56. *The Reversibility of the Adsorption of Catalyst Poisons. Part IV.* Revival of Poisoned Catalysts by Gas-phase Desorption.*

By E. B. Maxted and M. Josephs.

The revival of platinum hydrogenation catalysts, previously poisoned by thiophen or diethyl sulphide, by a method involving the desorption of the poison into the gas phase, has been studied as an alternative to the liquid-phase desorption method described in earlier papers of this series. This desorption has been carried out in three ways, namely, by simple evacuation, by circulating an inert gas through the poisoned catalyst, and by circulating gaseous ethylene all at room temperature. These procedures are gas-phase analogues of liquid-phase revivals by direct desorption into a solvent and by displacing the poison by the competitive adsorption of a second substrate.

It has been shown in an earlier paper of this series [1] that platinum or nickel hydrogenation catalysts which have been inactivated by various poisons, including dimethyl sulphide, thiophen, or toxic metallic ions, can be easily revived by a liquid-phase desorption or desorptive displacement method applied at room temperature and involving, respectively, the simple washing of the poisoned catalyst with a suitable solvent alone or with a solvent containing a displacing agent such as an unsaturated substance. In view of this rather unexpected reversibility of the adsorption of typical strong poisons even at room temperature, we have now studied the degree to which catalysts poisoned by volatile sulphur compounds can be revived by a similar desorption of the poison into the gas phase. In preliminary work [2] the activity of poisoned platinum catalysts was thus considerably improved but complete revival was not reached.

In the present, more systematic work, a complete revival of platinum catalysts poisoned either by thiophen or by diethyl sulphide was obtained at room temperature by three methods involving, severally, (i) the direct removal of the poison by evacuation, (ii) its removal by circulating an inert gas through the catalyst, and (iii) the desorptive displacement of the poison from the poisoned surface by circulating ethylene. Method (ii) is closely related to method (i), since if, as is known from other work, the poison–catalyst adsorption complex has a significant dissociation pressure, poison should be removed continuously from the poisoned catalyst either by direct evacuation or by continuously changing an inert atmosphere above the catalyst surface. Method (iii) corresponds to the liquid-phase procedure involving the displacement of the relatively small amount of adsorbed poison from the surface by the mass action of a relatively large concentration of a less strongly adsorbed species, which process was, in the liquid-phase work, carried out by washing the poisoned catalyst with a solution of an ethylenic compound.

EXPERIMENTAL

Apparatus.—This (Fig. 1) consists of a catalyst chamber, A, containing 12·5 g. of platinum black which, in the course of the work, was alternately poisoned and revived. B_1, B_2, and B_3 are porous sintered-glass discs, as a safety measure to retain the platinum in case of an accidental sudden change of pressure in the rest of the apparatus. The poison was contained as a liquid in a reservoir, C, which served as a source for the periodical filling of a poison-vapour reservoir, D, from which known amounts of poison vapour could be delivered to the remainder of the apparatus and eventually to the catalyst. Since circulation was required both for the determination of the catalytic activity of the platinum by the gas-phase hydrogenation of ethylene and for methods (ii) and (iii) of revival, an all-glass, magnetically operated circulating pump, E, was provided, with appropriate circuits for the circulation either of an ethylene–hydrogen mixture or, alternatively, either of nitrogen or of ethylene alone. The pressure in the pertinent section of the apparatus, by means of which either the adsorption of the poison vapour on the

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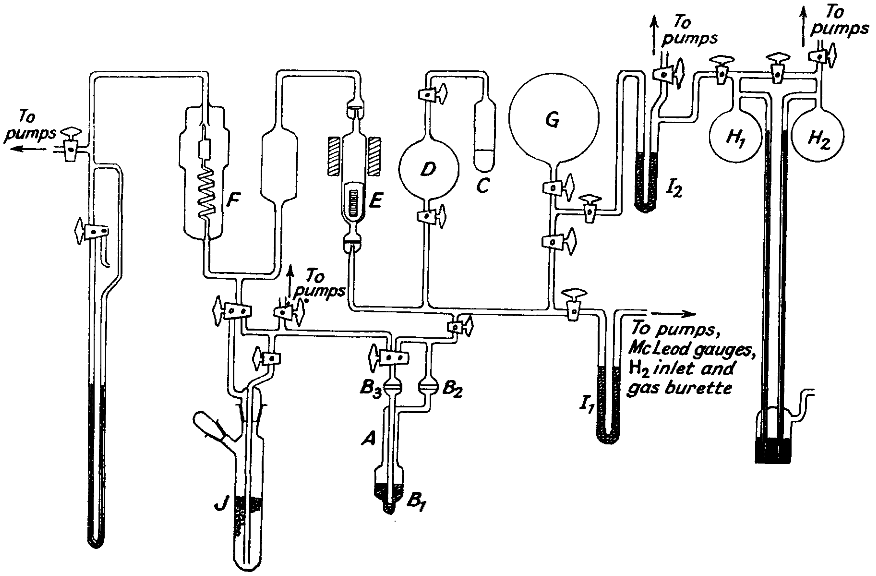
* Part III, *J.*, 1954, 2778.

[1] Maxted and Ball, *J.*, 1952, 4284 (Part I).

[2] G. T. Ball, Thesis, Bristol, 1953, pp. 126 *et seq.*

catalyst during a poisoning operation or the course of the hydrogenation during an activity determination was followed, could be read accurately on a Bourdon-type glass spiral gauge, *F*, from the mirror of which an optical image of the cross-wires of a lamp could be projected on to a distant scale. A storage bulb, for gaseous ethylene, *G*, was fed as required from liquid-ethylene reservoirs, H_1 and H_2, these liquid storage vessels being kept at −180° in liquid air, which was removed temporarily and with due caution when *G* was to be filled. The apparatus could be evacuated by a normal high-vacuum train; but a special feature of the apparatus was a provision for pumping off adsorbed poison from the catalyst by connection to a "cold-limb," *J*, which contained Fenske helices and could be immersed in liquid air. In this way, a very low poison pressure could, in the absence of other gases, be induced in the apparatus; and any poison pumped off from the platinum was condensed in a state having a very low pressure in the cooled limb. It was found that this acted as a very efficient pump: and it was, in all later stages of the work, used in preference to evacuation of the poisoned catalyst by means of the available high-vacuum system, particularly since the latter system had to be protected from contamination by poison. The apparatus included some mercury-filled gauges and safety valves; but the access of mercury vapour from these and from the mercury diffusion pump to the platinum was prevented by traps, I_1 and I_2, containing gold leaf and cooled in liquid air. The volumes of all pertinent parts of the apparatus were determined by calibration.

FIG. 1.



General Procedure.—In the cycle represented by poisoning followed by subsequent revival, the activity of the catalyst was measured at at least three stages, namely, in its original, poisoned, and revived states. In poisoning, a known amount of diethyl sulphide or thiophen vapour was admitted from the bulb, *D*, and the adsorption read off on the spiral pressure gauge. In the experiments in which the revival was carried out either by cold-limb pumping or by the circulation of an inert gas, the amount of poison adsorbed by the catalyst, and subsequently removed during the revival and condensed at −180° in the cold limb, *J*, could be checked by removing the liquid-air bath from this limb and allowing the condensed poison to evaporate into the spiral pressure gauge; but, at the time of the revival by ethylene circulation, this checking method had not yet been developed.

Activity Determinations.—In these, an equimolecular ethylene–hydrogen mixture, initially at approximately atmospheric pressure, was circulated through the catalyst by means of the magnetic pump, the fall in the pressure with the time as the hydrogenation proceeded being followed by reading the movement of the beam of light from the spiral pressure gauge.

The ethylene-hydrogenation velocity, at 0°, which was used as a measure of the activity of the catalyst at any given stage, is known [3] to vary approximately directly with the partial pressure of the hydrogen, at any rate up to not too advanced stages of the hydrogenation, after which the ethylene partial pressure begins also to exercise some control of the rate, though far less at 0° than at higher temperatures.[4] Consequently, during early stages of the hydrogenation at constant volume, in which the pressure falls continuously as a result of the process, the change in pressure with the time will follow a course which in its integrated form becomes $kt = \log\{p_0/(p_0 - p)\}$, in which p_0 is the initial partial pressure of the hydrogen, p the fall in the pressure of the system after time, t, and k is a reaction velocity constant. This relation should give a linear plot of $\log\{p_0/(p_0 - p)\}$ against the time, from the slope of which the value of k can conveniently be read off.

Revival Procedure.—The removal of the poison from the catalyst by simple evacuation at room temperature, by either of the methods described, needs no special description.

In revivals by nitrogen or ethylene circulation, the cold trap was used, not as a pump but as a means of freeing the circulating gas from entrained poison carried over from the catalyst, in such a way that clean gas was continuously re-passed through the platinum, the trap being placed in the gas circuit on the exit side of the catalyst chamber. The trap was maintained at −180° during the circulation of nitrogen and at −80° during ethylene circulation.

FIG. 2. *Revival by simple evacuation.*

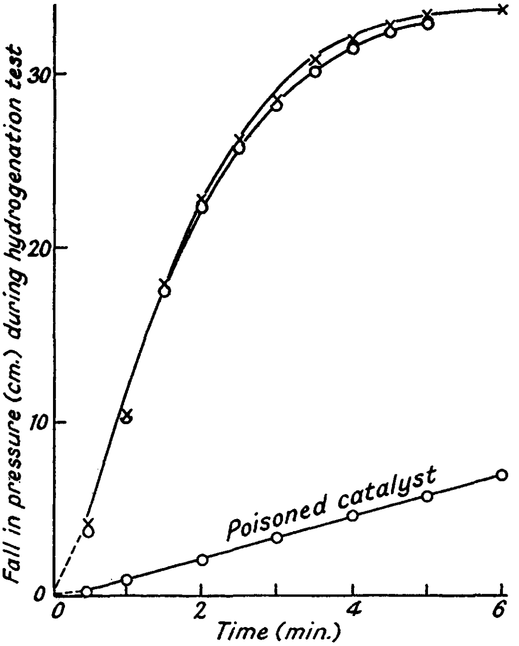
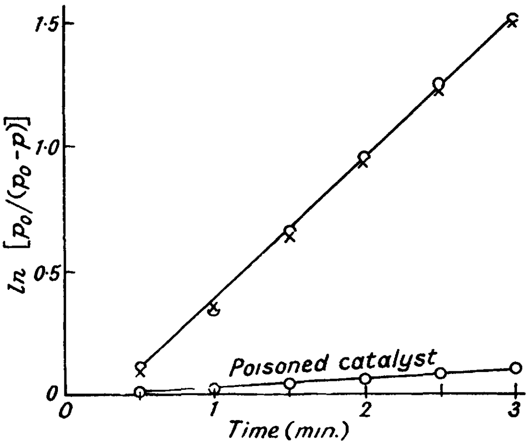


FIG. 3.



○ Original catalyst. × Poisoned catalyst after revival.

Typical Revival Cycles.—Revival by the circulation of ethylene was studied first, by reason of the previous successful revivals of poisoned catalysts in the liquid phase by desorptive displacement of poisons by treatment with a dissolved unsaturated substance. This was followed by a series involving revivals by simple evacuation and by a single set of runs in which an inert gas was circulated through the poisoned catalyst. During the work, the general accuracy of the measurements was progressively increased, mainly by increasing the efficiency and constancy of operation of the magnetic circulating pump and also by the introduction of the analytical method already described for checking the amount of poison on the catalyst. It is considered that conditions in the simple evacuation series were more precise than in the ethylene series, the revival by nitrogen circulation occupying an intermediate position. Accordingly, in the

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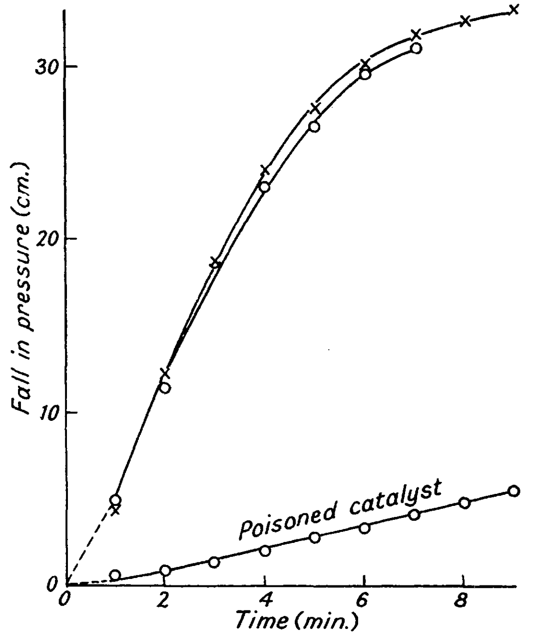
[3] Beeck, Smith, and Wheeler, *Proc. Roy. Soc.*, 1940, *A*, **177**, 62.

[4] Rideal, *J.*, 1922, **121**, 309; Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196.

following account, the various revival types have been arranged in the above order of their probable precision, in place of the order in which the work was carried out.

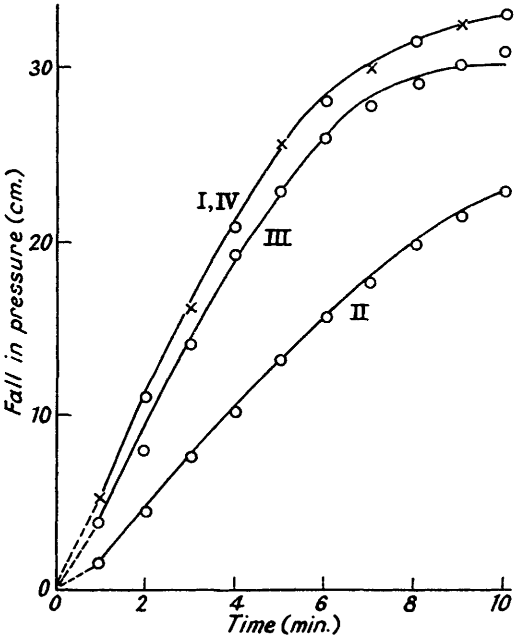
(i) *Revival of the catalyst by simple evacuation.* A representative revival by this method, using the cold limb as a vacuum pump, is summarised in Fig. 2, which contains the hydrogenation curves given by the platinum catalyst, first in its original unpoisoned state, secondly after being poisoned by $1\cdot5 \times 10^{-4}$ mole of diethyl sulphide down to about 7% of its unpoisoned activity, and, finally, after having been revived by evacuation for 13 hr. at room temperature. In each of the hydrogenation tests, a period of about 0·5 min., from the starting of the magnetic pump circulating the mixture of ethylene and hydrogen, was required before steady hydrogenation conditions were established; but the curves for the original and for the revived platinum were identical within the experimental limits of accuracy and showed a complete recovery to the original activity. Good linear plots (Fig. 3) of $\log\{p_0/(p_0 - p)\}$ against the time were given over the period from ½—3 min., by which time about 80% of the total hydrogenation had taken place. From the slope of these lines, the velocity constants representing the relative activity of the platinum in its three states can be calculated to be 0·56, 0·04, and 0·56, respectively, for the original, for the poisoned, and for the revived catalyst.

FIG. 4. *Revival by circulation of inert gas.*



○ Original catalyst.
× Poisoned catalyst after revival.

FIG. 5. *Revival by circulation of ethylene.*



I, IV. Original and final activities (× final activity).
II. Poisoned catalyst.
III. Activity after 2 hours' revival.

TABLE 1.

Amount of poison (10^{-4} mole)		Activity (k) of catalyst		
Applied	Recovered in cold trap	Before poisoning	After poisoning	After revival
1·7	1·9	0·57	0·039	0·51 after 18 min. evacuation
				0·52 ,, 36 ,, ,,
				0·58 ,, 12 hr. ,,
1·9	1·7	0·57	0·038	0·57 after 13 hr. evacuation

Two other examples of revival by evacuation, in each case by cold-limb pumping, are summarised in Table 1. The poison was diethyl sulphide.

It will be seen that complete revival was obtained in each case after evacuation for 12—13 hr.

(ii) *Revival by circulation of inert gas.*—A set of hydrogenation curves for a revival by treatment with an inert gas is given in Fig. 4, the catalyst being first poisoned by 2×10^{-4} mole of ethyl sulphide and then revived at room temperature by circulation of nitrogen for 28 hr. in a closed circuit in which the gas passed continuously through the poisoned catalyst, then through the cold trap at $-180°$ to remove entrained poison from the gas stream, and again through the platinum. These curves give good linear plots of $\log\{p_0/(p_0 - p)\}$ against time from 1 to 5 min. The corresponding catalytic activity constants, k, obtained from these linear plots, are 0·30 for the unpoisoned catalyst, and 0·024 and 0·36, respectively, for the catalyst in its poisoned and in its revived state, the apparent increase beyond its original activity in this case being probably due to a variation in the circulating efficiency of the magnetic pump in the last activity determination.

(iii) *Revival by ethylene circulation.* In this series both diethyl sulphide and thiophen were used as poisons and, in general, the catalyst was not so heavily poisoned as in the later work already described: further, in the absence of the checking method, the amount of poison actually on the catalyst was not so accurately known as in the other series. A typical series of hydrogenation curves showing almost complete revival after 2 hours' and complete revival after 16 hours' circulation of ethylene over the catalyst, previously poisoned with diethyl sulphide down to 40% of its original activity is shown Fig. 5. The usual linear logarithmic plots for these hydrogenation curves give activity constants of 0·256 for the catalyst in its original state, 0·103 for the poisoned catalyst, and 0·215 and 0·254 for the catalyst, respectively, after 2 and after 16 hours' ethylene circulation.

Results of some other sets of runs with revivals by ethylene circulation are summarised in Table 2.

TABLE 2.

Poison	Original activity of unpoisoned catalyst	Poisoned activity	Activity after revival
Thiophen	0·22	0·08	0·22 after 4 hr. circulation
Thiophen	0·23	0·10	0·23 ,, 6 hr. ,,
Diethyl sulphide...	0·28	0·18	0·30 ,, 2 hr. ,,
Diethyl sulphide...	0·254	0·12	0·19 ,, 2 hr. ,,
			⟶ 0·256 ,, 13 hr. ,,

It will be noted that the known circulation rate of the early form of the magnetic pump gives, as would be expected, generally lower absolute values for the rate constants for the unpoisoned platinum than in, for instance, the direct-evacuation series; but the ratios of the original, poisoned, and revived activities within each set of the present series are of course strictly comparable with one another and allow the observation of the fall and subsequent restoration of the catalytic activity. Further, taking into consideration this lower circulation rate also of the ethylene during the revival operation, the circulation times required for the removal of the poison are often notably short. This will be seen in the first example of the thiophen series by the complete revival after 4 hours' circulation, and indeed in the diethyl sulphide series by a complete revival after 2 hr. only. In one case, the revival was slower, but in this no intermediate measurements of the activity between 2 and 13 hr. were made, and the latter time may have been longer than was necessary for the restoration of the activity. It would be expected, from experience in liquid-phase revivals, that ethylene circulation would be, under similar conditions, more effective than the circulation of an inert gas.

UNIVERSITY OF BRISTOL.

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