Errors in the Measurement of Sticking Probabilities of Gases on Metal Films

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IN a recent note, McKee and Roberts[1] have very properly pointed out that the earlier results of Roberts[2] for the sticking probabilities of nitrogen and carbon monoxide on evaporated molybdenum films are too low by factors of about 50 owing to the incorrect positioning of the ionization gauge which was used in an attempt to measure the gas pressure above the film. This effect has been emphasized previously by Nasini and Ricca.[3] Nevertheless, there are other important factors which have been incorrectly analysed by Roberts,[2] but which must be taken into account to obtain meaningful values not only of the magnitude of the sticking probability s but also of its variation with the amount adsorbed.

When the desorption rate is negligible s may be equated to the ratio, (rate of adsorption)/(collision rate of gas molecules with the adsorbent surface), both rates being expressed in units of molecules cm.$^{-2}$ sec.$^{-1}$. The rate of adsorption can be unambiguously and accurately evaluated from the rate of flow of gas into the adsorption cell because, in such experiments, the rate of change of the number of gas-phase molecules in the cell is always negligible compared with the rate of adsorption. However, the collision rate requires an exact knowledge of the gas pressure above the adsorbent and, except in a carefully designed apparatus and with the use of highly pure gases, this pressure may differ considerably from that recorded by the ionization gauge. Also, if the geometric surface area of the adsorbent is large and the gas is introduced asymmetrically with respect to the adsorbent, the collision rate will vary across the surface and no definitive pressure will exist within the cell. This difficulty may be overcome by drastically reducing the geometric area of the adsorbent as in flash-filament studies, or by constructing a spherically symmetrical system as in our work.[4] The essential features of this latter method are shown in the Figure. Gas is introduced at the centre of the cell *via* a specially designed diffuser D. During film preparation, a nickel disc is magnetically held across the mouth of the gauge G_2 to prevent deposition of the adsorbent within the gauge tubing, and the diffuser is retracted out of the cell. The ionization gauge G_2 correctly measures the gas pressure above the adsorbent provided that no pumping takes place in the gauge assembly. Even an invisible film deposited in the gauge tubulation gives rise to spurious values of s (often greater than 1).

An additional error may arise owing to pumping by the gauge itself; this is particularly serious if the gauge has been freshly outgassed before gas admission. To test this effect in our apparatus, nitrogen was introduced to the cell in the absence of a film at a rate of 6×10^{11} molecules sec.$^{-1}$. With a freshly outgassed gauge no substantial pressure rise was recorded during the first four minutes. If, however, the gauge was first flushed with nitrogen at a pressure of around 10^{-6} torr and subsequently re-evacuated to 2—3 $\times 10^{-10}$ torr, then on repeating the above procedure, the pressure in G_2 rose immediately at a constant rate commensurate with the rate of gas inflow. Similarly,

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[1] C. S. McKee and M. W. Roberts, *Chem. Comm.*, 1965, 59.
[2] M. W. Roberts, *Trans. Faraday Soc.*, 1963, **59**, 698.
[3] A. G. Nasini and F. Ricca, *Ann. New York Acad. Sci.*, 1963, **101**, 791.
[4] To be published.

in sticking probability experiments where the gauge was not flushed before film deposition, spuriously high values of *s* were obtained during the first few minutes of gas flow.

In contrast to the flash filament technique the present method is highly sensitive to the accumulation of non-adsorbable impurities in the cell. This problem has been analysed by Roberts in the Appendix to his paper,[2] but his arguments and conclusions are fallacious. In both our apparatus (see Figure), and that used by Roberts, the pressure in the storage vessel is maintained constant at $\sim 10^{-4}$ torr by controlling the relative rates of gas inflow and of pumping, both rates being high compared with the rate of gas-flow to the cell when the valve V is opened, *i.e.*, the pressure in the storage vessel is substantially independent of whether V is open or closed. If the nitrogen contains 1 in 10^4 parts of a non-adsorbable gas, the partial pressure of this impurity in the storage vessel is 1×10^{-8} torr. Thus, on opening V, the partial pressure of the impurity will rise rapidly to 10^{-8} torr and must remain constant at this value for the duration of the experiment. This conclusion follows because, in this pressure range, equilibration of the impurity between the cell and storage vessel is brought about by Knudsen diffusion and is therefore unaffected by the simultaneous flow of nitrogen. In Roberts' argument, however, it is assumed that the partial pressure of the impurity will increase to 10^{-4} torr, *i.e.*, the total pressure of gases in the storage vessel; this is, of course, not possible.

When the partial pressure of the impurity in the cell is significant compared with that of the total pressure measured by G_2, both the magnitude of *s* and its variation with amount of nitrogen adsorbed must be in error; in the extreme case, the apparent value of *s* is independent of the extent of adsorption except at very high and low coverages. The impurity content of the gas supply may be estimated experimentally since, if valve V is closed at any time before the film is saturated, the pressure in the cell will fall to that of the non-adsorbed impurity and then remain constant. In preliminary experiments at room temperature, using two separate glass ampoules of B.O.C., spectroscopically pure, nitrogen, we determined by this procedure the non-adsorbable impurity content to be 1 in 10^4 and 2 in 10^5 parts, respectively. This impurity was apparently completely adsorbed on the tungsten film at 78°K, since the above effect was not observed at this temperature. In the initial stages of adsorption utilising the first sample of nitrogen, the total pressure in the cell in a typical experiment was $1{\cdot}2 \times 10^{-8}$ torr, of which the partial pressure of the impurity was $1{\cdot}0 \times 10^{-8}$ torr. Thus, the sticking probability calculated from the total pressure was 0·07 whereas the true value determined from the partial pressure of nitrogen, *viz.*, 2×10^{-9} torr, was 0·4. In confirmation of this value, initial sticking probabilities of 0·38 on tungsten and 0·43 on molybdenum were obtained using nitrogen prepared from outgassed sodium azide, which was shown to be free of non-adsorbable impurities.

Other workers have operated with higher pressures in the cell and have thereby reduced the error arising from the presence of non-adsorbable impurities. Nevertheless, this greatly shortens the time period of the experiment with consequent loss of knowledge of the variation of *s* with amount adsorbed in the initial stages.

One further factor has to be considered when the adsorbent is maintained at a temperature different from that of the gauge G_2, since there is apparently some confusion about the pressure and temperature to be used in the equation for the collision rate of gas molecules at the surface, *viz.*,

$$Z = P/(2\pi m k T) \text{ cm.}^{-2}\,\text{sec.}^{-1} \qquad (1)$$

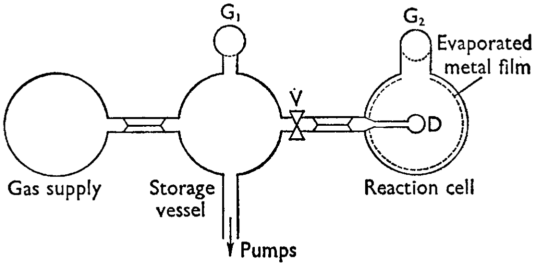
where m is the molecular mass, and P and T refer to the pressure and temperature of the gas over the adsorbent. If the temperature of the gauge is T^* and it records a pressure P^*, then P is related at these low pressures to P^* by the thermal transpiration equation, *viz.*,

$$P/P^* = (T/T^*)^{1/2} \qquad (2)$$

Substituting in equation (1) we obtain,

$$Z = P^*/(2\pi m k T^*)^{1/2} \qquad (3)$$

i.e., the collision rate is correctly obtained directly from the pressure P^* and the temperature T^* of the gauge, irrespective of the temperature of the gas over the adsorbent. It would appear from Roberts'[2] pressure measurements for adsorption at 78 and 295°K and from the sticking probabilities derived from them, that he has erroneously introduced a factor $(295/78)^{1/2}$ into his calculations for *s* at 78°K.



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