195. *The Detection of Adsorbed Gas Films on Heated Filaments.*

By GORDON VAN PRAAGH.

RECENT work by Roberts has shown that the accommodation coefficient of the rare gases on hot metallic surfaces, *i.e.*, the extent to which the gas molecules acquire the temperature of the surface on which they are impinging, is affected by small traces of adsorbed impurities. It is known that the thermal emissivity of metals is also affected, and it is important to investigate how far these two factors are changed by thick films and by unimolecular films.

It has been shown that the thermal emissivity of a metal is decreased when it is covered by a " thick " film of compound, *e.g.*, an iodide film some ten molecules thick on tungsten (Van Praagh and Rideal, *Proc. Roy. Soc.*, *A*, 1931, **134**, 385); but the emissivity is evidently unaffected by unimolecular layers, for Langmuir found that the emissivity of tungsten was that of the bare metal, when he knew from other considerations that the surface was covered by a monatomic oxygen film. Similarly a unimolecular platinum–iodine film is without effect on the emissivity of platinum (*loc. cit.*).

However, the accommodation coefficient is affected both by thick films and by unimolecular films, and the experiments described below show that the accommodation coefficient of argon on a platinum filament is increased when the metal is covered by a monatomic film of adsorbed iodine. In the present paper experiments are described in which this method was used to establish the presence or absence of such a film on the platinum after the latter had been heated to various temperatures in iodine vapour at various pressures. The results obtained are in accordance with deductions based upon a study of the kinetics of the attack of platinum by iodine.

EXPERIMENTAL.

The apparatus used has already been described (*loc. cit.*). Gas (99·5% argon, 0·5% nitrogen) from a cylinder was transferred to an evacuated reservoir, which was used as the source of argon for all the experiments. A certain pressure of argon was admitted to the vessel (surrounded by an ice-bath) containing the platinum filament, which was then heated with a " standard current." The extent to which the filament is cooled by the argon depends upon the accommodation coefficient. Hence a knowledge of the latter can be obtained by measuring the temperature to which the wire is heated by the standard current in a standard pressure of argon. The following detailed account of one experiment will make clear the procedure adopted throughout.

The wire was glowed out in a good vacuum at 1650° K. A pressure of 0·08 mm. of argon was admitted to the reaction vessel and the filament heated with the standard current. (Various current strengths were used.) The temperature, t_1°, of the filament was calculated from measurements of its resistance, the necessary corrections being applied, as already described. The argon was then pumped out and the wire heated to T° K. in iodine at 0·027 mm. pressure. Finally the iodine was removed, 0·08 mm. of argon admitted, and the temperature, t_2°, of the wire when heated by the standard current again measured. Some of the results are shown in the table.

Expt. No.	3.	8.	17.	21.
T° K.	310	1635	300	1565
t_1°	14·1	13·0	32·2	36·3
t_2°	12·8	13·0	30·6	35·5

The temperature t° was known to 0·2°. In Expt. 8 the temperature t° is the same before and after treatment with iodine, showing that no film has been formed, whereas the other experiments indicate the formation of a film.

DISCUSSION.

These experiments indicate that after the wire has been heated in 0·027 mm. of iodine to a temperature below 1565° K., it is covered by an adsorbed film, but that if the temperature is above 1635° K., no film forms. Owing to experimental difficulties it was not possible to make this range narrower and thus to decide whether the film behaved as a compound or as an adsorption complex. The difficulties arose as follows. In switching off the heating current and pumping out the iodine preparatory to testing for film formation, two dangers had to be avoided. (i) If, as the wire cooled from some temperature at which no film had formed, a sufficient iodine pressure remained unremoved from the vessel, a film would be formed on the cooling filament, whereas (ii) if the iodine was rapidly removed from a cooling filament on which a film had formed, the latter might evaporate off while the wire was still hot. In order to ensure the validity of the results obtained, the heating current was switched off before the iodine was pumped out when it was desired to show that no film was formed; whereas to demonstrate the formation of a film, the operations were done in the reverse order.

The rates of attack of platinum by iodine were found to follow the equation $-dp/dt = a + bp$ at the lower temperatures, but at the higher temperatures the rates fell off at the lower pressures, the divergence beginning at higher pressures the higher the temperature. These results were interpreted by assuming that the zero-order term, a, is due to the clean-up of iodine by the formation on the metallic surface of an adsorbed layer, which evaporates at a rate independent of the pressure; and that the component bp is due to the attack of the adsorption complex by iodine atoms at a rate proportional to the iodine pressure. Below a certain critical pressure, the surface of the metal was assumed to become bare, in order to account for the falling off in the rate of clean-up at the lower pressures. By extrapolation of the figures obtained, it is found that the critical pressure becomes 0·027 mm. at a temperature of about 1600° K., which is in accordance with the results obtained by measuring the accommodation coefficient.

SUMMARY.

The thermal emissivity of a platinum filament is not affected by the presence of an adsorbed monatomic film of iodine.

The accommodation coefficient of argon on the filament is increased by the presence of a film, and this method has been used to show that when the platinum is heated in iodine vapour at 0·027 mm. pressure, an adsorbed film is formed below 1565° K., but that above 1635° K. the platinum surface is bare. This result is in accordance with measurements of the kinetics of the attack of platinum by iodine vapour.

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