Sticking Probability of Gases on Metal Films Determined by the Flow Method. Nitrogen on Molybdenum

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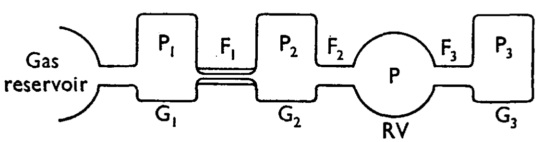
THE sticking probabilities of nitrogen and carbon monoxide on molybdenum films were determined recently[1] by a flow technique and at 23° the values were estimated to be about 2×10^{-2}. Sticking probabilities of this magnitude had been determined with other techniques for nitrogen on

[1] M. W. Roberts, *Trans. Faraday Soc.*, 1963, **59**, 698.

tungsten ribbons by Jones and Pethica[2] (0·035) and Ricca[3] (0·03) but higher values had been reported by Ehrlich[4] (0·1) and also by Pasternak and Wiesendanger[5] for nitrogen on molybdenum (0·35). Nasini and Ricca's[6] more recent studies suggest a higher value (0·1) than his earlier work. A discussion of the mechanism of the initial interaction of gases with metal films, in particular the details of how an adsorbed layer is formed, depends critically on the absolute value of the sticking probability. Two limiting cases are possible: (*a*) when the sticking probability is high, molecules will be adsorbed at almost the first point of impact and (*b*) with a low sticking probability molecules can seek out the more favourable adsorption sites.

Orr[7] has recently reported values between 10^{-2} and 10^{-1} for the sticking probability of oxygen on magnesium films; a feature of the experimental technique was that the pressure in the reaction vessel was monitored by an ion-gauge situated after the film, which is different to the arrangement used in our work[1] where the gauge was placed before the film. It has been pointed out[6] that such factors as gauge position and tube conductances may influence measured sticking probabilities; the consequences of using each of these two possible arrangements of film and gauge on the calculated sticking probability are therefore analysed in detail below.



Consider the experimental arrangement shown, where the metal film was formed on the walls of the spherical reaction vessel RV and gas leaked in at a known rate through a capillary of conductance F_1. During the initial stages of the interaction when the sticking probability α is likely to be constant equations (1)—(3) govern the gas flow. P is the actual pressure in the reaction vessel, P_2 and P_3 are the pressures measured with gauges G_2 and G_3 respectively, N (l. cm.$^{-2}$ sec.$^{-1}$) the volume of gas striking the surface of area A (cm.^{2}), F_1 (l. sec.$^{-1}$) is the conductance of the capillary, and F_2 (l. sec.$^{-1}$) that of the glass tubing connecting G_2 and RV. The pressure above the film is assumed to be negligible before gas is leaked in *via* F_1 and ion-gauge pumping is nglected. There is a net flow of gas from G_2 to RV so that $P_2 > P$ (equation 1) but since there is no net flow into G_3 (when α is constant) then $P = P_3$ (equation 2). In equation (3) $F_1 (P_1 - P)$ is the rate of adsorption of NAP, the rate at which molecules strike the film; during the early stages of the interaction $P_1 >> P_2$. In the previous work[1] the sticking probability Pr of nitrogen on molybdenum films was calculated by using equation (4) and the readings of gauge G_2, without applying the correction of equation (1). Therefore equation (4) holds.

$$P = P_2 - F_1P_1/F_2 \qquad (1)$$

$$P \times P_3 \qquad (2)$$

$$\alpha = F_1(P_1 - P)/NAP \qquad (3)$$

$$Pr = F_1 (P_1 - P_2)/NAP_2 \qquad (4)$$

From equations (1), (3), and (4) it can be shown that Pr is related to the real value (α) of the sticking probability by equation (5).

$$Pr = \left(\frac{1}{\alpha} + \frac{NA}{F_2}\right)^{-1} \qquad (5)$$

The film area A used in these experiments[1] was 40 cm.^{2} and F_2 was estimated to be between 5 and 20 l. sec.$^{-1}$. Therefore, by assuming various values for α the corresponding Pr values can be calculated from equation (5) and for $F_2 = 5$ l. sec.$^{-1}$ the variation of Pr with α is shown below.

Variation of the observed sticking probability Pr *with the real sticking probability* α

α	0·8	0·4	0·1	1·01	0·001
Pr	0·0104	0·0102	1·0094	0·005	0·001

It is clear that the values of Pr bear little relation to the real sticking probability α if the latter is $\geqslant$ 0·01. Also it can be seen that when $\alpha >$ 0·01 changes in area or of absolute sticking probability that may occur during a study of the influence of sintering of the film will not be reflected by appreciable changes in Pr. If α is, say, 0·4 then Pr will change by about only 8% (0·0102 to 0·0094) for a four-fold decrease in the pumping

[2] P. L. Jones and B. A. Pethica, *Proc. Roy. Soc.*, 1960, *A*, **256**, 454.
[3] G. Saini, F. Ricca, and A. G. Nasini, *Ricerca Sci.*, 1959, **29**, 1523.
[4] G. Ehrlich, *J. Phys. Chem.*, 1956, **60**, 1388.
[5] R. A. Pasternak and H. U. D. Wiesendanger, *J. Chem. Phys.*, 1931, **34**, 2062.
[6] A. G. Nasini and F. Ricca, *Ann. New York Acad. Sci.*, 1963, **101**, 791.
[7] W. H. Orr, "Transactions of the 9th National Vacuum Symposium," 1962, 484.

speed of the film. It can also be shown from equations (1) and (3) that

$$\frac{F_1P_1}{F_2P_2} = \left(\frac{F_2}{NA\alpha} + 1\right)^{-1} \quad (6)$$

Therefore, if the correction term (F_1P_1/F_2) in equation (1) is to be a reasonably small fraction of the measured pressure P_2 the conductance F_2 must be increased to an experimentally inconvenient value if $\alpha \geqslant 0{\cdot}1$. For example, with $A = 40$ cm.^{2} and $\alpha = 0{\cdot}4$ a conductance F_2 of ~ 200 l. sec.$^{-1}$ would be required to make $F_1P_1/F_2 = 0{\cdot}5\ P_2$. Hence for a metal–gas system where α is $\leqslant 0{\cdot}01$ either of the two experimental arrangements will suffice but when $\alpha > 0{\cdot}01$ both the absolute value and any small changes in this value can only be determined with any degree of certainty by using gauge G_3.

If the sticking probability α of nitrogen on molybdenum is high then difficulties can also arise from traces of film deposited in the connecting tubes F_2 and F_3 so that experiments have now been carried out with films formed on a small glass disc (3·5 cm.^{2}) and an arrangement such that G_3 (see diagram) monitored the pressure. The procedure was to form the molybdenum film in one compartment of a reaction vessel and then lower it into a second compartment where it was sealed off from the first by means of an all-glass valve. At 23° the sticking probability–coverage curve had an initial constant region where $\alpha \simeq 0{\cdot}3$; this could be a minimum value due to the vacuum conditions ($\sim 10^{-8}$ mm.) before gas admission in these experiments. The ion-gauge emission current used was 0·1 mA but as with Nasini and Ricca,[6] α was shown to be dependent on the current, being about a factor of two less with a current of 0·01 mA. Therefore, the sticking probability of nitrogen on molybdenum films is obviously within the range where α and *Pr* values (Table) would be expected to differ so that mechanistic deductions[1] based on the invariance of *Pr* with pressure, sintering conditions, and film weight must for the present be regarded with some caution.

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