357. *The Relative Effect of Inhibitants on Adsorption and on Catalytic Activity. Part II.*

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The effect of a catalyst poison on the velocity of adsorption of hydrogen by a hydrogenation catalyst, on the one hand, and on its activity for catalytic hydrogenation, on the other, has been found to be very similar throughout the whole of the poisoning graph. The correspondence found in Part I for early stages of poisoning thus extends also to later stages.

In certain respects, the adsorption of hydrogen by metals such as platinum resembles ordinary catalytic reactions catalysed by the metal; for instance, the velocity of the adsorption of this gas is retarded by catalyst poisons in a very similar way to the inhibition of the velocity of catalytic hydrogenation. From this standpoint—in that both the chemisorptive addition of hydrogen to platinum and the activation of hydrogen for addition to an external reactant seem to be dependent on contact with active metal—this union of hydrogen with platinum may perhaps be viewed as a special and particularly simple type of catalytic process in which the platinum is not only the catalyst but also the ultimate acceptor of the hydrogen. This process also occurs as the first stage in the general activation of hydrogen for hydrogenation, in which it is however followed by a further stage in which the hydrogen is passed on to a third body.

In Part I (J., 1938, 1228) the action of a poison on the adsorptive velocity has been compared with its action on the velocity of an ordinary hydrogenation reaction catalysed by the same platinum; and it has been found that the slope of the catalytic-poisoning graph, in which the activity is plotted against the poison content, is, for not too advanced stages of poisoning, of the same order as the corresponding part of the graph representing the fall, with increasing poison content, in the velocity of adsorption of hydrogen during early stages of adsorption. It has now been considered of interest to extend this work; and the present results indicate the close general similarity of the complete poisoning graphs for adsorption velocity and catalytic activity, *i.e.*, the correspondence found in Part I for early stages of poisoning also holds for later stages.

Experimental.

The general technique and method of calculation have already been described in Part I, which should be read in conjunction with the present paper; and, as before, hydrogen sulphide was used as the poison.

General Kinetics of the Adsorption.—Before dealing with the variation of the adsorption velocity with the poison content of the platinum, we give a single long run in detail in order to show the course of the adsorption process. The general course is of the same type both with unpoisoned and with partially poisoned platinum; and, in the example given, the adsorption of hydrogen, at 0° and at atmospheric pressure, by 16·2 g. of platinum black at an early stage of poisoning (0·075 c.c. of hydrogen sulphide per g. of Pt) was followed for about 1600 mins., the results being summarised in Table I.

Table I.

Time, mins.	Adsorption, in c.c. of H_2 at N.T.P., per g. of Pt.	ϕ_{10}.	Time, mins.	Adsorption, in c.c. of H_2 at N.T.P., per g. of Pt.	ϕ_{10}.
$\frac{1}{3}$	0·925	−0·381	5	0·995	−0·325
$\frac{1}{2}$	0·937	−0·371	$7\frac{1}{2}$	1·002	−0·320
$\frac{2}{3}$	0·944	−0·366	10	1·007	−0·316
$\frac{5}{6}$	0·952	−0·359	15	1·015	−0·309
1	0·955	−0·357	20	1·021	−0·305
$1\frac{1}{4}$	0·962	−0·351	30	1·029	−0·298
$1\frac{1}{2}$	0·967	−0·347	45	1·035	−0·294
$1\frac{3}{4}$	0·970	−0·345	60	1·040	−0·290
2	0·974	−0·342	90	1·048	−0·283
$2\frac{1}{2}$	0·980	−0·337	700	1·097	−0·244
3	0·984	−0·334	1575	1·108	−0·235
4	0·990	−0·329			

In plotting the adsorption, it is convenient to use functions of the volume and time which lead to a linear graph in place of a curve; and, as before, the function $\phi = \log\{\log a/(a - x)\}$, which gives a linear plot against log t, has been employed. This expression is the logarithmic form of Bangham and Sever's equation (*Phil. Mag.*, 1925, **49**, 938):

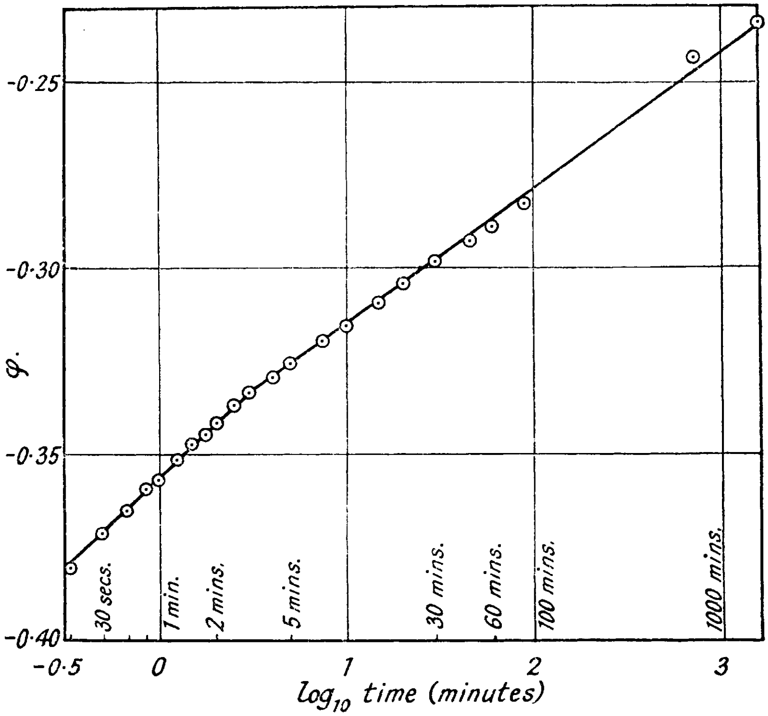
$$\log a/(a - x) = kt^n$$

or

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

in which x is the volume adsorbed after time t, and a is the saturation value (about **1500 c. mm.** of hydrogen, at N.T.P., per g. of Pt). On plotting ϕ against log t, Fig. 1 is obtained.

FIG. 1.



It will be seen that this is of a flexed linear type, the linear relationship between the time and volume functions being continued, after the break point, with a slightly different slope. In earlier work, this second process was found to be still taking place, without deviation from a linear course, even after several months. The general form of the graph suggests either the presence, in the early stages, of disturbing factors, or, alternatively, the real presence of a distinct initial adsorption process which takes place either prior to or concurrently with the main process of adsorption and, in the example given, comes to an end after about 4 minutes. This point is discussed on p. 1753.

From the values of ϕ and the slope of the ϕ–log t graphs, the product, nk, which constitutes a convenient velocity constant (see Part I, pp. 1230, 1231) for processes following the above equation, may be obtained. In comparing adsorption velocities, it is unnecessary to use natural logarithms, which the derivation of the original differential equation presupposes, since, although ϕ_e and ϕ_{10} are connected by an addition constant, $\phi_e = 0{\cdot}8340 + 2{\cdot}3026\phi_{10}$, yet this addition constant disappears in the derivation of k and of n, and the ratio of two values of k is not affected by the logarithmic scale used.

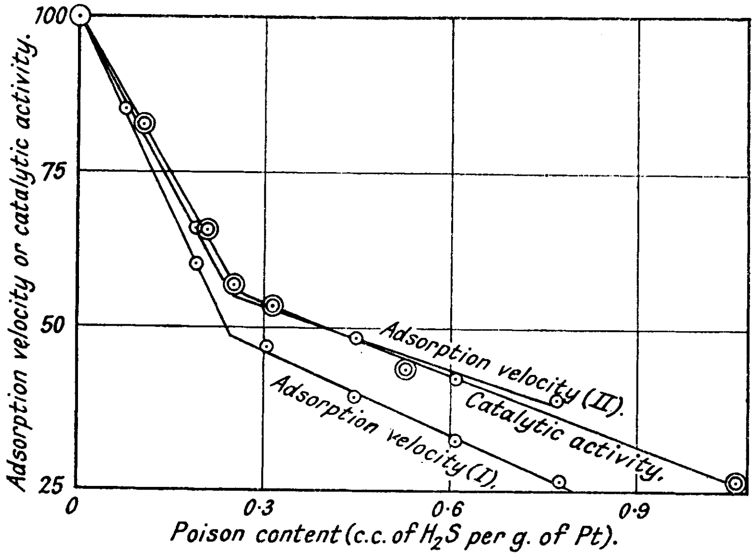
Relative Depression of Adsorption Velocity and of Catalytic Activity.—Parallel measurements, in which the same stock of platinum black was, as before, poisoned by hydrogen sulphide, were made of the effect of this poison on the adsorption velocity, on the one hand, and on the catalytic activity—measured by the rate of hydrogenation of crotonic acid—on the other. In the adsorption measurements, about 17 g. of the platinum were sealed and progressively poisoned in the apparatus previously described, the velocity of the adsorption of hydrogen being measured at each stage of poisoning; but, in this series, in order to avoid the necessity for opening the adsorption bulb for the removal of samples at the various stages, the poisoning coefficient for the catalytic activity was determined in the ordinary way with a further portion of the same platinum black. The results of the adsorption-rate measurements are summarised in Table II, in which n_1 and k_1, and n_2 and k_2, refer respectively to the adsorption rates before and after the point of inflexion (see Fig. 1). The poison content of the catalyst is given in c.c. of hydrogen sulphide, at N.T.P., per g. of platinum.

TABLE II.

Adsorption Rates.

Hydrogen sulphide content.			Adsorption velocity.			
Increment added.	Volume adsorbed.	Total poison content.	n_1k_1.	Relative velocity.	n_2k_2.	Relative velocity.
0·0	0·0	0·0	0·0231	100	0·0132	100
0·0749	0·0749	0·0749	0·0172	74·0	0·0112	84·8
0·1140	0·1140	0·1889	0·0139	60·2	0·0087	65·8
0·1173	0·1173	0·3062	0·0109	47·0	0·0083	62·8
0·1417	0·1417	0·4479	0·0091	39·4	0·0064	48·5
0·1621	0·1616	0·6095	0·0074	32·1	0·0055	41·6
0·1670	0·1667	0·7762	0·0059	25·6	0·0051	38·6

FIG. 2.



It will be seen that, up to the end of the poisoning range studied, nearly all the added poison is adsorbed; but the addition of quantities of hydrogen sulphide beyond this range introduced the complication of incomplete adsorption, as was shown by residual pressure in the McLeod gauge.

The corresponding depression in the catalytic activity, for the hydrogenation of crotonic acid under standard conditions, is given in Table III.

The comparison of the two poisoning effects, namely, on the adsorption velocity and on the catalytic activity, is given in Fig. 2. It will be noted that the general characteristics of the ordinary catalytic poisoning graph—including the inflected linear form—are reproduced in the adsorption graphs whether these are based on adsorption velocities during the initial period or in the time subsequent to this; and the rate of fall, with increasing poison content, is very similar in all three graphs. Actually, the catalytic graph corresponds more nearly with that involving adsorption velocities after the preliminary period; but, strictly, a slight correction for the small percentage of hydrogen sulphide not on the catalytic surface (*i.e.*, in the free liquid phase) in the hydrogenation reaction should be applied to the catalytic graph,

TABLE III.

Catalytic Activity.

Hydrogen sulphide content.		Activity of platinum.	
Mg. per 0·05 g. Pt.	C.c., at N.T.P., per g. of Pt.	*k*.	Relative activity.
0·0	0·0	9·0	100
0·0080	0·1055	7·4	82·3
0·0160	0·211	5·9	65·6
0·0192	0·253	5·1	56·7
0·0240	0·316	4·8	53·4
0·0402	0·530	3·9	43·4
0·0805	1·060	2·3	25·6

which would move it slightly to the left (see J., 1938, 2073, Fig. 1, for the order of magnitude of the correction with strong poisons). However, the degree of agreement of all the graphs in Fig. 2 of the present paper is sufficient to indicate the close similarity of the action of the poison both on adsorption and on catalytic activity.

DISCUSSION.

Form of the Adsorption–Time Graphs.—The adsorption of hydrogen on metals such as platinum is usually regarded—apart from components of van der Waals type, which are mainly operative at low temperatures—as consisting of a relatively rapid process, accompanied or followed by a slower one which has been attributed to non-surface factors such as the penetration of the gas into the interior of the metal. The presence, and the termination after a short time, of an initial adsorption phase or other initial factor is apparently also supported by the general form of the adsorption–time graphs (see Fig. 1) when time and volume are expressed as functions which give a linear plot between these quantities, the termination of the first phase being indicated by the change of slope.

Although the ending of the first phase after a short time seems clear, two alternative possibilities exist for the start of the process or processes represented by the subsequent slope, in that this process may either begin only after the termination of the first phase or actually start, like the first phase, at zero time, these processes being thus either consecutive or concurrent. In the latter case, the first slope of the graph would be composite and would represent a velocity-sum, the kinetic form of the components being related sufficiently for their summation also to lead to the observed linear plot. On the whole, the start also of the long-term adsorption process or processes from the beginning seems probable, since a linear plot for the secondary process alone is not obtained if observations of time and of volume adsorbed are begun from the time and volume corresponding with the break in the graph (which represents the commencement of any subsequent process, contrasted with a previously existing or concurrent one), whereas, as will be seen from the figure, a linear graph results also at advanced stages of adsorption if the time and volume are measured from the beginning of the total adsorption.

It should be noted, finally, that while the occurrence, in the early stages, either of a distinct short-term adsorption process or of initial disturbing factors is undoubtedly indicated, too much weight should not be laid on the form of the graph as confirmation, in itself, of distinct initial higher-velocity adsorption, since the transient disturbing factor may, for instance, be due to thermal contraction following an initial expansion caused by the almost immediate development of adsorption heat on contact of the hydrogen with the platinum, which contraction would simulate a contraction due to a true adsorption process and, when added to the normal adsorption, would apparently indicate the initial presence of a higher-velocity adsorption component. The hydrogen is of course present in excess and at atmospheric pressure, under which conditions the development of adsorption heat would be far more rapid than is the case in ordinary adsorption heat measurements at very low gas pressures and with restricted access of hydrogen. If this is the effective factor, it should be possible, by taking burette readings sufficiently quickly after contact between the gas and the metal, to observe the initial expansion phase, which would be in the opposite sense to adsorption and, when summed with the true adsorption, would thus simulate a subnormal adsorption velocity; but, under the experimental conditions used, stable observations could not be begun before the elapse of 10—20 seconds from the contact time, and although the 10-seconds reading in some cases indicated an apparent adsorption less than would be expected from the velocity from 20 seconds up to the break time, the system had not settled sufficiently after the first rush of gas into the evacuated adsorption bulb for the reading at 10 seconds to be trustworthy, particularly in view of the very rapid initial motion of the mercury in the gas-measuring burette and the necessity for rapid levelling of the mercury cups attached to this. It is hoped to deal more fully with the adsorption components in a later paper.

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