CHAPTER 1

Introduction to Catalysis

1.1. The Phenomenon of Catalysis

In the early part of the 19th century, when the scientific study of chemistry was just beginning, it was observed that the occurrence of a number of chemical reactions was conditional upon the presence of trace amounts of substances that did not themselves take part in the reaction. In 1836 the Swedish Scientist J.J. Berzelius tried to bring these observations into the body of chemical knowledge by attributing their action to what he called their *catalytic power*: this action he named *catalysis* by analogy, he said, with *analysis*, which is "*the separation of the component parts of bodies by means of ordinary chemical forces. Catalytic power means that substances are able to awake affinities that are asleep at this temperature by their mere presence ...*" The word 'catalysis' comes from Greek words meaning 'a breaking down', and had been used from the time of Ancient Greece to signify the collapse of moral or ethical constraints, so Berzelius applied the term to those phenomena where the normal barriers to chemical reaction were removed. In journalistic use it has however come to mean 'a coming together', which at first sight is the opposite of breaking down, but 'a breaking down' of a barrier inevitably leads to 'a coming together', and it is significant that in the Chinese language the same word is used for both catalysis and marriage broker.

The phenomenon of catalysis occurs very widely. Our life and health, and that of all living things, depends upon the action of biological catalysts called *enzymes* that usually consist of proteins, which sometimes have a metal–atom-containing prosthetic group such as the chlorophyll or haem molecule. These remarkably effective biocatalysts are at the pinnacle of catalytic power and all synthetic catalysts strive to emulate them. The substances that are of use in chemical processing and in environmental control are, however, inorganic in nature, and can be classified into (i) metals, (ii) oxides, (iii) sulfides, and (iv) solid acids, although practical catalysts often contain components drawn from two of these categories. In particular, as we shall see shortly (Section 3.1), metals need to be employed as very small particles in order to maximise their surface area, and because they are unstable in this state, it is necessary to separate them by attaching them to the surface of an oxide particle so that they are not in contact with each other. We then have a *supported metal catalyst*, and these materials will occupy our attention through much of this book (see Chapter 4 for ways of preparing them). In this form they occupy a phase that differs from the fluid phase in which the reactants exist, and they are therefore termed *heterogeneous catalysts*. However, there are many chemical species that can act catalytically when dissolved in a liquid phase in which one or more of the reactants are to be found: examples include the proton and hydroxyl ion, but of greater interest and importance to us are the salts and organometallic complexes of metals. These are termed *homogeneous catalysts*.

In the years following Berzelius, a number of further examples of catalytic action were discovered, but scientific appreciation of their mode of action had to await the arrival of experimental and theoretical techniques for the study of reaction rates. It then became possible for F.W. Ostwald to define a catalyst as "*a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process.*" This handy form of words encapsulates the essential truth of the catalytic effect, and has stood the test of time; it carries with it a number of important implications that we should now explore. The first of these is that the position of equilibrium attained in a catalysed reaction is exactly the same as that which would ultimately be arrived at in its absence: this must be so because the equilibrium constant K is determined by the Gibbs free energy of the process, and this in turn is fixed by the enthalpy and entropy changes, thus:

$$\Delta G = \Delta H - T\Delta S, \tag{1.1}$$

$$K = \exp(-\Delta G/RT). \tag{1.2}$$

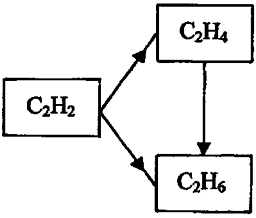
It is inconceivable that the same reaction could have two different sets of thermodynamic parameters, and this basic principle has been put to good use by using catalysts for determining heats of hydrogenation of alkenes at room temperature:[1] this would otherwise be impossible because reactions would be inordinately slow at all reasonable temperatures.

It is sometimes a source of confusion that different catalysts can effect different courses of reaction on the same molecule. A good example of this is the decomposition of ethanol, which when metal-catalysed undergoes dehydrogenation to ethanal and when oxide-catalysed is transformed by dehydration to ethene. The answer is, of course, that both reactions are thermodynamically favourable, but this example introduces the important concept of *catalytic specificity*, whereby a catalyst is able to select one particular route to the exclusion of others, through the kind of intermediate species that are formed on its surface. It is, however, important to appreciate that a catalyst can *only* assist a reaction which is thermodynamically allowed under the specified conditions, that is, for which the change in Gibbs free energy is negative. Considerable effort was spent in the last years of the 19th century attempting the catalysed synthesis of ammonia — under conditions where it later became obvious that the ammonia molecule was not stable.

There are a number of other qualities that catalysts possess which should be introduced at this point. It is not only different types of catalyst that afford different products: a single catalyst can also do this, so for example the hydrogenation of ethyne can lead with a platinum catalyst to a mixture of ethene and ethane, and ethene once formed can react further to ethane. The extent to which the intermediate product, which is often the desired one, is formed is measured by the *selectivity* S, where

$$S = r_{C_2H_4}/(r_{C_2H_4} + r_{C_2H_6}) \tag{1.3}$$

and the reaction scheme takes the form shown in Scheme 1.1. With certain metals such as palladium, nickel, copper (and gold, see Section 9.3.2), ethene is formed almost selectively. A second kind of selectivity is shown when two reactive molecules are present over a catalyst, and one of them reacts faster than the other because it is more strongly adsorbed on its surface. A further aspect of selectivity appears when there are two different reactive groups in the same molecule; thus for example styrene is easily reduced to ethylbenzene because the alkene side-chain is much more



Scheme 1.1: Reaction pathways in the hydrogenation of ethyne.

reactive than the aromatic ring. This is an example of *regioselectivity.* If a reaction is capable of giving stereoisomeric products, a catalyst may exhibit *stereoselectivity*: thus 1,4-dimethylcyclohexenes can lead on hydrogenation to either Z- or E-dimethylcyclohexane ($Z \equiv$ *cis*; $E \equiv$ *trans*). Of particular current interest is the reduction of *prochiral* molecules, that is, those that develop centres of optical activity in the product, which therefore contains optical enantiomers. It is often desirable to create one of the products selectively, and a catalyst showing *enantiomeric selectivity* is therefore required.

1.2. The Activation Energy of Catalysed Reactions

We now enquire how it is that a catalyst is able to accelerate the rate of a reaction. We may start with the concept proposed by Svante Arrhenius to describe the effect of temperature on a homogeneous (i.e. non-catalysed) gas-phase reaction: he stated that reaction rate r depended on the fraction of colliding molecules that between them had more than a critical amount of energy, which he called the *activation energy* E. This fraction increased exponentially with temperature in line with the Boltzmann distribution fraction, so that

$$r = Z \exp(-E/RT), \tag{1.4}$$

where Z is the collision number. The rate might be lower if collisions had to be orientationally acceptable, and so a *steric factor* P was later added to the right-hand side. It is not easy to compare a homogeneous gas-phase reaction proceeding in quite a large volume of space with a heterogeneous reaction occurring within a very much smaller volume at the surface of a solid, but, if the latter depends on the frequency of collisions of a reactant with the surface, this number expressed per cm^2 is typically about 10^{12} times smaller than the gas-phase collision frequency Z, and hence it has been concluded that to compensate for this the activation energy of a catalysed reaction has to be *at least* $65\,\text{kJ}\,\text{mol}^{-1}$ less than that of its homogeneous counterpart, and realistically must be $100\,\text{kJ}\,\text{mol}^{-1}$ less. This conclusion has been confirmed in cases where it has been possible to measure both. It has therefore become an article of faith in the theory of catalysis that *a catalyst acts by lowering the activation energy of the reaction.*

It must do this by creating a new and energetically more favourable reaction path, and we can visualise this by recalling that the activation energy can also be represented as the potential energy barrier that exists between reactants and products. This is the barrier that has to be broken down, so

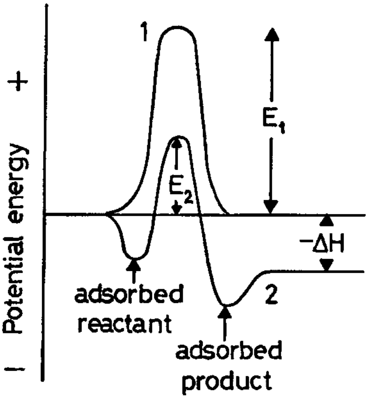


Figure 1.1: Potential energy profiles for (1) non-catalysed and (2) catalysed reactions.

the new reaction path is opened up as shown in Figure 1.1. This new path becomes possible because the reactants have first to be *chemisorbed* in the catalyst's surface, typically by the breaking of chemical bonds within the molecule and creating new bonds with the surface. A good example of this is the hydrogen molecule, which is quite stable and only dissociates into atoms at very high temperature; its dissociation energy is 410 kJ mol^{-1}. However, in the presence of an active metal such as platinum, it is chemisorbed even at liquid hydrogen temperature by dissociation into two atoms: this process is exothermic, and can be depicted as

$$H_2 + 2^* \rightarrow 2H^*, \tag{1.A}$$

where the asterisk stands for a univalent adsorption site on the surface. A weakly held intermediate state of *physical adsorption* effectively eliminates the potential energy barrier by allowing close approach of the molecule to the surface (Figure 1.2). Thus the catalyst succeeds in accomplishing the difficult act of dissociating the molecule, which is the hardest part in the process of hydrogenation. Quite generally *the catalyst surface acts by preparing the reactants for reaction, by converting them into forms that will react with minimum energy input, that is, with a lower activation energy than would otherwise be needed.* This concept is readily extended to cover homogeneous catalysis by metal compounds, where coordination of the reactants at the metal centre replaces chemisorption at the surface. A principal concern of scientists working on catalysis is to identify these

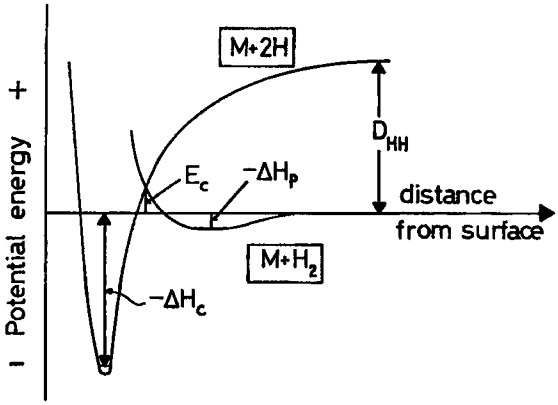


Figure 1.2: Potential energy curves for the approach of a hydrogen molecule and of two hydrogen atoms to a metal surface: E is the activation energy; $-\Delta H$ is the heat of adsorption; subscripts p and c are, respectively, physical adsorption and chemisorption.

new species and their modes of reaction, in other words, to establish the mechanism of the reaction.

If we display the temperature dependences of a reaction proceeding both homogeneously and heterogeneously catalysed as Arrhenius plots, using the equation in the form

$$\ln k = \ln A - E/RT, \tag{1.5}$$

k being the rate constant for the reaction, we see (Figure 1.3) that not only does the catalyst increase the rate, but also that it lowers the temperature at which the reaction achieves a useful rate, and it extends the temperature range in which these rates are available. In practice this is one of the most valuable attributes of a catalytic process, as it minimises the energy input needed, and hence the process costs.

1.3. Ways of Using Heterogeneous Catalysts

To get the best out of a catalyst, it has to be deployed in the most appropriate way. The considerations that determine what this should be are shown in the Catalytic Cycle (Figure 1.4). Reactants in the fluid phase have first to be brought to the neighbourhood of the surface, where they must find an *active centre* where they can be chemisorbed in the right form and with

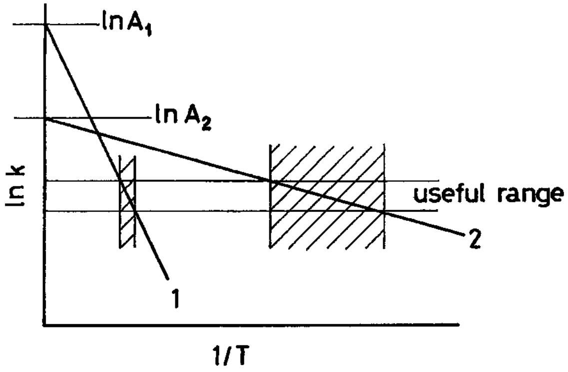


Figure 1.3: Arrhenius plots for (1) non-catalysed and (2) catalysed reactions: k is the rate constant; A is the pre-exponential factor.

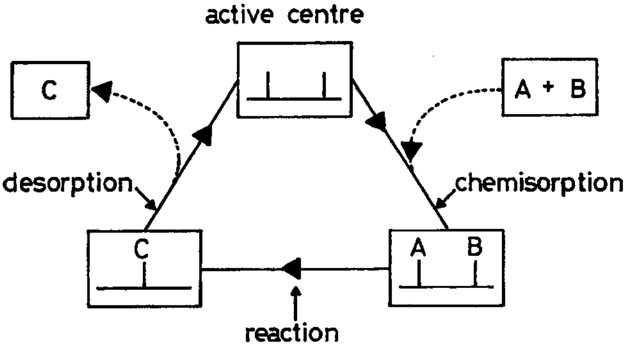


Figure 1.4: The catalytic cycle for the reaction of A + B → C.

the minimum energy, to ensure that their adsorbed states are sufficiently reactive. They react to form a product, which may itself be chemisorbed (Figure 1.1) and which must in that case desorb quickly, and diffuse away from the surface in order to recreate the vacant active centre. If the two diffusion steps are slower than the chemical reactions, the system is said to be under *mass-transport control*, and the catalyst is not being used efficiently, because the surface has to await the arrival of reactants or departure of products. For most purposes therefore it is better for the rate to be determined by the chemical steps at the surface, that is, to be under *kinetic control.* There are two simple ways of establishing which regime applies. (1) In a flow system, conversion should be a linear function of the

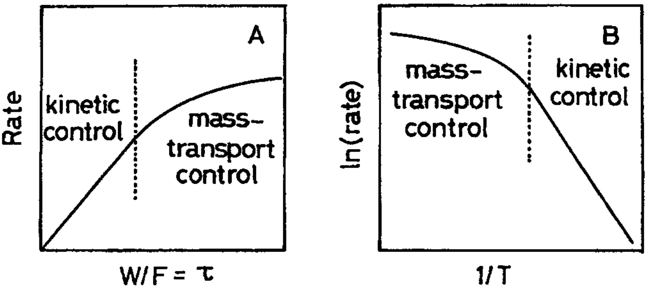


Figure 1.5: (A) Dependence of rate on contact time τ: W is the weight of catalyst; F is the flow-rate. (B) Arrhenius plot showing change from kinetic control to mass-transport control.

contact time τ, that is, to be inversely proportional to flow-rate F and proportional to catalyst weight (Figure 1.5(A)). In a stirred static reactor, it should be independent of speed of stirring, which affects the rate of diffusion of molecules close to the surface. (2) The temperature coefficient for mass-transport control is small and almost always lower than that for kinetic control: as temperature rises and the catalytic rate increases, a point is reached at which diffusion cannot keep pace, and mass-transport control sets in. This is most easily seen as a change in slope of the Arrhenius plot. (Figure 1.5(B)).

There are cases where it is actually desirable to operate under conditions of mass-transport control; this is so for example where it is an intermediate product that is wanted: fat-hardening is a case in point. More usually, however, one wishes to work under conditions where conversion is as close as possible to 100% and here it is inevitable that mass-transport control will apply, at least at the end of the catalyst bed. The physical structure of the catalyst then becomes of great importance, and much thought and skill is exercised in maximising access of reactants to the active centres. The form of reactor and the appropriate physical form of the catalyst have to be chosen with care.

If the reactants are in the gas phase, the reactor may be either *static* or *dynamic*. Small static reactors are convenient for basic research where either the reactants are expensive (e.g. isotopically labelled molecules) or the reaction slow. Dynamic reactors, where reactants flow through the catalyst bed, provide a better simulation of practical use: in a *fixed bed reactor* the catalyst remains in place, and it is in the form of large particles or pellets.

Alternatively it may take the form of a ceramic or metallic *monolith*, of which a variety of physical shapes is available; monoliths are now widely used as supports for the active catalyst, which lines the channels which permeate the structure. They find particular application for the control of exhaust from vehicles powered by internal combustion or diesel engines. If the catalyst particles are small enough, a fast flow of reactants causes the bed to expand and the particles to move about like molecules in a liquid. We then have *a fluidised bed reactor*, which affords a more uniform temperature profile than is possible in fixed bed reactors, and is therefore more apposite to strongly exothermic reactions.

In three-phase systems, where the solid catalyst is in contact with a liquid reactant or its solution plus a gaseous reactant, efficient agitation is required to effect dissolution of the gaseous molecule into the liquid and its transport to the catalyst surface. Such systems easily become mass-transport limited, especially when a very active catalyst is used. In *a batch reactor*, rapid shaking or stirring is needed, and catalyst particles must be small; it may operate at atmospheric pressure, or at superatmospheric pressure as an *autoclave*. Large catalyst particles can however be used with liquid reactants either in a *trickle-column reactor* or a *spinning-basket reactor*.

1.4. Understanding Catalysed Reactions

Under specified operating conditions, a reaction proceeds with a known amount of catalyst at a *rate* that can be expressed in units such as $\mathrm{mol\,s^{-1}}$. It is better given as $\mathrm{mol\,g_{cat}^{-1}\,s^{-1}}$, and if the fraction of the active component of the catalyst is known (and sometimes it is only guessed at) as the *specific rate*, in $\mathrm{mol\,g_M^{-1}\,s^{-1}}$ (M = metal or other component). The ultimate step is taken if the area of the active phase is known: we can then use $\mathrm{mol\,m^{-2}\,s^{-1}}$, which is the *areal rate*. For catalysts that adsorb carbon monoxide or hydrogen readily (see Sections 5.3 and 5.5), the number of surface metal atoms in a supported metal catalyst can be estimated by their chemisorption, obtained by measuring the amount needed to saturate the surface of the metal. Assuming each surface atom constitutes an active centre the rate can then be given as $\mathrm{mol\,mol_S^{-1}\,s^{-1}}$ where S is the surface atom, i.e. as a *turnover frequency* (TOF). When this is not possible, the quantity '$\mathrm{mol_S}$' can also be derived through estimation of particle size by transmission electron microscopy (TEM) or X-ray absorption fine structure (XAFS). For many purposes however the areal rate (rate per unit area of active surface) is sufficient, because it can be changed into TOF by dividing by the calculated average number of surface atoms per m^2 (ca.10^{15}). Since the actual number of active centres is rarely known with precision, and is certainly often less than the number of surface atoms, TOF is a quantity that needs to be treated with great care, especially where there is some possibility of involvement of the support in the reaction. This difficulty does not however apply in the case of homogeneously catalysed reactions, however, because there the concentration of the active species is precisely known and so values of TOF are readily obtained.

In a static reactor the rate changes with time as the reactants are consumed, and the *initial rate* is often used. In a dynamic reactor under steady state conditions the rate is independent of time, and with a known flow of reactant into the reactor the observed fractional *conversion* is readily changed into a rate. What is of great interest in understanding a catalysed reaction is the response of the rate to variations in operating conditions, especially the concentrations or pressures of the reactants, and temperature. It is frequently observed that, at least over some limited range of temperature, the Arrhenius equation in the form

$$\text{rate} = A\exp(-E/RT) \tag{1.6}$$

is obeyed, sometimes with great precision: if it is certain that the reaction is under kinetic control, E is the *apparent activation energy.*

For reactions of environmental interest, it has been customary to obtain the signature of a catalyst by a plot of conversion versus temperature, and unfortunately this procedure has been widely adopted for reactions catalysed by gold, especially the oxidation of carbon monoxide (Chapter 6) and the water-gas shift (Chapter 10). While it provides an easy means of ordering a series of catalysts into a qualitative hierarchy of activity, its limitations need to be stressed.

(1) 'Conversion' depends on the contact time or flow-rate, on the gas composition, on the amount of catalyst used and on the loading of the active component: changing any one of these could alter the relative activities of the members of the series.

(2) For highly exothermic reactions, such as carbon monoxide oxidation, it may be hard to keep the catalyst isothermal, and if the rate of heat dissipation no longer keeps pace with heat generation it becomes hotter than the temperature shown by the sensing device; the rate will then escalate

and quickly rise to 100% while the recorded temperature only rises by a few degrees. This phenomenon is known as *light-off* and the temperature at which this occurs is sometimes used as a measure of activity.

(3) At low conversions the rate is limited by the catalytic process on the surface (this is the *kinetic regime*), but when this becomes faster than the rate at which reactants can diffuse to the surface it becomes *diffusion-limited* (or *mass-transport-limited*). Its onset is gradual and can only be safely detected by changing conversion to a *rate* and then plotting its dependence on the measured temperature using the Arrhenius equation. When its slope starts to decrease, diffusion limitation is starting (Figure 1.5(B)): it may be noticeable at 50% conversion, and above 75% it will be dominant, so the comparison of high conversions only reveals aspects of the catalyst's *physical* structure and not of their true catalytic activity.

(4) It makes little sense to compare catalysts on the basis of the temperature of 50% conversion (or any other conversion) as is often done, because the statement that catalyst A is 10 degrees more active than catalyst B does not actually say by how much it is faster. Once again, comparison of *rates* at one or more temperatures is needed to show quantitatively how they compare. This does not work if these activities are vastly different, but other devices (such as showing the Arrhenius parameters as a compensation plot) can then be used.

(5) There is a danger that by forcing or allowing the catalyst to work at high temperature in order to obtain complete conversion, it may suffer structural damage such as sintering of the active component; this can be detected by following the reaction as the temperature is lowered back to its initial value, but this is rarely done. Deactivation due to structural change or any form of poisoning as the temperature is raised will clearly diminish the catalyst's ranking, and sometimes conversion fails to reach 100% for this reason. The activation energy will then also be false. The concept of *random* variation of temperature is hardly ever employed, although this is necessary to validate the activation energy. Running a catalyst to constant activity at low temperature before starting to raise it is no guarantee that further deactivation will not occur at higher temperature.

These cautionary words are needed because it is a matter for concern that conclusions about the merits of particular aspects of catalyst structure and composition are often based on very limited and sometimes unsatisfactory experimental work.

Deactivation of a catalyst is estimated by following the conversion as a function of time at a fixed temperature. It is of course pointless to do this when the conversion is close to 100%, as is sometimes done, because under such conditions the rate of the catalytic reaction can decline without affecting the observed conversion. Imagine a long catalyst bed in which initially all the reaction occurs in the first 10%; as this deactivates, the reactive zone moves further on, and this occurs progressively without apparent loss of activity, until all the catalyst is dead.

Consideration of how the rate of a catalysed reaction depends on the pressures or concentrations of the reactants in contact with it takes us into the realm of *chemical kinetics.* The simplest way of expressing this dependence for a reaction between two molecules is by an equation of the form

$$\text{rate} = kP_{\mathrm{A}}^{\mathrm{a}}P_{\mathrm{B}}^{\mathrm{b}}, \tag{1.7}$$

where k is a rate constant and the exponents a and b are the *orders of reaction*, respectively, of the reactants A and B, P being the pressure. This is an example of a *Power Rate Law.* Strictly speaking we should also provide for a possible effect of the pressure of the product on the rate, by including a term $P_{\mathrm{C}}^{\mathrm{c}}$, because occasionally the product is strongly adsorbed and inhibits the reaction. However, more often than not it is more weakly adsorbed than the reactants and does not interfere (i.e. $c = 0$), but all too frequently this is assumed without checking. It would be wise to check this by adding some product with the reactants to confirm that this is so. Now with catalysed reactions the values of a and b are often nonintegral, so that they do not allow of simple interpretation as is usually the case with noncatalysed reactions. The reason for this is that the rate is determined by the concentrations of the two reactants in chemisorbed states on the surface, usually expressed as their fractional surface coverages θ_{A} and θ_{B}, and these do not bear a straightforward relation to their concentrations in the fluid phase. They can however be connected by the *Langmuir adsorption equation* (sometimes called the Langmuir isotherm) which for reactant A takes the form

$$\theta_{\mathrm{A}} = b_{\mathrm{A}}P_{\mathrm{A}}/(1 + b_{\mathrm{A}}P_{\mathrm{A}} + b_{\mathrm{B}}P_{\mathrm{B}})^2, \tag{1.8}$$

where the b terms are the *adsorption coefficients* for each reactant, i.e. the equilibrium constants for their chemisorptions, and there is a corresponding equation for θ_B. The rate of reaction r is then proportional to the product of the two terms:

$$r = k\theta_A\theta_B = b_A P_A b_B P_B / (1 + b_A P_A + b_B P_B)^2. \tag{1.9}$$

This is the *Langmuir–Hinshelwood formalism.* We can see what this equation says by taking two extreme situations. (i) When the pressures of A and B are both low or when their adsorption coefficients are small, the rate is simply proportional to the product of the pressures, i.e. the reaction is first order in both reactants. (ii) If however θ_A is high because A is strongly adsorbed or its pressure is high, and if B is weakly adsorbed or its pressure is low, $b_A P_A \gg b_B P_B$, and then the reaction becomes first order in B and minus first order in A. Clearly there will be a range of intermediate conditions, and these can be summarised in Figure 1.6, which shows how the rate varies with P_A when P_B is held constant. It is however unusual for experimental measurements to reveal the whole of a curve of this type, and it is more usual for a section of it to be approximated by an exponent of the pressure, as in Equation (1.7). It is however important to appreciate that such an expression is only an approximation which applies over a limited range of pressure; however, it does provide a qualitative indication of the relative adsorption strengths of the reactants, but for quantitative work it is better to extract the adsorption coefficients from the appropriate form of the full rate equation (e.g. Equation (1.9)).

Although many reactions appear to proceed by a Langmuir–Hinshelwood mechanism, two other types are sometimes invoked and will receive passing mention in later chapters. In the *Rideal–Eley* (or

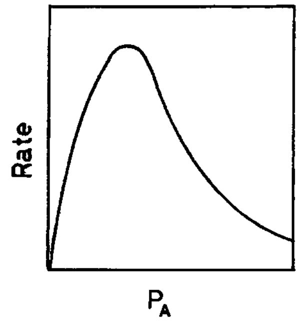


Figure 1.6: Langmuir–Hinshelwood formalism for a bimolecular reaction: dependence of rate on pressure of reactant A (see text).

Eley–Rideal) *mechanism*, one of the reactants comes directly from the fluid phase to react with the other, which is already chemisorbed. This procedure was devised to explain the kinetics of the hydrogen–deuterium reaction on certain metals (see Section 9.2), but has also been suggested for other reactions. The *Mars-van Krevelen mechanism* applies to oxidations catalysed by oxides that are easily reducible, and are therefore able to release their lattice oxide ions for the purpose of oxidising the other reactant; they are then replaced by the dissociation of molecular oxygen. With gold catalysts supported on such oxides, it is sometimes proposed that this mechanism plays a part in the total process.

Although orders of reaction for the oxidation of carbon monoxide in gold catalysts are sometimes reported,[2,3] application of rate equations based on Langmuir–Hinshelwood formalism (as Equation (1.9)) has only rarely been undertaken. In the case of this reaction, it is necessary to consider whether or not the reactants dissociate when they chemisorb and whether in either state they chemisorb competively (i.e. on the same site) or non-competitively (i.e. on different sites). Results obtained on Au/TiO_2 at 273–313 K were tested[4] against each of the four possible rate equations, and that based on non-dissociative non-competitive chemisorption gave best fit; spectroscopic measurements strongly suggested that carbon monoxide is chemisorbed on the metal and the oxygen on the support (see Section 6.2.5). The orders of reaction were ~ 0.4 for oxygen and 0.2–0.6 for carbon monoxide;[2] quite different values have been given for other catalysts and other experimental conditions,[2,3] but these could be accommodated by various values of the thermodynamic parameters for chemisorption.

Now the process of chemisorption is necessarily exothermic, so the operation of Le Chatelier's principle requires the surface coverages to decrease when temperature rises. This has important consequences for reaction kinetics, because the inhibition due to a strongly adsorbed reactant becomes less, and negative orders become more positive; the curves shown in Figure 1.7 illustrate this. A moment's consideration shows that the temperature coefficient of the rate must be a function of P_A; specifically, the activation energy will increase with P_A, thus justifying the term *apparent* activation energy. It is not always appreciated that activation energies derived from the temperature dependence of *rates* are not unique quantities, but depend on reactant pressures. The Arrhenius equation (1.5) describes the effect of temperature on the rate *constant*.

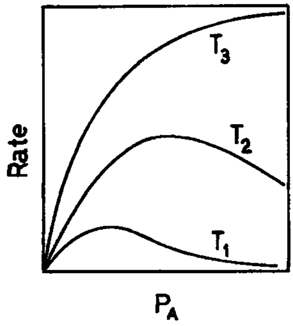


Figure 1.7: Dependence of rate on pressure of reactant B at three temperatures, $T_3 > T_2 > T_1$.

This matter can be resolved in the following way. The temperature dependence of an adsorption coefficient is given by

$$\mathrm{d}\ln b_{\mathrm{A}}/\mathrm{d}T = \Delta H^{\circ}_{\mathrm{A}}/RT^2, \tag{1.10}$$

where $\Delta H^{\circ}_{\mathrm{A}}$ is the standard heat of adsorption of A: thus is the *Van't Hoff isochore.* The observed effect of temperature on rate is therefore the consequence of two opposing effects, viz. (i) the positive effect on the rate of reaction of two adsorbed molecules assuming their surface coverages to be constant, and (ii) the negative effect of their decreasing coverages. We may associate (i) with the true activation energy E_t derived from the temperature-dependence of the rate constant k, so that

$$E_t = E_a - \Delta H^{\circ}_{\mathrm{A}} - \Delta H^{\circ}_{\mathrm{B}}. \tag{1.11}$$

Thus E_a will be less than E_t because the rate does not increase with temperature so fast as it would if surface coverages were constant; the heat terms are however negative from the system's point of view, so their values have to be *added* to E_a to obtain E_t. Of course the extent to which each heat term has to be taken into account depends upon how much the coverage term changes with temperature. If both reactants are very strongly adsorbed, the rate of coverage change will be small, in which case $E_a \approx E_t$; the 'orders' a and b will both be zero; but if both are weakly adsorbed, coverage change will be rapid, and the 'orders' both unity; both the heat terms then apply. In 1935, the Russian Scientist M.I. Temkin therefore devised the following equation to cover these and intermediate conditions:

$$E_t = E_a - a\Delta H^{\mathrm{o}}_{\mathrm{A}} - b\Delta H^{\mathrm{o}}_{\mathrm{B}}. \tag{1.12}$$

This analysis helps to explain one of the biggest mysteries of heterogeneous catalysis, namely *compensation phenomena.* It is often found that when the same reaction is followed over a series of different catalysts, or at different reactant pressures, or when a series of related reactions is used on the same catalyst, there is a correlation between the activation energy and the logarithm of the pre-exponential factor $\ln A$ (Equation (1.6)) of the form

$$\ln A = mE + c. \tag{1.13}$$

An example of this is shown in Figure 1.8. It means that if activation energy rises, and the rate in consequence of Equation (1.6) falls, the $\ln A$ term is increased in order to *compensate.* It is a simple algebraic consequence of this equation that there must be a temperature T_i at which all the rates in the series are the same, and only below this temperature does a lower activation energy betoken a faster rate. There has been very much discussion in the literature concerning the meaning and significance of this relation, but it has recently become clear that in every case compensation only occurs when *rate* measurements are used, and when therefore *apparent* activation energies are involved. What is of interest is the cause of the

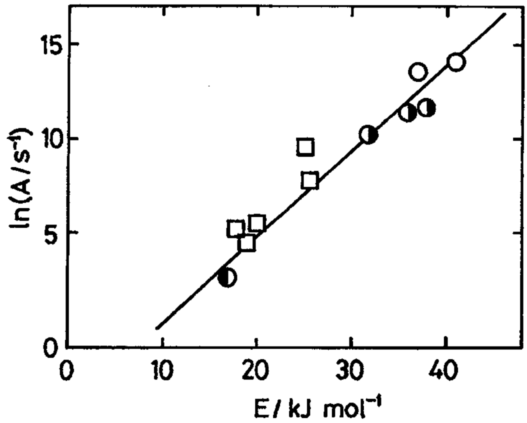


Figure 1.8: A 'compensation' plot showing a linear dependence of $\ln A$ upon E: □ Au/TiO$_2$ (*Catal. Today* **36** (2001) 153); ○ Au/TiO$_2$, ◑ Au/Al$_2$O$_3$, ◐ Au/SiO$_2$ (*J. Molec. Catal. A: Chem.* **199** (2003) 73).

variation of the activation energy, rather than the origin of the compensation, and the cause lies in the Temkin Equation (1.12). *Apparent* activation energies alter because of various inputs from heats of adsorption; the true activation energy remains the same.

The basic concepts of chemical kinetics as applied to heterogeneously catalysed reactions have been presented above because of their overriding importance in understanding how they proceed. There are however many other ways in which the structure and composition of adsorbed species can be explored and identified. The applicability of each method depends on the physical structure of the catalyst: for flat surfaces (single crystals, 'model' surfaces) low-energy electron diffraction (LEED) and sum-frequency generation (SFG) are appropriate, while for powdered materials infra-red spectroscopy (FTIR, RAIRS/IRAS) and X-ray absorption fine structure (XAFS) are suitable procedures. The last three methods can be used with dispersed systems such as supported metal catalysts. There is however one danger associated with all of them, namely, that they most easily notice the adsorbed species that are present in the greatest concentration, and since the key reactive species may only be a minor component great care has to be taken to ensure that these are accurately identified, and that their appearance correlates with the rate of reaction. Kinetic analysis is perhaps the only way of gaining direct access to the heart of the reaction, but a word of warning is still necessary; it is impossible to deduce a unique reaction mechanism simply from the reaction kinetic, because (as Karl Popper said) you cannot prove that all other mechanisms are excluded. However the converse is true: *no reaction mechanism can be valid that does not agree with the observed kinetics.*

1.5. The Catalytic Activities of Metals

The kinds of reactions catalysed by various types of solid are determined by the ability of the surface to convert the reactants into adsorbed forms that are conducive to making the desired product. So, for example, the metals of Groups 8–10 are particularly adept at reactions that require the dissociation of hydrogen molecules, i.e. hydrogenation and hydrogenolysis. Metals of Group 11 have the reputation of adsorbing hydrogen only weakly, and they are not therefore versatile catalysts for reactions needing hydrogen atoms. The base metals are useless for oxidations because they so readily become oxidised, and it is only the noble metals of these Groups that are useful oxidation catalysts, and then it is generally for non-selective or deep oxidation. Many transition metal oxides make splendid selective oxidation catalysts, and some of them, and particularly mixtures of them, are renowned for catalysing the selective oxidation of alkenes, alkanes and aromatic molecules. Acidic solids such as silica-aluminas, and especially zeolites, their crystalline analogues, are excellent for catalysing reactions of the carbocation type, which are initiated by protons.

With metals it is possible to drive our understanding further, and to see in a more quantitative way the principles that govern activity. Maximum rates will be found when the catalytic system, that is, the combination of reactants and catalyst, is such that the reactants (i) are so strongly adsorbed that the whole of the surface is utilised, but not so strongly that they are unreactive or poison the surface and (ii) are adsorbed in the forms that are appropriate for forming the desired product. The first consideration leads to the idea of the Volcano Curve (Figure 1.9), which exhibits a maximum rate when the two opposing needs are optimally balanced. This implies that strength of reactant adsorption enters into the picture *twice*, once to determine coverage and then to control reactivity. An additional requirement is for two reactants to be adsorbed with comparable strengths, since the rate depends on the product of their surface concentrations (Equation (1.9)), but this need cannot always be met.

Strength of adsorption is conveniently measured by the heat released when adsorption takes place, and for several molecules there is evidence to show that the strength decreases on passing from left to right across each of the three transition series; with some molecules (hydrogen, alkenes)

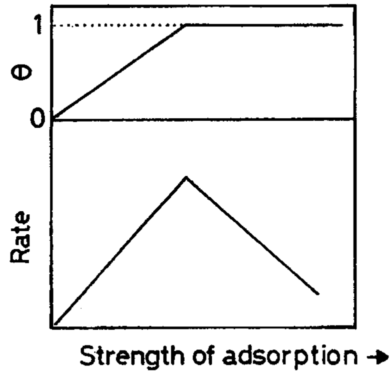


Figure 1.9: Volcano plot showing dependence of rate on strength of adsorption: the upper part shows the corresponding variation of surface coverage θ.

there is little variation within Groups 8–10, and with others (e.g. nitrogen) the ability to be chemisorbed cuts out at Group 8. These trends have been attributed to variation in the number of unpaired *d*-electrons or vacancies in the metal's *d*-band; the Group 11 metals, having filled *d*-levels, therefore fail to be very active in chemisorption. Drawing these concepts together, it is not surprising to find the most active metals for hydrogenation towards the end of each transition series (rhodium takes the prize for ethene hydrogenation but nickel is the most active base metal), with most metals occupying places on the right-hand side of the Volcano Curve (Figure 1.9) and only copper, and perhaps the other Group 11 metals (and possibly manganese) on the other side. Other classes of reaction however show somewhat different behaviours.

For example, maximum activity for alkane hydrogenolysis is to be found in Group 8 (Ru, Os) rather than in Group 9 or 10, because the hydrocarbon intermediates have to be multiply bonded to the surface, and metals in the later Groups have insufficient unpaired electrons for this purpose. Palladium is outstandingly the best metal for hydrogenating alkynes, but is of little use for hydrogenating aromatics.

There is one other important aspect of the catalytic activity of metals to introduce before concluding this brief survey; this is the concept of *structure sensitivity*, which will turn out to be relevant to much of the catalytic chemistry of gold. The idea of the active centre has already been noted (Section 1.3). For some reactions this comprises perhaps only one or two metal atoms, and it does not matter too much what their surroundings are; these reactions are termed *structure-insensitive.* Other reactions seem to require a larger assembly or ensemble of atoms arranged in a quite specific way; they are named *structure-sensitive.* Experimental evidence for the classification of reactions into these groups is of three kinds: (i) variation of specific rate with particle size, which alters the coordination number of surface atoms (particle size sensitivity, see Section 3.4); (ii) dependence of rate on the structure of single-crystal surfaces, including those having straight or kinked steps on them (surface structure sensitivity, see also Section 2.5.2); and (iii) dependence of rate on the composition of bimetallic particles containing one active and one inert metal (e.g. Pd–Ag, see Section 1.6).

1.6. Catalysis in Bimetallic Systems

In the wider field of heterogeneous catalysis, very much use has been made of catalysts containing two or more metals. Some of these have achieved industrial prominence, notably the platinum–iridium and platinum–rhenium combinations in petroleum reforming, and platinum–tin in alkane dehydrogenation, but much academic work has focused on catalysts containing an element of Groups 8–10 plus one of Group 11. The initial motivation for this work, which started in earnest in the middle of the last century, was to determine the importance of electronic structure of a metal in determining its activity,[5] but this was based on the mistaken belief that electrons from the two metals forming the bimetallic system were shared in a common pool. Although this work was misguided,[6,7] results of great interest were obtained, and the electronic theory came to be supplanted by concepts based on the size of the ensemble of the active metal and electronic modification of the active atoms by a ligand effect due to the vicinity of the other metal.[8] The probability of finding an active ensemble of a specified size is a function of the ratio in which the two metals are present, but note has to be taken of the tendency of the component of lower surface energy to segregate preferentially at the surface and liking best to occupy low coordination number sites. There has been much discussion over the years as to the relative importance of the ensemble and ligand effects; in the great majority of cases, the former is more usually predominant.

While in many cases addition of an inactive metal leads immediately to a decrease in activity, in some cases there is an initial increase. This has often been attributed to a decrease in the mean size of the active ensemble, which in turn, in the case of hydrocarbon reactions, minimises the formation of strongly-bonded dehydrogenated species that would lower the rate of the desired reaction, although sometimes improving its selectivity; a possible example of the effect of gold in doing this will be found in Section 13.5. There are, however, several instances of gold improving the activity of palladium in reactions involving only hydrogen (see Section 9.2). Bimetallic catalysts containing gold show activity that is superior to that of either component separately in the synthesis of hydrogen peroxide (Section 8.5), of vinyl acetate (ethenyl ethanoate) (Section 8.4), and in a number of other selective oxidations (Section 8.3). Sound explanations for these effects are not always available, but in some cases it is clear that the role of the gold is to modify favourably the performance of the palladium. It is not feasible to record all the many instances described in the literature[5,9,10] of gold acting purely or predominantly as an inert diluent, whatever benefits this may bring to the active component in terms of higher activity or better selectivity. In the following chapters, attention will to be largely confined to cases where the presence of gold leads to a significant and sustained improvement in performance.

For a further discussion of the structure and properties of bimetallic systems, see Sections 2.6 and 3.2.3; for the preparation of bimetallic catalysts, see Section 4.6; and for the mechanisms by which they work in oxidations, see Section 8.2.2. Most textbooks of physical chemistry have sections on adsorption and catalysis, but they frequently focus on studies made under ultra-high vacuum conditions with single crystal surfaces. While this work produces beautiful pictures, it has limited relevance to the more mundane world of practical catalysis. Other introductory treatments of about the level of this chapter, or slightly more advanced, are available,[5,7,11] as are deeper discussions of the kinetics of catalysed reactions.[12–14] Industrial processes using catalysts have also been described in detail.[15,16]

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