THE DISSOCIATION OF HYDROGEN INTO ATOMS. III.—THE MECHANISM OF THE REACTION.

By Irving Langmuir.*

A NEW theory of heterogeneous reactions avoiding certain assumptions of the earlier one, which experiment has recently proved untenable, is advanced. The earlier hypothesis considered that the surface of a tungsten wire in contact with hydrogen contained atoms and molecules of the gas in chemical equilibrium with each other, the two forms escaping at rates respectively proportional to their concentrations in the wire, and being absorbed at rates proportional to the corresponding pressures in the gaseous phase. The equation for heat loss from the wire thereby deduced agreed extremely well with experimental results over a range from 0.01 to 760 mm. pressure and 1000 to 3500 ° K. temperature. But the velocity of the reaction by which hydrogen in contact with a hot tungsten wire is dissociated is so enormous as to preclude the possibility of the existence of the gas as a solid solution in the metal with the attendant necessarily low rate of diffusion. Moreover, experiment has shown that, while 68 per cent. of all hydrogen molecules striking the filament at high temperatures reach chemical equilibrium before leaving it, at lower temperatures, up to 1500° K., only 19 per cent. reach thermal equilibrium, a fact for which the earlier theory offers no explanation. Work in gases at low pressures has demonstrated that electron emission is dependent upon the composition of the surface layer of atoms, and that reaction between gas and solid is also dependent upon the composition or structure of the same. It has become necessary, therefore, to assume that reaction occurs directly on the surface of the metal and involves no diffusion through even a single layer of atoms.

The new theory involves the view that on the surface of the metal the forces which hold its atoms together tend to be chemically unsaturated, and atoms or molecules of gases may be firmly held by them. In general accordance with the law of multiple combining proportions, each metal atom of the surface will be capable of holding a definite integral number of atoms of gas, or perhaps two metal atoms may hold one gas atom. Atoms or molecules so held are a part of the solid body, a real continuation of the space

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lattice of the solid, and may be said to be adsorbed. The surface of the metal is thus looked upon as a sort of checkerboard of a definite number per square centimetre of elementary spaces, each capable of holding an atom or a definite part of a molecule of adsorbed gas.

Application of this theory to the dissociation of hydrogen leads to equations identical with that derived by the older theory, which had previously (Parts I and II) been shown to be in complete accord with experimental results.

All the hypotheses considered lead to the conclusion that only a small fraction of the surface is covered with hydrogen, and that phenomena within the metal do not affect the reaction. This conclusion is confirmed by the difference in the accommodation coefficient of hydrogen in contact with tungsten at low and high temperatures, which is now easily explained by supposing the surface of the metal to be largely covered by adsorbed hydrogen at the lower temperatures and practically bare at the higher temperatures. The 19 per cent. may then correspond to the fraction of molecules condensing when they strike a surface already covered and 68 per cent. when they strike a bare surface. That the surface of tungsten is practically bare at the higher temperatures is strongly influenced by the fact that the electron emission is not perceptibly influenced by the presence of pure hydrogen.

A HIGH VACUUM MERCURY VAPOR PUMP OF EXTREME SPEED.

By Irving Langmuir.*

A NEW high vacuum mercury vapor pump, called the diffusion pump, has been devised, and its operation is explained and illustrated by a diagram. It has the advantages of extremely high speed of exhaustion, constant at all pressures, and absence of lower limit to which pressure may be reduced. The maximum speeds of exhaustion so far obtained have been 4000 c.c. per second for air and 7000 c.c. per second for hydrogen at pressures below 10 bars. Theoretical considerations indicate that this speed should remain constant down to the very lowest pressures. Further advantages are reliability and simplicity, in which respects the pump has been much improved by modifications in form and material, which will be described in later papers.

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