

232. *The Relative Effect of Inhibitors on Adsorption and on Catalytic Activity. Part I.*

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The gradient of the poisoning graph for the deactivation, by means of hydrogen sulphide, of platinum for catalytic hydrogenation has been compared with that representing the corresponding action of the poison on the adsorptive properties. Although the relative rate of decrease in the total adsorption of hydrogen by the metal as the poison content is progressively increased is in any case not widely different from the corresponding fall in the catalytic activity, yet a better agreement between the slope of the two graphs is obtained if the fall in the velocity of the adsorption, rather than in the total amount adsorbed, is compared. The correspondence is of interest in connexion with the existence of active points in the catalysing surface.

At sufficiently low gas pressures, the rate-controlling factor in the adsorption may change from the condition of the adsorbing surface to the rate of impingement of the gas molecules on the adsorbent.

THE relative action of a poison on the adsorptive power of a metallic catalyst and on its activity for catalysis is of considerable importance in connexion with the question as to whether all adsorbing elements in the surface are potentially catalytically active or whether, on the other hand, catalytic activity is confined to certain so-called active points.

In earlier work of Pease and Stewart (*J. Amer. Chem. Soc.*, 1925, **47**, 1235), carbon monoxide was used as a poison towards a copper catalyst; and it was observed that the addition of a small volume of this poison was followed by a far greater fall in the catalytic activity for the hydrogenation of ethylene than would be expected from the ratio between the volume of carbon monoxide added and the total volume which the copper was capable of sorbing. In view of the importance of this observation, it has been considered of interest to undertake a somewhat more extensive correlation of the relative depression of adsorptive power and of catalytic activity. Carbon monoxide is not a permanent poison and may readily be removed, for instance by degassing at 250°: further, the apparent adsorptive power of a metal for this gas—also the actual adsorbed concentration—might possibly be affected by reaction of the carbon monoxide with hydrogen, including any residual hydrogen present in the metal, although the hydrogenation of carbon monoxide certainly occurs far less readily on copper than, for instance, on nickel. Accordingly, in re-examining this point systematically, it appeared desirable, for the sake of simplicity, to employ a permanent poison which remains unchanged in amount on the metal surface throughout a given series of determinations and which, particularly, is not removed by any necessary degassing between adsorption measurements. In the second place, it was felt that considerations based on the total adsorptive power only, *viz.*, on the volume of a given gas which is adsorbed after an arbitrary time, or at saturation, by the unpoisoned metal, are not in themselves very definite evidence for active points, if only in view of the complex nature of the total sorption process and of the inclusion in this of non-surface components corresponding with the penetration of the gas to the interior. For this reason, it is considered that a fuller discussion of the implications is better postponed until the experimental data have been adequately examined.

In the present paper, in addition to measuring the total adsorption, an attempt has been made to correlate the velocity of the adsorption process—for hydrogen on platinum—at various known stages of poisoning with the corresponding catalytic activity, since this velocity, rather than the total volume of gas which the metal is capable of sorbing, may well be a controlling factor in determining the rate of catalytic activation.

It was found that the relative depression in the catalytic activity, with increasing poison concentration, does not in any case differ greatly from the corresponding fall in the total adsorption, provided that the time at which the observation of total adsorption is made is short; but, as was expected, a closer degree of correspondence in the value of the poisoning coefficients for catalysis and for adsorption, respectively, is obtained if the values

of the adsorption velocity during the early stages of adsorption are employed in place of those representing total adsorption.

EXPERIMENTAL.

The apparatus employed was similar to that previously used for other adsorption work involving hydrogen and deuterium (J., 1936, 1542). The kinetics of the adsorption of hydrogen by platinum at various stages of poisoning by hydrogen sulphide were found to be of the same type as for adsorption on unpoisoned platinum; and the general technique and method of expressing the adsorption velocities were as described in this previous paper. The platinum was prepared, as before, by Mond, Ramsay, and Shields's method (*Phil. Trans.*, 1895, A, 186, 657): the hydrogen was purified by desorption from palladium, and the hydrogen sulphide by liberation from magnesium hydrosulphide, followed by liquefaction and distillation.

Before a series of measurements was begun, the platinum was freed from its original oxygen content by repeated treatment with hydrogen and stabilised at 200°, all subsequent degassing being carried out at 100°. All measurements of adsorption were made at 18°. In poisoning, a known small volume of hydrogen sulphide was admitted to the previously degassed platinum at room temperature, the completeness of the adsorption of each small increment of poison being checked by testing for residual pressure by means of a McLeod gauge. The platinum containing the hydrogen sulphide was then heated to 100°, during which no sulphur was removed, and the adsorption of hydrogen, with the adsorption bulb immersed in a thermostat maintained at 18°, was subsequently followed in the usual way. The same specimen of platinum-black, of gradually increased poison content, was of course used throughout each series of measurements; and each series was started with a new preparation of unpoisoned platinum. Measurements of the catalytic activity of the platinum at known stages of poisoning were made by observing its activity for the hydrogenation of crotonic acid at 40° under standardised conditions (J., 1935, 393; *Trans. Faraday Soc.*, 1917, 13, 36).

When small specimens of platinum had to be removed from the adsorption bulb for determination of the catalytic activity, great care was necessary in order to avoid a change in the activity due to exposure to the air. To this end, after thorough degassing, the bulb was filled with helium in order to form a protective covering over the finely divided metal; and the extraction and testing of the small quantity of platinum required for the catalytic measurement were carried out as quickly as possible; further, the absence of change in the condition of the platinum was checked by duplicate measurements before and after this operation. If these precautions are not observed, the residual hydrogen content of the platinum may, on exposure to air, lead to a rise in temperature accompanied by sintering, and to the subsequent loss of activity by surface change rather than by the action of the poison added.

Preliminary Measurements of Total Adsorption.—In this preliminary series, measurements were made of the relative influence of hydrogen sulphide on the catalytic activity and on the total adsorptive power for hydrogen at atmospheric pressure. The initial weight of platinum taken was 16.1 g.; and small samples were removed at the various stages of poisoning in order to determine the catalytic activity. The results are summarised in Table I.

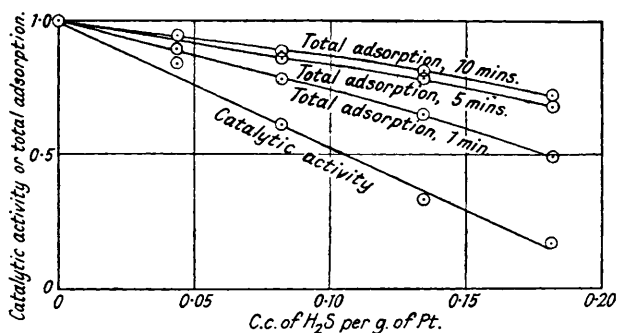
TABLE I.

H ₂ S content (c.c. at N.T.P. per g. of Pt).	Total hydrogen adsorption, in c.c. at N.T.P. per g. of Pt, after			Activity for catalytic hydrogenation (c.c. H ₂ per min.).
	1 min.	5 mins.	10 mins.	
0	0.820	0.913	0.953	19.0
0.043	0.730	0.870	0.903	16.0
0.082	0.642	0.793	0.843	11.6
0.134	0.535	0.719	0.775	6.4
0.181	0.405	0.621	0.686	3.4

In comparing the relative effects of the poison in this way—in place of, as was later done, studying the kinetics in greater detail and comparing the adsorption velocities—it is necessary to choose a standard time at which the total adsorption by the platinum at the known stage of poisoning is compared with the corresponding total adsorption by the unpoisoned metal; and, since this time is arbitrary, the influence of the poison on the total adsorption at all three times, *viz.*, at 1, 5, and 10 mins., has been plotted on the same graph as that showing the corresponding fall in the catalytic activity. In this graph (see Fig. 1) the values of the unpoisoned catalytic activity and of the unpoisoned total adsorption have in each case been taken as unity; accordingly, the figure represents on a comparable scale the fractional fall in the adsorp-

tion and in the catalytic activity, respectively, caused by a gradually increased concentration of the poison.

FIG. 1.



The disparity in slope of the activity and of the adsorption graphs is not very great if consideration be taken that this total sorption, in addition to including non-surface processes not directly concerned in surface catalysis, merely represents the aggregate amount of gas fixed by processes the velocity of which diminishes continuously with the time; and it will be noted that the slope of the adsorption graphs gradually approaches that of the line representing the fall in catalytic activity as the time at which the total adsorption is compared is decreased.

Since the secondary components in the total sorption—corresponding, for instance, with the penetration of the gas, by diffusion or by activated migration, to the interior of the metal—are, as is shown by the kinetics, relatively slow compared with the main process of primary adsorption, the proportionate effect of these processes in the total sorption should become greater as the time at which the total sorption is observed is increased; *i.e.*, the complicating influence of these factors should become less as this time is decreased. Thus the observed gradual approach in slope, with diminishing time, to that of the catalytic activity graph suggests that, as would be expected, the main rapid adsorption process is that responsible for catalysis and that a still greater degree of concordance between activity and adsorptive properties might be obtained if the relative degree of incidence of the slow secondary process could be minimised by further reducing the time of observation or, better, by following the adsorption kinetics—particularly during the early stages, during which the primary adsorption process is dominant—and comparing the adsorption velocity constant, at various stages of poisoning, with the corresponding catalytic activity.

Adsorption Velocities at Normal Pressure.—In this series, 17.2 g. of platinum-black were progressively poisoned by the addition of known increments of hydrogen sulphide; and the velocity of the adsorption of hydrogen by the original and by the poisoned catalyst was followed by observations made, in the early stages of adsorption, at intervals of a few seconds, the velocity measurements being in many cases checked by duplicate runs at the same poison content. The influence of various quantities of this poison on the adsorption during the first two minutes is summarised in Fig. 2.

On examining the kinetics of the adsorption, these were found to follow a course of the same type as that previously found for hydrogen or deuterium on unpoisoned platinum (J., 1936, 1542); *i.e.*, the volume adsorbed, during early stages of the adsorption, followed Bangham and Sever's relationship (*Phil. Mag.*, 1925, 49, 938):

$$\log a/(a - v) = kt^n \dots \dots \dots (1)$$

in which v is the volume of gas adsorbed after time t , and a the saturation capacity. If this equation is written in its logarithmic form:

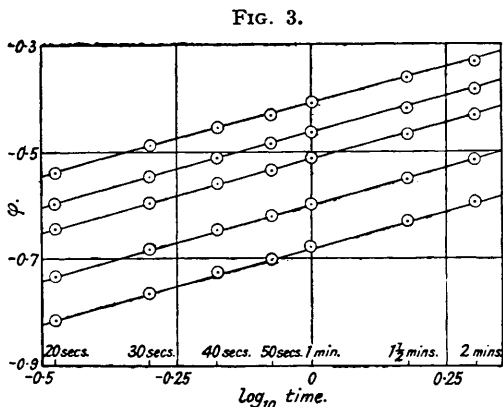
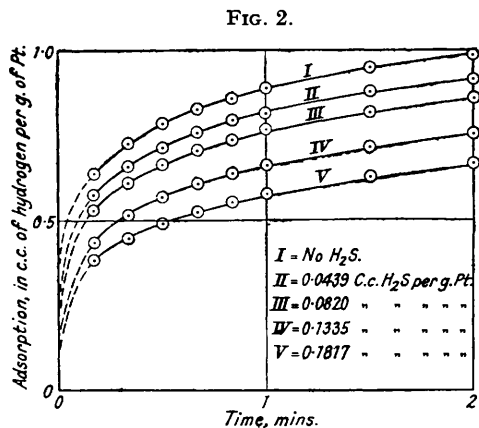
$$\log\{\log a/(a - v)\} = \log k + n \log t$$

it will be seen that a linear plot should be obtained between $\log\{\log a/(a - v)\}$ and $\log t$; and the agreement of the observed kinetics with a course of the above type is shown in Fig. 3, in which ϕ is the above function.

Equation (1) may, as before, be regarded as being derived from a rate equation of the type

$$dx/dt = nk(a - v)t^{n-1} \dots \dots \dots (2)$$

Consequently, provided that the index, n , in equation (1) does not change appreciably as the platinum is poisoned, the product nk may be employed as a velocity constant, the value of which, at a given stage of poisoning, is a measure of the velocity of the adsorption. The variation of

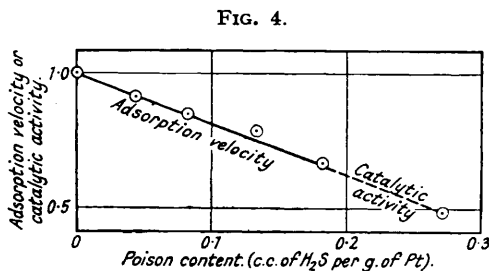


this adsorption rate constant with the hydrogen sulphide content is summarised in Table II, the general method of calculating n and k being as already described (J., 1936, *loc. cit.*).

TABLE II.

H ₂ S content (c.c. at N.T.P. per g. of Pt.)	k .	n .	nk .	Relative velocity of adsorption.
0	0.375	0.28	0.105	1.00
0	0.393	0.27	0.106	1.01
0.0439	0.354	0.27	0.096	0.92
0.0820	0.330	0.27	0.089	0.85
0.1335	0.286	0.29	0.083	0.79
0.1817	0.241	0.29	0.070	0.665
0.1817	0.245	0.29	0.071	0.675
0.1817	0.250	0.28	0.070	0.665

If the values of nk are plotted against the poison content (see Fig. 4) a straight line is obtained, *i.e.*, the adsorption velocity varies linearly with the poison content; and since, as has already been found, the catalytic activity also decreases linearly with the poison, it was considered preferable in the present series, in place of removing part of the platinum between each adsorption, to interrupt the measurement of adsorption once only, *viz.*, at the final stage shown in Table II (corresponding with the reduction of the original adsorption velocity by about 33% by the 0.1817 c.c. per g. of platinum of hydrogen sulphide added) and to continue the poisoning from this stage—with measurement of the catalytic activity—in order to ascertain whether the gradient of the poisoning graph was identical with that obtained for the adsorption velocity. This alternative method was adopted in order to minimise the possibility of an uncontrolled change in activity which may follow the repeated taking out and handling of a sensitive catalyst. The ease of handling is greatly increased if the activity has been reduced by partial poisoning; and the taking out of the catalyst was of course done with the precautions already described, including the use of an inert gas.



On continuing the poisoning graph from the above point, it was found that, whereas the platinum containing 0.1817 c.c. of hydrogen sulphide per g. possessed a catalytic activity of 6.6, this activity fell to 4.7 on increasing the hydrogen sulphide content to 0.2704 c.c., *i.e.*, by 0.0887 c.c. From these figures, the value of the poisoning coefficients, α (J., 1934, 26, 672), for the depression, respectively, of the adsorption velocity and the catalytic activity, can be calculated by means of the usual relationship $k_c = k_0(1 - \alpha c)$ or the equivalent expression

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$k_c/k_0 = (1 - \alpha_c)/(1 - \alpha_0)$ in which k_0 is the original unpoisoned catalytic activity, or the unpoisoned adsorption velocity, and k_c is the activity, or the adsorption velocity, in the presence of a concentration, c , of the poison. From these,

$$\alpha_{\text{ads.vel.}} = 1.8 \text{ and } \alpha_{\text{cat.act.}} = 2.0.$$

It will be seen that the agreement is reasonably close. The continuation of the adsorption-velocity line by that representing, on an equivalent scale, the slope of the observed further fall in catalytic activity per unit of poison has also been inserted in Fig. 4.

Influence of Poisoning on Low-pressure Adsorption.—In view of the special catalytic significance which has been ascribed to the low-pressure adsorption of hydrogen and other gases, work was also carried out on the relative effect of hydrogen sulphide on adsorption under these conditions, compared with its action on the catalytic activity. To this end, hydrogen at a relatively low pressure (*ca.* 0.06 mm. in each case) was admitted to progressively poisoned platinum, a small sample of which was—with proper precautions—removed at each stage of poisoning in order to enable the catalytic activity to be determined. This low-pressure series of adsorption measurements was combined with the first series of the present paper (total adsorption at normal pressure); consequently, the fall in the catalytic activity is identical with that already given in col. 5 of Table I, *i.e.*, 0.1813 c.c. of hydrogen sulphide per g. of platinum reduced the activity of the platinum to 17.9% of its unpoisoned value.

The rate of adsorption at these low pressures was followed by a McLeod gauge, since it was not practicable in the apparatus employed to measure the adsorption at a constant low pressure of this order. The results, with the platinum at various stages of partial poisoning, are summarised in Table III.

TABLE III.

Wt. of Pt, g.	H ₂ S content (c.c. at N.T.P. per g. of Pt).	p_0 , mm.	t , mins.	H ₂ adsorption, in c.c. at N.T.P.	k_1 .	$k_1/\text{wt. Pt.}$
16.11	0	0.0671	2	0.0163	0.121	0.0075
			5	0.0270	0.107	0.0067
			10	0.0353	0.112	0.0070
16.11	0.0433	0.0567	2	0.0143	0.127	0.0079
			5	0.0239	0.117	0.0073
			10	0.0302	0.120	0.0075
15.78	0.0820	0.0586	2	0.0142	0.120	0.0076
			5	0.0247	0.117	0.0074
			10	0.0312	0.119	0.0075
15.36	0.1340	0.0531	2	0.0131	0.123	0.0080
			5	0.0226	0.119	0.0078
			10	0.0284	0.126	0.0082
15.03	0.1813	0.0653	2	0.0161	0.123	0.0082
			5	0.0274	0.116	0.0077
			11	0.0352	0.116	0.0077

It will be seen that, on the whole, the rate of adsorption at these low pressures is, under the conditions of the measurements, not greatly affected by the presence of the poison, although the latter is ultimately present in amount sufficient to reduce the catalytic activity to less than one-fifth of its original value. On the other hand, the adsorption rate appears to be controlled by the hydrogen pressure, *i.e.*, by the frequency of the molecular impingement of the gas on the adsorbing surface. It will be noted that the rate-controlling factors under these conditions of low pressure and restricted gas supply are apparently quite different from those which are dominant in ordinary high-pressure adsorption. Further, if in these circumstances—in which the molecular impingement is relatively low compared with the available surface elements, even if four-fifths of these are covered by poison—the velocity of the adsorption is strictly proportional to the gas pressure rather than being a function of the condition of the surface, it should be possible very simply to correct for the variation in pressure during adsorption and to test the degree of this direct proportionality by evaluating the appropriate constant at each stage of the poisoning.

If $dv/dt = kp$, where p is the pressure in mm. at time t , and k is the required constant, and if p_0 is the initial hydrogen pressure, then introduction of the appropriate conversion factor for expressing volumes of gas present in terms of the pressure exerted (for the apparatus in question, 1 c.c. of gas = 1.754 mm. pressure) gives

$$p = p_0 - 1.754v$$

where v is the volume, in c.c., of gas adsorbed from the original volume introduced, this original volume corresponding with an original pressure, p_0 . Accordingly,

$$dv/dt = k(p_0 - 1.754v)$$

and, by integration,

$$(1/1.754) \log p_0/(p_0 - 1.754v) = kt$$

or

$$(1/t) \log p_0/(p_0 - 1.754v) = \text{const.}$$

The approximate constancy of the above expression, at all the stages of poisoning studied, is shown in the last two columns of Table III, in which k_1 is $(1/t) \log p_0/(p_0 - 1.754v)$. Since a small quantity of platinum was, as already mentioned, removed for testing between the additions of poison, it is necessary to make a small correction for the weight of platinum present. This has been done in the last column of the table; and, if the smallness of the individual adsorptions is taken into consideration, the degree of constancy of the corrected constant is quite good, and indicates a reasonably strict linear variation of the adsorption velocity with the pressure. Certainly, at these low pressures and under these conditions, the velocity does not sink as the catalyst is progressively poisoned, at any rate up to the stage investigated, namely, up to that corresponding with the removal of over 80% of its catalytic activity.

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