CCVIII.—*The Influence of Arsenic on the Catalytic Activity of Platinum for the Oxidation of Sulphur Dioxide.*

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The poisoning of a platinum catalyst by means of arsenic is intimately connected with the development of the contact process for the manufacture of sulphuric acid. In spite, however, of the technical and historical importance of this case of inhibition, relatively little has been published on its quantitative aspect; the present work was therefore undertaken with the object of correlating the activity of a progressively poisoned platinum catalyst with its arsenic content.

The kinetics of the reaction between sulphur dioxide and oxygen on the surface of a solid catalyst are complicated (see, for instance, Bodländer and Köppen, *Z. Elektrochem.*, 1903, **9**, 559); but, by working under conditions such that only a small percentage of the possible change takes place, even with an unpoisoned catalyst, the degree of conversion obtained may be regarded as a measure of the activity of the catalyst. For this reason, the measurements were carried out at a relatively low temperature, this being also desirable in order to preclude the possibility of loss of arsenic by volatilisation and in order to eliminate the complication of an equilibrium state appreciably below complete conversion.

The general form of the poisoning curve was found to be similar to that obtained for other reactions (J., 1921, **119**, 225; 1922, **121**, 1760). In the first stages of poisoning, the activity of the catalyst varies approximately linearly with the poison content. This portion of the curve corresponds probably with the saturation by the inhibitant of the regions of special activity which, according to the evidence recently put forward by H. S. Taylor (*J. Physical*

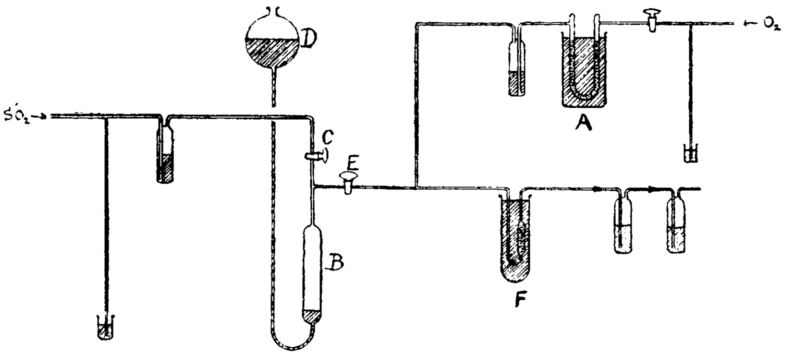
Chem., 1926, **30**, 145; see also Rideal, Deuxième Conseil de Chimie, 1925, Solvay Reports, p. 469) and others, occur on the surface of the catalyst and are apparently responsible for the greater part of its activity. This initial portion of the poisoning curve is followed by a region in which the continued addition of arsenic affects the activity to a far smaller degree.

With the catalyst studied, about 0·0016 g. of arsenic was found to be required to reduce the activity of 1 g. of platinum to one-half of its original value; but this ratio will necessarily be influenced by the degree of subdivision of the platinum.

EXPERIMENTAL.

The apparatus employed is shown diagrammatically in Fig. 1. Electrolytic oxygen, which was passed through the apparatus at a known constant rate, was freed from traces of hydrogen by passage through a tube, *A*, containing platinised asbestos and heated in an oil-bath, following which it was dried by means of sulphuric acid, and allowed to flow, together with sulphur dioxide, over the catalyst. The sulphur dioxide was similarly dried and, by opening the stopcock *C* and closing *E*, a constant volume of the gas was stored in the reservoir *B*, which had a capacity of approximately 80 c.c. This reservoir contained petroleum as the sealing liquid, which was forced into *D* by the pressure of the gas. For each experiment, the constant volume of sulphur dioxide was, by the action of the head of oil in *D*, allowed to flow, together with the oxygen, over the catalyst, the height of *D* being sufficiently above that of *B* to cause an approximately uniform rate of flow throughout the run. In each case, the time of passage of the above volume of sulphur dioxide was 30 minutes, the rate of flow of oxygen being 240 c.c. per hour.

FIG. 1.



The catalyst tube, which is shown at *F*, had a capacity of about 6 c.c., and contained 0·35 g. of platinum, supported on pumice and prepared by the reduction of platinic chloride with hydrogen. It was heated by immersion in a mercury bath, which contained a thermostat, by means of which the temperature was maintained at 300° with a maximum variation of 2°. The products of the oxidation were passed through two small wash-bottles in series, containing iodine solution, in order to determine—by titration with thiosulphate—the volume of sulphur dioxide which remained unoxidised, the original volume of sulphur dioxide being in each case accurately calculated, by correcting the volume of *B* for the prevailing conditions of temperature and pressure. All parts of the apparatus were sealed together, with the exception of the two wash-bottles which had to be detached for analysis and were connected by ground-in joints.

The solution used for poisoning the platinum contained 0·5 mg. of arsenic per c.c., and was prepared by dissolving the appropriate amount of arsenious oxide in water containing the requisite quantity of sodium hydroxide. After the initial activity of the catalyst had been measured, a known weight of poison was introduced by adding the required volume of the above solution, the water being removed by gentle heating in a current of oxygen. The activity of the partially poisoned catalyst was now determined, following which a further quantity of inhibitant was added, and the measurement of activity repeated, a series of readings being taken at each stage of poisoning. In order to obtain consistent results, it was found necessary, before beginning a test, to allow the sulphur dioxide and oxygen to flow for some time over the catalyst under the conditions subsequently used; and, with this precaution, the method of control and analysis was found to be sufficiently accurate to give reasonably consistent and reproducible results, as is shown by the agreement of the duplicate runs.

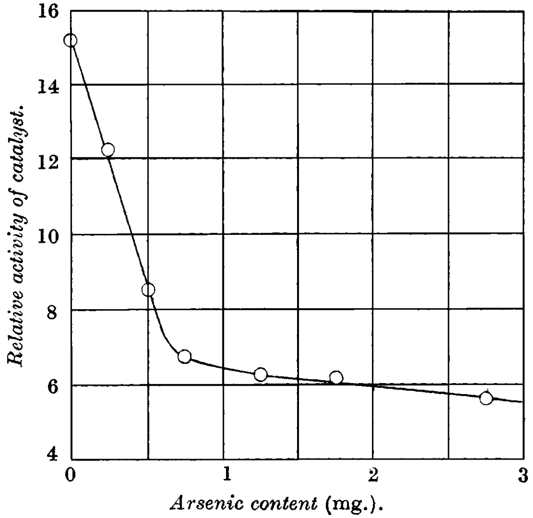
The results of the measurements are in Table I. The average values of the activity at various stages of inhibition have been plotted graphically in Fig. 2 in order to show the form of the

TABLE I.

As content, mg.	G. As per g. Pt.	% of SO_2 oxidised.	Mean.
0	0	15·10, 15·26, 15·12, 15·02, 15·15	15·13
0·25	0·00071	12·12, 12·30, 12·33, 12·39, 11·82, 12·06	12·17
0·5	0·00143	8·56, 8·48, 8·18, 8·90	8·53
0·75	0·00214	6·99, 6·68, 6·63	6·77
1·25	0·00357	6·23, 5·68, 6·65, 6·31, 6·50	6·28
1·75	0·0050	6·08, 6·26, 6·11	6·15
2·75	0·0079	5·65, 5·55	5·60
10·0	0·0286	4·07, 3·99	4·03

poisoning curve. The approximately linear first portion is clearly marked, and after about 0·7 mg. of arsenic, a region of the curve is reached in which the slope towards the activity axis is far less than in the first stages of poisoning; for the first 0·7 mg. of arsenic reduces the activity to 45% of its original value, and a further 9·3 mg., *i.e.*, 13 times the first weight of poison, only depresses the activity from the above value to 26% of the original activity. This is in agreement with the form of curve previously obtained for reactions involving the hydrogenation of an ethylenic linkage in the presence of a solid catalyst and for the decomposition of hydrogen peroxide.

FIG. 2.



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