394. *The Distribution Factor in Catalytic Toxicity.*

By Edward B. Maxted and Herbert C. Evans.

The toxicity of a number of simple poisons towards a platinum catalyst has—in place of expressing toxicity in terms of the total poison present—been correlated with the actual adsorbed concentration of these poisons on the catalytic surface. The results obtained are of interest from the standpoint of the effective homogeneity of the surface elements in such catalysts, since they may be interpreted as evidence for the existence of at least two types of potential catalysing or adsorbing elements, all elements of a given type being apparently mutually equivalent. The mutual equivalence of the range of surface elements suppressed during not too advanced stages of the obstructive adsorption of a poison by a potentially active catalytic surface is confirmed by earlier work; and the present extension is not incompatible with the adlineation theory of Pietsch and Schwab.

The toxicity of an inhibitant in heterogeneous catalysis is, in general, determined by factors of two types involving, first, the area of catalytic surface influenced by each molecule of the poison in an adsorbed state and, secondly, the mean adsorbed life of the poison on the catalyst.

Although the adsorption—particularly with strong poisons and if the ratio of poison to catalyst is not too high—may, under favourable conditions, be sufficiently complete for the adsorbed concentration to be regarded, without great error, as equal to the total amount present, yet a definite distribution of the poison between the free gas or liquid phase and the adsorbed phase will in every case occur; and, for the accurate expression of the true toxicity, on the basis of adsorbed concentrations, it is necessary to correct the effective toxicity, which is based on the total amount of poison present, by the introduction of a distribution factor. This factor is intimately connected with the mean adsorbed life of the poison on the catalytic surface and with the ease of removal of the poison by degassing or by washing with an inert solvent.

In the case of poisons possessing relatively long adsorbed lives, corresponding with substantially complete adsorption if the total concentration of the poison is not too high, the distribution factor representing the fractional adsorption will approach unity, and the correction required for converting effective into true toxicity will be negligible. Thus, at not too advanced stages of adsorption, the residual pressure after the admission of gaseous hydrogen sulphide to a platinum catalyst is too low to give an appreciable reading on a McLeod gauge; and, under these conditions, the effective toxicity—which in such cases is identical with the true toxicity—will depend principally on the individual molecular coverage in the way already discussed (J., 1937, 603, 1004; this vol., p. 455). On the other hand, the effective toxicity of substances, for which the partition between the adsorbed and the free phase is low towards the adsorbed side, will depend not only on the individual molecular coverage but also—and to an increasing degree as the adsorbed life decreases—on the distribution ratio.

The object of the present work has been, by determining both the effective toxicity and the distribution ratio for a number of simple inhibitants of varied toxicity, to plot the fall in the catalytic activity of a platinum catalyst against the actual adsorbed concentration of the poison on the catalytic surface, rather than against the total quantity of poison present, and thus to follow more accurately the true variation of the activity with the concentration of that part of the total poison which, by virtue of its obstructive occupation of potentially active catalytic surface, is responsible for the deactivation observed. This method of treatment has given what appears to be important new evidence with regard to the degree of participation of the various types of surface elements in adsorption or catalysis and particularly with respect to uniformity among these catalysing or adsorbing elements, in that indications were obtained of the existence of more than one, within itself uniform, range of such elements.

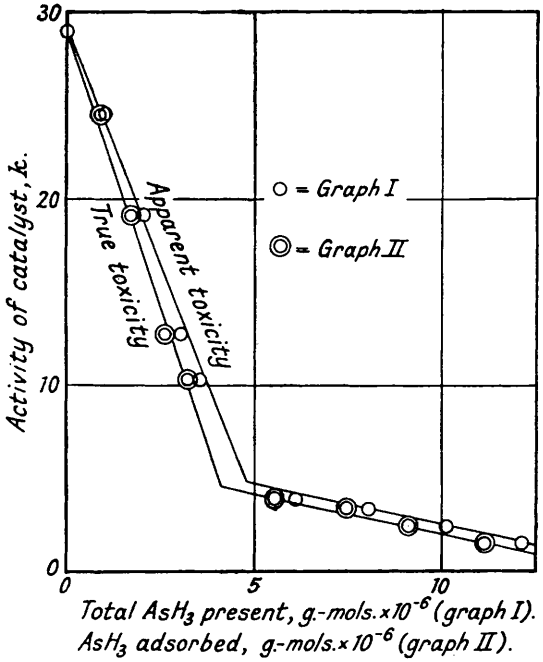
EXPERIMENTAL.

Two series of determinations were necessary for each inhibitant studied, *viz.*, (i) a poisoning graph of the usual type connecting activity with the total amount of poison present, and (ii) measurements of the variation in the quantity of poison adsorbed on the catalyst as the total poison present is increased. For details of the technique and method of expression, reference should be made to earlier papers dealing with measurements of catalytic toxicity (*loc. cit.*, and J., 1934, 26, 672) and with the adsorption of poisons by catalysts (J., 1925, **127**, 73). The measurements both of catalytic activity and of the adsorption were made in liquid systems of similar composition; and, in general, the determinations of the distribution of the poison between the adsorbed and the free liquid phase were made by allowing a known initial concentration of poison to remain in contact with a standard weight of catalyst, after which the residual poison content of the free liquid phase was determined by measuring the toxicity of the solution towards a standard catalyst. This method of analysis was necessary in view of the very small amounts of poison which are involved. The same stock of platinum catalyst was, save in some preliminary work, used throughout; and, as a convenient standard reaction for measuring the activity of this platinum for catalytic hydrogenation at various stages of poisoning, the hydrogenation of crotonic acid, in acetic acid solution, was, as usual, employed. Each charge, in the case of the poisoning measurements, contained 5 c.c. of a 2N-solution of crotonic acid in acetic acid, 0·05 g. of the catalyst, and a known amount of the poison, dissolved in a further 5 c.c. of acetic acid. The poisons chosen were in each case relatively simple in order to minimise as far as possible factors associated with the coverage of large molecules.

Preliminary Measurements with Arsine.—In order to obtain information as to the order of the correction required with strong poisons, a preliminary series of measurements was carried out with arsine in the presence, in each case, of 0·05 g. of platinum-black; but, since this was not taken from the same platinum stock as that used throughout the main series, the results are not directly comparable with those obtained with the other poisons studied. They can, however, conveniently be used to show the not very great change involved, with strong poisons, in going from an apparent poisoning graph, based on the total poison present, to a true poisoning graph, based on the poison actually adsorbed on the catalyst, and, as such, have been summarised in Fig. 1. Details of procedure are omitted, since this was, in general, very similar to that described below.

Relative True Toxicities of Various Simple Poisons.—In this main series of measurements, an attempt was made to compare the true toxicities of a number of simple poisons, including hydrogen sulphide, methyl sulphide, the cyanide ion, arsine, and a typical catalytically poisonous metal such as zinc. The results are, for the first poison studied, given numerically for the sake of completeness. In other cases, they are merely summarised in graphical form.

FIG. 1.



Catalytic Toxicity of Cyanides.—The effective toxicity, in catalytic hydrogenation, of the cyanide ion, in the form of potassium cyanide, towards 0·05 g. of the particular preparation of platinum used throughout the remainder of the present work and in a liquid system the volume of which was 10 c.c. in every case, is summarised in Table I. The activity of the catalyst is, as in earlier papers, expressed in c.c. of hydrogen fixed per minute in the hydrogenation of crotonic acid under standardised conditions.

TABLE I.

Poison content of system :									
KCN, mg.	0	0·078	0·156	0·261	0·393	0·524	0·786	1·048	1·307
KCN, g.-mols. × 10^{-6}	0	1·20	2·40	4·02	6·04	8·05	12·10	16·14	20·01
Activity of catalyst, k	14·1	12·1	10·3	7·4	4·4	3·5	2·4	1·6	0·8

If the data of Table I are plotted graphically, the usual linear relationship is obtained, the region of inflexion occurring at a concentration of about 6 × 10^{-6} g.-mol. of the poison in the 10 c.c. of acetic acid used. For purposes of comparison with the other poisons studied, this graph has also been included in the first of the collective diagrams (see Fig. 2).

The next step was to determine the amount of poison adsorbed by the platinum at each stage of total concentration. The variation of the adsorbed amount with the total poison introduced is shown in Table II, the volume of the system being 10 c.c. and the weight of catalyst 0·05 g., as before.

FIG. 2.

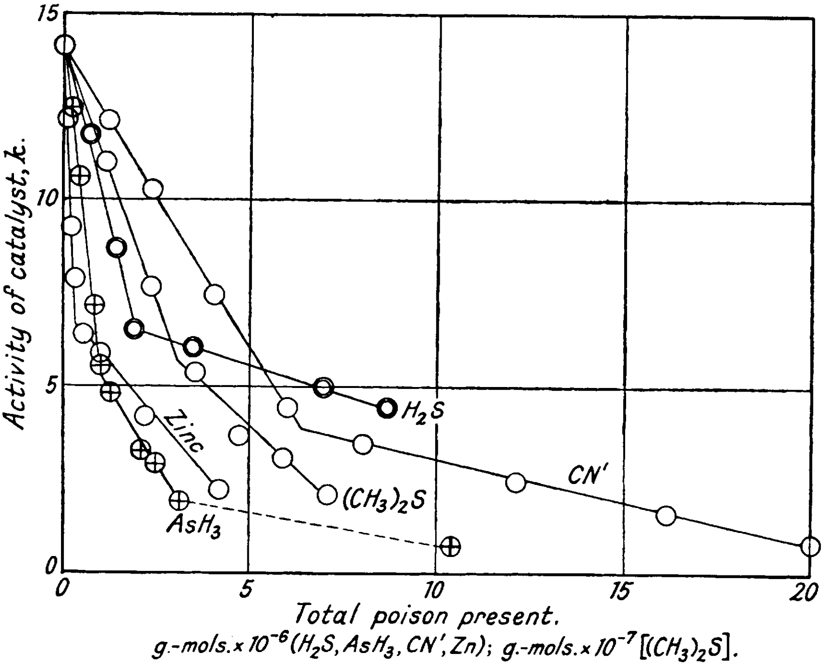


TABLE II.

Total KCN content (g.-mols. × 10^{-6}) in 10 c.c.	KCN adsorbed (g.-mols. × 10^{-6}) on 0·05 g. of catalyst.	KCN present in liquid phase, g.-mols. × 10^{-6}.	Distribution ratio. (*a*) KCN adsorbed to total KCN present.	Distribution ratio. (*b*) KCN adsorbed to KCN free in 10 c.c. of solution.
1·20	0·75	0·45	0·62	1·67
2·40	1·52	0·88	0·63	1·72
4·02	2·55	1·47	0·63	1·73
6·04	3·85	2·19	0·64	1·76
8·05	5·10	2·95	0·63	1·73
12·10	7·72	4·38	0·64	1·76
16·14	9·42	6·72	0·58	1·40

It will be seen that a poison such as the cyanide ion is by no means completely adsorbed; further, that the poison present in an adsorbed state on the platinum varies linearly with the total amount of the poison present, provided that this total poison is not in excess of a concentration which falls slightly below 16 × 10^{-6} g.-mol. Consequently, within this range, there is an approximately constant distribution ratio of poison between the adsorbed phase and the free liquid phase, as is shown in the last two columns of the table. This adsorption graph is, for comparison, included in Fig. 3.

It is now possible, by combining Tables I and II, to plot the catalytic activity of the platinum against the actual concentration of poison adsorbed on its surface. This has been done in Graph III of Fig. 4, from which it will be seen that an inflected linear relationship between these two quantities, very similar in form to that of the effective toxicity graphs shown in Fig. 2, is obtained. The probable implications of this relationship are discussed on p. 2077.

Toxicities of Zinc, Arsine, Hydrogen Sulphide, and Methyl Sulphide.—The effective poisoning graphs for these inhibitants, based on the total poison present, are summarised in Fig. 2, and the corresponding adsorption graphs in Fig. 3. The zinc was employed as sulphate, it having been previously found that the sulphate ion was non-toxic; the arsenic was introduced as arsenious oxide which, in the presence of catalytically activated hydrogen, passes into arsine;

Fig. 3.

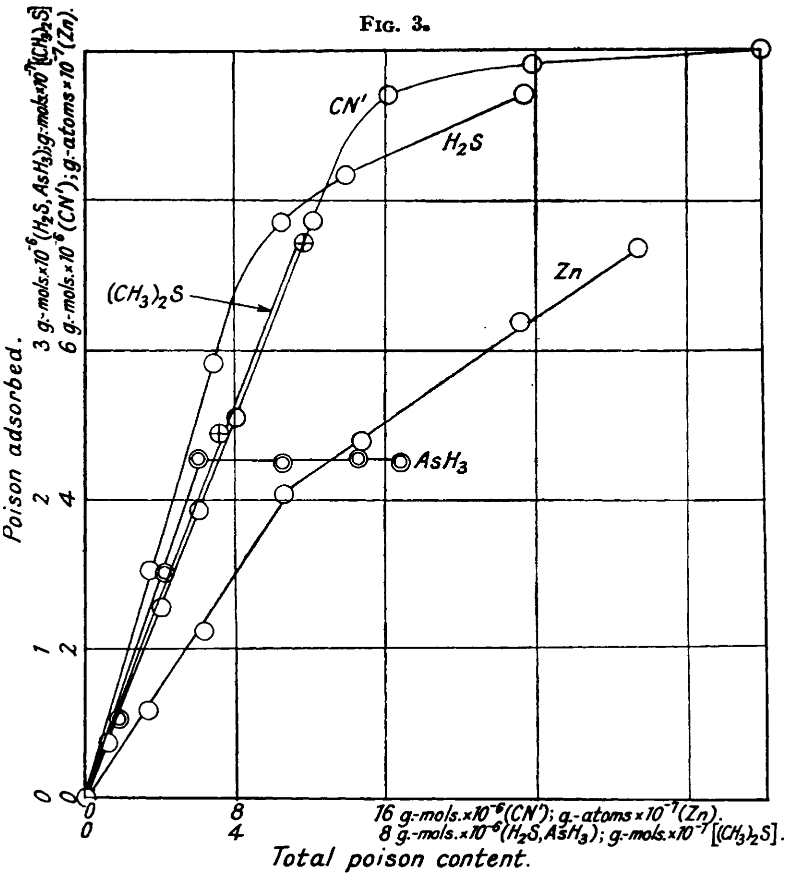
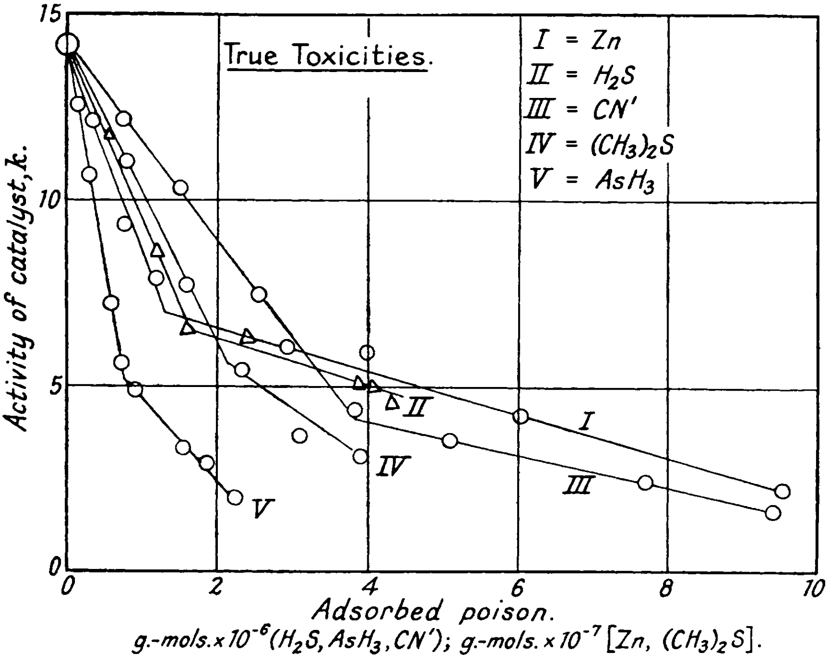

Poison adsorbed.
3 g.-mols.×10⁻⁶(H₂S, AsH₃); g.-mols.×10⁻⁷[(CH₃)₂S]
6 g.-mols.×10⁻⁶(CN′); g.-atoms×10⁻⁷(Zn).
0
1
2
0
2
4
CN′
H₂S
(CH₃)₂S
Zn
AsH₃
0
8
16 g.-mols.×10⁻⁶(CN′); g.-atoms×10⁻⁷(Zn).
0
4
8 g.-mols.×10⁻⁶(H₂S, AsH₃); g.-mols.×10⁻⁷[(CH₃)₂S].
Total poison content.

Fig. 4.


15
10
5
0
Activity of catalyst, k.
True Toxicities.
I = Zn
II = H₂S
III = CN′
IV = (CH₃)₂S
V = AsH₃
I
II
III
IV
V
0
2
4
6
8
10
Adsorbed poison.
g.-mols.×10⁻⁶(H₂S, AsH₃, CN′); g.-mols.×10⁻⁷[Zn, (CH₃)₂S].

and the hydrogen sulphide and methyl sulphide were applied in the form of dilute solutions of these inhibitants as such. From the distribution ratios derived from Fig. 3, the fall in catalytic activity may, as before, be plotted against the adsorbed concentrations of the respective poisons. This has been done in Fig. 4, the resulting graphs being of the inflected linear form similar to that obtained for the cyanide ion.

Correction of Effective Toxicity to True Toxicity.—If, for the time being, toxicities only for total poison contents not beyond the first linear portion of the effective poisoning graphs, *i.e.*, up to the respective points of inflexion in Fig. 2, are considered, the following values for the true toxicities, based on the actual adsorbed concentration of the poison on the catalytic surface, are obtained by applying the appropriate distribution factors. In Table III, α_a and α_r are, respectively, the effective and the true poisoning coefficients (J., 1934, 26, 672) derived from the usual relationship, $k_0 = k_c(1 - \alpha c)$, in which k_c is the activity of the catalyst in the presence of a concentration, c, of the poison (c being either the total or the adsorbed amount, according to whether α_a or α_r is being calculated), and in which k_0 is the original unpoisoned activity. K_1 is the distribution factor under the conditions employed, *viz.*, the ratio of the poison adsorbed to the total poison present.

TABLE III.

Inhibitant.	K_1.	K_2.	$a_a \times 10^{-5}$.	$a_r \times 10^{-5}$.	Relative values of a_r.
Cyanide ion	0·63	17·3	1·14	1·89	0·60
Hydrogen sulphide	0·86	58·5	2·82	3·17	1·00
Arsine	0·75	30·0	6·06	8·33	2·63
Methyl sulphide	0·67	19·0	19·6	28·6	9·00
Zinc ion	0·39	6·1	14·3	39·6	12·5

Since the value of K_1—which represents the distribution factor in a convenient form for direct use within the present work—will vary with the volume of the solution used for the hydrogenation, the factor has also been expressed in a more general form, *viz.*, as the ratio of the adsorbed concentration per unit surface of platinum to the free concentration per c.c. of liquid phase in equilibrium with this, the surface exposed by the 0·05 g. of the platinum catalyst being taken as unity. This factor, K_2, should be independent of the volume of the solution, but will of course vary with a change in the platinum, in virtue of its dependence on the effective catalysing or adsorbing surface exposed per unit of mass.

Two points of interest occur in connection with the variation of the true toxicity, α_r, with the nature of the inhibitant. In the first place, if simple inhibitants only are considered, the true toxicity increases with the atomic radius of the poisonous element. Thus the atomic radii of sulphur, arsenic, and zinc, *i.e.*, 1·04, 1·25, and 1·33 A., respectively, are in the same order as the relative toxicities of the simple compounds of these elements used; but, before any relationship between atomic radius and true toxicity can be discussed quantitatively, further systematic work, including consideration of the probable state of toxic ions on a catalytic surface and of valency, is necessary, especially since ionic radii, for instance of zinc, differ from the atomic radii. Secondly, it may be noted that the correction for the adsorbed concentration raises the relative toxicity of methyl sulphide from the previously observed effective value of 7 ($H_2S = 1$) to 9, based on adsorbed concentrations. The latter figure actually represents the number of platinum surface elements which can, on trial, be covered by a scale model of a methyl sulphide molecule superimposed on a model of a platinum lattice and anchored to this by its sulphur atom.

Influence of Molecular Size on the Break Point.—In the above discussion of Table III, it was noticed that the true toxicities of the various simple poisons increased qualitatively in the same order as the molecular or atomic size. This order appears also to be followed both for the break points in the adsorption graphs, *viz.*, for the critical adsorbed concentration at which signs of saturation of the surface by the poison in question begin to be shown by the departure of the adsorption graph from its original linear slope, and also for the break points in the true toxicity graphs. This is shown in Table IV.

With regard to the adsorption break point, it would be expected on first principles that a lesser number of larger molecules than of smaller molecules could be accommodated on a given surface (which was, in the present work kept constant throughout the series at that presented by the 0·05 g. of standard platinum catalyst used), particularly—even in stoicheiometric adsorption—if the effective radius of the poison atom exceeds that of the platinum, by virtue of a crowding effect; but it will also be noticed that the catalytic break points, although in the same sequence, occur consistently at lower adsorbed concentrations of poison than correspond with the adsorbed break. This has also been given consistently in another investigation involving true toxicities and distribution factors in the alkyl sulphide series, and it would appear that, in the catalytic curve, the adsorbed coverage must reach a critical value before inflexion sets in. There is, of course, on a partly poisoned surface—or even on a surface to which excess of a poison has access—an equilibrium between the occupation of surface area by the poison and by the normal reactants and resultants of the catalytic process, the equilibrium being strongly displaced towards the poison side; further, an important—but not the only—factor in this equilibrium will be the relative average adsorbed lives of the poison and of the reactants.

TABLE IV.

Inhibitant.	Relative true toxicity.	Break point in adsorption graph, g.-mols. × 10^{-6}.	Break point in true toxicity graph, g.-mols. × 10^{-6}.
Cyanide ion	0·6	9·5	3·8
Hydrogen sulphide	1·0	3·5	1·65
Arsine	2·6	2·25	0·75
Methyl sulphide	9·0	Not determined	0·23
Zinc ion	12·5	0·4	0·13

Implications of the True Toxicity Graphs.—The most probable general significance of a linear relationship between the adsorbed poison content and the catalytic activity is the mutual equivalence of the catalysing surface elements concerned; since, if this surface contained elements of abnormally high potential catalytic activity, their suppression by occupation by a poison would be reflected in a correspondingly greater fall in catalytic activity than would be caused by the suppression of any existing less active surface elements. This mutual equivalence of, at any rate, the surface elements involved in early stages of the adsorption both of poisons and of non-toxic bodies is apparently confirmed by a number of investigations of the homogeneity of this range of adsorbing or catalysing elements carried out by many methods of approach (J., 1931, 3313; *Trans. Faraday Soc.*, 1933, **29**, 698; J., 1933, 502; 1934, 26, 272; 1935, 393; see also Schwab, *Z. physikal. Chem.*, 1934, *A*, **171**, 421). The present investigation into the effect of poisons also at relatively advanced stages of adsorption, and the plotting of the actual adsorbed concentrations at these advanced stages against the residual catalytic activity—which has resulted in graphs of the flexed linear type shown in Fig. 4—apparently indicate the existence of a second type or range of homogeneous catalysing or adsorbing elements, which are mutually equivalent among themselves but are less effective both for adsorption and for catalysis than the—also mutually equivalent—primary range. This is by no means incompatible with the adlineation aspect of catalytic and general activity which has been developed by Schwab, Pietsch, and their co-workers (Pietsch, Kotowski, and Berend, *Z. physikal. Chem.*, 1929, *B*, **5**, 1; Schwab and Pietsch, *Z. Elektrochem.*, 1929, **35**, 135; Schwab and Rudolph, *Z. physikal. Chem.*, 1931, *B*, **12**, 247); indeed, it may be regarded as a necessary accompaniment of adlineation effects. If adsorption or catalysis at, respectively, crystal corners, edges or faces is involved, in accordance with the adlineation view, investigations at still more advanced stages of adsorption should show the presence of a third linear portion, of still smaller slope—due to adsorption or catalysis by the crystal face—in graphs of the type reproduced in Fig. 4. Evidence of this has not yet been found, although the still smaller slope of the advanced portion of the relatively steep effective arsenic graph in Fig. 2, which has been indicated by the dotted line, may perhaps be viewed as some preliminary indication of this. Further, since the number of surface elements situated at crystal corners should be far less than that at crystal edges, and since the number of elements at crystal edges should, in turn, be far less than that of those situated in the normal surface layer of the crystal face, this disparity should, in spite of possible overlap, be reflected in the length of the corresponding ranges along the poison concentration axis of Fig. 4, in which it will be seen that the first linear portion extends along this axis in each case to a far smaller length than the second portion. Light on this point should be obtained by studying the effect of sintering on the region of inflexion. An alternative aspect is obviously the participation, in adsorption or catalysis, of a second or even of more deeply seated lattice layers in the catalyst—or catalysis or adsorption on an already adsorbed layer—both of which cases would give a secondary range of, within themselves mutually equivalent, catalysing or adsorbing points.

The authors acknowledge the receipt from the Colston Research Society of a grant for the provision of materials.

UNIVERSITY OF BRISTOL. [*Received, November 7th,* 1938.]