16. *Heterogeneous Catalysis in Solution. Part III.*[1] *Heterogeneous Catalysis and Other Types of Interaction Between Metals and Oxidation–Reduction Reactions.*

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A series of tests is given for distinguishing between genuine heterogeneous catalysis by a metal and catalysis caused by three other forms of interaction of the metal and the reacting solution. The tests have been applied to the Ce(IV)–H_2O, Ce(IV)–Hg(I), Ce(IV)–Br^-, $Cr_2O_7^{2-}$–I^-, and $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$ redox reactions studied in the preceding Paper.

IN Parts I and II,[2,1] evidence was put forward to show that heterogeneous catalysis by metals of oxidation–reduction reactions in solution occurs largely by an electron-transfer mechanism. In the course of this work we had to be certain that any catalytic effects found were truly heterogeneous in nature since certain other kinds of catalytic metal–solution interaction can be postulated, and have in some cases been observed. The various types of interaction are therefore described below, together with a series of tests by which they may be recognized and differentiated from genuine heterogeneous catalysis. Most of the examples cited refer to platinum, with which we have been particularly concerned, but the principles apply equally to similar catalysts.

Let us suppose that the rate of the redox reaction

$$\mathrm{Ox_1 + Red_2 \longrightarrow Red_1 + Ox_2} \qquad (1)$$

is enhanced by the presence of a metal, M, such as platinum, and that the rate is greater the more metal is added. This phenomenon may be caused either by real heterogeneous catalysis or else by one of the following three effects.

(1) *Reaction between the Catalyst and the Oxidant* Ox_1.—Whether attack on the catalyst according to

$$\mathrm{Ox_1 + M \longrightarrow Red_1 + M^{n+}} \qquad (2)$$

is thermodynamically feasible depends upon the electrode potentials of the Ox_1/Red_1 and M^{n+}/M couples in the solution concerned. Since, initially, the concentrations of Red_1 and M^{n+} are uncertain, we can use instead for discussion purposes the standard electrode potentials, E^0. Eqn. (2) shows that base metals of low E^0 are not suitable as heterogeneous catalysts, and so we need consider only relatively noble ones like platinum, which have indeed been often employed.[1,2] Few couples possess an E^0 high enough to oxidize platinum in perchlorate or nitrate solutions where E^0 of Pt^{2+}/Pt is +1·2 v,[3] but many more are thermodynamically capable of doing so in halide media since E^0 is only +0·7 v [3] for $PtCl_4^{2-}/Pt$ and $PtCl_6^{2-}/Pt$ and +0·6 v [3] for platinum couples involving the corresponding bromo-complexes. Nitric acid, for example, cannot dissolve platinum or gold although aqua regia can. In 1961 Cohen and Taylor[4] discovered that dissolution of platinum was the real reason why this metal appeared to catalyse the reduction in chloride media of Np(VI) to Np(V) and Np(IV) (E^0[Np(VI)/Np(V)] = 1·15 v,[3] E^0[Np(V)/Np(IV)] = 0·75 v [3]).

Catalyst dissolution shows itself in two different ways. If reactions (1) and (2) run side by side, the introduction of the metal into the reaction mixture will actually appear to decrease the rate of reaction (1) if the change in concentration of Red_2 or Ox_2 is being followed, and will seem to increase the rate only if the concentration of Ox_1 or Red_1 is

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[1] Part II, Spiro and Ravnö, preceding Paper.

[2] Part I is considered to be Spiro, *J.*, 1960, 3678.

[3] Latimer, " Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N.J., 2nd edn., 1952. Latimer uses the American sign convention whereas the European-I.U.P.A.C. sign convention is employed in the present Paper.

[4] Cohen and Taylor, *J. Inorg. Nuclear Chem.*, 1961, **22**, 151.

measured. The following tests can then distinguish between attack on the metal and genuine heterogeneous catalysis:

(1a) Weighing the metal before and after the reaction and comparing any loss of weight with that calculated from the apparent change of rate and equation (2).

(1b) Analysing the reaction mixture for the presence of metal ions (M^{n+}) by means of spot tests, examination of spectra, radioactivity determinations after previous neutron irradiation of the metal,[5] or other means, and comparing the amount present with that expected from equation (2).

(1c) Carrying out a blank experiment to see if the oxidant Ox_1 alone reacts with the metal. This test is not adequate if the reducing species itself or its co-ion (*e.g.*, halide ion) could assist in the attack on the metal, as in the examples above.

(2) *Dissolution and Re-precipitation of the Catalyst.*

$$\left.\begin{aligned} Ox_1 + M &\longrightarrow Red_1 + M^{n+} \\ M^{n+} + Red_2 &\longrightarrow M + Ox_2 \end{aligned}\right\} \qquad (3)$$

Such chemical participation of platinum occurs with certain reactions in very hot sulphuric acid in which, according to Delépine,[6]

$$Pt + 8H^+ + 2SO_4^{2-} \longrightarrow Pt(IV) + 2SO_2 + 4H_2O$$

The platinum ions can then be reduced by ammonium ions [6] or by hydrogen: [7]

$$3Pt(IV) + 4NH_4^+ \longrightarrow 3Pt + 2N_2 + 16H^+$$

$$Pt(IV) + 2H_2 \longrightarrow Pt + 4H^+$$

with the result that platinum catalyses the reduction of hot concentrated sulphuric acid to sulphur dioxide by ammonium sulphate [6] or by hydrogen.[7] A corollary of this is that platinum cannot be used as a catalyst in Kjeldahl's method of nitrogen estimation.[6]

The following tests can differentiate between this double-pronged form of interaction and straightforward heterogeneous catalysis.

(2a) Inspection and weighing may show that the metal surface has been corroded away and that the metal has reappeared in a finely dispersed or colloidal form.

(2b) Control experiments could decide whether the oxidant alone dissolves the metal and whether the reductant by itself reduces the metal ions at rates fast enough to account for the observed catalysis. As in case (1c), above, the possibility must not be overlooked that in the mixture one reagent aids the chemical attack of the other.

(2c) Corroborative evidence can be provided by seeing if the overall reaction is catalysed by some similar metal which is not attacked by the oxidant. Thus Delépine [6] found that gold and iridium were not attacked by hot sulphuric acid nor did they cause nitrogen evolution on being added to a hot solution of ammonium sulphate in sulphuric acid.

(3) *Homogeneous Catalysis by Catalyst Ions.*—M^{n+} ions might enter the solution either through slight oxidation of the metal as in (1), above, or through dissolution of the oxide film on the metal surface, a process that would be aided by high acidity and the presence of complexing species. The ions so introduced could then speed up the redox reaction homogeneously, passing through different oxidation states in doing so

$$M^{n+} \xrightarrow{Ox_1 \text{ or } Red_2} M^{n'+} \xrightarrow{Red_2 \text{ or } Ox_1} M^{n+}$$

or else becoming part of a reactive intermediate.

Whether catalysis is really homogeneous or heterogeneous can be tested as follows:

(3a) By comparing the effect on the rate of initially adding an aliquot of spent reaction

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[5] Lossew, Dembrowski, Molodow, and Gorodezki, *Electrochim. Acta*, 1963, **8**, 387.
[6] Delépine, *Compt. rend.*, 1905, **141**, 886, 1013.
[7] Millbauer, *Z. phys. Chem.*, 1911, **77**, 380.

mixture, and, in another run, of adding an aliquot of spent solution that had been catalysed by the metal.

(3b) By analysing a solution reacting under catalysis for the presence of metal ions as in (1b), above, and seeing whether the deliberate addition of this amount of metal ions to an " uncatalysed " reaction mixture reproduces the catalytic rate.

(3c) By observing the effect of intermittently shaking or stirring the reaction mixture containing the metal. The rate will be high during the periods of agitation and low in each period of rest if the catalysis is both heterogeneous and at least partly diffusion-controlled.

If it is suspected that the metal oxide on the catalyst surface is responsible for such homogeneous catalysis or for some direct chemical action, then one test would be the effect of removing the oxide coating or deliberately adding to it by mechanical, chemical, or electrolytic pre-treatment of the metal. It would have to be borne in mind, however, that the metal oxide might be a heterogeneous catalyst in its own right.

EXPERIMENTAL

In Part II[1] we studied the effect of platinum metal on the rates of 11 redox reactions. Four of those that exhibited positive catalysis, Ce(IV)–H_2O, Ce(IV)–Hg(I), Ce(IV)–Br^-, and $Cr_2O_7^{2-}$–I^-, involved oxidants thermodynamically capable of attacking platinum in the media employed, and the catalysis of another process, $Fe(CN)_6^{3-}$–$S_2O_3^{2-}$, was theoretically unexpected. All five reactions have therefore been investigated further to see if the observed catalysis was truly heterogeneous or caused by some other type of platinum–solution interaction. The result of using the various distinguishing tests is described below, the different reactions providing good examples of how the theory above can be applied.

Reaction $2Ce(IV) + H_2O \longrightarrow 2Ce(III) + 2H^+ + \frac{1}{2}O_2$.—The oxidation of water by 5×10^{-4}M AnalaR $Ce(SO_4)_2$ in 2M-AnalaR $HClO_4$ at 18 ± ½° was strongly catalysed when 114 cm.² platinum foil was added.[1] Test 1a showed no loss in weight of the platinum although a 5 mg. loss would have occurred if the metal had itself dissolved. Effect 2 is impossible for this reaction since the reductant is the solvent itself and test 3c (Fig. 1) ruled out homogeneous catalysis by platinum ions. The catalysis is therefore heterogeneous and at least partly diffusion-controlled (test 3c, Fig. 1).

Reaction $Ce(IV) + Hg(I) \longrightarrow Ce(III) + Hg(II)$.—Strong catalysis by 114 cm.² platinum foil was observed[1] when $4{\cdot}2 \times 10^{-4}$M Hopkin and Williams $Ce(SO_4)_2$ reacted at 15 ± ½° with 5×10^{-3}M $Hg_2(NO_3)_2$ in a medium of 2M-AnalaR $HClO_4$. In this reaction the reductant Hg(I) could not aid any attack on the platinum by the oxidant Ce(IV) and therefore tests 1c and 2b are satisfied by the evidence produced for the Ce(IV)–H_2O reaction that there is no appreciable chemical interaction between ceric ions and platinum. This result, together with tests 3a and 3c (Fig. 1), proved that the catalysis was purely heterogeneous, with diffusion to the metal surface a slow step.

Reaction $2Ce(IV) + 2Br^- \longrightarrow 2Ce(III) + Br_2$.—The rate of the reaction between 5×10^{-4}M Hopkin and Williams $Ce(SO_4)_2$ and 5×10^{-2}M AnalaR KBr in 0·92M AnalaR H_2SO_4 at 20 ± 1° was greatly increased when 114 cm.² platinum foil was added.[1] Since any chemical attack on the foil would be aided by bromide ions, interaction of types 1 and 2 could not be ruled out by the fact[1] that the Ce(IV)–H_2O reaction in sulphuric acid is not catalysed by platinum. Absence of platinum dissolution was therefore tested by weighing the foil after the reaction (tests 1a and 2a); a decrease of 3 mg. would have been expected on the basis of the catalytic rate and a loss of only 0·4 ± 0·2 mg. was found. Once more, tests 3a and 3c disposed of the possibility that platinum ions rather than the metallic surface caused the catalysis. Test 3c [which produced a plot similar to that drawn in Fig. 1 for the Ce(IV)–Hg(I) reaction] demonstrated as well that the catalysis involved a slow diffusion step.

Reaction $Cr_2O_7^{2-} + 14H^+ + 9I^- \longrightarrow 2Cr(III) + 7H_2O + 3I_3^-$.—Kinetic measurements at 5° with solutions 5×10^{-4}M in AnalaR $K_2Cr_2O_7$, 0·015M in AnalaR KI, 0·04M in AnalaR $HClO_4$, and 0·4M in AnalaR NaCl revealed slight catalysis by 114 cm.² platinum foil.[1] This effect cannot be attributed to a simple dichromate–platinum attack of category 1 because in the kinetic runs the rate of formation of iodine was followed and not the rate of disappearance of dichromate. A control test of type 2b showed that PtCl$_6^{2-}$ and PtCl$_4^{2-}$ were not reduced by iodide ions, so overruling the possibility that catalysis was caused by consecutive dissolution and re-precipitation of the metal. Because the catalysis was only slight, homogeneous catalysis by platinum ions was hard to test for. A modified form of test 3c was tried in which a solution was allowed to react in the presence of platinum for 10 min. with shaking and for a further 10 min. without shaking. The thiosulphate titre was rather less than expected from a catalytic rate for 10 min. followed by a non-catalytic rate for a similar period, whereas homogeneous catalysis by platinum ions would have required a titre appreciably greater. Heterogeneous catalysis was thus established.

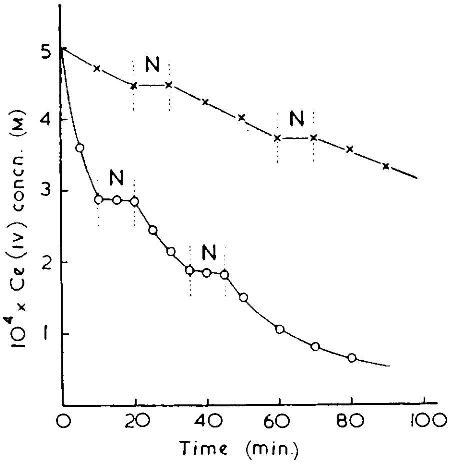

FIG. 1.

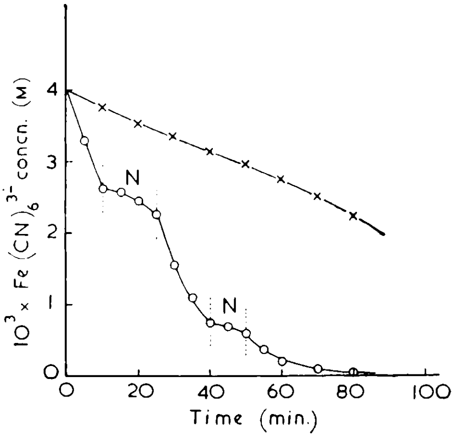

FIG. 2.

FIG. 1. The effects of intermittent shaking (test 3c) on the reactions between 5 × 10^{-4}M-Ce(SO$_4$)$_2$ and water (×), and between 5 × 10^{-4}M-Ce(SO$_4$)$_2$ and 5 × 10^{-3}M-Hg$_2$(NO$_3$)$_2$ (○), both in 2M-HClO$_4$ at 18° in the presence of 114 cm.^{2} platinum foil. The intervals of time labelled N refer to periods of quiescence, the solutions being well shaken the rest of the time.

FIG. 2. Circles show the effect of intermittent shaking (test 3c) on a reaction mixture 4 × 10^{-3}M in K$_3$Fe(CN)$_6$, 4 × 10^{-2}M in Na$_2$S$_2$O$_3$, 0·1M in CH$_3$·CO$_2$H, 0·125M in CH$_3$·CO$_2$Na, and M in KCl, in the presence of 114 cm.^{2} platinum foil at 18°. The homogeneous run under identical conditions is denoted by crosses. The intervals of time labelled N refer to periods of quiescence, the solutions being well shaken the rest of the time.

Reaction $2Fe(CN)_6^{3-} + 2S_2O_3^{2-} \longrightarrow 2Fe(CN)_6^{4-} + S_4O_6^{2-}$.—Marked catalysis by 114 cm.^{2} platinum foil was found [1] at 20 ± 0·3° with a reaction mixture 0·004M in K$_3$Fe(CN)$_6$, 0·04M in Na$_2$S$_2$O$_3$, 0·100M in CH$_3$·CO$_2$H, 0·125M in CH$_3$·CO$_2$Na, and M in KCl, all chemicals being of AnalaR grade. The standard electrode potential of the Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ couple (0·36 v [3]) is too low to permit platinum dissolution and this was confirmed (tests 1a and 2a) by the finding that 33 cm.^{2} platinum foil lost no weight during the reaction. Tests 3a and 3c (Fig. 2) gave negative results for homogeneous catalysis. Test 3c indicated that the heterogeneous catalysis was at least partly diffusion-controlled.

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