

*The Form of Catalyst Poisoning Curves.*

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The form of the catalyst poisoning curve representing the variation of the activity of a progressively poisoned platinum catalyst with the poison content of a hydrogenation system, has been remeasured. Additional precision has been possible by the use of a specially stabilised stock of platinum black and by taking into account the mobile nature of the competitive adsorption of the poison and of the unsaturated substance used in the hydrogenation tests. The poisoning curve is initially very nearly linear but is slightly curved even at early stages of poisoning, although formerly thought to be strictly linear there.

A FURTHER study of the form of the curve expressing the relation between the activity of a hydrogenation catalyst and the poison content of the system hydrogenated was suggested by the availability of two ways recently developed for increasing the precision of the measurements involved. The first consists in a simple and effective method for stabilising the grain size of catalysts such as platinum black when these are used in liquid-phase hydrogenation. The second lies in the rather unexpectedly easy reversibility of the adsorption of many types even of strong poisons, and of the mobility of the competitive adsorption between the poison and the unsaturated substance for the occupation of catalyst surface (Maxted and Ball, *J.*, 1952, 4284; 1953, 3153; 1954, 2778). As a result of this mobility, an adsorbed poison can be readily displaced by desorption, assisted by mass action, on applying a relatively large concentration of an unsaturated substance; or conversely, in the course of the hydrogenation of a system containing both a poison and an unsaturated species, additional poison, over and above that originally adsorbed, will move continuously from the free phase on to the catalyst as the concentration of the unsaturated substance in the system is decreased as a result of its hydrogenation to a saturated and therefore weakly adsorbed form.

By determining the individual points on the poisoning curve under conditions which are certainly more precise than those previously available, it has been found that, although initially the activity varies very nearly linearly with the poison content, yet this more exact study shows the graph to be slightly curved from its inception and to increase progressively in curvature; as the poison content of the system is still further increased, there is a region of rather sudden inflexion away from the activity axis. This is of interest since the initial, quasi-linear portion of the graph was formerly thought to be strictly linear (Maxted, *J.*, 1921, 119, 225, and later papers).

## EXPERIMENTAL

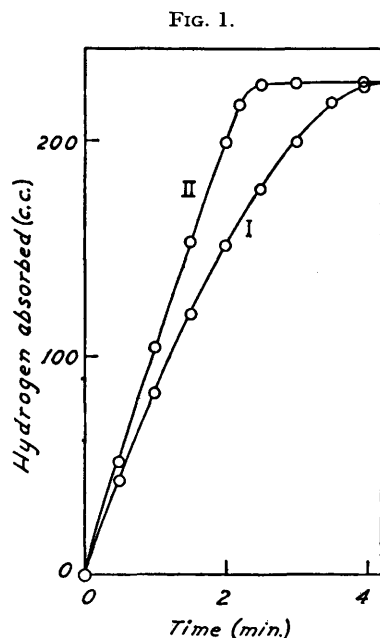
The reaction used for assessing the activity, at various stages of poisoning, of a known weight of platinum catalyst, weighed out as required from a stabilised stock, involved the liquid-phase hydrogenation of *cyclohexene* or crotonic acid. The activity tests were carried out in a thermostat at 30° in conjunction with a hydrogenation shaker operated under standardised conditions. This shaker, which has been developed over a number of years in order to obtain a high degree of reproducibility, actuates a small, vertically shaken hydrogenation pipette at a rate the constancy of which can be checked continuously throughout each run. The absorption of hydrogen is read off directly on a gas-burette system. Methyl sulphide was taken as the poison; and the usual hydrogenation charge consisted of 1 c.c. of *cyclohexene* (or 0.01 mole of crotonic acid), 9 c.c. of acetic acid containing a varied weight of the poison, and either 0.025 or 0.05 g. of platinum.

*Stabilisation of the Catalyst.*—Platinum black, made from chloroplatinic acid by alkaline formate reduction, is liable to change appreciably in grain size and consequently in surface area during its use for catalytic hydrogenation, with corresponding activity variations due to partial peptisation or coagulation rather than to poisoning.

It has been found that platinum black can be stabilised and activated if the usual exhaustive washing by decantation is supplemented by shaking the platinum rather vigorously in a mechanical shaker with successive changes of hot distilled water containing 5% of acetic acid,

the catalyst being separated from the supernatant liquid, at each change, by centrifuging. After this treatment, the platinum was dried at 100°, lightly ground in an agate mortar to remove lumps, and stored. From this stock, charges were weighed out as required; they gave closely reproducible results, together with a close adherence to zero-order reaction kinetics in an unpoisoned system. The improved kinetics and the general activation effect induced by this treatment are illustrated, for an unpoisoned system, in Fig. 1. In this, Curve I shows the course of hydrogenation obtained with a stock of platinum which had been exhaustively washed by decantation only. Curve II was given by the same platinum stock after it had been subjected to the stabilising treatment. Both systems consisted of *cyclohexene*, acetic acid, and platinum (0.025 g.), as above.

The stabilising effect of the new treatment may lie in a more thorough leaching of alkali salts (from the alkali formate reduction) out of the internal pores of the catalyst grains than can be obtained even by long-term washing by ordinary decantation, since the presence of such salts is known to cause instability and especially coagulation during the use of the catalyst; further, this extension of the available internal surface within the grains would account for the increase in activity which is also obtained. It may be noted that Feulgen (*Ber.*, 1921, 54, 360) has used intermittent violent shaking to prevent the passage of platinum into a difficultly washable, highly dispersed form during ordinary washing by decantation.



*Kinetic Form of Individual Hydrogenation Runs.*—In the absence of a poison, the linear zero-order form of the reaction path allows a direct and accurate evaluation of the reaction velocity. If a poison is present, two superimposed effects will cause curvature in the ordinary graph of total hydrogen absorption against time. First, poison will move from the free phase on to the catalyst as the concentration of the unsaturated substance decreases by reason of its hydrogenation. Secondly, unless the poisoned hydrogenation system has been allowed to remain in contact with the catalyst for the very long time (see *J.*, 1954, 2778) required for the attainment of equilibrium before starting the hydrogenation run, the adsorption will still be incomplete, and some poison will also move on to the catalyst by the continuation of simple adsorption during the test. The incidence of the latter process, which is additional to adsorption

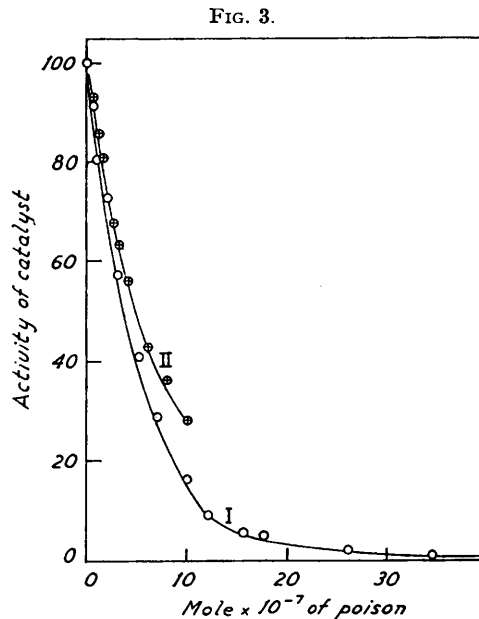
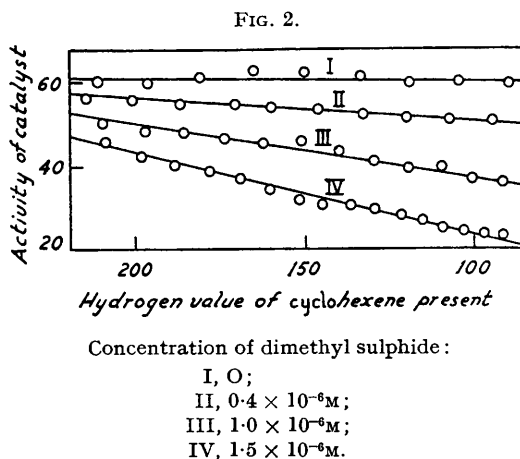
of poison caused by the gradual disappearance of the unsaturated component from the system, can be reduced to a negligibly low amount for the short period of the test by allowing the system to remain in the thermostat for about 1 hr. before starting the test. Even if this adsorption of poison were allowed to proceed until a very low rate had been reached before the hydrogenation is started, it is doubtful whether, at any rate in fast runs, the shift in the adsorbed poison content of the catalyst would keep pace with the changing conditions induced by the disappearance of the unsaturated component. In view of this probable time lag and of the lack at present of sufficient data to separate the two factors inducing a curved reaction path in the presence of a poison, curvature during a run has to be dealt with experimentally by reducing this complicating factor to a minimum.

The progressive fall in the reaction rate as hydrogenation proceeds in poisoned systems is most clearly seen if—instead of plotting the total hydrogen absorption against time—the instantaneous hydrogenation velocities are plotted against the residual concentrations of the unsaturated component, which for convenience can be expressed in terms of its hydrogen value, *i.e.*, as the number of c.c. of hydrogen required for its saturation. This is illustrated in Fig. 2 for a series of hydrogenation runs with various concentrations of poison. The system in each case was that mentioned on p. 3947, together with the amount of dimethyl sulphide indicated for the individual graphs. The unpoisoned run (I) is, of course, unaffected by any "moving-on" effect and is of zero-order, with a uniform hydrogenation rate throughout. In each of the poisoned runs, on the other hand, the activity of the catalyst, expressed in the Figure as the instantaneous hydrogenation velocity, in c.c. of hydrogen per min., falls continuously and

approximately linearly with the decrease in the concentration of the unsaturated substance, which effect is evidently the major factor in causing curvature in the ordinary hydrogenation graphs.

A further set of similar graphs was obtained by using  $10^{-2}$  mole of crotonic acid as the unsaturated substance, in place of 1 c.c. of *cyclohexene*, but in an otherwise similar hydrogenation system. In this case, the departure from zero-order kinetics in the presence of the poison was less marked. This was to be expected, since crotonic acid is known from other work to be less strongly adsorbed than *cyclohexene*; and, consequently, its progressive disappearance as the hydrogenation proceeds should have a smaller effect on the moving of additional poison on to the catalytic surface during a hydrogenation run.

*Form of the Poisoning Curve.*—This curve, which is based on a series of hydrogenation runs in which the poison content of the system is varied from run to run, gives the influence of the total poison content on the initial activity of the catalyst, before additional poison has begun to move on to the catalyst as a result of the progressive disappearance of the unsaturated



substance. In order to reduce the incidence of this moving-on factor to a lower value than that observed with *cyclohexene*, crotonic acid was used as the unsaturated substance. The system taken for Curve I of Fig. 3 consisted of 10 c.c. of a *N*-solution of crotonic acid in acetic acid, containing in the individual runs the various amounts of dimethyl sulphide shown in the abscissæ, and 0.025 g. of stabilised platinum catalyst. The poisoned system was allowed to remain in the hydrogenation pipette in contact with the platinum for about an hour in the thermostat at  $30^\circ$  before the admission of hydrogen and the starting of the hydrogenation shaker. The activities are expressed in the Figure as percentages of the original unpoisoned activity of the catalyst.

The evaluation of the initial activity of the platinum in the run carried out without poison presents no difficulty since, in this case, the hydrogenation velocity is substantially constant throughout the run; but in the poisoned runs, in which the moving-on effect causes curvature in the hydrogenation graph (namely, a progressive fall in the instantaneous hydrogenation rate as the run proceeds), the initial velocity has to be obtained by extrapolating the instantaneous rate at various times back to that at zero time, or by the equivalent method of extrapolating graphs of the type of Fig. 2 back to the hydrogen value corresponding to the amount of unsaturated substance present at the start of the run.

It will be seen from Fig. 3 that, although the variation of the activity with the poison content is at first not far from linear, the graph is never strictly linear and corresponds to a continuous curve in which the very slight initial curvature increases progressively and, at a later stage, undergoes a rather sharp inflexion away from the activity axis, after which it falls far less

steeply with still further increased poison concentrations. Curve II in Fig. 3 summarises a further, shorter series of measurements, made with 0.05 g. of a different and less active specimen of stabilised platinum, this series of tests being carried out mainly to confirm the existence of curvature in the initial portion of the poisoning graph.

Curves of the above nature, in which the inhibitive effect measured by the fall in activity is plotted against the total poison introduced, are called effective toxicity curves to distinguish them from those in which the observed inhibition is plotted against the amount of poison actually adsorbed on the catalyst, which are called true poisoning curves. It will be obvious, from the mobility of the competition between a poison and an unsaturated substance for the occupation of catalyst surface, that the accurate determination of true toxicity curves is more difficult than that of effective toxicity curves, since the assessment of instantaneous adsorbed poison concentrations involves dealing with a far more complex equilibrium than was previously supposed and would involve a knowledge both of the respective adsorption equilibrium constants and especially of the attendant rate constants which govern the adsorption and desorption of the particular poison and unsaturated substance used. All these are at present not known. For this reason, it seems certain that the structure of true, as distinct from effective, poisoning curves should receive renewed attention; and it is hoped to deal with this subject in a subsequent paper.

In this connection it may be noted that Kubokawa (*Rev. Phys. Chem. Japan*, 1937, 11, 202), who examined the poisoning of a platinum catalyst for the decomposition of hydrogen peroxide, obtained a linear relation between the logarithm of the reaction rate and the logarithm of the amount of poison adsorbed; but this adsorbed concentration was not determined with consideration of the poison mobility factors (*i.e.*, the reversibility of the adsorption of the poison alone, and any interference by virtue of the competitive and poison-displacing adsorption of the reactant). A similar logarithmic relation was also observed by the same author (*loc. cit.*, p. 82) for the non-specific and probably mechanical covering effect of the layer of carbon deposited on platinum during the decomposition of methane on a platinum wire at 1200°.

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