Homogeneous Catalysis by Transition Metals

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Introduction

In homogeneous catalysis, the reactants and products are in the same phase. Normally, we are studying the liquid phase, since there is little basis for distinguishing the theory of homogeneous gas phase catalysis from that of homogeneous gaseous reactions generally.

At the research and development stage it is often quicker and simpler to work with homogeneous catalysts, and then find ways of making the system heterogeneous for industrial application. The chief advantage of homogeneous catalysis as a preparative method is that there is good contact with reactants, and so a much greater effective concentration of catalyst than with heterogeneous catalysts. This means that to achieve the same rate milder conditions can be used. However, the catalyst needs to be separated after reaction, which can involve distillation. In some cases this makes catalyst recovery difficult because the temperature needed for the distillation can destroy the catalyst. This is why heterogeneous catalysts are predominantly used industrially.

Examples of homogeneous catalysts include transition metal ions and complexes, inorganic acids and bases, and enzymes.

The particular role of Transition Metals

Inorganic acids and bases are used to catalyse a wide variety of homogeneous organic reactions (e.g. acid-catalysed hydration of alkenes to produce alcohols), and transition metals catalyse redox reactions. [1] Whereas transition metals and transition metal oxides tend to be used as heterogeneous catalysts, their ions and complexes are usually employed as catalysts in homogeneous contexts.

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[1] Remember that acid-base and redox are the only two types of reactions in Chemistry.

A catalyst increases the rate of a chemical reaction without itself being permanently changed by the reaction. The emphasis on permanently changed is important when discussing homogeneous catalysis because the catalyst does undergo chemical change in providing an alternative reaction pathway of lower energy.

The ability of transition metal ions to change oxidation state makes them suitable as homogenous catalysts. A new activated complex can be formed with the catalyst, because transition metals are able to form stable compounds in more than one oxidation state.

The reaction between peroxodisulphate ions and iodide ions

This is a lovely solution reaction that you may well only meet in the context of catalysis. Peroxodisulphate ions, $S_2O_8^{2-}$, are very powerful oxidising agents. Iodide ions are very easily oxidised to iodine. If you look at the reduction potentials below, you can see that the reaction is feasible, and yet the reaction between them in solution in water is very slow.

$$\tfrac{1}{2}S_2O_8^{2-} + e^- \longrightarrow SO_4^{2-} \qquad E^{\ominus} = +2.01V$$

$$\tfrac{1}{2}I_2 + e^- \longrightarrow I^- \qquad E^{\ominus} = +0.54V$$

Hence:

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2 \quad E^{\ominus} = +1.47V$$

Looking at the equation, it is easy to see why that is. The reaction needs a collision between two negative ions, and so repulsion hinders the progress of the reaction considerably.

The catalysed reaction avoids that problem completely. The catalyst can be either iron (II) or iron (III) ions which are added in solution into the reaction mixture.

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad E^{\ominus} = +0.77V$$

Transition Metal Oxidation The peroxodisulphate ions oxidise the iron (II) ions to iron (III) ions, reducing the peroxodisulphate ions to sulphate ions.

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+} \quad E^{\ominus} = +1.24V$$

Transition Metal Reduction The iron (III) ions are strong enough oxidising agents to oxidise iodide ions to iodine, thus being reduced back to iron (II) ions again.

$$2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+} \quad E^\ominus = +0.23V$$

Both of these individual steps involve collision between positive and negative ions. This is found to be much more likely to be successful than collision between two negative ions in the uncatalysed reaction[2].

During the catalysed reaction, the transition metal ion is oxidised by one reactant up to a higher oxidation state. This is then reduced back to the original form by reaction with the other reactant. The overall result is that the reactants are converted into the same products formed without the catalyst's action, but this can occur more quickly due to the lower activation energy of the alternative pathway.

Original pathway
$A + B \longrightarrow C + D$
Catalysed pathway
A + TM ion in high ox. state ⟶ C + TM ion in low ox. state
B + TM ion in low ox. state ⟶ D + TM ion in high ox. state

Catalysis by a transition metal complex

Potassium sodium 2,3-dihydroxybutanedioate (potassium sodium tartrate or just Rochelle salt) contains tartrate ions ($C_4H_4O_6^{2-}$) which are oxidized by hydrogen peroxide, with the evolution of carbon dioxide gas. The reaction can be catalysed by the addition of Co2+ ions in cobalt (II) chloride solution.

$$5H_2O_2\ (aq) + C_4H_4O_6^{2-}\ (aq) \longrightarrow 4CO_2\ (\uparrow) + 6H_2O\ (l) + 2OH^-\ (aq)$$

This reaction occurs in two steps, the first of which has a high kinetic barrier and therefore a slow rate.

1. $3H_2O_2 + C_4H_4O_6^{2-} \longrightarrow 2CO_2 + 4H_2O + 2HCOO^-$
2. $2HCOO^- + 2H_2O_2 \longrightarrow 2CO_2 + 2H_2O + 2OH^-$

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[2] If you use iron (III) ions as the catalyst instead of iron (II) ions, the reactions simply happen in a different order.

Consider the first step, which we wish to catalyse. The reduction potentials below show that the reaction is feasible. Also included is the potential for the cobalt catalyst.

$$\mathrm{H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O} \qquad \mathrm{E^{\ominus} = +1.77V}$$

$$\mathrm{2HCOO^- + 2CO_2 + 6H^+ + 6e^- \longrightarrow C_4H_4O_6^{2-} + 2H_2O} \qquad \mathrm{E^{\ominus} = +0.20V}$$

$$\mathrm{Co^{3+} + e^- \longrightarrow Co^{2+}} \qquad \mathrm{E^{\ominus} = +1.82V}$$

This doesn't appear very promising. Whilst the overall reaction certainly seems feasible ($\mathrm{E^{\ominus} = +1.57V}$), $\mathrm{Co^{2+}}$ ions will not be oxidized by the hydrogen peroxide, and so our familiar alternative pathway for transition metal ions cannot get started.
The interesting feature of this reaction is that you can see the transition metal being oxidised up and then regenerated, since the two species have different colours. The $\mathrm{Co^{2+}}$ ions are a light pinkish colour and it changes to the deep green of $\mathrm{Co^{3+}}$ soon after adding the cobalt (II) chloride solution to the reaction mixture. After a short while, the green is replaced by the original pink, indicating that the reaction is complete, and the $\mathrm{Co^{2+}}$ is regenerated - the reaction is clearly catalysed by the cobalt ions in some form.

It turns out that the tartrate ions act as ligands for the cobalt ions in solution. Two bidentate tartrate ions surround each cobalt ion, forming a complex with a coordination number of four. The electrode potentials for complexes are often very different than those for ions, but are not always quoted in data books. In this case, it is really the cobalt ditartrate (II) complex which catalyses the reaction.

$$\mathrm{[Co(C_4H_4O_6)_2]^- + e^- \longrightarrow [Co(C_4H_4O_6)_2]^{2-}} \qquad \mathrm{E^{\ominus}} = x\mathrm{V}$$

$$\text{where} \qquad +0.20\mathrm{V} < x < +1.77\mathrm{V}$$

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