# 128. *The Energetics of Catalysis. Part I. The Energetic Homogeneity of a Platinum Surface.*

By Edward B. Maxted and Gordon J. Lewis.

The following work has been undertaken as a contribution towards the analysis of the energy distribution within the surface of a catalyst. If certain of the individual adsorbing or catalysing elements of such a surface possess a higher activity either for catalysis or for adsorption, it appeared conceivable that this higher degree of activity might be associated with an abnormal energetic condition compared with other, less active elements; and it was accordingly considered of interest to examine, for any convenient heterogeneous catalytic reaction, the possible variation, from element to element, in the critical increment, *viz.*, in the additional energy required for the raising of the given element, or of an adsorption complex associated with this, to reaction level. The problem is intimately connected with the existence and nature of so-called peak areas or centres of special activity within a catalytic surface.

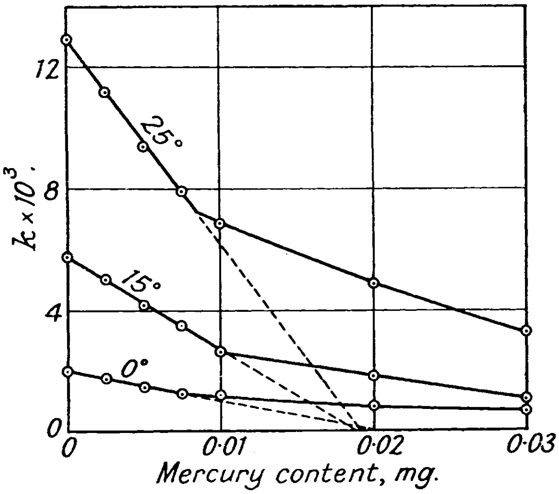
If the existence of such specially active centres is assumed, these centres should, from their nature, both catalyse and adsorb preferentially, compared with other potential catalysing or adsorbing centres; consequently, if a catalytic surface, *e.g.*, of platinum, be exposed to the action of a relatively small concentration of a poison, the latter should be adsorbed preferentially on the centres of relatively high activity, leaving the remainder of the surface free, or relatively free, for catalysis or for further adsorption. If, therefore, the energy of activation, first for the unpoisoned surface and, subsequently, for the gradually decreasing residual fraction left by progressive occupation of the surface by increasing concentrations of a poison, be measured, the variation in this energy should indicate a corresponding variation in the original energy of the adsorbing or catalysing centres.

The reaction chosen was the decomposition of hydrogen peroxide, for which the kinetics are simple and well known. The platinum-black, which was the catalyst, was progressively poisoned by known concentrations of mercury ions; and the energy of activation at various stages of poisoning was determined by means of the temperature coefficients in the usual manner.

## EXPERIMENTAL.

A standard suspension of Pt black, having a grain size sufficiently large to be washed by decantation and sufficiently small for a constant quantity of the metal to be transferred to the reacting system, when required, by means of a pipette, was, after considerable trial, made by the reduction of $H_2PtCl_6$ with $CH_2O$ according to Löw's method (*Ber.*, 1890, **23**, 289). The Pt, after prolonged washing, was stored in conductivity $H_2O$ in the form of a suspension containing about 0·25 mg. of Pt per c.c. The aq. $H_2O_2$ employed contained 30 g. per l.; and the $HgCl_2$ aq. used for poisoning contained 0·0025 mg. Hg per c.c., a solution of 4 times this concn. being taken when more convenient. All measurements were carried out in a thermostat, the temp. of which could be adjusted within 0·02°. It was shown, by means of tests with KCl, that the Cl′ ion exerted no measurable influence on the activity of the Pt, poisoning being due to the adsorption of the $Hg^{\cdot\cdot}$ ion, as previously investigated (J., 1925, **127**, 73).

In carrying out each expt., 1 c.c. of the suspension of Pt and the appropriate quantity of $HgCl_2$ were made up to 50 c.c. and kept over-night in the thermostat. The partially poisoned catalyst was diluted to 250 c.c. and stirred in the thermostat for a further 3 hr. 25 C.c. of the aq. $H_2O_2$ were now added, and the decompn. was followed by titration with $KMnO_4$ in the usual way, the catalyst in the samples withdrawn being rendered inactive by immediately bringing each into contact with a relatively large quantity of $HgCl_2$, in order to inhibit further reaction during the titration.



The results of a number of such measurements are summarised in the following table, *k* being the unimol. reaction const.

| Series 1. | | | | | | Series 2. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Poison content of system. | | | Poison content of system. | | | Poison content of system. | | | Poison content of system. | | |
| Hg, mg. | Mg. of Hg per mg. of Pt. | $k \times 10^5$. | Hg, mg. | Mg. of Hg per mg. of Pt. | $k \times 10^5$. | Hg, mg. | Mg. of Hg per mg. of Pt. | $k \times 10^5$. | Hg, mg. | Mg. of Hg per mg. of Pt. | $k \times 10^5$. |
| | At 0°. | | | At 15°. | | | At 0°. | | | At 25°. | |
| 0 | 0 | 203 | 0 | 0 | 575 | 0 | 0 | 200 | 0 | 0 | 1290 |
| 0·0025 | 0·01 | 171 | 0·0025 | 0·01 | 500 | 0·0025 | 0·01 | 177 | 0·025 | 0·01 | 1120 |
| 0·005 | 0·02 | 147 | 0·005 | 0·02 | 415 | 0·005 | 0·02 | 149 | 0·05 | 0·02 | 940 |
| 0·0075 | 0·03 | 115 | 0·0075 | 0·03 | 350 | 0·0075 | 0·03 | 123 | 0·075 | 0·03 | 791 |
| 0·01 | 0·04 | 108 | 0·01 | 0·04 | 265 | 0·01 | 0·04 | 122 | 0·01 | 0·04 | 685 |
| 0·02 | 0·08 | 85 | 0·02 | 0·08 | 189 | 0·02 | 0·08 | 85 | 0·02 | 0·08 | 487 |
| 0·03 | 0·12 | 65 | 0·03 | 0·12 | 110 | 0·03 | 0·12 | 70 | 0·03 | 0·12 | 335 |
| | | | 0·04 | 0·16 | 55 | | | | | | |

On plotting the above results graphically, poisoning curves of the type previously found (J., 1921, **119**, 225; 1922, **121**, 1760) are obtained, in which the activity of the Pt decreases initially linearly with an increase in the poison content, this stage being followed by a less rapid, but also approx. linear, decrease in activity with a still greater increase in the poison content. This is shown in the fig. It is probable that the initial linear portion of each of the graphs corresponds with the section of the $Hg^{\cdot\cdot}$ ion adsorption isotherm for which the adsorbed concn. is linearly proportional to the initial bulk concn. of $Hg^{\cdot\cdot}$ ions in the solution (J., 1925, **127**, 73); indeed, the bulk concn. at which the point of inflexion occurs corresponds in order of magnitude with these earlier measurements, although the method of preparation of the Pt black was not the same; so that, for this section of the graphs, the initial bulk concn. of poison may be taken as a measure of the adsorbed concn. of poison at the Pt surface. Beyond this point, equiv. bulk concns. of poison will not necessarily correspond with the equiv. adsorbed concn. which is necessary for the determination of the temp. coefficient of the catalyst at a given stage of partial poisoning; and the method is thus limited to stages of poisoning corresponding with the first part of the poisoning graph, unless, as was previously done, a separate estimation of the adsorbed concn. at each bulk concn. is made.

On calculating the activation energy for various stages of poisoning up to the point of inflexion, by means of the relationship

$$E = 1{\cdot}98 \times 2{\cdot}3026[T_1T_2/(T_2 - T_1)] \log k_{T_2}/k_{T_1}$$

the following values are derived.

| | Poison content of system (mg. of Hg) | 0 | 0·0025 | 0·0050 | 0·0075 |
|---|---|---|---|---|---|
| $E$ (cals.) | Series 1 : $T_1 = 273°$; $T_2 = 288°$ | 10,900 | 11,100 | 10,800 | 11,600 |
| | Series 2 : $T_1 = 273°$; $T_2 = 298°$ | 12,000 | 11,900 | 11,900 | 12,000 |

It will be seen that, for each temperature difference, *viz.*, from 0° to 15° in the first, and from 0° to 25° in the second series, the value of the energy of activation remains approximately constant as the poison content is increased to that corresponding with the point of inflexion. The figure, moreover, shows that the first linear portion of each of the poisoning graphs intersects the poison concentration axis at approximately the same point.

The constancy in the values of $E$ indicates merely that, if peak areas of special activity exist, these are of such a nature that, at any rate up to the fraction of the surface corresponding with the point of inflexion, a constant energy increment is required for the raising of each, or of an adsorption complex associated with each, to a condition which permits catalysis. Presumptive evidence for energetic homogeneity, not only among the surface elements involved in catalysis but also for the entire range of points capable of adsorption, is, however, derivable from the constancy of the differential heat of adsorption (Ward, *Proc. Roy. Soc.*, *A*, 1931, **133**, 506; Maxted, J., 1931, 3313; Beebe, *Trans. Faraday Soc.*, 1932, **28**, 761; Schwabe and Brennecke, *Z. physikal. Chem.*, 1932, *B*, **16**, 19). The linear form of the poisoning graph itself may also be regarded as evidence of homogeneity. These points are discussed elsewhere.

UNIVERSITY OF BRISTOL.

[*Received, March 3rd*, 1933.]