

Understanding the Rates of Chemical Reactions

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Abstract. A review is given of the key steps that have led to our current understanding of the rates of chemical reactions. These steps include the law of mass action, the Arrhenius equation, catalysis, collision theory, potential energy surfaces, transition state theory, unimolecular reactions, and classical trajectories.

Introduction

This paper gives a historical view of our understanding of the rates of chemical reactions. The topic covers approximately 200 years. Almost as soon as people carried out reactions that we would recognise today as chemical, they asked how fast they went. The subject has matured to the point that the foundations on which it has been built are unlikely to be removed. Yet there is still a long way to go before we can predict the rate of a new reaction with confidence. Also, we have pushed forward the questions we ask about a reaction; not just how fast it goes but what are the details of the energy changes that accompany the reaction.

The Law of Mass Action

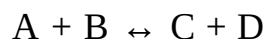
In 1777 Wenzel [1] proposed that as a measure of chemical affinity one could take the rate at which chemical reactions occurred. For the affinity of dilute acids for metals he noted that “If an acid liquid dissolve a drachm of copper or zinc in an hour, a liquid half as strong will require two hours to effect the same, provided that the surfaces and the heats be equal in the two cases”. According to the famous 19th century physical chemist Ostwald this was the first statement of the Law of Mass Action, but it took another 50 years before the laws describing the rates of chemical reactions were formulated more precisely.

An understanding of chemical formulae, and of the difference between compounds and mixtures was achieved early in the 19th century, and at that time many new chemicals were being synthesised in a manner that we would now recognise as typical of modern chemistry. The importance of

chemical mass in determining the rates of chemical reactions (we would today normally talk about concentrations), was first proposed by Berthollet in several papers and books at the beginning of the 19th century. He also made the very important observation that chemical reactions do not always go to completion, and that the position of equilibrium was affected by the quantity of chemicals involved. In his book ‘Recherches sur les Lois de Affinité’ published in 1801 (translated into English in 1804) [2], he states that ‘In opposing the body A to the compound BC, the combination AC can never take place completely, but the body C will be divided between the bodies A and B in proportion to the affinity and quantity of each, or in the ratio of their masses’.

Many experiments were performed to confirm or refute Berthollet’s conclusion, and a dynamical view of chemical equilibrium as a balance of two opposing reactions, forward and backward, gradually gained acceptance. In 1850 Williamson [3] said ‘ it is clear that the relative velocity of interchange must be greatest between the elements of that couple of which the quantity (*at equilibrium*) is least’. More succinctly Malaguti [4], in 1853, said that equilibrium is reached when the velocities of the two opposing reactions are equal.

If we consider a simple chemical equilibrium



and write the equilibrium constant¹

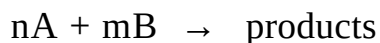
$$K = [C][D]/[A][B]$$

then we can take the rate of the forward reaction to be equal to the product $k[A][B]$, and the rate of the backward reaction to be equal to $k_{\text{A}}[C][D]$, where k and k_{A} are called rate constants. If at equilibrium the two rates are equal, then $K=k/k_{\text{A}}$

A study of the equilibria established in esterification reactions was made by Berthelot and St. Gilles [5], and they deduced that the rate of the forward reaction was proportional to the product of the alcohol and acid

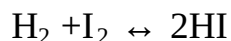
¹ What is meant by the square brackets depends on the phase being studied. For example, in solution it would represent concentration, or more exactly, the thermodynamic activity.

concentrations. This work stimulated two Norwegian scientists, Guldberg and Waage [6] to examine a large number of reactions, and they made the first clear and general statement of the law of mass action for chemical reactions. They made two new important points. Firstly, that the quantities entering the rate law could be raised to integer powers other than one, and secondly, for reactions in solution, it is concentration not mass that enters the equations. Thus if a reaction follows the chemical equation



then, according to Guldberg and Waage, the rate of reaction is proportional to the product $[A]^n[B]^m$. They followed this by stating that 'If the number of molecules in unit volume be denoted by p and q, the product pq will represent the frequency of the encounters of these molecules'. In the meantime, van't Hoff [7] had also looked at the work of Berthelot and St. Gilles, and he also recognised the importance of reaction velocities in determining the balance at equilibrium.

One of the most convincing of many later studies which confirmed the law of mass action was that of Lemoine [8] on the reaction



He measured the rates of the forward and backward reactions (in the presence of a platinum catalyst), and showed that they approached equality as the reaction approached equilibrium. The rate constants in both directions were later determined through extensive work by Bodenstein [9], although it was much later to be shown that the $H_2 + I_2$ reaction was not a simple bimolecular reaction [10].

Rate Equations and Integration

In a typical kinetic experiment the concentration of one or more of the chemical components is followed as a function of time, and the rate of the reaction is then deduced from the rates of change of the reactants. These rates of change are the target of the kinetic theories which will be described later.

In some simple but very important examples the relation between the concentrations of reactants or products and the rates of change of these concentrations can be deduced by simple calculus, and the first such analysis was made by Wilhelmy in 1850 [11]. He used a polarimeter to follow the inversion of cane sugar (sucrose) by dilute acid (it takes up

water to give dextrose and levulose), and showed that the initial rate was proportional to the concentrations of both sugar and acid. He set up a differential equation for the rate of loss of sucrose and integrated it to show how the concentration of sugar decreased with time. His analysis agreed with his experimental observations.

A more thorough examination of the kinetics of simple reactions was made by Harcourt (a chemist) and Essen (a mathematician) [12]. They analysed the differential equations for what we now call first order and second order reactions, and for consecutive second order reactions. The term 'order' was first used by Ostwald to describe the powers of the molecular concentrations which enter into the rate equations, although others had earlier implied this term. Incidentally, Harcourt and Essen were the first to make a detailed kinetic study of the famous iodine clock reaction (the oxidation of an iodide by hydrogen peroxide in which the iodine formation is followed by a starch-thiosulphate indicator).

The Arrhenius Equation

The next important step in understanding the rates of chemical reactions was the interpretation by Arrhenius of the effect of temperature on the rate constant; as we shall see this lead to the idea that many reactions have to surmount an energy barrier to proceed.

The fact that the rates of most chemical reactions increase with a rise in temperature was well known, for example from the work of Berthelot and St Gilles already mentioned [5]. Wilhelmy [11] was the first to propose a specific temperature law for rate constants from his studies on the inversion of cane sugar, mentioned above. He concluded that the rate of inversion had an exponential dependence on the reciprocal temperature (the logarithm of the rate constant is proportional to $1/T$). Other early workers who found an exponential temperature law were Hood [13] in his experiments on the oxidation of ferrous sulphate by potassium dichromate, and Bodenstein [9] in studies of the thermal decomposition of HI.

Van't Hoff [14] pointed out that an exponential temperature dependence of rate constants could be anticipated from the fact that equilibrium constants are the ratio of forward and backward rate constants, because it was known from thermodynamics that equilibrium constants followed an exponential temperature law. For a reaction at constant pressure the equilibrium constant is given by

$$\ln K = -\Delta G/RT = -(\Delta H - T\Delta S)/RT$$

(1)

where ΔG is the Gibbs free energy change for the reaction. Taking the temperature variations of the enthalpy ΔH and entropy ΔS to be negligible over a small temperature range, this leads to

$$(d \ln K/dT) = \Delta H/RT^2$$

(2)

The dependence on temperature of the forward and backward reactions must be such that from their ratio one must arrive at equation (2). This was the starting point for van't Hoff's deduction that the rate constants would vary with temperature according to the law

$$(d \ln k/dT) = B/T^2$$

(3)

which would integrate to

$$\ln k = -B/T + C$$

(4)

B and C being constants.²

When examining the temperature effects on the rates of reactions Arrhenius concluded that they were much too large to be attributed to factors such as the temperature increase in the energy of collision of the molecules, or in the decrease in the viscosity of the solutions [15]. He reached the important conclusion that there was an equilibrium between normal molecules which had the potential to react and those which actually do react, and that B in expression (4) could be identified as the energy needed to create these reactive molecules. He specifically commented on the cane sugar inversion reaction studied by Wilhelmy [11], and used the term 'active cane sugar' for the form that undergoes the reaction. He speculated that the active form was related to the inactive "by displacement of atoms or addition of water". He noted that there must

² One could add an arbitrary function of temperature to equation (3) and recover equation (2) if this function was exactly the same for the forward and backward reactions, but this is an unlikely possibility.

be a 12% increase in the proportion of active cane sugar per degree rise in temperature.

Arrhenius's law is traditionally written

$$k = A \exp (-E_a/RT) \quad (5)$$

where E_a is called the activation energy (which is not a term that was used by Arrhenius), and A is called the frequency factor; or together they are called the Arrhenius parameters. It is often said that the exponential term in (5) can be interpreted as the fraction of molecules with energy greater than E_a . The basis for this is that the population of energy levels is given by the Boltzmann distribution function

$$P(E) = N g(E) \exp(-E/RT) \quad (6)$$

where $g(E)$ is a degeneracy factor for the number of states with energies E , and N is chosen so that the total population is unity. The fraction with energy greater than E_a is obtained by integrating this from E_a to infinity, and this would be equal to the Arrhenius exponential if $g(E)$ was unity. However, this is not true even for collision energies (for which $g(E)$ varies as E^2), so this simple interpretation of the term is incorrect.

A full understanding of the significance of E_a took some time to emerge. There were a number of suggestions that reactions required the formation of intermediate species, but although this is true for certain reactions, there was no evidence for its generality. Marcelin [16] was the first to advance our understanding when he said that molecules in their average state as regards their internal energy were not capable of reacting, and they only became reactive when their internal energy rose above a critical value. Lewis [17] later called the difference between the energy of the average state and the critical state the 'critical increment', and he identified this with E_a . Rice was following a similar line of argument [18]. Tolman [19], in an important paper dealing with the statistical mechanics of chemical reactions, showed that the activation energy could be equated to the difference between the average energy of reacting molecules and the average energy of all molecules.

It is worth emphasising that if a reaction is studied over a short temperature range, then the results can often be fitted by other temperature laws; a straight line relationship between $\ln k$ and $\ln T$ can, for

example, almost always be achieved. The Arrhenius equation is widely accepted because its interpretation leads to the important concept of the barrier to reaction, and the theories which follow from this, rather than because of its superior fit to the data.

The question of how molecules acquire their energy of activation was tackled by several workers, and the most popular early view was that it was provided by infra-red radiation. Trautz [20], Lewis [18,21], and particularly Perrin [22] developed this idea, using Wien's law for the radiation density. This theory was finally rejected (except for reactions which are specifically photochemical) by Langmuir [23] who showed for several examples that the reactants did not absorb light in the frequency region required to reach the activation barrier, and at higher frequencies where they do absorb, there was insufficient radiation density to produce the experimental reaction rate. The fact that an exponential function appears in both the Arrhenius equation and the Wien radiation law is just a consequence of the statistical basis of both laws; one for molecules and one for photons. It was eventually concluded that for most reactions a sufficient concentration of activated molecules could be produced by molecular collisions alone to give the observed reaction rate. An interesting discussion on this point occurred in a Faraday Society Discussion [24]. It is interesting to note that as late as 1920 Tolman [19] in his paper said that the importance of radiation in producing activated molecules was "unescapable"

One can take van't Hoff's approach to reactions further by noting that expression (2) can be written

$$\ln k - \ln k_{\text{A}} = -\Delta G^{\ddagger}/RT \quad (7)$$

where k and k_{A} are the rate constants for the forward and backward reactions respectively. This led Kohnstamm and Scheffer [25] (following less precise ideas of Marcelin [26]) to write a rate constant as

$$k = \nu \exp(-\Delta G^{\ddagger}/RT) = \nu \exp(-\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT) \quad (8)$$

where $\Delta S^{\ddagger}$, and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation respectively, and ν is a constant for all reactions. By equating $\Delta H^{\ddagger}$ to the activation energy, we get the Arrhenius equation if $\nu \exp(-\Delta S^{\ddagger}/R)$ is identified with the frequency factor A . It should be noted that this approach gives rate constants for the forward and backward reactions which are consistent with their ratio being the equilibrium constant, a

property that is not generally held by the collision theories which are described later.

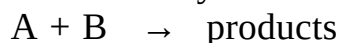
Catalysis

The rate of a chemical reaction can be strongly influenced by adding substances to the medium in which it is carried out. Many examples of this had been discovered early in the 19th century, and in 1835 Berzelius had introduced the concept of a catalytic force (katalyska kraft), to cover many of them [27]. 'The nature of the catalytic force seems to consist essentially in the circumstance that substances are able to bring into activity some affinities which are dormant at this particular temperature, and this not by their own affinity, but by their presence alone.' In his catalytic reactions Berzelius included enzyme processes which had been already identified in fermentation reactions, and the role of metals in heterogeneous catalysis which had been known for a long time; Davy [28], in particular, had noted that platinum and palladium wires glowed in mixtures of air and combustible gases. Berzelius was keen to attribute catalysis to some electrical phenomenon as this was his principal interest at the time.

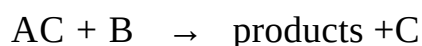
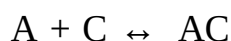
Ostwald took the study of catalysis further, first studying homogeneous reactions which were accelerated by the addition of acids [29]. He was given a Nobel Prize for this work in 1909. Ostwald defined catalysis as the acceleration of a slowly occurring chemical change by the presence of a foreign body, a body which is not necessary for the reaction. He later proposed an alternative definition that a catalyst is any substance that alters the rate of a chemical reaction without appearing in the end product [30]. He also recognised the existence of negative catalysts or inhibitors, which slow reactions by their presence. His most important proposal was that the total energy change in the reaction should be the same with and without the catalyst; it follows that a catalyst will not alter an equilibrium constant, and hence it alters the rate constants of the forward and backward reactions in the same proportion.

Ostwald did not support Berzelius's idea that there exists a catalytic force, and although he had no specific theory of catalysis of his own, he liked to use analogies such as 'the effect of oil on machinery, or of a whip on a horse'. His views that there is no reaction that cannot be catalysed, and that there is no substance that cannot act as a catalyst are too strong for today, but they do emphasise the point that catalysis is a very widespread phenomenon.

One of the most influential workers in the field of catalysis was Paul Sabatier, who in his book 'La Catalyse en Chemie Organique' [31], first published in 1912, emphasised the importance of understanding the mechanistic or chemical interpretation of catalytic action, and this can be quite specific to the reaction in question; he was awarded a Nobel Prize for this work in 1912. The simplest mechanistic case would be where the catalyst forms a complex with one of the reactants, and it is this complex which reacts. Thus if we start with the uncatalysed reaction



then the catalytic mechanism might be



Such a mechanism would alter the energy profile of the reaction; the intermediate AC would be associated with a minimum on the reaction path, but the important point is that the energy barrier from AC + B to products plus C will be lower than the barrier for the uncatalysed reaction. An important point to note is that with the above mechanism the rate of the reaction would depend on the concentration of C; it is not true that catalysts are always effective in very small concentrations.

If the mechanistic role of the catalyst is more complicated than the simple one given above, then it may completely change the route (path) of the reaction. This led Hinshelwood [32] to liken the catalytic role to the opening of a by-pass road with easier gradients. Given the broad range of catalytic mechanisms, we must conclude that the only statement that embraces all catalytic processes is that catalysts alter the topography of the energy surface leading from reactants to products; we say more about such energy surfaces later in this essay.

Collision Theory of Chemical Reactions

Once the atomistic view of chemistry had been established, it was natural to think of chemical reactions as taking place through the collisions of atoms and molecules. In solution this process will be moderated by the solvent; indeed the rate determining step might be the rate of diffusion together of the reactants rather than the energy of their collision. For gas phase reactions, however, an understanding of collision dynamics is essential for the reaction process, and this task began with the work of Maxwell, Clausius and others who developed the kinetic theory of gases in the 19th century. Early theories only treated atoms and molecules as hard spheres.

Two hard spheres with diameters d_A , and d_B , will collide when the distance between their centres is

$$d = (d_A + d_B)/2 \quad (9)$$

and the collision cross section will be

$$\sigma = \pi d^2 \quad (10)$$

The mean relative speed of these molecules at the time of collision can be calculated from the Maxwell-Boltzmann distribution of velocities as

$$v = (8kT/\pi\mu)^{1/2} \quad (11)$$

where μ is the reduced mass of the two molecules, $m_A m_B / (m_A + m_B)$. It follows that the collision frequency per unit concentrations of molecules A and B, which can be equated to the Arrhenius frequency factor, is [33]

$$A = \sigma v = d^2 (8\pi kT/\mu)^{1/2} \quad (12)$$

Note that A depends on T, so that in this theory a strict Arrhenius law ($\ln k \propto 1/T$) would not be found. However, one does not usually have rate constants measured over a sufficiently large temperature range to detect any deviation from the strict law.

The first application of this result to a gas reaction was by Lewis [21]. For the thermal gas phase decomposition of HI he found ‘satisfactory’ agreement with experiment, and for the reverse reaction of H_2 and I_2 , he found ‘moderate’ agreement with experiment. He concluded that the main error in his theory was in the estimation of d, the distance between the centres of the molecules at collision. Guggenheim and Prue [34] analysed more recent data on the decomposition of HI and found that collision theory gave good agreement with experiment if d was 4.12 Å.

A more detailed treatment of the collision theory of reactions was given by Fowler and Guggenheim [35] (see also [36]). By applying the Maxwell-Boltzmann expression to the relative velocity of collisions, it can be shown that the number of collisions per unit volume per unit time in which the relative velocity lies between v and $v+dv$, and the angle between $\underline{v}$ and the line of centres on impact lies between ϑ and $\vartheta+d\vartheta$, is

$$n_A n_B (\mu/2\pi kT)^{3/2} 8\pi^2 d^2 \exp(-\mu v^2/2kT) v^3 dv \sin\vartheta \cos\vartheta d\vartheta \quad (13)$$

If the two molecules are of the same species then this expression has to be divided by a symmetry number of 2.

If we now say that the probability of a reactive collision is $\kappa(v, \vartheta)$, and note that for a bimolecular reaction the number of reactive collisions per unit volume per unit time is $n_A n_B k$, then the second order rate constant is

$$k = (\mu/2\pi kT)^{3/2} 8\pi^2 d^2 \iint \kappa(v, \vartheta) \exp(-\mu v^2/2kT) v^3 dv \sin\vartheta \cos\vartheta d\vartheta \quad (14)$$

This formula is based on the assumption that either the two reactant molecules are of different species, or that if they are of the same species then both molecules react. It also assumes that only one internal state (rotation, vibration, electronic) is relevant for each species (which is not usually the case).

For the two molecules to be approaching one another ϑ must lie between 0 and $\pi/2$. If the probability of reaction is independent of ϑ (an extreme assumption in most cases), we can integrate over ϑ to give the result

$$k = (\mu/2\pi kT)^{3/2} 4\pi^2 d^2 \int \kappa(v) \exp(-\mu v^2/2kT) v^3 dv \quad (15)$$

The kinetic energy of collision is $E = \mu v^2/2$, and changing the variable in (15) to E gives

$$k = (\mu/2\pi kT)^{3/2} (8\pi^2 d^2/\mu^2) \int \kappa(E) \exp(-E/kT) E dE \quad (16)$$

If we now take $\kappa(E)$ to be zero below the energy barrier E_0 , and one above it, then we can integrate (16) to give

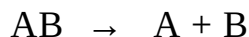
$$k = (8\pi kT/\mu)^{1/2} d^2 (1 + E_0/kT) \exp(-E_0/kT) \quad (17)$$

The energy independent factor is identical to that obtained by the simple collision analysis given above, except for the extra term E_0/kT , which is usually small. In the HI reaction at 556K, for example, this term has the value 0.04.

Although this form of collision theory leads to a broadly satisfactory interpretation of the Arrhenius equation, it requires the adoption of several highly questionable assumptions. In addition, the ratio of the collision theory rates for forward and backward reactions is not equal to the equilibrium constant because there is no explicit treatment of entropy changes in the reaction. However, the Arrhenius form is certainly more robust than is implied by simple collision theory.

To develop collision theory further one has to start by defining a reaction cross section, and determining how this depends on the collision energy and the internal quantum states of the reactants. Some analytical developments have been made along these lines (see Gardiner [36]), but they have been overtaken by the advances that have come along with high speed computers and the work that has emerged from classical trajectory calculations; this will be looked at later.

An interesting application of collision theory was made by Herzfeld [37], who obtained an expression for the rate constant of the unimolecular dissociation process



This work came before an understanding of the role of pressure in such reactions, which we will discuss later. Herzfeld used the fact that the ratio of the backward to the forward rate constants was equal to the equilibrium constant, and he took the backward rate constant from collision theory. The equilibrium constant could be calculated from statistical mechanics, the case of diatomic molecule dissociation having been analysed by Stern [38]. Herzfeld obtained the result

$$k_u = N(kT/h)(d^2/s^2)(1 - \exp(-h\nu/kT))\exp(-\Delta E/RT) \quad (18)$$

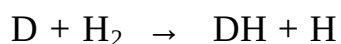
where d is the collision diameter for the atomic collision, s is the diatomic bond length, ν is the vibration frequency of the diatomic molecule, and ΔE its dissociation energy. Herzfeld went on to equate d and s , which is certainly not acceptable. The most important feature of this work was that by using equilibrium theory he obtained an expression containing the factor (kT/h) , which was later to enter the transition state theory developed by Eyring and others.

The Potential Energy Surface

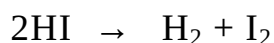
From the Arrhenius interpretation of reaction rates we have a picture of a reaction proceeding along a potential energy path and crossing a barrier. The first developments of this idea were by Marcelin [39], and Rodebush [40], who refer specifically to the rate at which the system crosses a critical surface in phase space; a concept used in statistical mechanics in which the phase space variables are the coordinates and momenta of the atoms in the system.

For the collision between two atoms the potential energy is just a function of the distance between the two, but for collisions involving molecules the potential energy will depend on the molecular orientations, and also on the internal geometries of the molecules themselves. This is where the important concept of a potential energy surface comes in (some use the term hypersurface to emphasize that it is multidimensional). This is the energy of the reacting system as a function of a set of coordinates which define completely the instantaneous relative positions of all the atoms in the molecules. If there are N atoms in the reacting molecules there will be $3N-6$ relative position coordinates; $3N$ is the number needed to define the absolute positions of all the atoms in space, and we can subtract from this the 3 coordinates of the overall centre of mass and the 3 which define the overall orientation of the system.

Fritz London [41] was the first to make some conjectures about the nature of such surfaces, indeed he was the first to state explicitly that the majority of chemical reactions could be considered as the motion of atoms on a single surface that extended from reactants to products; what we call an adiabatic process. There are reactions that can only be interpreted by considering jumps between surfaces, but these non-adiabatic processes are a small fraction of the total. London examined the general features of simple gas phase reactions involving only three or four atoms [42], such as



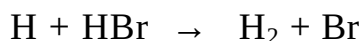
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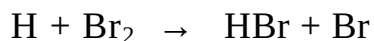
From the new theory of the chemical bond [43], which he had jointly authored, he concluded that for certain three atom reactions of the above type, which are model substitution or abstraction reactions, the lowest energy barrier on the reaction path occurs when the atoms are collinear.

More detailed calculations on such potential energy surfaces, with the collinear restriction, were made by Eyring and Polanyi [44], using a

similar Heitler-London model. As well as the hydrogen atom exchange they looked at the two reactions



and



The collinear H_3 potential energy surface possesses a col or saddle point in the region where the two H-H distances are equal (both about $1\text{\AA}$), and this leads to an important extension of the one-dimensional Arrhenius view; not all reactions pass exactly through the lowest point on the saddle, but they do pass through the saddle region. The curve that passes from the bottom of the reactant valley, through the saddle point, and emerges at the bottom of the product valley is called the reaction coordinate; this can be defined for any number of coordinates although its precise form depends on the coordinate system used.

Eyring and Polanyi went on to consider the dynamics of motion on their potential energy surfaces according to classical mechanics, and a more thorough analysis was given soon after by Pelzer and Wigner [45] who stressed the importance of the region around the saddle point. For a particular set of initial conditions of the reactants (these will be the initial positions and momenta of all the atoms which according to classical mechanics will determine a particular outcome), it is in principle possible to calculate a trajectory across the potential energy surface. Some of these trajectories will end up back in the region of the reactants, and will be representative of a non reacting collision, and others will pass over the saddle to the product region and be representative of a reactive collision. Pelzer and Wigner derived an expression for the rate of reaction by considering the number of trajectories that passed over the saddle. For the collinear atom plus diatomic molecule collision of the type examined by Eyring and Polanyi, a trajectory can be pictured as the motion of a ball rolling over a surface, but only if the surface is drawn in skew coordinates; for three atoms of equal mass the appropriate angle is 60° .³

³ This was pointed out by Eyring and Polanyi but they had an incorrect sign in their analysis so their axes were at an angle of 120° rather than 60° . The correct result appears to be due to J.O.Hirschfelder in his PhD Dissertation (Princeton University, (!935). The basis of this result is to find orthogonal coordinates which give the classical kinetic energy as a sum of diagonal terms.

We might now take the view that the degree to which we ‘understand’ a chemical reaction (at least in the gas phase) is the degree to which it can be interpreted by a potential energy surface, using one of the dynamical theories which allow us to calculate the rate expected from that surface. The potential energy surface can, in principle, be calculated from the quantum mechanical Schrodinger equation for the electrons of the reacting molecules, and we can deduce some information from experiments. For reactions in solution, we can usually obtain only a little information about the full surface; for gas reactions it may be possible to obtain quite a lot of information.

Transition state theory

In all types of experiment there is some loss of idealised data due to limitations in the measuring equipment; the temperature range may not be as large as one would like, there is always some averaging over the conditions of the reactants or the state of the products. In highly averaged experiments, particularly those in which only the temperature is a specified condition, we expect statistical theories to be very useful, and the most important of these is called transition state theory.

The work of Eyring and Polanyi [44], and of Pelzer and Wigner [45], and indeed most of the people who adopted Arrhenius’s view that reactions were due to activated molecules, lead to a thermodynamic view of reactions which we call transition state theory (also called activated complex theory) [46,47,48].

Evans and Polanyi say that their work was forshadowed in several earlier paper [49,50,51].

Evans and Polanyi were the first to use the term transition state to refer to the region of the

potential energy surface in the vicinity of the saddle point, and they and Eyring derived a rate constant for the reaction by assuming that the transition state (or activated complex) was in equilibrium with the reactants. Of course there cannot be a true equilibrium because there can be no uniquely defined area in which the transition state can be said to exist; it is only defined by the coordinate surface that passes through the saddle point and is orthogonal to the reaction coordinate. The transition state is at best a transient species whose lifetime is related to the rate of passage across the barrier, although with modern fast spectroscopic techniques the properties near the barrier can be examined.

If X represents the transition state arising from a bimolecular reaction between A and B, then the equilibrium constant is

$$K = [X]/[A][B] \quad (19)$$

We can obtain an expression for this equilibrium constant using formulae derived from statistical mechanics; it can be written

$$K = (q_X/q_A q_B) \exp(-E_0/kT) \quad (20)$$

where the quantities q are called partition functions, and E_0 is the height of the potential energy barrier. There are specific formulae for the partition functions of molecules which take into account their translational, rotational, and vibrational motion, and any electronic degeneracy they may possess. The important question is what to use for that part of the partition function of the transition state which represents the motion along the reaction path. In the original formulation due to Eyring this was taken as the translational partition function of a molecule confined to a one-dimensional box of length δ , and the final expression for the rate constant was shown to be independent of δ . In an alternative treatment, perhaps more difficult to justify, it has been taken as the vibrational partition function for a one-dimensional harmonic oscillator in the limit that the vibrational frequency approaches zero. Both methods lead to the same answer for the rate constant, namely [52]

$$k = (kT/h) (q^\# / q_A q_B) \exp(-E_0/kT) \quad (21)$$

where $q^\#$ is the partition function for the transition state except for that part representing motion along the reaction coordinate.

The only modification to the above theory which was in the original work was the introduction of a multiplying factor κ in expression (21) called the transmission coefficient. This took into account the possibility that some systems that passed through the transition state might not end up as products, but would be turned back by other features of the potential energy surface and emerge again as reactants. One would not expect κ to be much less than unity, but a weakness of the original theory was that there was no way of determining its value. In a much later development of the theory it was argued that it was not necessary to define the transition state by a surface that passed through the saddle point. If another surface, orthogonal to the reaction coordinate, was selected so that

all trajectories which passed through it went on to emerge as products, then κ would be unity. This led to a modification called variational transition state theory (VTST), in which a surface was chosen to minimise the subsequent calculation of the rate constant [53] This theory is particularly appropriate for reactions which do not usually have a saddle point on the potential energy surface, such as molecular dissociation reactions and the bimolecular addition of free radicals.

The problem with VTST is that the transition state surface is not independent of the energy at which the reactants collide, and hence it must be temperature dependent. It is therefore necessary to formulate the theory in terms of phase space rather than coordinate space, as in the early statistical theory of Marcelin [39], and later of Wigner [54].

The development of VTST is largely due to Keck [55], although there were others having similar ideas at the time, and later there were further generalisations. In his review article Keck shows how his theory relates to several other theories of reaction rates, including conventional transition state theory. He also deals in detail with the problem of three-body recombination.

Unimolecular Reactions

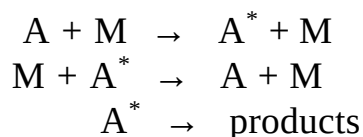
A unimolecular reaction is one represented by the process



but the rate of such a reactions may not be proportional to the concentration of A, that is be a first order reaction. Indeed in the early history of gas kinetics it was not certain whether first order reactions should exist. If A is a normal stable molecule then there must be some intervention to make it undergo a reaction. This may, for example, be the absorption of light, or, more commonly, it is the effect of molecular collisions, either by some species that is not chemically involved in the reaction, or between molecules A themselves. To understand unimolecular reactions one needs to understand the mechanism through which A first has enough energy to react, and then does so.

A characteristic of unimolecular gas reactions is that their apparent order depends on the pressure of the system. Lindemann [56] was the first to

suggest that such reactions could take place by collisions,⁴ and Hinshelwood [57] explained why first order behaviour was maintained down to lower pressures than would be expected on the basis of simple collision theory. The so-called Lindemann-Hinshelwood mechanism is described by the following equations



A^* is a molecule which has sufficient energy to give products. If the rate constant for collisional excitation is k_1 , and for de-excitation is k_2 , and k_a is the rate constant for the formation of products from A^* , then in the steady state (when the amount of A^* is constant), the effective first order rate constant for the disappearance of A is

$$k_u = k_1 k_a / (k_2 + k_a / [M]) \quad (22)$$

In a gas phase reaction the concentration of M will be proportional to the pressure.

In the so-called high pressure limit ($k_2 > k_a / [M]$), the reaction will be strictly first order, with a rate constant of ($k_1 k_a / k_2$); at low pressures the reaction is second order, the rate being $k_1 [A][M]$. The effective first order rate constant k_u falls off with decreasing pressure from $k_1 k_a / k_2$ to $k_1 [M]$, and a graph of this against pressure is known as the fall-off graph. The position of the fall-off region in this graph provides a measure of the relative importance of the energizing-deenergizing process and the rate at which A^* gives products.

Although the Lindemann-Hinshelwood mechanism explains the passage from high to low pressures, it simplifies the problem by assuming that there is a single species A^* which can be assigned a rate constant. But the population of A^* cannot be taken to conform to the Boltzmann formula, that is to be in a true equilibrium with A. There are several reasons for this but the main one is that for A^* to react its energy must be in particular modes. Molecules that undergo reaction will be those whose extra energy is in vibrations rather than translations or rotations; moreover, not all vibrational modes will be equally effective. Important

⁴ J.A.Christiansen also proposed the Lindemann model in a PhD thesis titled Reaktionskinetisch Studier, of the University of Copenhagen in 1921.

early work by Chambers and Kistiakowsky [58] showed that for the isomerisation of cyclopropane to propene, only between one half and two thirds of the 21 vibrational modes of cyclopropane were effective in leading to reaction.

Theories of unimolecular reactions have to tackle the energizing-deenergizing processes, and the rate of reaction of A^* . The first theory to do this is known as the RRK theory after the work of Rice and Ramsperger [59], and of Kassel [60]. Central to their work is the distinction between a molecule which has sufficient energy to undergo reaction (A^* , an energised molecule), and one that will pass quickly to products because the energy is in a favourable bond or bonds; this is called the activated complex, $A^\ddagger$. The passage from A^* to $A^\ddagger$ is assigned a rate constant k_a , and the passage of $A^\ddagger$ to products a rate constant k_3 . However, in this theory it is always assumed that $A^\ddagger$ goes very rapidly to products so that the rate of reaction is independent of k_3 .

Marcus developed a quantum mechanical version of this theory, which is referred to as RRKM theory [61]. Its main feature is to recognise the importance of zero point vibrational energy as this is unavailable for the reaction process.⁵

In RRKM theory the energy dependence of k_a is calculated by taking the available energy in A^* and determining how much of this is in a particular vibrational mode that leads rapidly to reaction. Assuming that the vibrational states can be taken in the harmonic model, then if there are s oscillators having j quanta, the probability that a particular oscillator has m quanta is equal to

$$(j-m+s-1)!j!/(j-m)!(j+s-1)! \quad (23)$$

and if j is very large this is approximately equal to

$$((j-m)/j)^{s-1} = ((E - E^*)/E)^{s-1} \quad (24)$$

⁵ A molecule does not have to be very large before its zero point energy is bigger than its dissociation energy, although the difference between the zero point energy of the reactant and the products is usually small compared with the dissociation energy.

where E is the total energy and E^* is the minimum energy that is necessary for the reaction to occur.

The theory further assumed that energy passes between modes very rapidly so that the rate at which energy appears in the particular mode is proportional to expression (24) (ie k_a is proportional to (24)). The amount of energy needed in the vibrational modes to produce a reaction is usually too large to validate the harmonic model, but in a strictly harmonic model there would be no energy transfer between modes. It is therefore the anharmonic part of the potential energy which validates the assumption that energy flows rapidly between modes.⁶

Although the essential element of RRKM theory is that k_a depends on energy, the basis for its success is that s , the number of normal modes relevant to the reaction, is treated as a parameter. As mentioned above, the value of s which gives agreement with the fall-off curve is usually about half the total number of normal modes possessed by the molecule.

The literature on unimolecular reactions is extensive, and is thoroughly treated in several books and reviews (eg the book by Forst [62]).

Classical or Quantum mechanics

We know that the dynamics of individual atoms and molecules is governed by the equations of quantum mechanics, yet most practical theories of reaction rates are based on classical mechanics, the mechanics of massive bodies. It is important therefore to know why classical mechanics is successful, and to know when it fails.

In quantum mechanics particles of momentum p have an associated wave whose wavelength λ is given by the de Broglie equation

$$\lambda = h/p \quad (25)$$

⁶ An alternative approach to the vibrational energy was given by Slater [6] who took a strictly harmonic model (ie no energy transfer between modes) and calculated the rate at which the cooperative motion of the modes led to a critical displacement appearing in a breaking bond. This theory does not seem to be as successful as RRKM theory and is now little used.

A quantum mechanical approach is usually required if this wavelength is large compared with the range over which particles interact; typical classical systems are those for which the wavelength is small even by comparison with the size of the body.

Wave motion is characterised by diffraction and interference, which are easily recognised, and by the phenomenon of tunnelling which is less obvious; none of these is found in classical mechanics. In classical mechanics an initial discrete set of coordinates and momenta of interacting particles will evolve into a specific discrete final set of these variables. In quantum mechanics one cannot have a system with discrete coordinates and momenta; there is a distribution of these variables which can be represented by wave packets, and under the influence of potentials an initial wave packet will evolve to a final wave packet.

At standard temperatures in the gas phase molecules typically travel at about the speed of sound, say 300m/sec, and a hydrogen atom at these speeds have a wavelength of about 10^{-9}m (10Å). We would therefore expect hydrogen atoms to easily show quantum phenomena, but for atoms heavier than carbon, say, the wavelengths will typically be less than 1Å and quantum behaviour will be difficult to observe. However, even for light atoms one can only observe diffraction and interference in experiments for which the momenta of the particles are highly discrete; one does not observe these wave phenomena for a continuum of wavelengths (eg for white light). It follows that chemical reactions in which the molecules have a range of velocities determined only by the temperature of the system can usually be interpreted by classical dynamics. The only exception to this statement is for the phenomenon of tunnelling. This is the property of quantum systems to pass through a potential barrier even if their total energy is less than the height of the barrier. So, even for a temperature averaged system, light atoms such as hydrogen can be transferred in a reaction if their energy is less than the activation energy. The usual way that this is established is to show that isotope substitution (eg D for H), slows a reaction much more than is expected from a classical picture. Also, if there is tunnelling a reaction will not follow the Arrhenius law for variation of the rate constant with temperature. There is certainly evidence for tunnelling being significant for the $\text{H} + \text{H}_2$ reaction, and for several proton transfer reactions in solution [63,64].

The Crossed Beam Experiment

In temperature averaged chemical reactions there are usually only two quantities that can be extracted from experimental data, namely the two Arrhenius parameters. For any substantial understanding of the potential energy surface this is clearly inadequate. Other types of experiment must be used to extract such information, and most of these are based on the crossed beam experiment. The origins of beam experiments can be traced back to Rutherford, who showed by passing α particles (He^{2+}) through metal foils that atoms possessed a small positively charged nucleus. The first crossed beam experiments to determine the potentials between atoms (alkali metals and mercury), were by Fraser and Broadway in 1933 [65], and the first experiments to study chemical reactions were by Taylor and Daz on $\text{K} + \text{HBr}$ in 1955 [66].⁷

The normal set-up for the experiment is to have two beams of atoms or molecules directed along lines at right angles to one another, which meet in a collision chamber, and the products of the collision are detected and analysed at various angles in the plane of the incident beams. A laser beam is often applied to the collision region at right angles to this plane.

The density in the collision chamber is sufficiently low that the outcome can be explained by single collisions of the reactants. Ideally both incident beams should have narrowly defined velocities, so that their collision energy is narrowly defined. Again, ideally, the reactants should be in specific rotational, vibrational and electronic quantum states. The products should be analysed to give their velocities, and their quantum states, and this should be done in narrowly collimated beams over a range of angles of the detector.

The experiment leads to reaction cross sections (with the scattering angle as variable) for each value of the collision energy, and for specific quantum states of the reactants, with as wide a range of the collision energy as possible. This is a huge amount of information, which, in principle, would specify in fine detail the features of the potential energy surface. However, any lack of resolution in the energy spread of the reactants or products, or lack of resolution in the scattering angle will ultimately lead to a loss of detail in the potential energy surface. Some loss is inevitable in the experiment, not least because there is a compromise between angular resolution and the need to have sufficient intensity in the exit beam.

⁷ A slightly earlier crossed beam study of the reaction between Cs and CCl_4 by Bull and Moon did not have velocity resolution in the beams [7].

The main snag in determining the potential from the experimental data is that there is no direct route for this (we say there is no inversion procedure). The only way to determine the potential is by the indirect route, which is effectively by trial and error. Given a potential we can calculate the reaction cross sections that this would lead to. If these agree with the experimental data we conclude that the potential is accurate within the limits of the data.

Classical trajectory calculations.

Given a potential energy surface, or more specifically given an algebraic function that describes the energy of the surface with the coordinates as variables, we can calculate the dynamics on that surface by classical or quantum mechanics. We have already seen that quantum features do not emerge in most experiments; putting that another way we can say that if one wants to observe quantum features then special systems have to be studied and special care taken to obtain the highest resolution. Classical mechanics has therefore been used much more extensively than quantum mechanics to interpret chemical reactions, even those arising from crossed beam experiments.

Potential energy functions for molecular reactions are almost always sufficiently complicated that numerical methods have to be used to determine the resulting dynamics, using either classical or quantum theory. This was clear from the earliest studies of potential surfaces by Polanyi, Eyring and others, but the computational facilities were not available at that time. Hirschfelder and co-workers [67] were the first to calculate a trajectory on the collinear $\text{H} + \text{H}_2$ surface, and showed how it became trapped in a shallow minimum at the top of the surface (a minimum later shown to be an artefact of the method of calculation). Such 'by-hand' calculations were extremely laborious and could not be done in sufficient numbers to explore the dynamics. The first serious numerical studies of classical trajectories were by Wall and co-workers in 1958 [68], using the ILLIAC computer and the Runge-Kutta-Gill method for numerical integration of Hamilton's equations. They calculated several hundred trajectories for the collinear $\text{H} + \text{H}_2$ surface, and then in 1961 [69] calculated 700 trajectories for the three dimensional surface of this reaction. Sufficient trajectories to determine a statistically significant rate constant were calculated by Karplus and co-workers [70], using a more accurate potential surface. The technique has not changed greatly to the present, and is well described in reviews [71]. The first widely available computer programs were for atoms colliding with diatomic

molecules, but within about 10 years collisions between atoms and triatomic molecules were being studied [72].

In a classical trajectory study there are a certain number of variables that have to be chosen to specify the initial conditions. Some of these have values determined by the conditions of the crossed beam experiment; the relative velocity of the colliding species, for example, and perhaps the quantum state energies of the reactants. Other quantities are unspecified by the experiment such as the initial orientations of the molecules with respect to the collision axis, and the perpendicular displacement of the initial collision vector from this axis (called the impact parameter). The unspecified parameters are chosen either serially or randomly to cover the full variation they may have, with appropriate statistical weighting, and a set of trajectories is calculated covering these.

The number of trajectories that must be calculated for each set of collision energies and initial quantum states to give statistically significant results depends on the type of analysis that is made of the product states. For example, if one is just interested in whether there has been a chemical reaction or not, then about 1000 trajectories may be enough. If one is interested in knowing the energy states of the product molecules then one could well ask for about 100 trajectories for each possible energy state. If one is interested in the scattering angle that these products and their energy states emerge from the collision, then one would need this number for each band of angles that is covered. In short, the number of trajectories depends on the experimental data being examined or predicted.

By calculating the fraction of all trajectories leading from specified initial conditions to specified final conditions, and multiplying by the area spanned by the impact parameter, one obtains cross sections for specified initial conditions leading to specified final conditions, and these can be summed or averaged to give quantities measurable in experiments. For example, cross sections for scattering into specified angles of emergence (in a relative coordinate system), which are called differential cross sections, can be summed over all angles to give total cross sections; total cross sections can be averaged over initial states and summed over final states to give reaction cross sections, $S(E_r)$, for collision energies E_r . The rate constant for a temperature averaged system is obtained by further averaging of these cross sections over the collision energy, using the Maxwell-Boltzmann formula. The final expression has the form

$$k = (8/\pi\mu(kT)^3)^{1/2} \int E_r S(E_r) \exp(-E_r/kT) dE_r$$

(24)

However, one might conclude at the end of such calculations that a lot of work has gone in to produce a single quantity, moreover, a quantity that could perhaps be obtained directly by one of the transition state theories. In fact, one is unlikely to embark on trajectory calculations unless one is interested in quantities other than the rate constant; for example the experiment may show the populations of different energy states in the products, and this is most easily obtained from trajectories. Seminal papers along this line were published by John Polanyi and co-workers in 1969, in which they showed how the product energy in an atom-diatomic reaction was disposed according to the position and height of the potential energy saddle point [73,74].

Conclusions

I am aware that there are several important topics within the field of chemical reactions which I have not dealt with, or have touched on only briefly: photochemistry (particularly time-resolved), explosions, reactions in condensed phases (particularly atom recombination), and quantum mechanical calculations, are some of the more obvious. Each of these has been associated with key ideas that advanced our understanding of the subject. But finally I should be clear on what is the most important step for understanding the rate of a reaction, and I have no doubt that this is to be able to write down the mechanism in terms of the primary chemical steps which occur. Many chemical reactions are multi-step, but detailed understandings, and particularly numerical calculations, are always made on single step reactions.

I have read many books and reviews specializing in reaction kinetics, and would like to acknowledge particularly the information I received on historical matters from two of these. The first is Partington's epic volumes 'A History of Chemistry' [75], and the second is Laidler's 'The World of Physical Chemistry' [76]. I also acknowledge many helpful discussions with my colleague Tony Stace.

I never worked closely with Per-Olov

Lowdin, but I sometimes sent preprints of my papers to him to see if they were nonsense; occasionally they were.

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