

CCXCIX.—*Studies in Gaseous Adsorption. Part I.*
The Influence of Hydrogen Sulphide on the Rate
of Adsorption of Hydrogen by Platinum.

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THE adsorption of hydrogen by hydrogen-activating metals normally follows a course such that the bulk of the gas is taken up relatively quickly. Further adsorption then occurs at a far slower rate; and equilibrium between the adsorbed and the gaseous phase is only approximately reached after a time which may be of the order of several days.

The slow process which follows the primary adsorption is usually ascribed to the penetration of the hydrogen into the interior of the metal. Taylor (*J. Amer. Chem. Soc.*, 1931, **53**, 578) postulates two modes of adsorption, each associated with its own critical energy, and corresponding with the adsorption of hydrogen in the molecular and in the atomic state respectively. According to Taylor's views, the activation energy required for molecular adsorption is relatively low; and hydrogen adsorbed primarily in the molecular state may pass into a condition of atomic adsorption if it attains the higher critical energy required for this.

It appeared of interest, in the light of Taylor's conception, to examine the effect of a catalyst poison on the rate of adsorption, in order to attempt to obtain some indication of the degree of applicability of these two postulated variations to primary and to secondary adsorption; for, in a surface of non-uniform energy distribution, if the adsorbing units of the highest degree of unsaturation are occupied obstructively by preferentially adsorbed molecules, in place of being free for normal adsorption, the probability within a given time of the attainment by an individual adsorbed hydrogen molecule of the necessary higher critical energy for atomic adsorption will be decreased. The mechanism by means of which the energy of an adsorbed hydrogen or other molecule is raised to a level higher than that corresponding with its initial adsorbed state is not definitely known; it appears, however, reasonable to postulate that this occurs through the mobility of an adsorbed molecule on a surface—by virtue of adsorption and re-adsorption at another adsorbing point—until re-adsorption ultimately takes place at an adsorbing unit of a sufficient degree of unsaturation to raise the energy content to that required, in accordance with the method of activation discussed in a previous paper (Maxted, *Chem. and Ind.*, 1931, **50**, 149).

The results now obtained show a general retardation of the whole process of adsorption by the presence of a poison, the degree of retardation increasing with the poison content. It should be pointed out, however, in connexion with Taylor's conception of the dual nature of adsorption, that this general retardation would also be exerted by a poison if one mode only of adsorption on an assumedly non-uniform surface took place.

EXPERIMENTAL.

The apparatus and general technique resembled that employed in earlier work with palladium (J., 1919, **115**, 1050; 1920, **117**, 1280), save that the relative smallness of the adsorption of hydrogen by platinum rendered unnecessary the second, larger gas burette.

The platinum was prepared by the reduction of hydroplatinic acid with alkaline potassium formate (Mond, Ramsay, and Shields, *Phil. Trans.*, 1895, A, **186**, 657). After being sealed in the adsorption tube, it was heated to 100° for several hours in a stream of hydrogen to remove free oxygen as water, then degassed as completely as possible by evacuation at the same temperature. This degassing was repeated between individual adsorption measurements, the temperature not being raised above 100° in order to avoid the risk of structural changes in the platinum. The hydrogen sulphide was made by decomposing magnesium hydrosulphide.

As was previously found for palladium, small quantities of hydrogen sulphide are almost completely adsorbed by platinum. This adsorbed gas is not removed to any great extent by evacuation at room temperature, but on degassing at 100° an equal volume of hydrogen is evolved, and the sulphur remains on the platinum; further, the influence of a given concentration of the inhibitant on the subsequent adsorption of hydrogen is—as with palladium—not the same for hydrogen sulphide in the freshly adsorbed state as for the equivalent quantity of sulphur left behind after removal of the hydrogen component by evacuation.

The influence of hydrogen sulphide on the total volume of hydrogen which can be subsequently adsorbed was, within the limits studied, not very great, provided that sufficient time was allowed for the hydrogen adsorption to attain an equilibrium value. Table I refers to the total subsequent adsorption of hydrogen, at 20°, by 6.72 g. of platinum-black having the hydrogen sulphide content indicated. All gas volumes are corrected to N.T.P. The adsorptions marked A are direct and include the volume of hydrogen resulting from the dissociation of the hydrogen sulphide increment; those marked B are adsorptions after removal of the hydrogen resulting from the dissociation of the poison, by evacuation at 100°.

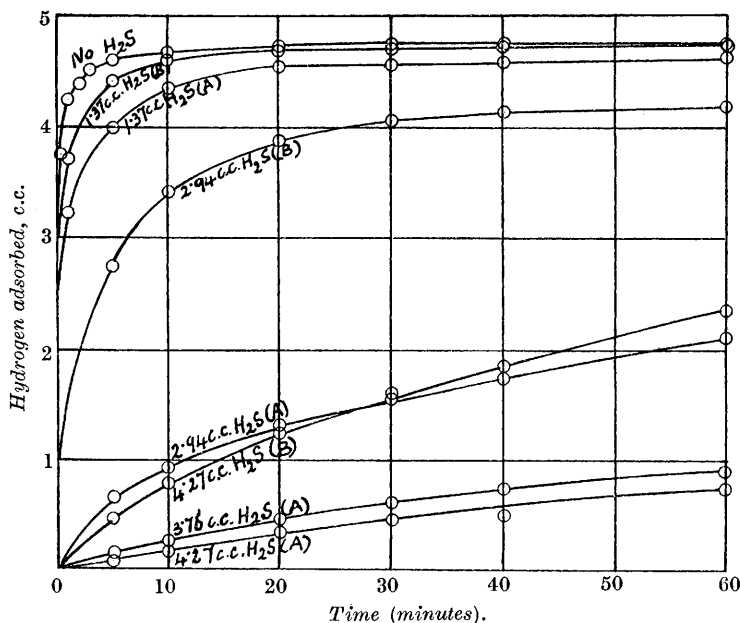
TABLE I.

Total H ₂ S content, c.c.	H ₂ subsequently adsorbed, c.c.	Total H ₂ S content, c.c.	H ₂ subsequently adsorbed, c.c.
None	5.17	2.94	A 4.81
	4.89		B 5.15
	4.96	3.76	A 4.64
	4.93	4.27	A 4.49
	1.37	A 4.81	B 4.00
	B 4.91	7.22	B 4.45

It will be seen that a gradual general decrease in the total hydrogen subsequently adsorbed is observed on increasing the hydrogen sulphide content; but the slight variation in the volume of hydrogen taken up from one experiment to another under similar conditions is sufficient to render impossible the quantitative expression of this

influence of the poison on the total hydrogen adsorption without further work. In order to obtain a platinum-black having a hydrogen sulphide content of 7.22 c.c. for the 6.72 g. of platinum used, exposure to hydrogen sulphide for a period of 3 days was necessary. It should be noted that the value, 4.0 c.c. of hydrogen, observed for a hydrogen sulphide content of 4.27 c.c., is probably low, since it was obtained after exposure to hydrogen for 21 hours only, whereas approximate equilibrium with this poison content requires several days. For attainment of hydrogen equilibrium

FIG. 1.



with a hydrogen sulphide content of 7.22 c.c., 9 days' exposure to hydrogen was necessary.

While, within the limits studied, the effect of hydrogen sulphide on the total hydrogen adsorption is not very great, the poison exerts a very marked and interesting action on the velocity of this adsorption, the retardation being greater for hydrogen sulphide in the initial form than for the equivalent sulphur left after dissociation and removal of the hydrogen.

The influence of various concentrations of the poison on the rate of adsorption, and the difference in the effect of hydrogen sulphide in its original and in its dissociated form, are seen from the curves of Fig. 1, in which the adsorption of hydrogen is plotted against time

for various hydrogen sulphide contents. (The significance of the letters A and B is explained on p. 2205.)

The form of the curves is somewhat difficult to explain on the basis that the main process of primary adsorption, or a substantial part of this, is a molecular one associated with a relatively low critical energy, since, in this case, the obstructive occupation of the peak areas should result only in the retardation or suppression of atomic adsorption, whereas the effective absence of these highly unsaturated areas retards the adsorption as a whole. Thus, the presence of, and possibly the activation of hydrogen by, free adsorbing units of a high degree of unsaturation influences also the rate of adsorption by less highly unsaturated adsorbing elements. From this standpoint, the main process of adsorption would be a catalytic reaction dependent on, or accelerated by, previous association with the highly active areas. This aspect will be discussed in greater detail in a later paper.

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