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Chemisorption and Displacement Processes on Molybdenum Films

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The chemisorption of hydrogen, carbon monoxide, and nitrogen has been investigated on molybdenum films. Evidence is obtained for carbon monoxide being bonded differently on a nitrogen-covered surface than on a clean surface. Surface potential and other data gave no indication of any surface complexes involving nitrogen and hydrogen. Presorbed hydrogen and nitrogen had little influence on the krypton monolayer while carbon monoxide reduced it substantially.

Presorbed hydrogen was desorbed by adsorbing nitrogen under certain conditions of hydrogen coverage and temperature. The kinetics of hydrogen adatom recombination and subsequent desorption have been investigated and the specific nature of nitrogen chemisorption emphasized. The activation energy of hydrogen desorption ($\sim$20 kcal mole^{-1}) is close to the heat of hydrogen adsorption at the same coverage. On the basis of a two-dimensional gas model the molecular desorption process is shown to be very inefficient.

INTRODUCTION

In order to unravel the possible processes occurring during simple surface reactions it is important to consider the chemisorption on the surface of individual gases and, what is probably more important, mixtures of gases. By monitoring the gas phase during mixed adsorption information regarding surface displacement, the formation of complexes, and the acceleration or retardation of surface processes can be ascertained. Each of these may occur during catalysis and may not be detected during normal catalytic studies.

The use of physical adsorption data and the BET theory has been particularly significant in the interpretation of surface reactions. Although field emission and other data have suggested that inert gas interaction can be specific, little information has been obtained on the possible significance of specificity in influencing surface area estimates. This paper is, therefore, concerned with some aspects of the chemisorption of both single and mixed gases, the use of surface potential data for establishing the existence or otherwise of new surface species, and the application of physical adsorption techniques in estimating the surface areas of metal surfaces on which gas has been adsorbed.

EXPERIMENTAL

In its main features the apparatus is similar to that used in a previous investigation (*1*). It allows adsorption isotherms, rates of adsorption at constant pressure, and surface areas to be evaluated. Surface potential measurements were determined by a capacitor technique with a different apparatus (*2*). The molybdenum films were prepared as previously described (*3*) and pure gases were obtained in sealed bulbs from the British Oxygen Company Limited.

A calibrated Pirani gauge enabled analysis to be carried out of nitrogen-hydrogen mixtures, the gauge being first calibrated with the individual gases and checks made that our interpolation gave accurate analysis of mixtures of known composition. It was usual to carry out analysis at a total pressure of about 10^{-2} mm, when the absolute accuracy was about 5%.

RESULTS

Adsorption of CO and H_2

The adsorption of CO at −195° consisted of an extensive process which was immeasurably fast, but above a pressure of 10^{-5} mm a slow adsorption of limited extent occurred. Table 1 shows the extent of CO uptake at −195° and a pressure of 10^{-3} mm (V_{CO}), the volume of krypton required to form a monolayer before (V_{m_1}) and after (V_{m_2}) adsorbing CO, and the ratios V_{CO}/V_{m_1}, V_{CO}/V_{m_2}, and V_{m_1}/V_{m_2}. A comparison of the extent of CO adsorption at −195° and at 0° was made by first adsorbing the gas at 0° to a pressure of 10^{-3} mm, cooling the film to −195° and adding gas to a pressure of 10^{-3} mm. The value of V_{CO} $(-195)°/V_{CO}$ $(0°)$ is approximately equal to 1.3. The V_{CO}/V_{m_2} ratio at 0° and at a CO pressure of 10^{-3} mm was 2.6 ± 0.1, as can be seen from Table 2.

TABLE 1

INTERACTION OF KRYPTON AND CARBON MONOXIDE WITH MOLYBDENUM FILMS AT −195°

V_{m_1} (ml × 10^3)	V_{m_2} (ml × 10^3)	V_{CO} (ml × 10^3)	V_{CO}/V_{m_2}	V_{CO}/V_{m_1}	V_{m_1}/V_{m_2}
25.6	18.7	58.7	3.14	2.29	1.37
28.6	17.1	61.4	3.59	2.15	1.67
37.0	24.4	80.6	3.30	2.74	1.52
34.5	21.3	66.6	3.13	1.93	1.62

TABLE 2

ADSORPTION OF CARBON MONOXIDE AT 0° AND 10^{-3} MM IN RELATION TO THE KRYPTON MONOLAYERS

V_{CO} (ml × 10^3)	V_{m_2} (ml × 10^3)	V_{CO}/V_{m_2}	V_{CO}/V_{m_1}[a]
44.0	17.4	2.53	1.6
108.4	42.3	2.56	1.6
88.5	33.0	2.68	1.7
145.4	55.7	2.61	1.7

[a] Estimated from the mean V_{m_1}/V_{m_2} ratio in Table 1.

Carbon monoxide isotherms were determined in the temperature range −23° to 43°, the procedure being to admit a dose of gas at the highest temperature, then measure the equilibrium pressures on successively cooling the film in stages to −23°. The temperature was then raised to 43° and the equilibrium pressure again noted to ensure reversibility of the adsorption process. Isosteric heats were calculated for different coverages by means of the Clausius-Clapeyron equation; in order to compare values for different experiments $\theta = 1$ is taken to correspond to the volume of CO adsorbed at 0° ~ 4 × 10^{-2} mm. Equation (1) describes the variation of the heat of adsorption ΔH (kcal mole^{-1}) with the coverage θ in the range stated

$$\Delta H = 50\theta - 50.5 \qquad (1)$$

where θ is 0.75 to 0.95.

The low heats (~10 kcal mole^{-1}) at $\theta \simeq 0.8$ are compatible with the fact that about 15% of the gas adsorbed at 0° may be removed by pumping at 50° for 50 min. Also the small values of about −5 kcal mole^{-1} at $\theta = 0.9$ certainly suggest that the molecules may be "physically" adsorbed, the interaction being possibly of the charge-transfer type.

The value of V_{H_2}/V_{m_2} was 1.55 ± 0.05 where V_{H_2} is the volume of hydrogen adsorbed at 0° and 10^{-3} mm and V_{m_2} is the volume of krypton required to form a monolayer on the hydrogen-covered surface. Hydrogen was shown to have very little effect on the adsorption of krypton since $V_{m_1}/V_{m_2} = 1.1$ where V_{m_1} is the volume of krypton required to form a monolayer on the clean film. Hydrogen isotherms were determined by a procedure similar to that described for CO and at a film temperature of 60° and a hydrogen pressure of 5 × 10^{-3} mm ($V_{H_2}/V_{m_2} \simeq 1.3$) ΔH was ~ −15 kcal mole^{-1}. These measurements are particularly helpful in elucidating the mechanism of H_2 displacement by nitrogen and under certain conditions used in the displacement experiments (see section on displacement) we estimated ΔH to be ~ -18 kcal mole^{-1}.

Adsorption of N_2

At 0° 80% of the total nitrogen uptake at 10^{-2} mm was adsorbed instantaneously at a pressure less than 10^{-5} mm. The kinetics of the slow nitrogen uptake was investigated at constant pressure and successively increasing temperatures. Between 0° and 100°C, Eq. (2) summarizes the data at a given coverage θ ($V_{N_2}/V_{M_2} \simeq 0.75$)

$$\text{rate } (\theta) = kp^{0.85} \exp [(-9{,}000 \pm 1{,}000/RT] \quad (2)$$

where k is a constant and p the pressure. The activation energy is the mean of eleven separate experiments and over the restricted range of coverage studied no trend in the activation energy was observed. However, at about 200° the value was somewhat greater ($\sim$14 kcal mole^{-1}) and may represent nitridation although $V_{N_2}/V_{m_2} < 1.0$. The pressure dependence value of 0.85 is taken to imply a dependence of unity.

The adsorption at 0° was virtually irreversible since evacuating for 1 hr at 100° and readsorbing nitrogen at 0° resulted in only 3×10^{-4} ml being adsorbed, i.e. about 1% of the initial uptake. This fact is reinforced by our inability to distinguish nitrogen isotherms in the temperature range −40° to +40°C. The low coverage attained by nitrogen on transition metals is well known as also is the ability of such nitrogen "covered" surfaces to absorb further such gases as H_2 and CO (*4*, *5*). Table 3 shows the maximum volume of nitrogen, V_{N_2} adsorbed at 0° and 10^{-5} mm, the volume of hydrogen or carbon monoxide, V_g, which can be subsequently adsorbed, V_{m_1} the volume of krypton required to form a monolayer, and the ratio V_{N_2}/V_{m_1} and V_g/V_{N_2} in each case.

It is clear that much more CO than H_2 is adsorbed by films on which nitrogen has been preadsorbed; the value of V_{CO}/V_{N_2} is about 1.7 while V_{H_2}/V_{N_2} is only 0.5. Much of this CO (about 25%) can be removed by pumping for 40 min at 50°.

Adsorbed hydrogen does not induce the adsorption of nitrogen under our experimental conditions since when nitrogen was adsorbed to a pressure of 10^{-3} mm at 22° and hydrogen added there was no change in the gas phase composition. This behavior is, therefore, quite different from that recently observed by Tamaru (*6*) with an iron catalyst under ammonia synthesis conditions.

Surface Displacement Processes

Analysis of the gas phase during the interaction of hydrogen with a nitrogen "covered" surface at 60° showed that the gas phase was always pure hydrogen and no evidence was obtained for nitrogen displacement. We have studied the displacement of absorbed hydrogen by nitrogen under various conditions, in the first place to determine whether there was some critical coverage of hydrogen below which displacement would not occur at a film temperature of about 60°. It was shown that for values of V_{H_2}/V_{m_2} less than unity displacement of adsorbed hydrogen did not occur on admitting nitrogen to a film maintained at 60°, i.e. nitrogen was adsorbed without simultaneous hydrogen desorption. However, at values of V_{H_2}/V_{m_2} greater than unity rapid displace-

TABLE 3

ADSORPTION OF NITROGEN BY MOLYBDENUM FILMS AT 0° AND THE SUBSEQUENT ADSORPTION OF HYDROGEN AND CARBON MONOXIDE

V_{N_2} (ml × 10^3)	Gas (g)	V_g (ml × 10^3)	V_{m_1} (ml × 10^3)	V_{N_2}/V_{m_1}	V_g/V_{N_2}
33.6	H_2	15.9	44.8	0.75	0.48
31.7	H_2	16.6	44.0	0.72	0.52
47.4	CO	77.4	60.0	0.79	1.63
47.3	CO	90.0	66.0	0.72	1.90

ment of hydrogen by nitrogen was observed. In order to study the kinetics of hydrogen displacement it was usual to adsorb hydrogen at 60° to a pressure of about 2×10^{-4} mm and to cool the film to 20° when the pressure fell to $<10^{-4}$ mm. A dose of nitrogen was then admitted and the gas phase composition monitored by the Pirani gauge as a function of time and temperature. Figure 1 shows an analysis of the gas phase when nitrogen was admitted to the film maintained at 20° and subsequently when the film temperature was increased first to 40° and finally to 60°. A rapid adsorption of nitrogen occurs at 20° with no comparable fast hydrogen desorption but this is quickly followed by hydrogen desorption with simultaneous nitrogen adsorption. When the film temperature was increased to 40° there was a fast hydrogen desorption but no comparable nitrogen adsorption. Subsequently the expected displacement–adsorption process took place. The value of the ratio V_{N_2}/V_{m_2} (where V_{N_2} and V_{m_2} are the volumes of nitrogen adsorbed at 40° and of krypton required to form a monolayer) is 0.2, which compares with 0.7 for nitrogen on a clean film. From a comparison of the rates of hydrogen desorption at different temperatures but at fixed coverages the activation energy was 20 ± 1 kcal mole^{-1}. The value of V_{H_2}/V_{m_2} during these experiments was about 1.2 and the activation energies were determined at the point at which displacement at 20° was becoming slow.

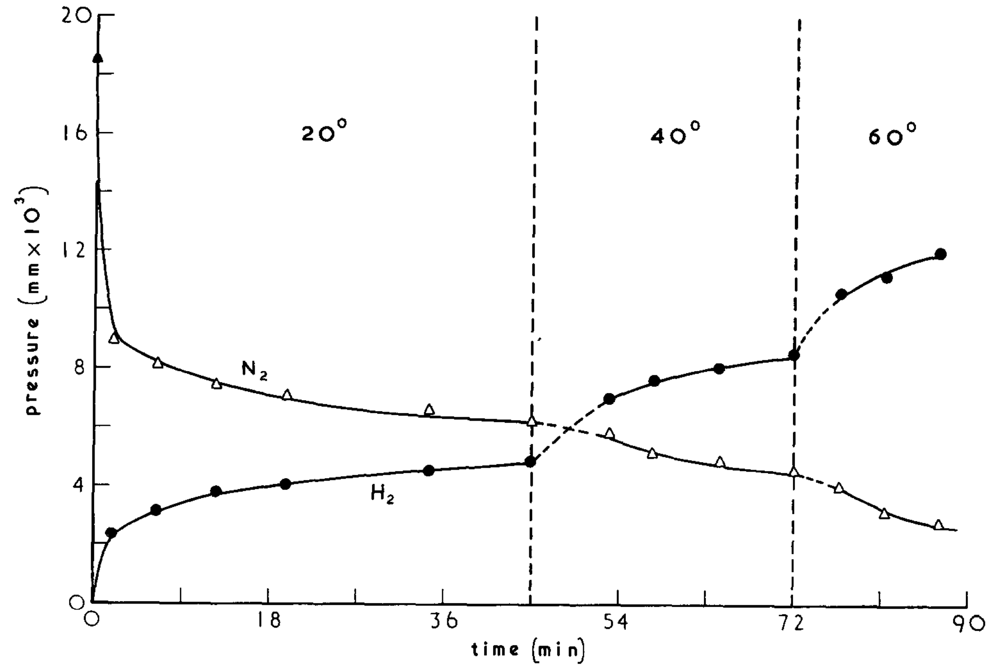


Fig. 1. Analysis of gas phase when nitrogen interacted at 20°, 40°, and 60° with a molybdenum film covered with hydrogen to a pressure of $\sim 10^{-4}$ mm at 60°. ($V_{H_2}/V_{m_2} \simeq 1.2$) △, N_2; ●, H_2; ▲, N_2. Pressure calculated for zero time.

The pressure dependence of the displacement process at 20° was determined by measuring the rate of hydrogen displacement r_1 at a given nitrogen pressure p_1, then suddenly changing the pressure to p_2 ($p_2 \simeq 10p_1$) and measuring the new rate r_2 of hydrogen displacement [see Fig. 2 (b)]. Then from the relationship $r_1/r_2 = (p_1/p_2)^n$ the pressure dependence n of the process was calculated. Values ranging from about 0.25 to 0.5 were estimated for n and, although it is not possible to assign from our particular experiments a particular value of n due to

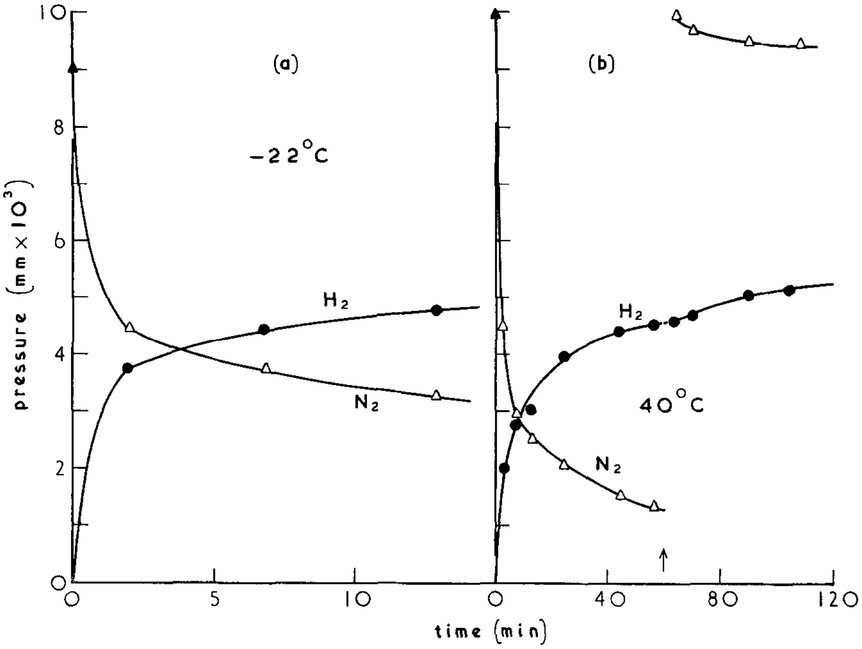


FIG. 2. (a) Analysis of gas phase when nitrogen interacted at −22° with a molybdenum film covered with hydrogen at −22° to a pressure of ~10^{-4} mm. ($V_{H_2}/V_{m_2} \simeq 1.5$). Symbols as for Fig. 1.

(b) Influence of nitrogen pressure on hydrogen displacement at 40°C. Symbols as for Fig. 1. ↓ indicates the point at which the nitrogen pressure was increased.

experimental difficulties, the value is clearly not unity and probably less than 0.5.

In some experiments, after the displacement-adsorption process had become very slow at 20° and a hydrogen pressure of 2×10^{-3} mm, the system was evacuated for about 30 min at 20°, hydrogen readmitted to a pressure of ~2×10^{-3} mm (to compensate for any loss from the surface during evacuation) and nitrogen added. Only a very slow displacement of hydrogen was observed, which proves that the nitrogen adsorbed during displacement was irreversible, since an enhanced rate of displacement would be expected had the adsorbed nitrogen been removed during evacuation.

Displacement experiments were also carried out at lower temperatures and at much higher hydrogen coverages than that used in the experiments described above. Hydrogen was adsorbed on a film at −22° until V_{H_2}/V_{m_2} was about 1.5 and addition of nitrogen to such a film at −22° gave rise to hydrogen displacement with simultaneous nitrogen adsorption. In this case (Fig. 2a) the nitrogen-hydrogen analyses as a function of time are virtually mirror images, and there is no fast nitrogen adsorption without a simultaneous hydrogen desorption (cf. Fig. 1).

A third type of displacement experiment was investigated, namely adsorbing hydrogen at 60° to a final pressure of ~3×10^{-4} mm, cooling to −22°, and then adding nitrogen. In this case the initial hydrogen coverage before nitrogen adsorption was the same as in the experiment at 20° (Fig. 1) but the film temperature was −22°. Nitrogen was adsorbed at the latter temperature but there was no evidence for hydrogen displacement; only when the temperature was increased to 20° was hydrogen desorption detected. In Table 4 are summarized the surface conditions, temperature, and the occurrence or otherwise of hydrogen displacement by nitrogen.

In some experiments after the displacement of adsorbed hydrogen by nitrogen had been completed at 60° the system was evacuated, the reaction vessel isolated, and

TABLE 4

Surface Conditions under which Hydrogen Adatoms were Desorbed by Nitrogen

H_2 coverage (V_{H_2}/V_{m_2})	Temperature (°C)	Displacement of H_2 by N_2
1.2	−22	No
1.5	−22	Yes
1.2	20	Yes
1.0	60	No

the −195° trap replaced by a −80° trap. The pressure of gas not condensable at −80° corresponded to about 6×10^{-5} mm. Since the vapor pressure of ammonia is negligible ($<10^{-6}$ mm) at −195° but about 40 mm at −80° any formed during displacement would be detected by this procedure. The quantity of noncondensable gas corresponds to less than 1% of the nitrogen adsorbed during displacement so that we have no analytical evidence for the formation of ammonia in these experiments.

Surface Potential Measurements

In view of our previous studies of hydrogen interaction with oxidized surfaces (*2*) and of Siddigi and Tompkins' data (*7*) for hydrogen interaction with surfaces which had presorbed carbon monoxide, it seemed particularly attractive to investigate surface potential changes $\Delta\phi$ during the displacement of hydrogen by nitrogen. The formation of surface complexes such as $=NH$, $-NH_2$ or "protonic" type species [cf. Haber, Gundry, and Tompkins (*8*)] with apparently very different surface potentials to both adsorbed nitrogen and hydrogen should be resolved by this approach. On the other hand if changes in $\Delta\phi$ only reflect a simple surface substitution, then the observed $\Delta\phi$ may be compared with a calculated $\Delta\phi$ value. Since there is no data available for the surface potentials of the separate gases on molybdenum it was necessary to study the gases both individually and mixed.

At 25° the $\Delta\phi$ for hydrogen at a pressure of 10^{-3} mm is about −0.3 volt, addition of nitrogen at this stage caused $\Delta\phi$ to increase (i.e. become more positive) by about 0.04 volt over a period of 40 min (Fig. 3). Cooling the film at this stage to −195° and adsorbing nitrogen to a pressure of $\sim 10^{-2}$ mm caused $\Delta\phi$ to increase by +0.60 volt to a value of about +0.30 volt for the composite surface. This increase of $\Delta\phi$ was completely reversible since on warming to 25° the value returned to −0.28 volt with simultaneous nitrogen desorption.

The value of $\Delta\phi$ for nitrogen on molybdenum at 25° was about −0.20 volt; cooling to −195° and adding nitrogen to a pressure

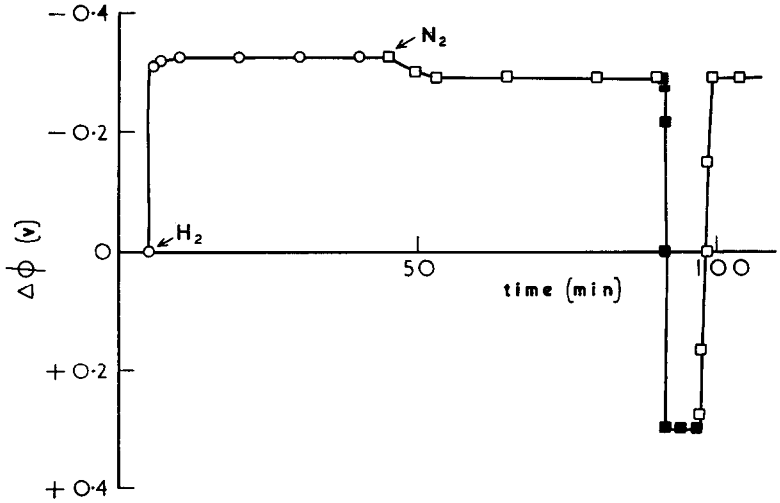


Fig. 3. Surface potential changes ($\Delta\phi$) during the adsorption of first hydrogen (○) and subsequently nitrogen (□) at 25°. The film was then cooled to −195°, nitrogen added to a pressure of $\sim 10^{-2}$ mm (■), and the film again warmed to 25° (□).

of 10^{-2} mm resulted in $\Delta\phi$ increasing by about 0.60 volt. The former value was obtained on rewarming to 25°. When the gas phase nitrogen was removed quickly (pumping for 30 sec at 25°) and hydrogen added there was an appreciable instantaneous adsorption and $\Delta\phi$ decreased by about -0.08 volt.

It is clear from these surface potential experiments that we have no evidence for surface complexes involving nitrogen and hydrogen and that a simple substitution of hydrogen by nitrogen can account for the small increase in the $\Delta\phi$ value during displacement. The further small decrease (0.08 volt) in $\Delta\phi$ on adding hydrogen to the nitrogen-covered surface is compatible with just adsorption, since we would expect on the basis of a simple additivity rule a decrease of about -0.10 volt due to hydrogen alone.

Two distinct states of nitrogen adsorption are distinguishable—that which results in the large reversible positive potential ($\sim +0.60$ volt) at $-195°$ and the very small irreversible value (~ -0.20 volt) at 25°. The former is undoubtedly molecular [cf. the γ state on ribbons (*9*)] and the latter atomic [cf. β state on ribbons (*9*)]. Thus, with molybdenum films at room temperature, adsorbed nitrogen increases the work function, in contrast to its reported behavior of lowering the work function of bulk tungsten (*10*). We believe that the divergence of values reflects a crystallographic factor in work function measurements and this point is discussed elsewhere (*11*).

DISCUSSION

Adsorption of Krypton

Clear evidence for crystallographic specificity of physical adsorption has been demonstrated by the field emission studies of Ehrlich and Hudda (*12*) and Rootsaert, van Reijen, and Sachtler (*13*) and, in general, the energy of binding is greatest for that surface region where maximum ligancy prevails. It, therefore, should not be surprising that the physical adsorption of krypton is also sensitive to presorbed gases (*14*). The constant C in the BET equation is related to the free energy of adsorption and Table 5 summarizes C values obtained in this and other investigations. We refrain from calculating heats of adsorption because of the assumptions involved. If for any particular system C increases on chemisorbing a gas, this reflects a decrease in the free energy of adsorption and, therefore, a probable increase in the heat of adsorption. Both chemisorbed nitrogen on molybdenum and hydrogen on iron films result in slightly larger C values than on the clean metal and, in fact, the decrease in the free energy of adsorption can be recognized by the form of the relevant isotherms at $-195°$. Instead of the volume of adsorbed krypton decreasing (e.g., as with O_2 on Fe, O_2 on Ni, and CO on Mo) there is a small increase ($\sim$15%) at p/p_0 values of $\sim 10^{-3}$ but at larger values the difference in the volumes adsorbed is less pronounced. Isosteric heat data (*18*) have in fact shown that in the CO_2–Ni sys-

TABLE 5

SUMMARY OF C AND V_{m_1}/V_{m_2} VALUES FOR THE INTERACTION OF KRYPTON WITH METALS AND METALS + CHEMISORBED GASES

System	C	V_{m_1}/V_{m_2}[a]	Reference	System	C	V_{m_1}/V_{m_2}	Reference
Kr–Mo Kr–CO–Mo	2300 1170	1.4	This work	Kr–Ge Kr–O_2–Ge	179 86	1.0	(*17*)
Kr–Mo Kr–N_2–Mo	2220 2500	1.0	This work	Kr–Fe Kr–H_2–Fe	520 670	1.0	(*14*)
Kr–Ni Kr–C_2H_4–Ni	1200 400	1.8	(*15*)	Kr–Fe Kr–O_2–Fe	420 1040	3.0	(*14*)
Kr–Ni Kr–H_2–Ni	2300 1000	1.0	(*16*)	—	—	—	—

[a] V_{m_1}/V_{m_2} values within 10% of unity are designated 1.0.

tem the initial heat of krypton adsorption is about 1 kcal $mole^{-1}$ less on the CO_2 "covered" surface than on the "clean" one (5 kcal $mole^{-1}$ as compared with 4 kcal $mole^{-1}$) so that changes in the shape of adsorption isotherms are not unexpected.

It is usual to explain values of V_{m_1}/V_{m_2} greater than unity by invoking induced sintering by chemisorbed gases. Calculations (*14*, *15*) suggest that the heat liberated during gas interaction *could* result in large increases in film temperature. We would, therefore, expect on this basis a close parallelism between heats of chemisorption and induced sintering for any given metal. Examination of Table 5 shows that this is clearly not so; presorbed CO on molybdenum decreases V_{m_1} [cf. also CO on Cu and Au (*19*)] while H_2 and N_2 have very little effect (slight increase). Now hydrogen is probably adsorbed with roughly the same heat as carbon monoxide while nitrogen is adsorbed with a much greater heat but to a somewhat lesser extent. Thus, to invoke induced sintering with CO is illogical and it would appear that the general concept of induced sintering of surfaces by chemisorbed gases has probably been overemphasized. For the case where the heat of krypton adsorption is decreased by presorbed gases the monolayer will only be completed at a much higher pressure than on the clean metal and we may, therefore, obtain a false monolayer value unless we examine the complete isotherm. This fact is emphasized in the recent data of Anderson and Baker (*16*) who found that for xenon on nickel the high ($0.04 < P/P_0 < 0.33$) and low ($P/P_0 < 0.04$) pressure regions do not give collinear BET plots.

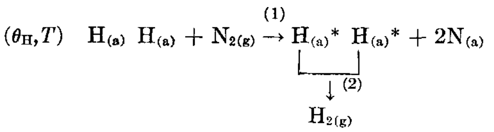
Adsorption of Nitrogen, Carbon Monoxide, and Hydrogen

In view of the preceding discussion on physical adsorption we prefer to relate the volumes of nitrogen, carbon monoxide, and hydrogen adsorbed at 0° and 10^{-3} mm to V_{m_1}, the krypton monolayer for the "clean," thermally stabilized film. Moreover, due to the high melting point of molybdenum, we would not expect appreciable induced sintering. The values of V_{H_2}/V_{m_1}, V_{CO}/V_{m_1}, and V_{N_2}/V_{m_1} are about 1.4, 1.7, and 0.7, respectively. Thus, using the value 19.5 A^2 for the cross-sectional area of a krypton molecule, the following concentrations of adsorbed molecules are present on a molybdenum film at 0° and 10^{-3} mm: CO, 8.8×10^{14} cm^{-2}; H_2, 7.2×10^{14} cm^{-2}; N_2, 3.6×10^{14} cm^{-2}. There are no values available for carbon monoxide and nitrogen on molybdenum ribbons, but for hydrogen Pasternak and Wiesendanger (*20*) have reported a value of about 8×10^{14} cm^{-2}. With tungsten ribbons Ehrlich (*21*) has reported maximum values of about 6.8, 7.0, and 2.8×10^{14} cm^{-2} for CO, H_2, and N_2, respectively, at room temperature. The close similarity between data obtained by the two schools of chemisorption (ribbon and film) is reassuring.

It is instructive to compare the extent of hydrogen and carbon monoxide adsorption on "clean" and nitrogen "covered" films at 0°. The surface concentration of nitrogen was 3.6×10^{14} molecules cm^{-2} and this surface was capable of adsorbing a further 1.8×10^{14} molecules cm^{-2} of hydrogen, whereas 6.8×10^{14} molecules cm^{-2} of carbon monoxide could be adsorbed. If we assume that all the CO on a nitrogen "covered" surface is bonded linearly then the number of "sites" per cm^2 is $[6.8 + (2 \times 3.6)] \times 10^{14}$ since nitrogen is adsorbed dissociatively at room temperature. This value of 14×10^{14} sites cm^{-2} is in excellent agreement with twice the value of the number of hydrogen molecules adsorbed at 0° and 10^{-3} mm. On the other hand a comparison of the CO and H_2 uptakes (8.8 and 7.2×10^{14} molecules cm^{-2}) on the clean films implies that most of the CO is adsorbed in the bridged form. Redhead (*22*) concludes from flash filament data that with tungsten, bridged CO ($\Delta H \simeq$ 70 kcal $mole^{-1}$) is first formed and that when the sticking probability begins to fall a gap-filling process resulting in linearly bonded CO of lower heat occurs. This data of Redheads' is, therefore, in general agreement with our results on clean films. Preadsorbing nitrogen, however, induces the formation of linearly bonded CO of low heat at 0°, and is compatible with the fact that nitrogen-covered surfaces adsorb far less H_2 than CO, presumably due to the prerequisite that hydrogen is adsorbed dissociatively so that adsorption only occurs if $X_1 + X_2 > D_{H_2}$, whereas no similar restriction operates with CO (X_1 and X_2 are the energies of adsorption of two adjacent hydrogen atoms, D_{H_2} the dissociation energy of the hydrogen molecule). Thus, presorbing nitrogen makes molybdenum behave more like an *sp* metal towards carbon monoxide, the adsorption forces being probably "electrostatic" in nature as suggested by Tompkins (*23*).

Surface Displacement

The displacement of an adsorbed species X at a surface coverage of unity by a second species Y is possible provided the free energy change is negative. Thus, we would expect from simple thermochemical considerations that, provided the energy of the bond formed D(M—Y) is much greater than D(M—X) and that the change in entropy is not too great, displacement could occur. The situation is, however, rather more complicated at coverages much less than unity when the species Y is a diatomic molecule and X is a hydrogen atom which can only exist in the gas phase as a molecule. An important process in our case is the recombination of hydrogen adatoms involving surface diffusion followed by molecular desorption. There is, therefore, an added condition that for displacement to occur hydrogen adatoms can not be retained at any part of the surface, although they may have been replaced at their original sites by nitrogen. The following scheme summarizes the situation at a hydrogen coverage θ_H and temperature T. The subscripts (a) and (g) denote adsorbed and gaseous species respectively, and the asterisks denote hydrogen atoms displaced from their original sites and held at other sites on the surface.



$$(\theta_H, T)\quad H_{(a)}\ H_{(a)} + N_{2(g)} \xrightarrow{(1)} \underbrace{H_{(a)}^*\ H_{(a)}^*}_{\downarrow (2)\ H_{2(g)}} + 2N_{(a)}$$

We can estimate D(Mo—N) and D(Mo—H) from 1/2 [D(molecule) $- \Delta H$] and for nitrogen and hydrogen the values at low coverage are roughly 140 and 70 kcal mole^{-1} since the ΔH values are about 80 and 40 kcal mole^{-1}, respectively. Therefore, for the simple displacement process:

$$N_{2(g)} + 2\text{Mo—H} \rightarrow 2\text{Mo—N} + H_{2(g)}$$

the initial process should be exothermic to the extent of about 70 kcal mole^{-1}. The process will, therefore, be thermodynamically feasible since entropy changes can have but little influence on ΔG, since $-\Delta H$ is so large. The rate at which molecular hydrogen desorption occurs will, in principle, depend on either the heat of adsorption or the activation energy for adatom mobility. For surface adatoms which are unstable with respect to the molecular gas the desorption rate will depend on the activation energy for mobility.

Thus, when the feasibility of displacement is investigated at $-22°$ with a surface covered with hydrogen at 60° to about 10^{-4} mm ($V_{H_2}/V_{m_2} \simeq 1.2$) the rate of desorption is small and nitrogen adsorption is not accompanied by desorption. At higher hydrogen coverages (e.g. $V_{H_2}/V_{m_2} \simeq 1.5$) at the same temperature hydrogen desorption will accompany nitrogen adsorption, but when $V_{H_2}/V_{m_2} \simeq 1.2$ the temperature has to be raised to 20° before the desorption rate becomes appreciable. When $V_{H_2}/V_{m_2} < 1.0$ the rate of hydrogen desorption during nitrogen adsorption is negligible up to 60°. Clearly, the smaller are the values of θ_H and T the more likely will displaced hydrogen adatoms be successfully retained by the surface and the process will not proceed beyond stage 1.

The small burst of hydrogen observed on increasing the temperature from 20° to 40° (Fig. 1) can be accounted for on the basis of hydrogen removal during nitrogen adsorption to less energetic sites. The important point is that these molecules must have originated from parts of the surface inaccessible to nitrogen (e.g., 110 and 111 regions) since these hydrogen bursts are not accompanied by a simultaneous nitrogen uptake.

For a second order molecular desorption process from a mobile layer of adatoms, the rate expression is (*24*):

$$r_{\mathrm{des}} = N^2 \alpha r_0 (\pi kT/m)^{1/2} \exp(-E/RT) \qquad (3)$$

in which r_0 is the internuclear distance of the activated complex, assumed to be 1 Å, α is a probability factor, N the number of adatoms which have a desorption energy E, and the other terms have their usual significance. We are assuming that the adatoms behave as a two-dimensional gas and that collision of atoms with energy exceeding E will lead to molecular desorption. Moreover, we regard the adatoms as existing in discrete patches and that desorption occurs completely from one patch before another, thus accounting for the stepwise nature of the desorption curve in Fig. 1. The rate of hydrogen desorption decreases rapidly at any one temperature; at 40° about 3×10^{16} molecules are desorbed within the first few minutes and the value of the activation energy at this stage in desorption is 20 kcal mole^{-1}. Thereafter little desorption occurs at this temperature due to an increase in the value of E with decreasing hydrogen coverage. We will, therefore, assume that $N \simeq 5 \times 10^{16}$, $r_{\mathrm{des}} = 10^{14}$ molecules sec^{-1}, and E has a value of 20 kcal mole^{-1}. Substitution in Eq. (3) gives a value of about 10^{-3} for α. Since the activation energy of hydrogen desorption (20 kcal mole^{-1}) is close to the estimated heat of hydrogen adsorption (~ -18 kcal mole^{-1}) at about the same coverage, our assumptions concerning the slow step and hence the value of E seem reasonable. The value of α, although only approximate, indicates inefficiency of the recombination process.

Thus, the displacement of hydrogen by nitrogen is dependent on the variation of the heat of hydrogen adsorption with coverage and is, therefore, related to the desorption of two adjacent hydrogen adatoms. The stepwise desorption is clear evidence for surface heterogeneity in our case. The small extent of displacement at 40°, when $V_{\mathrm{N_2}}/V_{\mathrm{m_2}}$ only attains a value of about 0.2 compared with 0.7 on a clean film, is due to the requirement that nitrogen adsorption is determined by the rate of hydrogen desorption.

We, therefore, have no evidence for the formation of surface complexes involving nitrogen and hydrogen atoms under the present conditions. Also, presorbed hydrogen has no influence on the rate and extent of the subsequent nitrogen uptake. This contrasts with the behavior of a typical iron catalyst under ammonia synthesis conditions and also with iron films at 25°.

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