coverages below 600 °K. It was not possible to ascertain whether dissociative adsorption also occurred below 450 °K.

Arguments derived from the present investigation relating to this question are presented in the following section.

Evidence for dissociative adsorption of carbon dioxide

The energy of adsorption

It does not seem feasible to account for the very large heats generally observed for the adsorption in terms of a pseudo carboxylate species. It has been suggested (Collins & Trapnell 1957) that the electron affinity of carbon dioxide is probably high enough to permit strong bonding with the surface. However, a review of the latest values of work function and ionization potentials shows that there is no correlation of the heat of adsorption with either of these quantities, and no support for an undissociated complex can be found in arguments of this kind.

If it is assumed that the adsorbed CO and O derived from the dissociative adsorption of carbon dioxide are comparable energetically to the adsorbed states derived directly from gaseous carbon monoxide and oxygen, it is possible to calculate a theoretical value, $Q_d(\mathrm{CO_2})$, for the heat of adsorption of carbon dioxide by means of the equation

$$Q_d(\mathrm{CO_2}) = Q(\mathrm{CO}) + \tfrac{1}{2}Q(\mathrm{O_2}) - 68$$

in which all quantities are expressed in kilocalories per mole. In table 5, the values of $Q_d(\mathrm{CO_2})$ are compared with the experimental values for the adsorption. Despite some discrepancies, there is an overall correspondence between the two which encourages acceptance of this hypothesis. Thus, it is possible to account in a general way for the heats of adsorption of carbon dioxide, some of which are surprisingly large, without introducing any *ad hoc* notions.

The case of iron and especially of cobalt and nickel merits special consideration here as in the later paragraphs. These metals have the lowest values for $Q(CO_2)$ which are noticeably larger than the calculated heats $Q_d(CO_2)$. It seems possible that, whereas dissociative adsorption occurs on the metals with larger values of $Q(CO_2)$, for these group VIII metals adsorption of carbon dioxide in an undissociated form might be energetically more profitable. This argument correlates with the infra-red spectroscopic evidence, but it is not sufficiently strong to warrant a clear conclusion.

Table 5. Comparison of the experimental heats of adsorption of carbon dioxide $Q(CO_2)$, with the heats, $Q_d(CO_2)$, calculated on the supposition of dissociative adsorption from the experimental heats of adsorption of carbon monoxide, $Q(CO)$, reported in the preceding paper, and of oxygen, $Q(O_2)$, reported by Brennan *et al.* (1960); all energies are in kilocalories per mole

	observed initial heats of adsorption			
metal	$Q(O_2)$	$Q(CO)$	$Q(CO_2)$	$Q_d(CO_2)$
Ti	236	153	191	203
Mn	150	78	63	85
Fe	136	46	68	46
Co	100	47	37	29
Ni	107	42	54	28
Nb	208	132	152	168
Mo	172	74	109	92
W	194	126	122	155
Ta	212	134	182	172
Rh	102	46	—	29
Pt	70	48	—	15
Pd	68	43	—	9

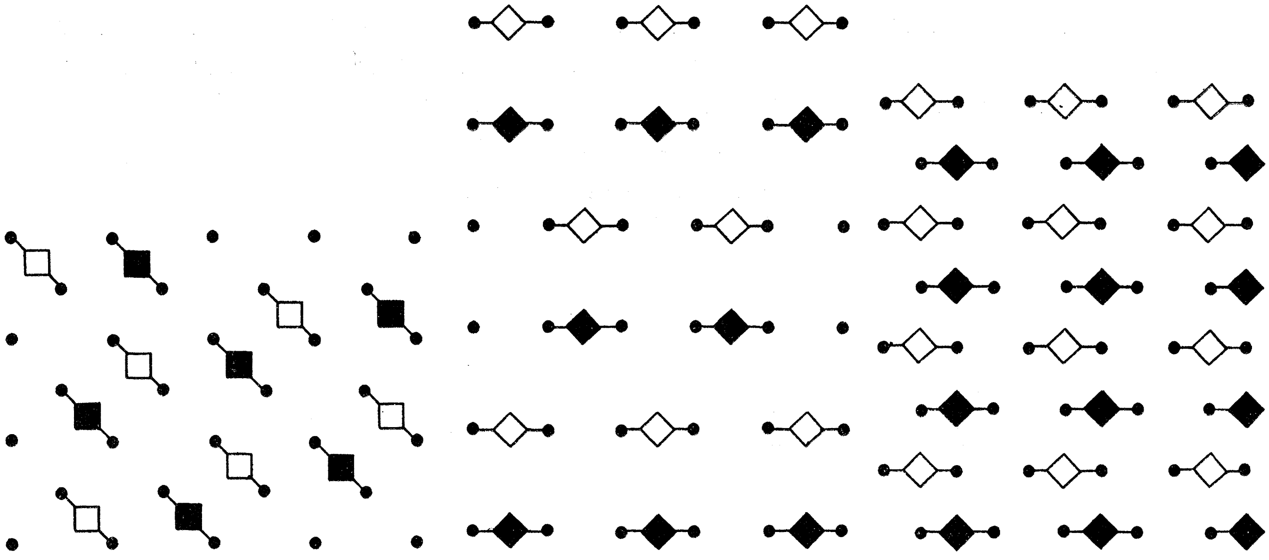
It is tempting to suppose that the reason why carbon dioxide does not adsorb on rhodium, platinum and palladium to any significant extent is because $Q_d(CO_2)$ is so small for these metals. However, as discussed below, a small net heat of adsorption of dissociatively held carbon dioxide does not imply weak surface bonds permitting recombination and desorption.

The irreversibility of the adsorption

For all the metals, the heat of adsorption falls sharply as the limiting coverage is reached. For iron, cobalt, and nickel the final heats are especially low, and these are the metals with the lowest coverages, so it could be that the heat of adsorption has fallen to a level at which coverage is controlled by thermodynamic equilibrium considerations. However, even for these metals, the adsorption in its later stages remains virtually irreversible, as shown by the impossibility of desorbing any significant quantity of carbon dioxide from the saturated surface by pumping for 30 min. This failure to observe desorption of carbon dioxide could be due simply to a slow rate of desorption associated with a rising heat as the coverage is reduced. Such an explanation would require the carbon dioxide to be held in an undissociated form, because, if it were dissociated, the CO and O fragments would be too strongly held to be mobile, despite the small heat of adsorption, and thermodynamic equilibrium would not be attained.

The low coverage

It is very difficult to see how an entity like the pseudo carboxylate group could give rise to the very low coverages which are a distinguishing feature of these adsorptions (cf. table 1); values for $p(CO_2)$ of about one-third those for $p(CO)$ are typical. It is unlikely that rotation of adsorbed CO_2 would be adequate to block adsorption on neighbouring sites, but, even if it were, it would still not provide an explanation of the low capacity of these surfaces for carbon dioxide, nor of their inability subsequently to adsorb appreciable quantities of hydrogen.



A, 100 face *B*, 110 face *C*, 111 face

FIGURE 3. Configuration for carbons dioxide dissociatively adsorbed on the face-centred cubic metals. ●, Centres of the surface metal atoms; -◇-, centres of bridge-bonded CO molecules; -◆-, centres of bridge-bonded O molecules.

Acceptance of the hypothesis of dissociative adsorption of carbon dioxide, provides a means of accounting for low p values. The configuration of lowest coverage which can plausibly be constructed is that subject to the following restrictions (cf. the conclusions of the preceding paper):

(i) Both CO and O are bridge-bonded to two surface metals atoms.

(ii) No one surface atom can participate in more than one bond.

These restrictions mean, in effect, that each adsorbed carbon dioxide molecule, existing as CO and O, occupies four metal atoms. In figure 3, the densest configurations possible, subject to these restrictions, have been drawn for the face-centred cubic metals; the p values are: 100 and 110, 0·5; 111, 0·75. Nickel has a short lattice spacing ($r = 1{\cdot}25$ Å), but it is not possible to attribute any significant intermolecular repulsions for these configurations, even for this metal. Similar conclusions apply to configurations on the other metals. Hence, on these arguments, values of p between 0·5 and 0·75 would be expected. Reference to table 1 shows that chromium, niobium, molybdenum, tantalum and tungsten all conform adequately to these limits. However, there is a regularity about the variation of the dependence of p on $Q(CO_2)$ (figure 4) which must be indicative of an additional factor.

A graph of p against metallic radius would have a form similar to that of figure 4 (cf. figure 5) and it might be surmised that increasing lattice spacing could account for extra adsorptive capacity. However, this is very unlikely to be so. If bonding of the adsorbed species to the surface atoms is strongly directional, as it must surely be for energies as large as these, then a smooth variation of coverage with increasing lattice spacing is not to be expected, nor, generally, is it found. We believe that the dominant factor in increasing p is the increasing heat of adsorption and tentatively propose that this is due to the influence of the heat of adsorption on the packing of the adsorbate. There is reason to believe from field ion microscopy that, when a diatomic molecule adsorbs with the liberation of a large quantity of heat, the two atoms come to rest on the surface at some distance apart. There is also reason to believe that adsorption from the gas phase can give rise to regular arrays of the adsorbed species and self-consistent results were obtained in the previous paper on the assumption that carbon monoxide molecules occupied metal surfaces in an ordered manner. The saturation coverage of dissociatively held carbon dioxide is probably a function of these two conflicting processes. The act of adsorption of carbon dioxide could conceivably require four unoccupied metal atoms in the correct configuration. As the adsorption proceeds, the number of site configurations suitable for adsorption will diminish, because both CO and O will be immobile on the surface. Eventually, the unavailability of adsorption sites, as opposed to residence sites, could terminate the adsorption. At appreciable coverages, adsorbed CO and O moving on the surface immediately subsequent to adsorption will collide with CO and O adsorbed previously, and it is probable that such collisions will dislodge these otherwise immobile species. The extent of the disturbance in the adsorbed layer will depend on the energy of CO and O in their mobile condition immediately after adsorption. The larger the heat

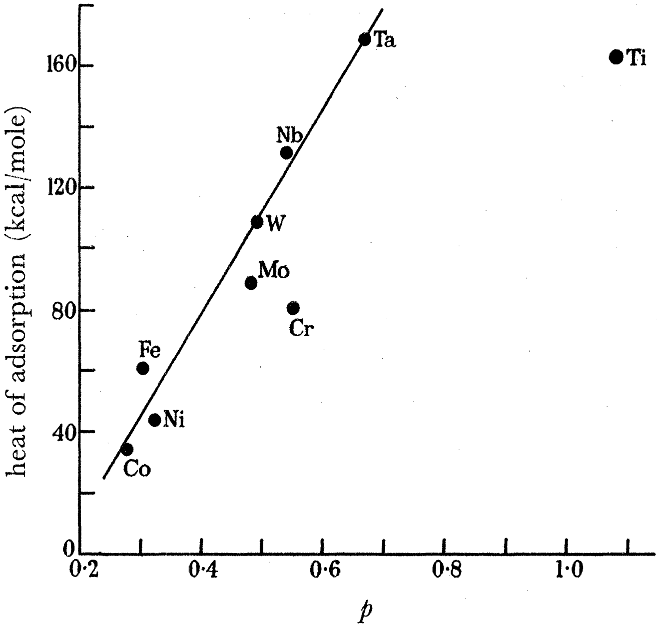


FIGURE 4. The dependence of the saturation coverage for carbon dioxide upon the heat of adsorption.

of adsorption, the greater the possibility of a redistribution within the adsorbed layer and an increase in the availability of adsorption sites for carbon dioxide. This hypothesis provides an explanation of the trend in the observed p values with heat of adsorption at the same time as the average value of p is accountable in terms of a four site adsorption. It also explains how the adsorption can still proceed even when the process has acquired an appreciable activation energy due to the activated nature of the surface diffusion necessary if the adsorption is to continue.

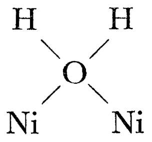
These arguments provide for a self-consistent interpretation of the saturation coverage for all the metals, including the group VIII metals. However, for these last metals, their very low coverages can be discussed in different terms, as was done above, and the present arguments do not detract from that earlier discussion.

The appearance of gaseous carbon monoxide

The appearance at saturation of a non-condensable gas (table 3) was most marked for the metals having the highest heats of adsorption. Assuming the identification of this gas with carbon monoxide to be correct, the observation is difficult to account for. For dissociative adsorption, the expectation is that the effect would be most marked with the metals for which the heat of adsorption was low. In the case of titanium, which is alone in exhibiting the effect to an appreciable degree, it might be that some oxidation of the metal has occurred and this would also explain the anomalously high value of p obtained with titanium.

The adsorption of hydrogen on surfaces saturated with carbon dioxide

If carbon dioxide were adsorbed as an undissociated entity, the smallness of the saturation coverage would give rise to the expectation of an appreciable adsorptive capacity for hydrogen, both on the grounds of the presence of unoccupied sites and the supposition that hydrogen is adsorbed close to or even within the surface, while an adsorbed CO_2 molecule would stand well above the plane of the surface. The fact that chromium, molybdenum and tungsten saturated with carbon dioxide do not adsorb more than one-fiftieth of the capacity of the clean surface is in keeping with the view that the adsorptive capacity of the metal atoms is already saturated and this accords with dissociative adsorption of carbon dioxide. The notion that hydrogen is being adsorbed on the few remaining metal atoms might, with reservations, also be applied to iron. However, with nickel, for which the $p(CO_2)$ value is close to that for iron, this argument breaks down, because the extent of the hydrogen adsorption on this surface saturated with carbon dioxide is one quarter of the adsorptive capacity of the clean surface. Quinn & Roberts (1962) have studied this system using the adsorption of hydrogen to determine the state of the surface layer. Unfortunately, their discussion is invalidated by failure to appreciate that carbon dioxide adsorption, even if it is dissociative, could not possibly be simulated by adsorption of a mixture of gaseous carbon monoxide and oxygen, because each species would distribute itself differently within the metal film. Further, in the case of experiments involving different coverages of oxygen, it is important to remember that the adsorbate is not uniformly distributed over the entire surface area of the film, as assumed by these authors, but is confined to that part of the surface which is most accessible from the gas phase. For these reasons, the conclusion of Quinn & Roberts in favour of dissociative adsorption cannot be regarded as strengthening the case for this hypothesis. Siddiqi & Tompkins (1962) have shown that atomic hydrogen can be adsorbed at −183 °C by nickel saturated with carbon monoxide, but most of the hydrogen desorbs on warming to room temperature. However, in the presence of adsorbed oxygen, it is conceivable (Siddiqi & Tompkins 1962) that strong complexing could occur, for example as



but it is difficult to see why nickel should exert this property and not its congeners. The hypothesis of adsorption of carbon dioxide in an undissociated form on nickel lends itself better to an explanation of the ability of this metal to adsorb an appreciable quantity of hydrogen when saturated with carbon dioxide. The presence of undissociated CO_2 molecules in low concentration would leave available the necessary space for the adsorption of hydrogen. For iron, the facts would be met by a contribution from both dissociated and undissociated forms of adsorbed carbon dioxide.

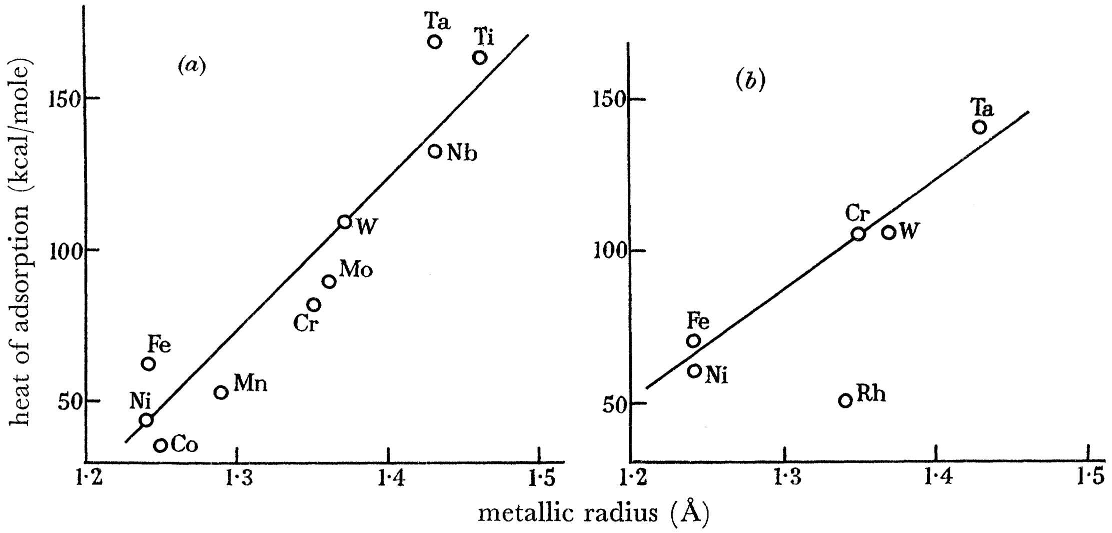


FIGURE 5. The dependence of the heat of adsorption of (*a*) carbon dioxide and (*b*) ethylene on the metallic radius.

Correlation of the heat of adsorption with metallic radius

Brennan *et al.* (1960) drew attention to an interesting correlation between the heat of adsorption of oxygen and metallic radius. In the preceding paper (p. 358), this correlation was shown to hold for the adsorption of carbon monoxide. In figure 5, the correlation is seen to apply also to carbon dioxide, using heats of adsorption reported in this paper, and to ethylene, using published values for the heats of adsorption. The horizontal branch is missing for carbon dioxide because the heats of adsorption are small on platinum, palladium and rhodium, but these metals would undoubtedly form a separate branch were the data available to define it. For ethylene, the existence of the horizontal branch is indicated by the point for rhodium.

The increase in the heat of adsorption with increasing lattice spacing could conceivably be related to directional bonding between neighbouring surface atoms and its disruption by the presence of an adsorbate molecule. Thus, in the absence of an adsorbate, bonding could occur between neighbouring surface atoms which is specific to the surface and, because of enhanced orbital overlap, is stronger the shorter the lattice spacing; such bonding would presumably involve the d_{xy} orbitals. If the bonding of the adsorbate molecule were to implicate these same metal orbitals, then, for a given overlap energy between adsorbate and metal orbitals, the net heat of adsorption would be greater the weaker the initial interaction between surface metal atoms. This explanation is no more than conjectural, and disregards the observations for the noble metals, but it does correlate in a general way with the notion of bridge-bonded CO and O, with only one orbital available per metal atom, as described in this and the preceding paper.

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