MODERN LIQUID KINETICS – NOTES

Modification of gas phase reaction kinetics to suit reactions in the condensed phase, or those at interfaces. Less well understood. The main difference is that in the gas phase reactive molecules are separated by space, while in solution they are separated by solvent molecules that might, and often do, affect the reaction.

Reactions are still defined in terms of a rate (in terms of concentration) and a rate constant, according to the Arrhenius Equation. Typical types of reaction to be considered:

- Relatively few reactions occur in both the gas phase and in solution, but when they do they occur at similar rates and show little solvent dependence. An example is $2N_2O_5 \rightarrow 2N_2O_4 + O_2$.
- Some reactions do not occur in the gas phase at all, and have rates which vary greatly with solvent, e.g. $Et_3N + EtI \rightarrow Et_4N^+ + I^-$. In this particular reaction, the rate increases greatly as the solvent becomes more polar, as the ions formed are stabilised in polar liquids.
- Reactions between ions. It takes a very large amount of energy to form ions in the gas phase, but a polar solvent decreases this. They can also be formed electrochemically. Thus, these reactions are usually confined to the liquid state (with a few exceptions).
- Some reactions in solution are very slow, although some are extremely fast. Can this be understood using a single basic theory?
- Free radical reactions are often very fast, and are considerably different in the gas and liquid phases. Recent research into Spin Chemistry by observing these reactions as they proceed, and studying the effect of magnetic fields on them. Pairing of radicals (e.g. $CMe_3 + CMe_3$) requires that the spins are correctly orientated antiparallel (introduces spin distribution statistics).
- Fluorescence quenching reactions. Absorbance of light and the emitting radiation from a higher electronic state. Anthracene is a good example – on its own spontaneous emission will occur, but in the presence of another molecule (e.g. perylene) the excitation energy is transferred to this instead of being radiated (quenching). This is called an energy transfer reaction, and these are some of the fastest reactions known in solution.

Comparison of Liquids and Gases –

Average Separation of Molecules:
(i) Gas Phase
Ideal gas, $pV = nRT$, or $pV_m = N_Ak_BT$
Volume occupied by a single molecule is the molar volume divided by the number of molecules it contains. This implies that each molecule is separated from its neighbours by the cube root. Taking p as atmospheric pressure and T = 300K we obtain:
$$(V/N)^{1/3} = 4 \times 10^{-9}m.$$
(ii) Liquid Phase
Clearly separation will depend on concentration. Consider the concentration needed to make the average distance between the molecules the same as in the gas at 1 atm.
A 1 mol m^{-3} solution would contain 6×10^{23} molecules. Thus the volume occupied by each molecule is $^1/_{Nc}$, where c is the molar concentration (in mol m^{-3}). Thus to obtain the same separation as in the gas phase we require that:
$$(N_A \times c)^{-1/3} = 4 \times 10^{-9}.$$
This gives c = 26 mol m^{-3}, i.e. 0.026M.

However, this only deals with the distance between solute molecules. Concentrations of solvent are typically 10M, which is 10^{-4} mol m^{-3} giving separations of 5×10^{-10}m. This also implies that the average solvent-solute distance is the same (since almost all the molecules present are solvent). Interestingly, this figure is less than the size of a typical molecule, which implies that the molecules in liquids are essentially touching one another (whilst moving around dynamically).

Fraction of the total volume occupied by Molecules:
(i) Gas Phase
Volume of a molecule approximately equals the molecular diameter cubed, i.e. $(0.4 \times 10^{-9})^3$. The volume available to the molecule will be the distance between the molecules cubed, i.e. $(4 \times 10^{-9})^3$. This gives the fraction of space occupied as 0.001, i.e. lots of space between the molecules which travel about unimpeded between collisions.

(ii) Liquid Phase
Again, diameter over separation cubed gives approx 0.5 for the fraction of space occupied. Thus, about half the space is full of molecules – very crowded.

How far do Molecules travel between collisions:
In the gas phase this is the mean free path,

$$\lambda = \frac{kT}{(\sqrt{2})\sigma P}$$

Where σ is the molecular diameter. At P = 1 atm and 300K this gives $\lambda = 6 \times 10^{-8}$m. This is about 100 molecular diameters.

In the liquid phase the density is about 1000 times that in the gas phase, which implies that the average distance a molecule travels between collisions is about 6×10^{-11}m (only 0.1 molecular diameters).

Collision Frequency:
In the gas phase the time between collisions is given by the mean free path divided by the average velocity, and the collision frequency is the reciprocal of this. This gives a value of about 10^{10} s^{-1}.

In solution we could again use the fact that the density is about 1000 times higher, which would imply a value of 10^{13}s^{-1}. This same figure can also be obtained using a different argument. As seen above, molecules in solution almost touch one another. This means that every time a molecule vibrates, which it does at a typical frequency of 10^{13}Hz, it collides with an adjacent molecule – there are about 10^{13} collisions a second, or one every 10^{-13}s. Since reactions can occur when molecules collide, the potential for very fast processes is seen. The fact that many reactions are not nearly as fast implies that other factors apply to slow things down, although these do not apply to all reactions.

Diffusion in Solution

(i) Translational Diffusion
In the gas phase this occurs comparatively easily and its rate can be calculated using the kinetic theory of gases. But both here and in solution, observation tells us that molecules tend to diffuse from regions of high concentration into ones where there are not. It is also apparent that the rate at which this occurs depends on how rapidly the concentration varies with distance, the concentration gradient dc/dx. This is expressed by Fick's 1st law of Diffusion, which relates this to J, the flux (number of moles of molecules passing through unit area in unit time) –
$$J = - D\left(\frac{dc}{dx}\right)$$
D is an important constant characteristic of the liquid and known as the Diffusion Coefficient. Its units are m^{2}s^{-1}. It is related to the viscosity, η, of the solution (viscosity being the bulk property which reflects diffusion at the molecular level) through the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta a}$$ | Where a is the molecular radius

It is interesting now to investigate how far a solute molecule in solution travels in a given time. (Strictly to do this we should use Fick's 2nd Law of Diffusion which gives a relation for dc/dt, but it will be of no further use to us and here we shall simply quote the result). Because the motion in

the liquid is so haphazard and random, all the molecules move different distances, and the best we can do is define a root mean square distance travelled, $\bar{x}$: $\bar{x} = (2Dt)^{1/2}$

This can be used to show that it takes a day for a molecule to move about 1cm in solution! Clearly, translational diffusion is extremely slow.

(ii) Rotational Diffusion
For completeness, this should be mentioned, even though it will not be used. A molecule typically takes 10^{-10}s to rotate, which has been shown to be slower than the number of collisions – this is why rotational energy is not usually quantised in solution. Although they do no rotate freely, they do rotate in a diffusive manner. This is particularly relevant for NMR spectroscopy (related to spin-lattice relaxation time).
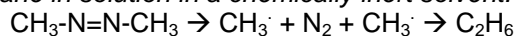
Basic Concepts of Reactions in Solution
Start from the assumption that molecules must collide to react, but in the liquid phase this is determined by the translational diffusion process we have discussed. We must also remember that the liquid phase is also crowded. This means that to move away from one point to another in solution, a molecule must move others out of its way. This is clearly an activated process (requires energy), so an energy barrier must be overcome (typically 10-15 kJ mol^{-1}) to move from one minimum energy position to another. Incidentally, this is why the viscosity of a liquid varies with temperature.

In turn, this implies that if two molecules have diffused together, they are likely to remain together and make many collisions before they can separate again by diffusion – the solvent simply keeps them together in a way which cannot happen in the gas phase. This is termed the "solvent cage".

<u>Evidence for the Cage Effect –</u>
(i) Photolysis of diazomethane in solution in a chemically inert solvent:
$$CH_3\text{-}N\text{=}N\text{-}CH_3 \rightarrow CH_3^. + N_2 + CH_3^. \rightarrow C_2H_6$$
The exact same reaction with occur with deuterated diazomethane, forming C_2D_6.
Taking a 1:1 molar mixture of the deuterated and undeuterated, we would expect a mixture of 3 products (since now CH_3CD_3 could form). This does not occur, and shows that radicals do not exist long enough to move through the solution to meet a radical of a different type – they react within the solvent cage.

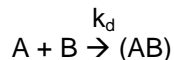*(ii) Photodissociation of iodine in solution*
It is possible to observe the loss of I_2 molecules per photon of light absorbed (the quantum yield). In the gas phase, this equals 1 (i.e. atoms form and move apart without recombining). In hexane, this drops to 0.66, i.e. some I atoms recombine to form molecular I_2 before they can separate.

Increasing the energy of the light absorbed by decreasing the wavelength increases the value – the atoms are less likely to recombine in the solvent cage. This is because the molecule is formed with far too much energy simply to dissociate and the excess energy is given to the I atoms formed on fragmentation – they blast their way through the surrounding solvent cage and have less probability of reacting within it.
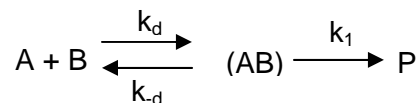
Finally, we increase the viscosity of the solution to make it more difficult to escape the cage: most of the I atoms now recombine in the cage.

Activation and Diffusion Controlled Reactions
We have seen that when a pair of molecules comes together in solution they remain together whilst a large number of collisions occur. There is therefore something special about them and we term them an "encounter pair". We write its formation as:
$$A + B \xrightarrow{k_d} (AB)$$

Where k_d is the rate constant for the diffusion of the molecules together. Now the molecules might react to form product with a first-order rate constant k_1, or they may separate again if no reaction occurs.

$$A + B \quad \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} \quad (AB) \xrightarrow{k_1} P$$

Now, providing that the reaction is occurring continuously we can treat the encounter pair as a reaction intermediate and assume that its rate of destruction to form product, or to re-form the separated reactants greatly exceeds its rate of formation. We may then apply the steady state approximation to the kinetics of the system:

$$\frac{d[AB]}{dt} = k_d[A][B] - k_{-d}[AB] - k_1[AB] = 0$$

$$\therefore [AB] = \frac{k_d}{k_1 + k_{-d}}[A][B]$$

And the overall rate of reaction is given by:

$$\frac{d[P]}{dt} = k_1[AB] = \left\{ \frac{k_1 k_d}{k_1 + k_{-d}} \right\}[A][B]$$

But experimentally we find the reaction is 2nd order with:

$$\frac{d[P]}{dt} = k_{exp}[A][B]$$

By comparison of the two equations we obtain:

$$k_{exp} = \frac{k_1 k_d}{(k_1 + k_{-d})}$$

Now consider two extreme cases:

(i) The **activation-controlled reaction** where $k_1 << k_{-d}$. This is the most common type of reaction in solution found, for example, in most preparative chemistry in which the pair is more likely to separate without reaction than to react. The inequality implies that:

$$k_{exp} = k_1\left(\frac{k_d}{k_{-d}}\right) = k_1 K_d$$

Where K_d is the equilibrium constant for the diffusive step. Both k_1 and K_d are temperature-dependent but we have seen that the activation energy for diffusion is small and we can ignore changes in K_d at normal temperatures. This implies that the overall rate of the reaction depends on the rate constant for product formation, and through the temperature dependence of the rate constant k_1 on its activation energy.

(ii) The **diffusion controlled reaction**. Here the rate of break up of the encounter pair << the rate at which it reacts to form products, $k_{-d} << k_1$, implying that:

$$k_{exp} = \frac{k_1 k_d}{k_1} = k_d$$

That is, the rate of the reaction is entirely controlled by the rate at which the reactants come together, with reaction occurring every time that this happens. This is the case provided that $E_A << E_d$; that is the activation energy for reaction does not have to be zero but rather less than the energy needed for the reactants to separate again. These reactions are obviously very much faster than those in the first category and are termed "fast reactions in solution". Some examples:

  a) The combination of small free radicals (larger ones may have considerable activation energies as a result of steric hindrance etc). This can be very important in radical-initiated

polymerisation, for example, whilst many human illnesses are now known to involve free radicals.
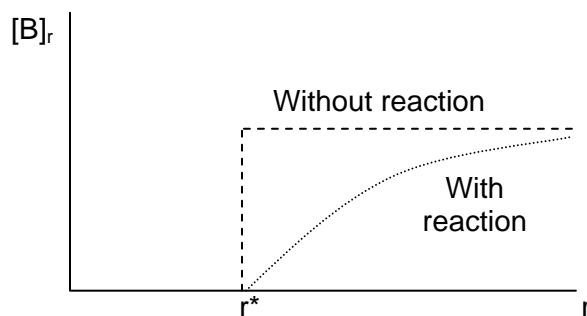
b) Reactions involving energy transfer, such as the quenching of the fluorescence of molecules.

Diffusion Controlled Reactions

Calculation of the rates of diffusion-controlled reactions –
We need, as in the gas phase, to calculate the number of collisions the reactant molecules make with one another. Our basic model is similar to that we use in the gas phase: we initially consider a static molecule A which is immersed in a solvent which contains reactant B molecules, and we consider that when B ones come within a critical distance r (known as the "encounter distance") of A they react.

When the reactants diffuse together and react this disturbs their local concentration and establishes a concentration gradient:

And we know from Fick's First Law that this creates a flux of material (in mol s^{-1}) through the solution which is given *per unit area* by:

$$J = D_B(dc_B/dx)$$

This implies a flux of $N_A J$ molecules s^{-1}, where N_A is the Avogadro number. We now have to remember that B can approach A from any side; assuming spherical symmetry.

Total flux of B towards A through a sphere of radius r = flux per unit area x the surface area of the sphere.

$$J = 4\pi r^2 J N_A = 4\pi r^2 N_A D_B \frac{d[B]}{dr}$$

Where D_B is the diffusion coefficient of the B molecules.
Re-arranging we obtain:

$$d[B] = \frac{J}{4\pi D_B N_A} \frac{dr}{r^2}$$

We can now calculate the concentration of B at any distance r from A:

$$\int_{[B]_r}^{[B]} d[B] = \frac{J}{4\pi D_B N_A} \int_r^\infty \frac{dr}{r^2}$$

The integration limits come from the fact that when r tends to infinity, $[B]_r$ tends to [B], the bulk value. Note that J is independent of r. This may seem strange from the equation we wrote above, but look at the diagram – the same three molecules which pass through the sphere of radius r would also pass through a smaller one since none are lost to reaction before they reach the critical value r*.

This gives:

$$[B]_r = [B] - {}^J/4\pi D_B N_A r$$

But now we introduce the fact that B reacts when it gets within a distance r* of A. It is then removed from the system so that $[B]_r* = 0$.

The flow of B towards A which leads to reaction is obtained by inserting this condition into the above equation and rearranging:

$$J = 4\pi r^*D_B N_A[B] \text{ molecules s}^{-1}.$$

In the solution as a whole the concentration of A is [A] so that there are $N_A[A]$ molecules of A. The overall rate of collision between A and B molecules, which is equal to the rate of reaction for a diffusion-controlled reaction, is therefore:

$$4\pi r^*D_B N_A^2[A][B] \text{ molecules s}^{-1} \text{ m}^{-3}.$$

This is almost the correct answer but we should remember that the A molecules move, too (just as we have to in the calculation of the collision rate in gases). It turns out that we can simply replace D_B by the sum of the diffusion coefficients of the different species: $D = D_A + D_B$ and obtain the final result that:

$$\text{Rate} = 4\pi r^*DN_A[A][B]$$

Note the direct dependence on the diffusion coefficient. From the Stokes-Einstein equation we have;

$$D_{A,B} = \frac{k_B T}{6\pi\eta r_{A,B}}$$

And if we assume that A and B are roughly the same size and that reaction occurs when they actually touch,

$$r_A \approx r_B \approx r^*\!/\!2$$

and,

$$k_d \approx \frac{8N_A k_B T}{3\eta} = \frac{8RT}{3\eta} mol^{-1}m^3s^{-1}$$

$$= \frac{8000RT}{3\eta} mol^{-1}m^3s^{-1}$$

In this approximation the rate constant is independent of the actual species involved in the reaction and, in particular, their size.

There is a correction factor that is necessary to make this equation valid over a wider range of conditions. The rate is given instead by:

$$k_d = \frac{8000RT}{3\eta}\frac{\sigma}{f}$$

σ is a factor introduced for radical recombination reactions. It brings in the requirement that antiparallel spins are necessary for bond formation. Only one radical encounter in four satisfies this – in the other three (triplet) states the electron spins are parallel. Therefore we multiply by a spin factor of ¼ .

f is a factor that comes into play particularly at higher viscosities, where the Stokes-Einstein relation begins to break down. This is because it was derived by treating the liquid as a bulk fluid whereas we are concerned with the diffusion of molecules. It turns out that this can be accounted for by introducing a "frictional constant" that has a different value for each solvent (and can be estimated from independent theory).

Some Examples
Besides the radical recombination and high viscosity cases, there are some other reactions that are worth mentioning.

Quenching of electronically excited states:
This is fluorescence quenching, e.g. Naphthalene + biacetyl. This type of reaction is always very efficient. Interpretation of the rate constant using the theory given above suggests that molecules

can exchange electronic energy when they get within 0.5-0.7nm of each other. That is they do not have to actually collide, and this tells us that there is a through-space mechanism by which they do it (electric dipole-electric dipole interaction).

$H^+ + {}^-OH$ equilibrium.
This reaction is quite abnormally fast. It is diffusion controlled, but the diffusion coefficients of the two species are abnormally high. This is explained by the fact that diffusion in the normal sense of one molecule moving towards another is not needed. Rather the proton, for example, simply hops from one molecule of water to another (the Grotthus mechanism), and protons are small compared with molecules. This actually relies on the water having local structure, and in fact the proton moves faster in ice than in liquid water. It is worth noting that the molecule must rotate before the next state of hopping. The mean lifetime of an individual H_3O^+ molecule is thought to be about 10^{-12}s.

It is worth remember however that although the diffusion controlled rate constant may be very high, a diffusion controlled reaction may not be very fast if the concentrations of one of the reactants is low.

Diffusion Controlled Reactions between ions
We might expect ions to behave differently due to the electrostatic charge effects. This either tends to hold them together or separate them by repulsion. The size of this effect is expected to be linked to the magnitude of the interaction (U) compared to the thermal energy (kT), through a Boltzmann type of relation. In fact, it is found that a simple multiplying factor in the equation for the rate constant –

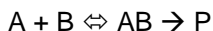$$k_d = 4000\pi r * DN_A \left\{ \frac{U/k_B T}{e^{U/kT} - 1} \right\},$$

$$U = \frac{Z_A Z_B e^2}{4\pi\varepsilon\varepsilon_0 r*}$$

$Z_A Z_B$ are the charges on the two ions, e the electronic charge, ε_0 the vacuum permittivity and ε the relative permittivity of the solution.

k_d is increased for ions of opposite charges, and decreased for ones of like charge. The effect is most pronounced in low relative permittivity (non-polar) solvents.

Activation Controlled Reactions

Basic scheme:
$$A + B \Leftrightarrow AB \rightarrow P$$
When $k_1 \ll k_d^{-1}$ the reaction proceeds with the second order rate constant now defined as k_2 which is given by $k_2 = k_1(k_d/k_d^{-1}) = k_1 K_{AB}$. The reaction rate constant is lower than that in the diffusion-controlled limit.

Reactions between ions:
We saw that ions affected diffusion controlled reactions by making the diffusion more or less difficult, depending on the charges of the ions. In activation controlled reactions this implies that the equilibrium constant K_{AB} is affected.
From thermodynamics we have $K_{AB} = \exp[{}^{\Delta G}/_{kT}]$, where we can write the Gibbs Free Energy change as the sum of the change in the absence of ions plus the electrostatic potential, U, between the ions:
$$\Delta G = \Delta G_0 + U$$
Where U is the same as it was above for diffusion controlled reactions.
However, we know that $k_2 = k_1 K_{AB}$ so:

$$\ln k_2 = \ln k_1 - \frac{\Delta G_0}{RT} - \frac{U}{RT} = \ln k_1 + \ln K_{AB}^0 - \frac{U}{RT} = \ln k_2^0 - \frac{U}{RT}$$
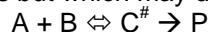
Where the superscript zeros refer to values with no ions present.

We see that if the product $Z_A Z_B > 0$, k_2 is decreased, but if $Z_A Z_B < 0$ it is increased. This is what we would expect – like charges repel and make reaction more difficult, whilst unlike charges attract the reactants together.

The same equation shows that the rate should vary with the solvent used, and in particular it should vary as $1/\varepsilon$. This is pretty much what is found experimentally.

Transition State Theory
In TST it is assumed that reactants encounter to form an "activated complex" or "transition state" which is in equilibrium with the reactants but which may dissociate to form products.
$$A + B \Leftrightarrow C^\# \rightarrow P$$
The activated complex is a molecular species en route to the product and should not be confused with the encounter pair we have been talking about. In the gas phase we can do the calculation in some detail using the partition functions of the species involved, but these are difficult to define in solution. We therefore move to the thermodynamic formulation of TST instead.

Our approach is however exactly the same – we calculate the concentration of the activated complex which decays unimolecularly to the product. Then we have:
$$\frac{d[P]}{dt} = k_{obs}[A][B] = k[C^\#]$$
Where we have assumed that experimentally we find the reaction to be second order.

Having assumed that the reactants are in equilibrium with $C^\#$ we obtain –
$$K_C = \frac{[C^\#]}{[A][B]} \text{ or } [C^\#] = K_c[A][B]$$
where K_C is the equilibrium constant written in terms of concentrations. It follows that $k_{obs} = kK_c$.

From thermodynamics we can relate the equilibrium constant with respect to pressure K_P to the Gibbs Free Energy change through $\Delta G = -RT \ln K_P$ and to use this we must first convert the equilibrium constant in terms of concentration to that in terms of pressure:
$$K_c = \left(\frac{RT}{p^0}\right) K_{p,c}$$
It then follows that:
$$k_{obs} = k\left(\frac{RT}{p^0}\right) e^{-\frac{\Delta G^\#}{RT}} \text{, where } \Delta G^\# \text{ is the free energy of activation.}$$

We could use the general result from transition state theory that $k = k_B T/h$ if we wished. This is obtained by assuming that it is a specific bond in the activated complex that vibrates to destruction. It is equal to $6\times10^{12} s^{-1}$ at 300K. This gives us a feel for the size of the pre-exponential factor (and the maximum rate of reaction).

Now writing $\Delta G^\# = \Delta H^\# - T\Delta S^\#$
We obtain,
$$k_{obs} = \frac{k_B T}{h}\left(\frac{RT}{p^0}\right) e^{\Delta S^\#/R} e^{-\Delta H^\#/RT}$$
where $\Delta S^\#$ and $\Delta H^\#$ are the activation entropy and enthalpy, i.e. the changes which occur to both in forming the activated complex.

This equation nearly has the same form as the Arrhenius equation, but we need the relation between the enthalpy of activation and the energy of activation. It turns out that for a reaction in solution there is little difference between $\Delta H^{\#}$ and $\Delta U^{\#}$ and we find $\Delta H^{\#} = E_A - RT$. Substituting gives:

$$k_{obs} = e.\frac{kT}{h}e^{\Delta S^{\#}/R}e^{-E_A/RT}$$

Note that we have an expression for the pre-exponential factor, A, and that it depends on the activation entropy of the reaction.

The thermodynamic treatment of the Absolute Rate Theory is also valid in the gas phase. Here, if two molecules come together to form an activated state the entropy change is from a less-ordered to a more ordered state and the change is negative. But if the reaction is in solution and involves oppositely-charged ions of the same charge, the entropy change is positive. This is because the ions are hydrated before they form the complex as a result of the charges attracting the dipoles of the water, but the complex itself is neutral and the ions are released from bondage – the entropy increases.

The reverse occurs if a neutral molecule dissociates into ions, or if two ions of the same charge come together so that the total charge, and dipolar attraction, is increased.

Summarising, if two ions react and have $Z_A Z_B < 0$ then $\Delta S^{\#} > 0$, but if $Z_A Z_B > 0$ then $\Delta S^{\#} < 0$. These are examples of ELECTROSTRICTION, which causes the number of attached solvent molecules, and the volume of the activated complex, to change over what it would be if the effect did not happen.

It is worth noting that this can have an enormous effect – we normally associate the major effects on reaction rates with activation energies, but entropy term can dominate.

A further unexpected consequence of this theory is that some reactions in solution are affected by the external pressure applied to them. This is because:
$\Delta G^{\#} = \Delta U^{\#} + p\Delta V^{\#} - T\Delta S^{\#}$ and this can be substituted into our original equation. Differentiating with respect to p yields:

$$\frac{d\ln k_2}{dp} = -\frac{\Delta V^{\#}}{RT}$$

That is, the rate constant changes with pressure if the reaction proceeds with a volume change, called the activation volume between reactants and the activated state. But in solution there are two contributions to this – the volume change on forming the encounter pair, and the change when the encounter pair becomes the activated complex.
$$\Delta V^{\#} = \Delta V_1^{\#} + \Delta V_2^{\#}$$
For bimolecular reactions, V_1 dominates and when ions are concerned we are again affected by electrostriction –
$Z_A Z_B > 0$, then $\Delta V_1^{\#} < 0$: k_2 increases as p increases.
$Z_A Z_B < 0$, then $\Delta V_1^{\#} > 0$: k_2 decreases as p increases.

Here the solvation of the ions reduces the volume occupied by the solvent molecules.

For unimolecular reactions, there is no V_1.

If a neutral molecule dissociates to neutral products then $\Delta V_2^{\#} > 0$ since the bond breaks and two molecules are produced in place of one. If the products are ions, then $\Delta V_2^{\#} < 0$ by electrostriction.

There is obvious correlation between the entropy and volume of activation as both are affected by electrostriction.

The Kinetic Salt Effect

It is found experimentally that the rates of reactions involving ions are affected by the presence of other ions, not themselves involved in the reaction, in solution. This is known as the kinetic salt effect. It can be understood using a combination of absolute rate theory and the Debye-Huckel theory for ions in solution.

Care must be taken not to use a salt that has an ion in common with the reacting species since then its presence would affect the ion equilibria ("common ion effect").

Debye-Huckel Theory tells us that for an ion, i:

$$\log_{10} \gamma_i = - A\, z_i^2\, I^{\frac{1}{2}} \,,$$

where I is the ionic strength $= \frac{1}{2} \Sigma\, c_j z_j^2$ (sum over all ions present – reactants and added salt).

We can combine this with our rate equation by taking logs and substituting for the activity (γ) terms. We also realise that the charge on the activated complex is the sum of the charges on the individual separate ions:

$$\log \frac{k_{obs}}{k_0} = \log \gamma_A + \log \gamma_B + \log \gamma_C$$

$$= -Az_A^2 \sqrt{I} - Az_B^2 \sqrt{I} + A(z_A + z_B)^2 \sqrt{I}$$

$$= 2Az_A z_B \sqrt{I}$$

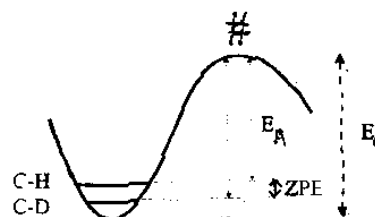where $A = 0.509$ dm$^{-3/2}$mol$^{-1/2}$ for water at 298K.

We predict, therefore, that the log of the rate constant should vary as $I^{1/2}$ and that the slope of the line should be $z_A z_B$. This is born out experimentally and it provides an extremely useful method for identifying the species involved in a reaction through its charge.

Mass Isotope Effects in Chemical Kinetics

Replacement of one isotope of an element by another can cause substantial changes in the rates of reaction of some types of reaction, if the bond involving the isotope is that which is broken. This has proved invaluable in the understanding of the reaction mechanisms of complex organic and bioorganic processes, for instance enzyme reactions, and has the effect of making ^2H_2O poisonous to biological systems at sufficiently high concentration. There are three main effects, the kinetic isotope (and inverse) effects, the equilibrium isotope effect, and tunnelling. All have a quantum origina and all depend on the mass of the isotope. There are other effects which depend on the fact that some isotopes have magnetic moments, which affects reactions involving free radicals.

Kinetic Isotope Effects

The activation energy of a chemical reaction is determined by the energy separation of the reactants and the transition state. But the energies are quantised and, in particular, the reactants possess zero point energy. This differs between molecules of different isotopic content, causing the activation energy, and the rate of reaction, to change.

The maximum possible size of this effect is obtained if it is assumed that isotopic substitution has no effect on the energy of the transition state.

Define E_0 to be the energy gap between the (unattainable) lowest point of the potential energy curve for the reactants and the transition state. The activation energy for breaking the C-H bond is then $E_0 - \frac{1}{2} h\nu_{CH}$, where ν_{CH} is the vibrational frequency of the C-H bond. Similar this can be done for the CD bond. Inserting this into the Arrhenius Equation gives:

$$k_H = Ae^{-\frac{(E_0 - 1/2 h\nu_{CH})}{k_B T}} = Ae^{-\frac{E_0}{kT_B}} e^{\frac{1/2 h\nu_{CH}}{k_B T}}$$

$$k_D = Ae^{-\frac{(E_0 - 1/2 h\nu_{CD})}{k_B T}} = Ae^{-\frac{E_0}{kT_B}} e^{\frac{1/2 h\nu_{CD}}{k_B T}}$$

$$\frac{k_H}{k_D} = \exp\left\{\frac{\frac{1}{2}h(\nu_{CH} - \nu_{CD})}{k_B T}\right\} = \exp\left\{\frac{\frac{1}{2}h\Delta\nu}{k_B T}\right\}$$

Treating the vibration of the molecule as a simple harmonic oscillator,

$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ where k is the bond force-constant (the same for both isotopic molecules), and μ is

the reduced mass. It follows that:

$$\frac{\upsilon_{CH}}{\upsilon_{CD}} = \left(\frac{\mu_{CD}}{\mu_{CH}}\right)^{1/2}$$

This has the value of $(13/7)^{1/2}$ if we just consider the CH fragment, but in reality CH is not a diatomic molecule so that using C=12 in this equation underestimates the mass of the second component involved in the vibration. The rest of the molecule is in fact so heavy that we may regard the CH bond vibrating as though the H atom was alone moving. Inserting this above shows that the value of the ratio rapidly tends towards $2^{1/2}$ as the molecule gets heavier.
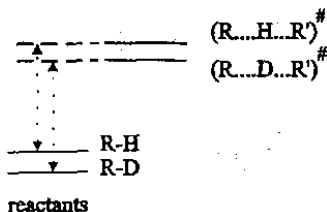In consequence we can write in general that:

$$\Lambda\upsilon \approx \upsilon_{CH}(1 - \frac{1}{\sqrt{2}})$$

This gives limiting values of $k_H/k_D \approx 7$ at 300K, and increases with decreasing temperature.
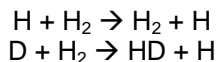
We note also that hydrogen is unique in having an isotope twice as heavy as itself. Mass isotope effects are consequently much more pronounced for H and D than they are for other elements (e.g. ^{12}C).

The magnitude of the kinetic isotope effect is decreased if the transition states involving the two isotopes have different energies. This would be expected to be the case in H or D atom transfer reactions:
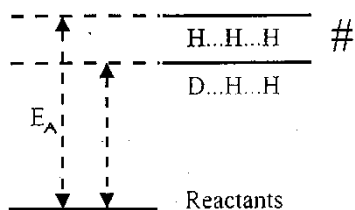

Now the difference in activation energies is less than the difference in the zero-point energies – the kinetic isotope effect is diminished in size.

Closely related to this is the Inverse Isotope Effect that is seen in the reaction of H and D atoms with the H_2 molecule:

$$H + H_2 \rightarrow H_2 + H$$
$$D + H_2 \rightarrow HD + H$$

Here the zero point energy of the reactants is that of the H_2 molecule in each case and the difference in activation energies originates only in the zero point energies of the transition state: the activation energy for the D reaction is now the lower.

Equilibrium Isotope Effects
Isotopic substitution can affect the position of an equilibrium and through it the rate of a chemical reaction. This is commonly seen in protonation reactions where H^+ adds to a molecule, S:
$H^+ + S \Leftrightarrow SH^+$ with equilibrium constant K, followed by
$SH^+ \rightarrow$ products, with rate constant k.
The overall rate constant for formation of products is then kK.

The size of the equilibrium constant is determined by the Gibbs Free Energy change in the process. Since H^+ and S are not bound, this affected by isotope effects only by the zero point energy difference in the SH^+ and SD^+ species, and this implies that ΔG is greater for SH^+, so that SH^+ is more dissociated (it is the stronger acid). That is, $K_H < K_D$. Typically $pK_A(SD^+)$ is about $pK_A(SH^+) + 0.6$

Everything else being equal, this has the effect of making the overall reaction to form products slower in H_2O than D_2O. But this conclusion must be made with care – it assumes that kinetic isotope effects on the reaction stage do not affect this result, and it assumes that tunnelling can be neglected – quite often H^+ transfer reactions are faster than D^+ ones. We must always remember that more than one effect can occur.

Quantum Mechanical Tunnelling
A characteristic of most simple chemical reactions is that they satisfy the Arrhenius equation. That is if k is measured as a function of temperature then a plot of ln k versus 1/T is a straight line with slope $-E_a/R$. The physical interpretation is that the reaction proceeds by the system overcoming an activation barrier that separates the reactants from the products. It is, however, found experimentally that certain sorts of reactions, notable proton- and hydrogen atom-transfer ones, show non-linear Arrhenius behaviour at low temperatures where the reaction proceeds faster than would be expected from a measurement of the (temperature-independent) activation energy at higher temperatures. That is, the reactants cannot surmount the activation barrier fast enough to account for the observed rate of reaction. It is apparent that the reaction proceeds by a quite different mechanism, which is quantum mechanical tunnelling.

Tunnelling actually proceeds at all temperatures, but it is only detectable when it becomes the dominant mechanism – at higher temperatures the reaction over the top of the barrier is much faster.

As has been seen above, the reactants are confined by a finite potential barrier. This always means that Schrodinger Equation has a solution inside the barrier itself, that is, the wavefunction is non-zero within the barrier. Since the square of the wavefunction gives the probability of a particle being at a position, this implies that it can actually penetrate into the barrier, and if the barrier is sufficiently narrow, get right through to the other side.

Solving for a simple potential step in one dimension gives two important consequences – only the lightest atoms tunnel, and different isotopes of them tunnel at appreciably different rates. We expect to see such effects in chemistry for reaction involving H and H^+ and their isotopic forms.

They show up in two ways, strong departure from Arrhenius behaviour at low temperatures, with the departures becoming apparent at substantially lower temperature for D and D^+ than for H and H^+, and abnormally and unexpectedly high ratios of k_H to k_D.

Electron Transfer Reactions
The reactions in solution which involve the transfer of an electron from one species to another are of considerable importance. They are commonly encountered in inorganic reactions between ions exhibiting mixed valence but are prevalent too in organic chemistry and biochemistry. They occur, for example, in photosynthesis in which early on the chemistry following absorption of a photon, a pair of radical ions is formed which would back-react and re-evolve the energy trapped from the sun if the positive and negative centres remained contiguous in the photosynthetic centre. Nature copes with this by providing an efficient and fast electron transport chain which whisks the electron away and separates the charges. Electron transfer also plays an important role in human respiration and other biological processes.

In inorganic chemistry, electron transfer reactions are of two different types. In one (the inner sphere mechanism) an actual bond is formed and broken, with the reactants sharing an atom or ligand in their coordination shells.

In the other (the outer sphere mechanism) no such bond is formed and the electron simply transfers from one species to the other, although through a complicated route.

An important sub-set is the "degenerate electron exchange" reaction between a radical anion and its parent molecule. This type of reaction has reactants and products that are the same, and it can be detected only using magnetic resonance methods (both ESR and NMR) where its occurrence strongly affects observations. This type of reaction is also important in biology.

We are primarily concerned with outer sphere reactions.

All of these reactions are concerned with ions and they are consequently strongly affected by their environment which plays a very real role in the reactions and can no longer be regarded as a passive medium. Sometimes the entire ion atmosphere surrounding a given molecule must change. Energy expended to accomplish these changes is known as "reorganisation energy".
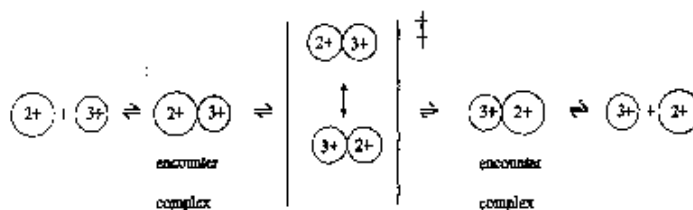
From a fundamental point of view the reactions also show special characteristics as a result of the electron being so light compared with the nuclei present. When an electron jumps from one molecule to another it does it so fast that the geometry of the molecules involved do not change during the transition, and nor do the positions of the dipoles. There is a direct analogy with the Franck-Condon Principle in spectroscopy in which an electron jumps from one orbital to another without the molecular framework changing.

Marcus Theory
Marcus envisaged the two reactants coming together to form an encounter complex in equilibrium with the reactants, which then formed a transition state which subsequently dissociated to form a second encounter complex, itself in equilibrium with the products. For example, for the reaction:

$$Fe(H_2O)_6^{2+} + Fe(H_2O)_6^{3+} \Leftrightarrow Fe(H_2O)_6^{3+} + Fe(H_2O)_6^{2+}$$
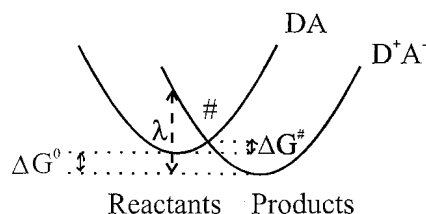
This can be depicted as follows – we draw the ions with charge 2 as bigger spheres than those with charge 3. This diagram also shows that in the transition state the reactants and products have attained the same size:

The reason for this is more clearly seen on a potential energy diagram. This is a little difficult to know how to draw since we have to depict the reaction in two dimensions on paper – as usual we label one axis the reaction coordinate, implying that this is the only coordinate which changes during the reaction.

Since, however, the ordering of the solvent (and therefore the entropy) enters the problem, the surface we should draw is a free energy one rather than simple potential energy one. We shall assume that the reactant and product curves are identical, and both parabolas (i.e. that the reactants and products are behaving are behaving as simple harmonic oscillators with identical force constants etc). For reaction to occur there must exist a route from the reactant state to the product one – both energy surfaces must pass through a common point on the reaction coordinate axis. We treat them as weakly interacting so that they can be drawn crossing one another, and the activation free energy is represented by the barrier the reactant must surmount between them.

Here the reactants are shown as the donor/acceptor (DA) encounter complex, and the products the D^+A^- encounter complex. $\Delta G^\#$ and ΔG^0 are the free energy of activation and the standard free energy change in the reaction respectively. λ is the new quantity, the reorganisation energy.

Inspection of the diagram shows that λ is the energy that the product would have to obtain to be formed if the electron was unable to find a lower energy route. In fact the free energy surfaces of the reactant and product intersect, and the transition state itself exists between them – the reactant seeks out this low energy path and goes over it to form the product. λ is consequently interpreted as the free energy required to distort the equilibrium nuclear framework of the products to that of the reactants without electron transfer in fact occurring. In practice this includes all the reorganisations mentioned above – the bond lengths, the dipole orientations and the changes in the ion atmosphere.

By writing in the mathematical equations for the parabolas the calculation of the free energy of activation becomes a simple problem in geometry which yields:
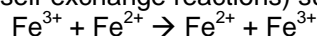
$$\Delta G^\# = \frac{(\Delta G^0 + \lambda)^2}{4\lambda}$$

As ever in transition state theory the observed rate constant can be expressed as the product of an equilibrium constant K (here for the formation of the reactant encounter pair) with the rate constant for the transition state reacting to form products (which we label k_{ET}):

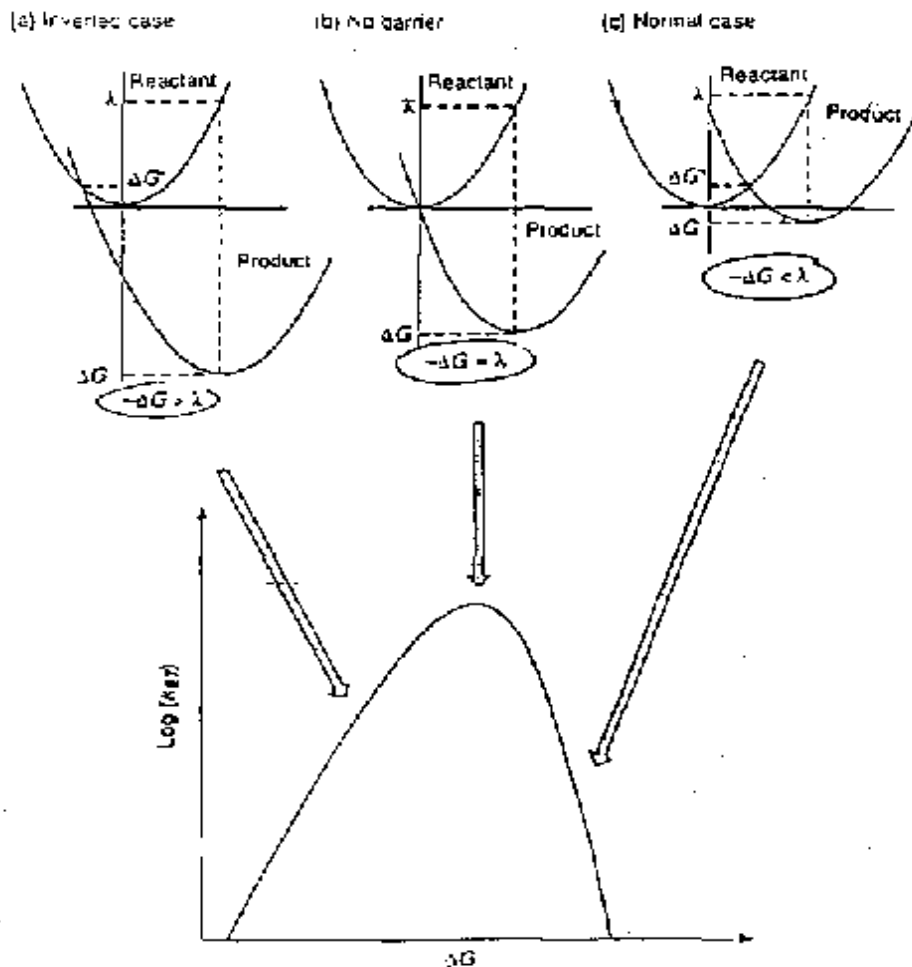$$k_{obs} = Kk_{ET} = KAe^{\frac{-\Delta G^\#}{RT}}$$

where A is a pre-exponential factor (but recall that entropy is included in the free energy).

For degenerate electron transfers (self-exchange reactions) such as:

$$Fe^{3+} + Fe^{2+} \rightarrow Fe^{2+} + Fe^{3+}$$

ΔG^0 is obviously zero, and $\Delta G^\# = {}^\lambda/_4$.

In cross reactions (A + D $\rightarrow$ A^- + D^+), the reorganisation energy is equal to the mean value of those of the two corresponding self-exchange reactions, whilst ΔG^0 can be measured from electrochemistry – the rates of these reactions can therefore be calculated from data obtained from the study of the self-exchange processes.

The approach we have given contains the principles of the Marcus Theory but is approximate. The value of the activation free energy should be amended to account for the work done in moving the reactants to the transition state. Also the free energy change in the reaction should include the work done in forming the initial reactant encounter pair, and in separating the final product encounter pair. But within these limitations further progress can now be obtained by introducing quantum theoretical aspects which we have so far ignored.

The rate of the electron transfer step depends on the mixing of the reactant and product wavefunctions at the transition state. The physical interpretation is that this occurs most efficiently if the vibrational wavefunctions of the two states overlap in that region of space. This is exactly analogous to the familiar calculation of the intensities of lines in the electronic spectra of molecules. Treating it as a simple two-level system gives:

$$V_R{}^2 = V_0{}^2 e^{-\beta R}$$

Where R is the edge-to-edge distance between donor and acceptor treated as spheres, β is a constant and V_R is the rate of electron transfer at a distance R.

This insight allows us to investigate how the variation of λ relative to ΔG^0 affects the rate of transfer: we find that overlap of the wavefunctions maximises, as does the rate, when $\lambda = -\Delta G^0$ (not surprisingly this corresponds in the classical treatment).