JOURNAL OF CATALYSIS 1, 458–467 (1962)

Successive Adsorption of Gases on Tungsten. Nitrogen and Carbon Monoxide at Room Temperature

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Received April 10, 1962

Successive adsorption of nitrogen and carbon monoxide on a tungsten sheet at room temperature was studied by dynamic measurements.

Maximum quantities adsorbed on clean tungsten are 10.1×10^{14} CO molecules/cm^2 and 4.5×10^{14} N_2 molecules/cm^2. The initial values of the sticking probability are 0.27 for CO and 0.10 for N_2.

Preliminary adsorption of N_2 produces an exactly equivalent decrease in the number of molecules of CO subsequently adsorbed at saturation. Previous adsorption of CO lowers the quantity of N_2 adsorbed at saturation of an almost equivalent number of molecules, only if less than 3×10^{14} CO molecules/cm^2 were preliminarily adsorbed. No adsorption of N_2 occurs after saturation with CO.

These results, together with the corresponding behavior of sticking probabilities, are discussed in terms of the different states of N_2 and CO chemisorbed on tungsten, as they are known from desorption spectra.

INTRODUCTION

Desorption spectra and field-emission measurements have recently given a good visualization of the existence of different forms of nitrogen and carbon monoxide adsorbed on tungsten.

For nitrogen, α, β, and γ forms were detected: γ-N_2 is characterized by low adsorption heats and is encountered only in low-temperature adsorption measurements, whilst α-N_2 corresponds to only a few per cent of the total adsorbed amount and, although very interesting for a study of the adsorption kinetics, it may be neglected in a first approximated evaluation of the surface coverage in room-temperature adsorption. Therefore we can consider that, at room temperature, all the adsorbed nitrogen is in the β form, which is generally admitted to consist of chemisorbed atoms, so that two adsorption sites are occupied by every adsorbed molecule.

For carbon monoxide, α and β forms were both detected in room-temperature adsorption, and characterized by their largely different heats of adsorption; whilst α-CO appears to correspond to a well-defined single state, β-CO was shown to split into at least three groups (β_1, β_2, β_3), of appreciably different adsorption energies.

The most typical features of the room-temperature adsorption of carbon monoxide on tungsten are probably given by the regular filling up of the different species: first β_3 and β_2 are formed, then β_1, and only after the β-CO has achieved at least two-thirds of its final concentration, α-CO begins to be populated to a significant extent.

A question of particular interest arises: As it has been ascertained that in all cases carbon monoxide is adsorbed without dissociation, to which kind of chemical bond and molecular structure does the CO correspond when adsorbed in these different forms?

An answer to this question can be only conjectural, as we have not yet such information as infrared absorption spectra for the W–CO system. However, through kinetic considerations, Redhead has quite recently suggested (*1*) that β-CO consists of molecules bridged over two tungsten atoms, and that the more energetic β_3 and β_2 forms are due to bridging of CO over two free tungsten atoms, whilst the successive β_1 type corresponds to the formation of new bridged bonds over tungsten atoms already involved in β_3 or β_2 bonds. In this hypothesis α-CO would be due to the single-bonded linear adsorbed molecules, filling the gaps allowed by bridged CO.

The present work is intended to provide new experimental data for a discussion of this hypothesis, through the study of the adsorption of both nitrogen and carbon monoxide on the same tungsten surface, in particular by the study of the adsorption of one of these gases on a surface partially covered by the other, in such a way that the relatively simple nature of the room-temperature adsorbed nitrogen can contribute to the interpretation of the more complicated state of adsorbed carbon monoxide.

EXPERIMENTAL

Measurements were performed using an apparatus of the type already illustrated in previous work (*2*), based on the Knudsen-flow capillary technique, connected to a typical ultra-high-vacuum system with an oil diffusion pump, giving a residual pressure of 10^{-10} Torr.

Particular attention was given to avoid misleading effects due to the limited conductances within the apparatus, whilst electron ionizing currents of 0.01 ma were used to reduce to a minimum the activation of gaseous molecules by the Alpert gauges (*3*).

Due to the fact that the linearity of the ion current with pressure extends to relatively high pressures when operating at sufficiently low ionizing currents, the Alpert gauges at 0.01 ma were calibrated for nitrogen and carbon monoxide directly against a McLeod gauge in the range from 10^{-6} to 10^{-3} Torr.* Calibration curves are given in Fig. 1.

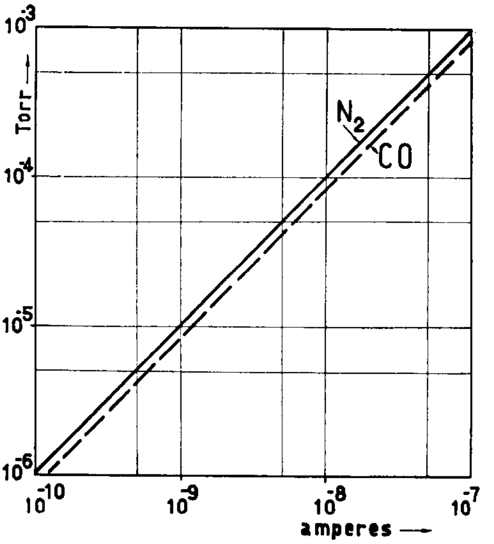

FIG. 1. Alpert gauge calibration curves for nitrogen and carbon monoxide. Electron ionizing current: 0.01 ma.

The adsorbent was a cylindrically shaped tungsten sheet (0.0025 cm in thickness) having a surface area of 30 cm²; it was heated by means of induced eddy currents for 48 hr at 2000°C.

The tungsten sheet, kindly provided by Metallwerke Plansee, contained less than 0.03% impurities.

Nitrogen was supplied by British Oxygen Gases; carbon monoxide was prepared by following essentially the Weinhouse method (*4*), and then spectrographically controlled.

The conductance of the capillary was 9.7 $cm^3\ sec^{-1}$.

Measurements were performed by regulating the pressure in the manifold P_m at the desired value, keeping it constant and recording the variations of the pressure on the adsorbent P_a, until this pressure attained the maximum value of 2.5×10^{-8} Torr: then, in order to avoid the inconveniences connected to a larger increase of the pressure in the adsorbent cell (in particular for CO) the pressure was kept constantly at this value by the continuous careful regulation of the pressure on the other side of the capillary.

As an example, a typical diagram (time, pressure) is given in Fig. 2.

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* Thanks are due for calibration to T. Giorgi, of SAES-Getters Research Lab. (Milan).

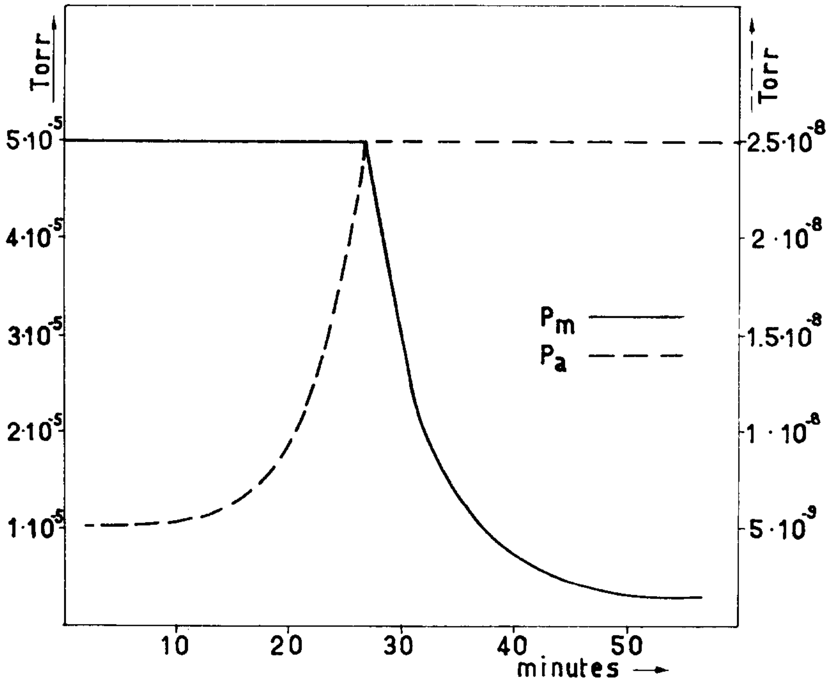

FIG. 2. Pressure variations with time.

Sticking probabilities at different times are immediately obtainable from it. Adsorbed quantity as a function of time is obtained through graphical integration of pressure curves. The adsorption process will then be followed through curves giving the sticking probability as a function of the adsorbed quantity.

For the evaluation of the total adsorbed quantity, the surface was considered as saturated when the sticking probability had fallen to 2×10^{-3}, due to the experimental error in measuring very low adsorption speeds.

When the gas flow is stopped before saturation, the pressure on the adsorbent immediately drops to very low values, so that a few minutes suffice to attain the value of about 1.5×10^{-10} Torr, very near to the initial value. It is therefore possible, for a two gas adsorption measurement, to introduce the second gas in exactly the same manner as the first one.

RESULTS AND DISCUSSION

In a first series of measurements, the influence of preadsorbed nitrogen on the adsorption of carbon monoxide by tungsten was explored.

Adsorption of carbon monoxide was studied on a clean tungsten surface, on a surface partially covered with preadsorbed nitrogen in different amounts, and on a surface saturated with nitrogen.

For the adsorption of carbon monoxide on clean tungsten, the sticking probability is given as a function of the adsorbed quantity in the diagram of Fig. 3.

This curve shows the usual almost flat initial portion which corresponds to a little dependence of the sticking probability on the surface coverage; such an initial behavior extends until 3 to 4×10^{14} molecules of carbon monoxide are adsorbed per square centimeter of apparent area of the tungsten surface; thereafter the sticking probability begins to fall more decidedly.

For the last part of the adsorption a rather complicated behavior is indicated by the sticking probability curve; this behavior was found in all our measurements, also when the adsorption occurred over tungsten with preadsorbed nitrogen, and it is also clearly revealed in the curves

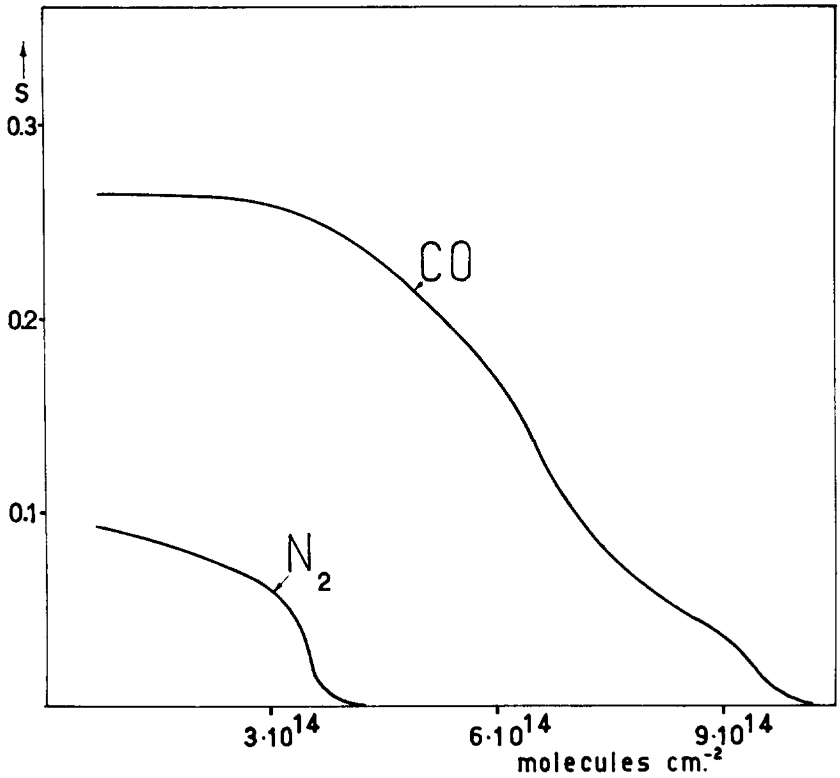

FIG. 3. Sticking probability curves for N_2 and CO on the clean tungsten sheet.

recently published by Redhead (*1*). It seems likely that such a behavior could be attributed to the multiplicity of the states of carbon monoxide adsorbed on tungsten.

The initial value of the sticking probability which was found in our measurements is compared, in Table 1, to the values obtained by other authors working on clean tungsten surfaces.

Data collected in Table 1 do not show very good agreement, for which many factors may be responsible: different features of the measuring system (ionizing currents and interposed conductances) (*3*), minor impurities in the adsorbed gases and, of particular importance, differences in the prevailing crystal faces at the surface of the polycrystalline tungsten.

This last reason is obviously the only one capable of explaining the largely different results quoted in Table 1 and obtained by Ehrlich (*8*) in exactly similar conditions on two different tungsten samples.

TABLE 1
ADSORPTION OF CO ON W

	Author and reference					Present experiments
	Eisinger (*5*)	Becker (*6*)	Schlier (*7*)	Ehrlich (*8*)	Redhead (*1*)	
Initial sticking probability	0.18	0.36	0.62	0.49 0.28	0.50	0.27
Maximum adsorbed quantity (molecules/cm^2)	5.3×10^{14}	6.5×10^{14}	5×10^{14}	4.8×10^{14} 4.5×10^{14}	9.5×10^{14}	10.1×10^{14}

Different features of the surface of the adsorbent may also provide the only reasonable explanation for the discrepancies found in measured total amounts of adsorbed gas, if the calibration of the gauges is to be considered correct.

The sticking probability curves found for the adsorption of carbon monoxide on tungsten covered with nitrogen to different extents are given in Fig. 4 together with the already discussed curve for the adsorption of carbon monoxide on clean tungsten.

The values of the initial sticking probability range from 0.26 to 0.29, with the exception of the value of 0.21 for the adsorption of carbon monoxide on the surface previously saturated with nitrogen.

Keeping apart this last case, to which we shall return, the spreading of the initial sticking probabilities does not show any regularity (e.g. a regular decrease when increasing the partial preliminary coverage with nitrogen), so that any particular significance can hardly be attached to it besides that of an imperfect reproducibility of the adsorbing surface.

As a consequence, we preferred in Fig. 4 to refer the measured sticking probabilities to their initial values taken as unit, in order to avoid any misleading intersections of the curves.

For the last curve, corresponding to the adsorption on a tungsten surface saturated with nitrogen, measured sticking probabilities were referred to the mean value of the

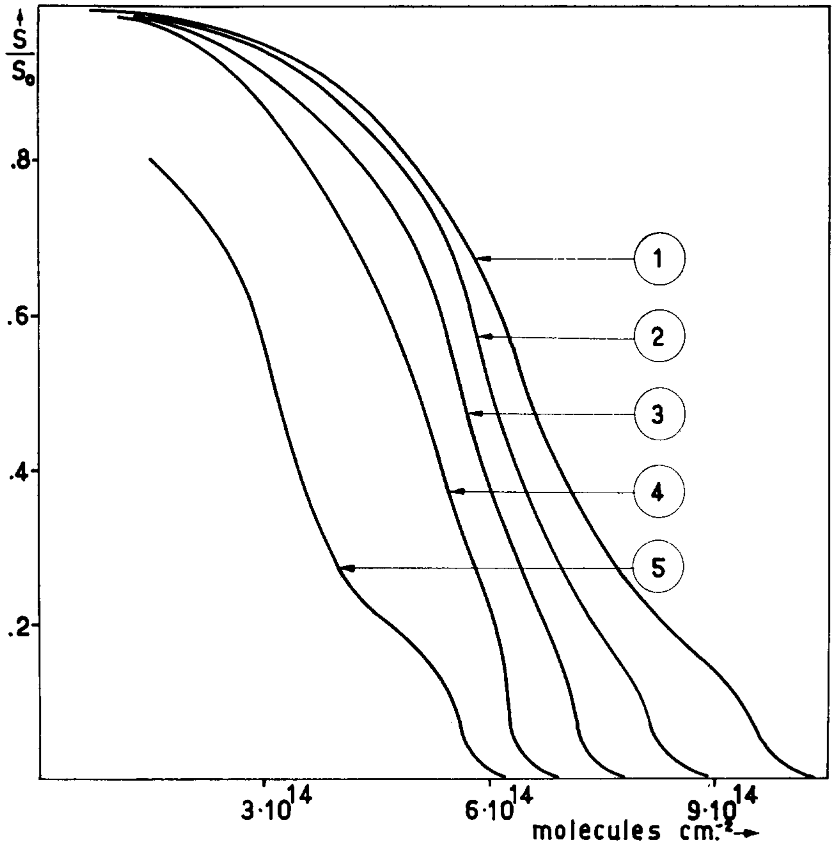

FIG. 4. Sticking probability curves for CO on a tungsten surface differently covered with preadsorbed N_2. 1—Clean tungsten surface; 2—1.1 × 10^{14} molecules/cm^2 of preadsorbed N_2; 3—2.2 × 10^{14} molecules/cm^2 of preadsorbed N_2; 4—3.3 × 10^{14} molecules/cm^2 of preadsorbed N_2; 5—tungsten surface saturated with N_2(4.5 × 10^{14} molecules/cm^2).

initial sticking probabilities measured in the other cases. This mean value was of 0.27 which is also the value quoted in Table 1.

The general form is similar for all the curves, even if with some increase in the slope of their falling portion with the increasing quantity of preadsorbed nitrogen; this regularity is partially altered only in the case of the preliminary saturation with nitrogen.

In particular, the initial flat portion of the curves clearly shows that a previous limited adsorption of nitrogen does not alter this typical feature of the adsorption kinetics of carbon monoxide. However the length of the flat portion reduces when increasing the quantity of preadsorbed nitrogen, until it disappears at saturation.

This behavior, together with the already discussed values of the initial sticking probabilities, strongly suggests that a fraction of the adsorption sites at the tungsten surface may alternatively by occupied either by carbon monoxide or by nitrogen.

Better information may be achieved on this point by considering the total quantities of gas adsorbed in the different cases, which are given in Table 2.

For all the degrees of preliminary coverage of the tungsten surface with nitrogen, the sum of the adsorbed quantities of nitrogen and of carbon monoxide gives a constant value of approximately 10×10^{14} molecules/cm^2, which is perfectly in agreement with the value found for the adsorption of carbon monoxide on clean tungsten.

This result may be accounted for by assuming that the same number of adsorption sites are occupied by a molecule of nitrogen and by a molecule of carbon monoxide.

As it was established that nitrogen is adsorbed as atoms by tungsten at room temperature, two sites are obviously needed for every nitrogen molecule. This would involve, for carbon monoxide, the bridged bonded form of Redhead's hypothesis.

Also the lower value of the initial sticking probability found in the case when the surface was preliminarily saturated with nitrogen would appear comprehensible from this point of view.

Because in this case a quantity of nitrogen was adsorbed greater than 4×10^{14} molecules/cm^2, and if the same adsorption sites are involved in the adsorption of nitrogen and in the initial adsorption of carbon monoxide, we again may interpret the fall in the sticking probability as due to the adsorption of carbon monoxide in the less strongly bonded forms.

The second series of mesurements concerns the influence of preadsorbed carbon monoxide on the successive adsorption of nitrogen.

Tungsten surfaces partially covered with carbon monoxide were shown to be able to adsorb nitrogen, but no adsorption occurred on the tungsten saturated with carbon monoxide.*

This confirms that adsorbed nitrogen and carbon monoxide are bonded to the same

TABLE 2

MAXIMUM ADSORBED QUANTITIES FOR ROOM-TEMPERATURE ADORPTION OF CO ON A TUNGSTEN SURFACE PARTIALLY COVERED WITH N_2

Preliminarily adsorbed N_2 (molecules/cm^2)	—	1.10×10^{14}	2.20×10^{14}	3.30×10^{14}	4.50×10^{14}[a]
Adsorbed CO at saturation (molecules/cm^2)	10.10×10^{14}	8.90×10^{14}	7.75×10^{14}	6.80×10^{14}	5.65×10^{14}
Total adsorbed quantity (N_2 + CO) (molecules/cm^2)	10.10×10^{14}	10.00×10^{14}	9.95×10^{14}	10.10×10^{14}	10.15×10^{14}

[a] This amount is for saturation of tungsten surface with nitrogen, at room temperature.

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* It may be recalled that some qualitative results in agreement with ours (no adsorption of nitrogen on a surface saturated with carbon monoxide; adsorption of carbon monoxide on a surface saturated with nitrogen) were obtained by Wagener working on evaporated films of titanium and tungsten. [Wagener, S., *J. Phys. Chem.* **61**, 267 (1957)].

tungsten surface atoms, and shows that all the tungsten atoms able to adsorb nitrogen at room temperature can also bind the carbon monoxide molecules, whilst it was previously seen that nitrogen cannot exhaust the adsorption sites for CO.

For the adsorption of nitrogen on clean tungsten, the sticking probability as a function of the adsorbed gas is given in Fig. 3.

In this case too the general features of the curve are the same as found by other authors. We do not reproduce here the very initial part of the sticking probability curves for the adsorption of nitrogen, as some doubts may be advanced about the measurement conditions in this region, and more detailed measurements are required, but a dependence on the coverage more pronounced than generally admitted was found.

The initial value of the sticking probability may be given as approximately 0.1, and the adsorbed quantity at saturation was 4.5×10^{14} molecules/cm^2.

Initial values of sticking probabilities and adsorbed quantities at saturation found by different authors are given in Table 3.

TABLE 3

ADSORPTION OF N_2 ON W

	Author and reference					Present experiments
	Becker (*9*)	Schlier (*7*)	Eisinger (*10*)	Kisliuk (*11*)	Ehrlich (*12*)	
Initial sticking probability	0.55	0.42	0.3	0.3	0.28 0.11	0.10
Maximum adsorbed quantity (molecules/cm^2)	3.5×10^{14}	1.8×10^{14}	5.5×10^{14}	3.2×10^{14}	2.3×10^{14}	4.5×10^{14}

Here too, the same reasons already discussed for the discrepancies in the literature concerning the CO data may be recalled.

However it must be pointed out that the tungsten sample which in Ehrlich's measurements presented an initial sticking probability of 0.28 for CO, gives an initial sticking probability of 0.11 for N_2, which is in nice agreement with our results (0.27 for CO and 0.10 for N_2, respectively).

The nitrogen sticking probability, for different degrees of previous coverage of the tungsten surface with carbon monoxide, is given in Fig. 5a, as a function of the quantity of adsorbed nitrogen.

The most striking difference from the reverse case of the adsorption of carbon monoxide on the surface partially covered with nitrogen, is given by the large influence of the preadsorbed CO on the initial sticking probabilities for nitrogen.

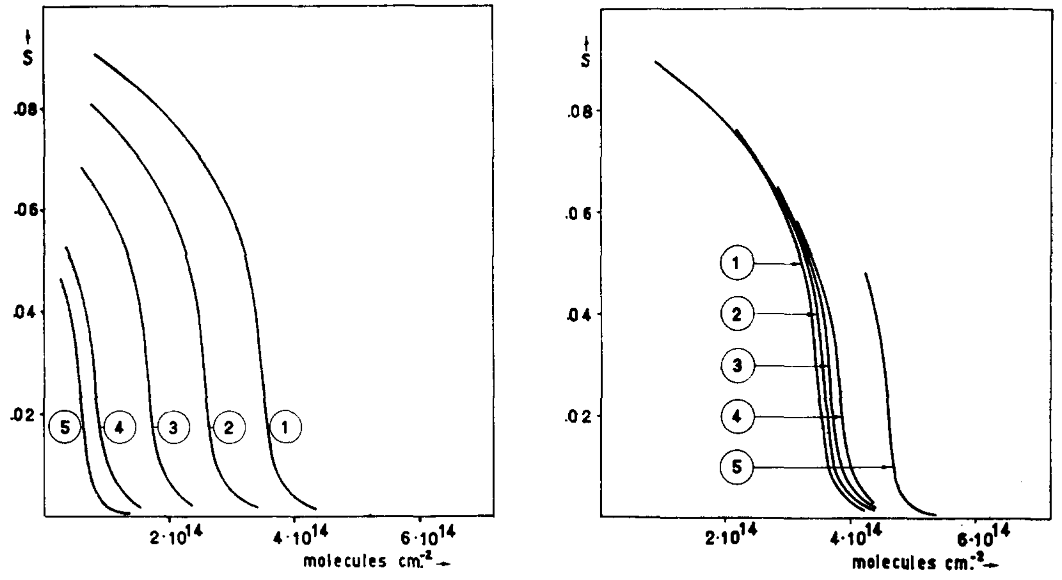
This can, however, easily be explained by considering that the sticking probability curves for nitrogen start to fall at markedly lower values than for carbon monoxide. Thus, if initial CO adsorption occupies the sites generally available for N_2, the fall in the initial sticking probability is just what must be expected.

This is more clearly shown in Fig. 5b, where the nitrogen sticking probability is given as a function of the total quantity of adsorbed gases ($N_2 + CO$): it presents a very reasonable arrangement of the sticking probabilities, with the only apparent exception the last curve, obtained when approximately 4×10^{14} molecules/cm^2 were preliminarily adsorbed.

But again this corresponds to the changes that have been revealed, both in desorption spectra and in rate of adsorption measurements, as occurring when more than 3×10^{14} molecules of CO/cm^2 are adsorbed.

The fall in the sticking probability and the appearance of the β_1 peak in desorption spectra show that at these coverages a different type of adsorption of carbon monoxide is involved, either due to a second valence bond or to surface metal atoms differently coordinated.

This suggests that a certain quantity of



(a) (b)

FIG. 5. Sticking probability curves for N_2 on a tungsten surface differently covered with preadsorbed CO. The sticking probability is given as a function: (a) of the quantity of adsorbed N_2; (b) of the total quantity of adsorbed gases ($N_2 + CO$). 1—Clean tungsten surface; 2—1×10^{14} molecules/cm^2 of preadsorbed CO; 3—2×10^{14} molecules/cm^2 of preadsorbed CO; 4—3×10^{14} molecules/cm^2 of preadsorbed CO; 5—4×10^{14} molecules/cm^2 of preadsorbed CO.

CO may in this way be adsorbed without involving those sites which are suitable for the adsorption of nitrogen.

In the same way, of course, the little splitting of the first four curves could be explained.

This is strongly supported by the adsorbed amounts of gases given in Table 4.

TABLE 4

MAXIMUM ADSORBED QUANTITIES FOR ROOM-TEMPERATURE ADSORPTION OF N_2 ON A TUNGSTEN SURFACE PARTIALLY COVERED WITH CO

Preliminarily adsorbed CO (molecules/cm^2)	—	1.00×10^{14}	2.00×10^{14}	3.00×10^{14}	4.00×10^{14}
Adsorbed N_2 at saturation (molecules/cm^2)	4.50×10^{14}	3.65×10^{14}	2.70×10^{14}	1.70×10^{14}	1.30×10^{14}
Total adsorbed quantity ($CO + N_2$) (molecules/cm^2)	4.50×10^{14}	4.65×10^{14}	4.70×10^{14}	4.70×10^{14}	5.30×10^{14}

The sum of the adsorbed nitrogen and carbon monoxide is approximately constant at the value which corresponds to the saturation of the clean tungsten surface with nitrogen, until the quantity of the preadsorbed carbon monoxide exceeds 3×10^{14} molecules/cm^2.

This confirms that, as was previously pointed out, the same adsorption sites at the surface of the tungsten may alternatively be occupied either by carbon monoxide or by nitrogen, but it restricts such an alternative possibility only to those sites which are able to adsorb carbon monoxide strongly, giving the β_2-CO and β_3-CO forms.

Whilst no elements are supplied by these data for defining the nature of more weakly bonded α-CO and β_1-CO, they seem to enable us to distinguish them from the β_2 and β_3 states, through the ability of corresponding sites to adsorb or not to adsorb nitrogen at room temperature.

CONCLUSIONS

For room-temperature adsorption of nitrogen and carbon monoxide on tungsten, the following points were experimentally established:

(1) The total quantities adsorbed at saturation were 10.1×10^{14} molecules/cm^2 of apparent surface area for carbon monoxide, and of 4.5×10^{14} molecules/cm^2 for nitrogen.

The initial sticking probabilities were 0.27 for CO and 0.10 for N_2.

(2) The preliminary adsorption of nitrogen produces an exactly equivalent decrease in the number of molecules of carbon monoxide subsequently adsorbed at saturation.

Such a preliminary partial coverage of the surface with nitrogen does not produce appreciable changes in the initial sticking probability for the successive adsorption of carbon monoxide until the quantity of adsorbed nitrogen exceeds 3×10^{14} molecules/cm^2, after which a decrease is found, similar to that encountered in this region when studying simply the adsorption of carbon monoxide on a clean tungsten surface.

(3) The previous adsorption of carbon monoxide lowers the quantity of nitrogen adsorbed at saturation of an almost equivalent number of molecules, while the decrease in the initial sticking probability for nitrogen approximately corresponds to that one would have if all the adsorbed gas was nitrogen.

However, when more than 3×10^{14} molecules of carbon monoxide/cm^2 were preliminarily adsorbed, the sum of the quantities of the two gases adsorbed at the saturation with respect to the nitrogen largely exceeded the total quantity of nitrogen which can be adsorbed by the clean tungsten surface; a corresponding change may also be recognized in the behavior of the sticking probability.

By comparing these data with the results given for nitrogen and for carbon monoxide by desorption spectra, the following hypothesis may be formulated:

(1) The tungsten surface atoms involved in the strongest bonds with carbon monoxide (β_3-CO and β_2-CO), are the same atoms which are involved in the chemisorption of nitrogen at room temperature.

Due to the exact equivalence of the two gases at low coverages, one must admit that the undissociated molecule of carbon monoxide occupies two surface sites, probably through a bridged bond between two tungsten atoms.

(2) As more weakly bonded states of carbon monoxide (α-CO and β_1-CO) begin to be significantly populated, the equivalence of the two gases is stopped: The adsorption sites involved in the new forms of adsorption are no longer able to dissociate nitrogen molecules at room temperature.

(3) Preadsorbed nitrogen seems not to exert any significant influence on the subsequent adsorption of carbon monoxide in weakly bonded forms.

In terms of the hypothesis of Redhead on the second valence bond character of β_1-CO, one should admit the possibility of such a second valence bond for carbon monoxide on tungsten atoms already involved in a bond with nitrogen atoms. Obviously this must be experimentally tested through desorption spectra of a mixed phase, as one could expect in this case a rather consistent shifting of the β_1 peak.

The alternative possibility of the formation of β_1-CO (and eventually of α-CO) on surface sites of a different kind, e.g. on differently coordinated tungsten atoms, does no harm and seems to take better into account recent information about the atomic scale regular heterogeneity of tungsten surfaces and its role in chemisorption processes.

However, some difficulties arise from the rather high concentration of tungsten atoms able to adsorb carbon monoxide, which would be required in this case.

Finally it must be pointed out that the

study of mixed adsorption on a metal surface may enable us to achieve a more complete description of the surface itself, as it brings to light in a new manner the existence of different sites, capable of different behavior with respect to different gases.

REFERENCES

1. REDHEAD, P. A., *Trans. Faraday Soc.* **57,** 641 (1961).
2. NASINI, A. G., SAINI, G., AND RICCA, F., *in* "Actes du Congrès International de Catalyse," p. 241. Editions Technip, Paris, 1961.
3. RICCA, F., NASINI, A. G., AND SAINI, G., in press.
4. WEINHOUSE, S., *J. Am. Chem. Soc.* **70,** 442 (1948).
5. EINSINGER, J., *J. Chem. Phys.* **27,** 1206 (1957).
6. BECKER, J. A., *Solid State Physics* **7,** 379 (1958).
7. SCHLIER, R. E., *J. Appl. Phys.* **29,** 1162 (1958).
8. EHRLICH, G., *J. Chem Physics* **34,** 39 (1961).
9. BECKER, J. A., *Advances in Catalysis* **7,** 135 (1956).
10. EISINGER, J., *J. Chem. Phys.* **28,** 165 (1958).
11. KISLIUK, P., *J. Chem. Phys.* **31,** 1605 (1959).
12. EHRLICH, G., *J. Chem. Phys.* **34,** 29 (1961).