# 104. *Catalytic Toxicity and Chemical Structure. Part VI. The Poisoning of Platinum Catalysts by Metals.*

By E. B. Maxted and A. Marsden.

The toxicity of various metallic ions towards platinum in catalytic hydrogenation has been examined quantitatively. In general, the relative obstructive effect per atomic unit of metal adsorbed on the catalyst, namely, the relative coverage per adsorbed atom, appears to vary not only with the atomic size of the poisonous metal but also with its ordinary valency. This variation, and the regularities observed in Part V, are of interest in connection with the probable nature of the linkage involved in catalyst poisoning and in specific chemisorption generally.

Although it is well known that certain metals, such as mercury, zinc, and others, act as poisons towards platinum and similar catalysts, the list of definitely toxic metals appears to require more precise establishment, and little is known with regard to their relative toxicity. The occupation of a catalytic surface by the adsorption of, for instance, toxic metallic ions from a solution constitutes a particularly simple type of poisoning, since the adsorption of simple structures only is involved, although the nature of the obviously strong linkage—by virtue of which these metallic poisons are preferentially and obstructively adsorbed even when present only in very small concentrations—is less easy to understand than in the case of bonds between a platinum or other metallic catalyst and a non-metallic poison such as sulphur or phosphorus.

Two points are of special interest in connection with poisoning by these elementary poisons, *viz.*, the influence of atomic or molecular size and of valency, since it was considered that the relative toxicity of simple atoms of known size and of known probable valency might throw light on the packing of poison layers on catalytic surfaces and, particularly, on the influence of the ordinary effective valency of a poison atom on the relative number of poison atoms associated with each surface element. The latter point is of considerable interest as an approach to the wider problem of determining to what extent the chemisorption of catalyst poisons, and of strongly held adsorbed species generally, involves linkage by ordinary electronic valency bonds. With regard to the effect of size, it should be noted that, if mere mechanical covering—area for area—is involved, the toxicity should increase continuously with the atomic size, whereas, if the adsorption of these poisonous metals takes place stoicheiometrically, the toxicity per g.-atom adsorbed should (at any rate in the simplest type of placentation, involving a single poison atom on each surface element of the catalyst) remain constant, in place of increasing with the size of the adsorbed metal atom, until the effective radius of the toxic atom exceeds that of the adsorbing element, whereupon a packing factor, due to the overlap of the adsorbed atom beyond the boundary of the original adsorbing surface element, should be introduced. Further, stoicheiometric adsorption should involve valency as well as size.

For the strict comparison of relative coverage per atomic or molecular unit, except with poisons which are substantially completely adsorbed, it is necessary to compare true toxicities (J., 1938, 2071) based on the toxic effect observed per unit of poison actually adsorbed on the catalytic surface, rather than effective toxicities which are based on the observed poisoning effect per unit of total poison present, including that which remains unadsorbed in the free liquid phase.

It may be noted, in connection with these two toxicity scales, that effective toxicity, which is the toxicity observed in the ordinary way, will be dependent on factors of two types, *viz.*, (i) on a size or effective individual coverage factor, which controls the number of surface elements (or, in general, the surface area) of the catalyst obstructively occupied or influenced by each molecule or atom of poison in an adsorbed state, and (ii) a factor dependent on the average length of stay of the adsorbed molecule on the surface. This may be formulated by an expression of the type :

$$\text{Effective toxicity} = f(s),(\tau)$$

in which $s$ is the size factor and $\tau$ the adsorbed life. With all poisons, the adsorbed life is relatively long compared with that of normal adsorbed species: indeed, it is by virtue of this length of life—which is reflected in the low ratio of desorption to adsorption—that a poison acts obstructively, by accumulation in the adsorbed state, even when present only in traces; and, in the extreme case of an infinite adsorbed life, all the poison, provided that this is not present in excess of the amount required for saturation of the surface, will accumulate on the catalyst in this way, since the rate of desorption will be nil. Since the adsorbed life is intimately connected with the partition of the poison between the adsorbed and the free liquid or gas phase, it is possible, by determining this partition ratio and consequently the actual adsorbed concentration of the poison on the catalytic surface, to eliminate the adsorbed life factor altogether and to calculate the inhibitive effect exerted by each g.-atom of the poison in the adsorbed state, without the complication of the life factor.

In the present work, the various metals have been employed, usually as acetates, in alcoholic or acetic acid solution, the acetic ion being non-toxic; and their toxicity towards a standard preparation of platinum black has been measured for the hydrogenation of crotonic acid.

## EXPERIMENTAL.

*Preliminary Measurements.*—It was considered advisable, in the first place, to determine what metals are appreciably toxic towards platinum under these conditions. Paal and his collaborators (*Ber.*, 1911, **44**, 1013; 1913, **46**, 3069, 4010; 1918, **51**, 711, 894), who worked however with platinum or palladium supported on finely divided metals, or on their oxides or carbonates, rather than with poisons adsorbed from solution, found in general that an inactive catalyst resulted with platinum or palladium in conjunction with mercury, bismuth, lead, tin, zinc, cadmium, copper, aluminium or iron, but that the platinum or palladium acted normally if supported on magnesium, nickel or cobalt. The general catalytic toxicity of many of these metals, especially that of mercury, bismuth, lead, zinc, and cadmium, has subsequently become well recognised, at any rate qualitatively.

The results of a somewhat more extensive preliminary survey, in which the drop in activity was measured quantitatively, are summarised in Table I, which contains all the metals tested in the present work. Any division of these metals into toxic and non-toxic elements is in principle merely one of degree, since toxicity is of course a relative term. However, in practice, the division is fairly definite; and the metals grouped as toxic destroyed the activity of the platinum even when present in very small amounts (for the order of these, see later), whereas the elements marked non-toxic did not measurably depress the hydrogenation rate even when present in relatively large quantities, for instance in 100 to 1000 times the amount required for a substantial reduction of activity in the case of the poisonous metals.

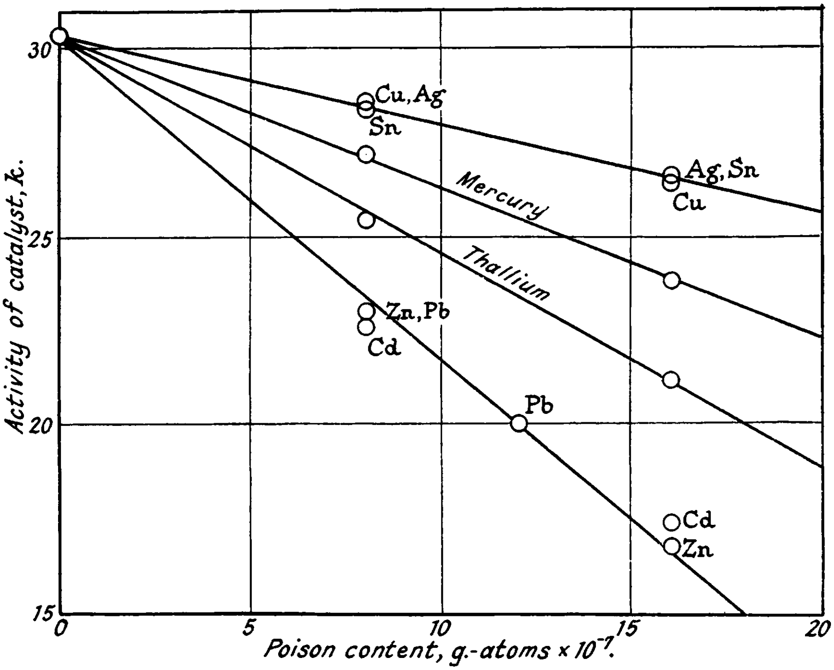
TABLE I.

| Periodic group. | Toxic. | Non-toxic. |
|---|---|---|
| I | Cu, Ag, (Au) | Alkali metals |
| II | Zn, Cd, Hg | Alkaline earths, Mg, Be |
| III | Tl, (In) | Al, La, Ce, and rare earths |
| IV | (Ti), Sn, Pb | Zr, Th, and rare earths |
| V | Bi | — |
| VI | — | Cr |
| VII | Mn | — |
| VIII | Fe, Co, Ni | — |

Toxic non-metals, such as sulphur, phosphorus, arsenic, and antimony, have been excluded from Table I; further, the metals enclosed in parentheses are only slightly toxic.

At first sight, many of the toxic metals, *e.g.*, copper or silver, are those which, in the presence of catalytically activated hydrogen, might be precipitated on the platinum in the form of metallic deposits stable in the solvents (acetic acid or alcohol) used, in which case loss of activity could occur by virtue of mechanical covering rather than by specific adsorption. However, mechanical deposits of metals such as zinc, cadmium or manganese are not likely to be formed and should not be stable in acetic acid; and it is difficult to account in this way for the low toxicity (see later) of the gold group. It should be mentioned that with some metals, especially in the case of silver, visible progressive coagulation of the finely-divided platinum occurred during catalysis (but not on adding the poison to the system or on merely allowing this to remain in contact with the poison), with corresponding mechanical reduction in the activity of the catalyst, by loss of surface, as the reaction progressed; and, although the activity at the start was obtained by extrapolation of the falling activity to zero time, this factor must necessarily affect the accuracy of the measurements in such cases. Coagulation during reaction could be prevented by using a supported catalyst, but, in this case, the complication of the adsorption of poison also by the support would have been introduced.

*Relative Toxicities.—Series* I. Cu, Ag, Zn, Cd, Hg, Tl, Sn, Pb. The relative effective toxicities of these metals, as acetates, in each case in alcoholic solution and towards the same stock of platinum (Platinum I), are shown in the figure. The method of measurement was similar to that used in earlier determinations of toxicity (J., **1934**, 26, 672; **1937**, 603, 1004; **1938**, 455, 839), to which reference should be made for experimental details and method of expression. The system taken consisted in each case of 0·1 g. of platinum, 10 c.c. of N-crotonic acid in alcoholic solution, and a known quantity of the poison. Hydrogenation was carried out at 25° in a shaker under standardised conditions.



It will be seen from the figure that copper, silver, and, perhaps rather unexpectedly, tin have approximately the same toxicity, which is the lowest in the series. Mercury is next in order of toxicity, followed by thallium, while zinc, cadmium and lead form another group of approximately equal toxicity, which is higher than that of the other metals. The grouping of zinc and cadmium together might be expected from their general similarity. It should be noted especially that these effective toxicities are based merely on the total poison present, rather than on the adsorbed amount, and that, accordingly, no regularity depending on atomic or ionic size or on valency would be expected, since no conclusions based on coverage alone can be drawn until corrections have been applied for unadsorbed poison.

From the slope of these poisoning graphs, the value of the poisoning coefficient, $\alpha$, which is a convenient measure of the toxicity on a quantitative scale, may be derived by means of the usual relationship $k_c = k_0(1 - \alpha c)$, in which $k_0$ is the original activity of the catalyst and $k_c$ its activity in the presence of a concentration, $c$, of the poison. This has been done in Table II.

TABLE II.

| Metal. | $\alpha \times 10^{-5}$. | Relative effective toxicity. | Metal. | $\alpha \times 10^{-5}$. | Relative effective toxicity. |
|---|---|---|---|---|---|
| Copper | 0·78 | 1·0 | Thallium | 1·97 | 2·5 |
| Silver | 0·78 | 1·0 | Zinc | 2·81 | 3·6 |
| Tin | 0·78 | 1·0 | Cadmium | 2·81 | 3·6 |
| Mercury | 1·37 | 1·8 | Lead | 2·90 | 3·7 |

The next step consisted in the determination of the partition of the various poisons between the adsorbed and the free liquid phases, for the calculation of the true toxicities. This was carried out by the method already described (J., 1938, 2071), with 0·1 g. of Platinum A and a total liquid volume of 10 c.c. as in the toxicity measurements, the unadsorbed poison being determined, as before, by measuring the toxicity of the supernatant liquid towards a standard catalyst previously calibrated against solutions containing known concentrations of the poison in question. The type of relationship found in previous papers, *viz.*, an approximately linear variation of the adsorbed amount with the bulk concentration, over and considerably beyond the range of bulk concentrations used in the toxicity measurements, was again observed. At still higher initial bulk concentrations, and with corresponding saturation of the adsorbing surface, this linear variation ultimately of course breaks (see J., 1938, 2075, Fig. 2, for the general form of these distribution graphs); but, in the range for which it is valid, the amount of poison actually adsorbed on the catalyst can be obtained from the total poison present by multiplying the latter by a simple factor. The partition ratios for all the metals of this series have been collected in Table III, from which it will be seen that, with all these metals, over 80% is adsorbed by the 0·1 g. of platinum under the conditions employed. $K_1$ is, as before, the fractional adsorption, *viz.*, the fraction of the total poison present which is adsorbed, and $K_2$ is the partition ratio, *i.e.*, 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 0·1 g. of the platinum catalyst being taken as unity. The values of $K_1$ and $K_2$ are of course only valid for the particular platinum—and, in the case of $K_1$, only for the particular volume (10 c.c.) of solution—used in the toxicity measurements. The true toxicities, $\alpha_r$, derived from the effective toxicities, $\alpha_e$, of Table II, by correcting for non-adsorbed poison, are also included.

TABLE III.

| Metal. | $K_1$. | $K_2 \times 10^{-2}$. | $\alpha_r \times 10^{-5}$. | Relative true toxicities. |
|---|---|---|---|---|
| Copper | 0·95 | 1·9 | 0·83 | 1·0 |
| Silver | 0·95 | 1·9 | 0·83 | 1·0 |
| Tin | 0·95 | 1·9 | 0·83 | 1·0 |
| Mercury | 0·97 | 3·2 | 1·41 | 1·7 |
| Thallium | 0·84 | 0·52 | 2·35 | 2·8 |
| Lead | 0·95 | 1·9 | 3·05 | 3·7 |
| Zinc | 0·83 | 0·49 | 3·38 | 4·1 |
| Cadmium | 0·83 | 0·49 | 3·38 | 4·1 |

*Series* II. Mn, Fe, Co, Ni. Owing to the exhaustion of the first platinum stock, a second preparation (Platinum B) had to be used for the remaining toxic metals; but, in order to co-ordinate the toxicities with those of the first series, measurements for zinc and cadmium, as reference substances of known toxicity relative to the metals of Series I, were again included in these toxicity determinations with Platinum B. The results, which were obtained under the same conditions as those used previously, but with 0·05 g. of the new platinum stock, are summarised in Table IV. It will be seen from the table that all these metals have approximately the same true toxicity per g.-atom adsorbed.

TABLE IV.

| Metal. | $\alpha_e \times 10^{-5}$. | $K_1$. | $\alpha_r \times 10^{-5}$. | Relative true toxicities. |
|---|---|---|---|---|
| Zinc | 5·1 | 0·63 | 8·1 | 1·0 |
| Cadmium | 5·1 | 0·64 | 7·9 | 1·0 |
| Manganese | 5·2 | 0·64 | 8·1 | 1·0 |
| Iron | 5·6 | 0·66 | 8·4 | 1·0 |
| Cobalt | 6·7 | 0·66 | 10·1 | 1·2 |
| Nickel | 4·8 | 0·65 | 7·2 | 0·9 |

*Confirmatory Measurements.*—Before comparing the toxicities of all the metals studied, it was thought advisable to re-examine two points, *viz.*, (i) to confirm the unexpected low toxicity of tin (which, as will be seen in Table II, was only approximately equal to that of the metals of the copper group), and (ii) to redetermine the relative toxicity of zinc or of cadmium, since these were used as reference substances in Series II. This later work was carried out with a further stock of platinum black (Platinum C), having a higher activity than that previously used; but the true toxicities of tin and copper were again found to be approximately equal to one another, and the relative toxicity of cadmium, compared with that of copper, was once more of the order of 4. The results, which are collected in Table V, may also be regarded as a further confirmation of the observation made in earlier work that, although the absolute values of the poisoning coefficients vary of course with the activity (*i.e.*, with the surface-to-mass ratio) of the catalyst, yet the ratio of the true toxicity of one poison to that of another, *viz.*, the relative true toxicity, does not vary appreciably with a change in the catalyst stock, provided that a given stock is used in making the comparison between the two poisons. This would be expected on first principles, since relative true toxicity merely represents the relative covering power, per molecular unit adsorbed, of the two poisons compared. The point is dealt with in greater detail elsewhere.

TABLE V.

| Metal. | $a_s \times 10^{-5}$. | $K_1$. | $a_r \times 10^{-5}$. | Relative true toxicities. |
|---|---|---|---|---|
| Copper | 0·82 | 0·98 | 0·84 | 1·0 |
| Tin | 0·91 | 0·97 | 0·93 | 1·1 |
| Cadmium | 2·50 | 0·82 | 3·05 | 3·7 |

## DISCUSSION.

In order to compare the toxicities of the metals of Series II with those of Series I, the metals zinc or cadmium, which are common to both series, have, as already mentioned, been used as connecting links, the real toxicity of cadmium being taken as about 4 on a scale in which the toxicity of copper is unity. On arranging all the metals examined in the order of their toxicity (save that cobalt has been placed with the related elements, iron and nickel), Table VI is obtained. In addition to these approximate relative toxicities, the ionic and atomic sizes of the various metals and their ordinary valencies have also been tabulated in view of the interest which is attached to the influence of valency and size on the toxicity from the standpoint of its bearing on the probable nature of the poison–catalyst bond and of the general disposition of the poison on the surface. In this connection, it may be noted that, in the corresponding work on poisoning with non-metallic ions (see Part V), it was shown that toxicity is not exhibited, even if these ions contain normally toxic elements such as sulphur or phosphorus, unless the structure of the molecule is such that the toxic element possesses unsaturated, *i.e.*, unshared, valency electrons, the presence of a completely shared electron octet being sufficient to prevent these poisonous elements from showing their characteristic toxic properties: accordingly, at any rate in this previously considered poison group, it appears that attachment to the surface may occur through linkages which are similar to ordinary, and probably covalent, valency bonds.

TABLE VI.

| Toxicity group. | Metal. | Relative true toxicity. | Atomic radius, $r_a$, in A. | Ionic radius, $r_i$, in A. | Probable effective valency, *n*. | $r_a^2n$. |
|---|---|---|---|---|---|---|
| I | Cu | 1·0 | 1·27 | *ca.* 0·95 | 1 | 1·61 |
| | Ag | 1·0 | 1·44 | 1·13 | 1 | 2·07 |
| | Sn | 1·0—1·1 | 1·40 | *ca.* 1·2 | 2 | 3·92<br>(1·96, $n = 1$) |
| II | Hg | 1·7 | 1·49 | 1·12 | 1 | 2·22 |
| | Tl | 2·8 | 1·99 | 1·47 | 1 | 2·89 |
| III | Pb | 3·7 | 1·74 | 1·32 | 2 | 6·06<br>(3·03, $n = 1$) |
| | Ni | 3·7 | 1·24 | 0·78 | 2 | 3·08 |
| | Fe | 4·1 | 1·27 | 0·83 | 2 | 3·22 |
| | Co | 5·1 | 1·25 | 0·82 | 2 | 3·12 |
| | Mn | 4·0 | 1·18 | 0·91 | 2 | 2·8 |
| | Zn | 4·0 | 1·33 | 0·83 | 2 | 3·5 |
| | Cd | 4·0 | 1·49 | 1·03 | 2 | 4·4 |

Although poisoning by toxic metals is more difficult to formulate by means of simple electronic valency bonds—particularly in view of the usual looseness and the exceptional character, from a valency standpoint, of most intermetallic compounds—it will be seen from Table VI that size alone is not sufficient to account for the toxicity sequence found experimentally. For instance, many of the more highly toxic metals have an atomic or ionic radius which is no greater than those of low toxicity.

If, however, the probable effective valency is also taken into consideration, a rough qualitative generalisation is at once apparent, in that, with the exception of tin, which is discussed later, the bivalent elements occur in the group of greatest toxicity at the foot of the table, *i.e.*, the bivalent toxic elements have in general a greater covering power per atom adsorbed than the univalent elements. In connection with the effective valency, it should be noted that metals of variable valency, such as mercury or iron, will, in the presence of catalytically activated hydrogen, be present in the lowest valency state, *viz.*, with these two metals, in the mercurous or ferrous form. The data available are obviously insufficient to permit any precise formulation of the way in which the toxicity varies with size and with valency; but if, for the time being, the toxicity is regarded as being a function of both these quantities, and if, as a rough approximation, their product—*viz.*, the projectional area of the poison atom (which is proportional to the square of its radius) multiplied by the valency—is tabulated against the toxicity, this product increases in approximately the same way and in roughly the same sequence as the toxicities. This is shown in the last column of the table. It will be noted that tin and lead give values approximately twice those which would be expected from their positions. This is discussed below.

If the table is considered as a whole, it will be seen that the toxic metals studied fall roughly into two extreme groups, (i) univalent metals having a toxicity of about 1, and (ii) bivalent metals having toxicities of the order of 4, together with an intermediate group of metals which apparently only differ from those of the first group by having a slightly greater atomic radius. The two apparent exceptions are of interest. Tin should not fall in Group I on account of its bivalency, which also causes, as already pointed out, a figure of the order of 4, in place of one of about 2, to be given in the last column. The case of lead is a little different. The figure given in the last column is again almost exactly twice that which would be expected from the position of lead in the sequence of relative toxicities; but this place in the toxicity sequence seems a reasonable one, and the abnormal valency–size product seems due to its large size. In this connection, the effect of size should also be noted for thallium, which, although univalent, apparently possesses an abnormally high toxicity for its valency by reason of its large atomic radius (1·99 A.). The apparent irregularity of tin could be completely—and that of lead partly—removed by assuming an effective valency of 1 for these two metals in the adsorbed state on platinum, as shown by the alternative figures in the last column of the table; but, although there is some evidence in the literature for univalent lead compounds, such as the suboxide and subchloride, these compounds are neither very definite nor usual, and there appears to be no evidence for univalent tin, save in gaseous radicals of short life (such as SnCl) at high temperatures and possibly in rather indefinite intermetallic compounds of the type KSn. Accordingly, these two irregularities must, for the time being, be left as an experimental result which, at any rate in the case of tin, has been confirmed by further toxicity measurements.

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# NOTE.

## 3 : 4'-*Dinitrodiphenyl—A Correction.* By WILLIAM A. WATERS.

HODGSON and MARSDEN (this vol., p. 211) have described 3 : 4'-dinitrodiphenyl as a "new compound of m. p. 137°." This substance was first prepared by Scarborough and Waters (J., 1927, 1139) by deaminating 3 : 4'-dinitro-4-aminodiphenyl, and was then reported as having m. p. 189°. This value for the m. p. was confirmed by Blakey and Scarborough (*ibid.*, p. 3005), who obtained 3 : 4'-dinitrodiphenyl by nitration of 3-nitrodiphenyl. Finzi and Mangini (*Gazzetta*, 1932, **62**, 664) prepared the same compound by still another method and gave its m. p. as 187°. It is evident, therefore, that the product obtained by Hodgson and Marsden from reactions between diazotised *m*-nitroaniline and nitrobenzene is a mixture: this would be expected (compare *inter alia*, Hey, J., 1934, 1968; Waters, J., 1939, 866).—SALISBURY, WILTS. [*Received, March 8th*, 1940.]