## Elementary Processes and Rate Theories

- An elementary process cannot be determined from the net stoichiometry of a reaction.
- For example, the combustion of octane is:

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

  but the reaction does not proceed by 25 oxygen molecules interacting simultaneously with two octane molecules.

  - Statistics works against this.
  - Instead the reaction proceeds by a sequence of elementary processes involving interactions of a small number of species at a time.
- **BUT** not all stoichiometric reactions that are bimolecular are elementary reactions.

## Elementary Processes

- Elementary Processes may be categorized as:
  - Unimolecular
  - Bimolecular
  - Termolecular
  - Photochemical
- See table 27.1 on page 1041 of Winn.

## Unimolecular Processes

- Isomerization and elimination are examples of unimolecular reactions.
- The rate of isomerization depends on temperature through the activation energy due to the intramolecular energy barrier.
  - If the activation energy is low (as in the case for conformal isomers such as boat and crown or staggered and eclipse), the rate of isomerization is rapid and is not strongly temperature dependent.
  - If the activation energy is high (as in the case of interconversion of optical isomers) then the rate of isomerization tends to be low at room temperature.
- In the case of an elimination reaction, the activation energy is related to the height of the potential energy barrier between isolated ground state reactants and isolated products.
  - Excitation of reactants can increase the rate of reaction.

## Bimolecular Processes

- There are many types of elementary bimolecular processes.
- Recombination **cannot** occur solely by a bimolecular collision due to conservation of momentum and energy.
  - An additional collision is required to carry off excess energy and momentum.
  - Therefore many recombination processes are density dependent.
- Recombination may also occur by *radiative association* where a photon is emitted to remove the excess energy.
  - This is an example of where the bimolecular process has at least two products. In this case one of the products is a photon.

- Whether a bimolecular reaction leads to products depends on the potential energy surface which describes the energy interaction of all the atoms involved in the system.
    - If there are large energy barriers between reactants and products then the reaction does not occur at an appreciable rate.

### Termolecular Reactions

- Pathways not accessible through bimolecular reactions may be accessed by termolecular reactions.
- Termolecular reactions require the simultaneous or nearly simultaneous interaction of three molecules.
    - The rate of reaction is often strongly pressure dependent.
- Consider recombination of I in Ar:

$$I + I \longrightarrow I \cdots I$$

- If $I \cdots I$ collision pair can interact with Ar before it fall apart, then energy may be transferred to or from the Ar atom.
    - If Ar takes away energy, $I \cdots I$ is stabilized to $I_2$.
    - If Ar delivers energy, $I \cdots I$ is further destabilized.
- Because termolecular reactions require the simultaneous or nearly simultaneous interaction of three molecules, the rate may increase as the speed of the interacting species is slowed down.

    - Termolecular reactions may be faster at lower temperatures.
- Consider a termolecular reaction as occurring in two stages:
    - transient association:

$$A + A \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} A \cdots A$$

    - collisional stabilization:

$$A \cdots A + M \overset{k_2'}{\rightarrow} A_2 + M$$

    - If the second process occurs immediately upon the first occurring, the interaction of three bodies may be regarded as simultaneous.
- The chaperone mechanism is a variant of this:
    - chaperone complex foundation:

$$A + M \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} A \cdots M$$

    - bimolecular atom transfer:

$$A \cdots M + A \overset{k_2'}{\rightarrow} A_2 + M$$

- Both mechanisms give the same rate law.
    - Which one is preferred depends on the stability of the complex formed.
    - The more stable the complex formed in the first step, the more likely the second step will occur.

### Photochemical Processes

- Light must be absorbed to cause a chemical change.

  - Each photon absorbed leads to one photochemically active molecule.
- The rate of reaction depends on the availability of photons:

$$HI + h\nu \rightarrow H + I$$

- One mole of photons is an *einstein.*
  - However the intensity of the light and the duration of irradiation must be considered.
- The Beer-Lambert Law is:

$$I_a = I_0(1 - e^{-abc})$$

  where:
  - $a$ is the absorbance coefficient
  - $b$ is the optical path length of the sample
  - $c$ is the concentration of the absorbing species.
- The product $abc$ is dimensionless and there are a number of choices.
  - If $c$ is in units of molecules per unit volume, $b$ is in units of distance, then $a$ has units of area and is known as the absorbance cross section.
- Not every photon absorbed leads to the photochemical product of interest.
  - Photochemical product quantum yield $\Phi$ is:

$$\Phi = \frac{\text{number of molecules produced}}{\text{number of photons absorbed}}$$

  - If competing processes may occur, then $\Phi < 1$.

- Photochemical processes include:
  - Excitation of the molecule vibrationally, rotationally, and/or electronically.
  - Dissociation
  - Ionization
  - Isomerization
- Energy from absorbed photons may also be lost photophysically.
  - Fluorescence
  - Phosphorescence
  - Collisional Quenching

## Simple Collision Theories of Reactions

- Can be used to predict rate coefficients for simple bimolecular processes.
- Must take into account
  - Collision or encounter rate
  - Probability of reactive collision.

- Collision or encounter rate determined from:

  - Relative collision velocity
  - Collision cross section
  - Number densities of colliding species
- Probability of a reactive collision takes into account:
  - Energy requirements
  - Quantum mechanical (spin) requirements
  - Collision geometry requirements (steric factor).

**Gas Phase Reactions**

- Consider the associative detachment reaction:

$$H \ + \ H^- \ \rightarrow \ H_2 \ + \ e^-$$

  - Well-studied both experimentally and theoretically.
  - Observed rate coefficient at 300 K is $1.17 \times \ 10^{12}$ $\mathrm{M}^{-1}$ $\mathrm{s}^{-1}$.
- Compare the rate coefficient with the collision rate.
  - Recall that:

$$Z_{12} =< g\sigma > n_H n_{H^-}$$

    therefore

$$k = N_A < g\sigma > .$$

  - and recall that:

$$< g >= \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}$$

  - The hard-sphere cross section is:

$$\sigma_{12} = \pi(r_1 + r_2)^2$$

  - Assuming that the radii of each of H and $\mathrm{H}^-$ are approximated by the bohr radius $a_0$ of $5.3 \times 10^{-11}$ m gives:

$$\sigma_{12} = 3.5 \times 10^{-20} \ \mathrm{m}^2$$

- This gives a bimolecular collision rate of

$$k = \frac{Z_{12}}{n_H n_{H^-}} = 7.5 \times 10^{10} \ \mathrm{M} \ \mathrm{s}^{-1}$$

  at 300 K.
- Why is this less than the observed rate?
- Is the hard-sphere cross section a reasonable estimate?
  - What value of the collision cross section would be consistent with the observed rate coefficient?

$$\frac{k}{< g >} = 5.5 \times \ 10^{-19} \ \mathrm{m}^2$$

- How do you explain this?
  - Is the bohr radius a reasonable estimate of the radius of $\mathrm{H}^-$?

- The rate coefficient is observed to be nearly independent of temperature.
  - No activation energy is apparent.
  - This is typical of ion-molecule reactions.
- Consider a reaction that does have an activation energy:

$$Cl\ +\ H_2\ \rightarrow\ HCl\ +\ H$$

  - Observed rate coefficient at 300 K is $9.4 \times\ 10^6$ $M^{-1}$ $s^{-1}$.
  - Observed Arrhenius activation energy is $\sim$ 18.3 kJ $mol^{-1}$.
  - From the observed rate coefficient, a hard-sphere cross section is estimated to be $8.6 \times 10^{-24}$ $m^2$, which is absurdly small.
- Probability of reaction must be considered.
  - Fraction of collisions with energy in excess of cross section is $6.5 \times 10^{-4}$.
  - This appears to be sufficient to account for the difference between the collisional rate and the reaction rate.
- For other reactions, this is not sufficient.
  - Directness of collision may matter.
  - Usually accounted for by the "steric factor".

### Solution Reactions

- Differs from gas phase reactions in that reactants must diffuse toward each other.
- Concepts from gas phase such as activation energy is still valid.
- In solution, molecules are always interacting with the solvent molecules.
- As reactant molecules diffuse toward each other, the molecules of solvent can form a "cage" around them.
  - This means that the reactant molecules will be in proximity for a long time.
  - Energy can be rearranged within the reactants and gained or lost from the solvent molecules.
- Reactions in solution can fall into two classes in accordance with the activation energy.
- Reactions with low activation energy take place in the diffusion limited regime.
  - The rate of reaction is controlled by the rate of diffusion of reactants toward each other.
- Reactions with high activation energy take place in the activation limited regime.
  - Reaction depends on fluctuations within the solvent cage that are occasionally large enough to provide the activation energy.
  - The reaction sequence may be represented as:
    $$\mathrm{A + B \rightleftharpoons A\cdots B}$$
    which represents reactant diffusion in the forward direction and dissociation of the encounter pair in the reverse direction and:
    $$\mathrm{A\cdots B \rightarrow C + D}$$
    which represents reaction of the encounter pair.
  - Applying steady state analysis to A$\cdots$B leads to the overall rate law:

$$\Re = \frac{d[C]}{dt} = k_1'[A\cdots B] = \frac{k_2 k_1'}{k_{-1} + k_1'}[A][B]$$

with

$$k_{exp} = \frac{k_2 k_1'}{k_{-1} + k_1'}$$

- This expression allows us to assess the relative roles of diffusion and dissociation of the encounter pair,
  - In the diffusion controlled regime,

    $$k_1' >> k_{-1} \text{ and } k_{exp} = k_2$$

  - In the activation limited regime,

    $$k_1' << k_{-1} \text{ and } k_{exp} = \frac{k_2 k_1'}{k_{-1}} = k_1' K_{eq}$$

    where $K_{eq}$ is for the diffusive formation of the encounter pair.
- $K_{eq}$ is usually small because:
  - The entropy of formation of the encounter pair is negative.
  - The enthalpy of formation of the encounter pair is positive or slightly negative.
  - Thus $\Delta_r \overline{G}^\circ$ is usually positive.
- The diffusion rate coefficient $k_2$ may be estimated from the diffusion transport equation.
- The diffusion coefficients $D_A$ and $D_B$ are important.
  - These are functions of temperature, the viscosity of the solvent, and molecular radii since:

    $$D = \frac{k_B T}{6\pi\eta R}$$

- If either A or B are ions, then electrostatic forces play a role.
- Also to be considered is detailed balance.
  - Detailed balance uses concentrations, not activities.
  - Connected to thermodynamic equilibrium by fugacity, activity, and other corrections for nonideality.
- Initially consider uncharged reactants.
  - A is a spherical molecule with characteristic radius $R_A$.
  - Spherical molecules of B diffuse around A in a structureless continuous solvent.
  - An encounter complex A$\cdots$B forms when A and B are separated by R$^*$.
- Because B is now part of A$\cdots$B, [B] = 0 at R$^*$.
- This gives a radial concentration gradient which drives the diffusion of B towards A.
- This described by Fick's First Law:

  $$J_{B,r} = -D_B \frac{\partial n_b}{\partial r} = -D_B \frac{d[B]}{dr} N_A (1000 \text{ L m}^{-3})$$

  where:
  - $J_{B,r}$ is the radial flux,
  - $D_B$ is the diffusion coefficient for B in that solvent system

  - $n_B$ is B number density
  - $N_A$ and (1000 L m$^-3$) convert from concentration in moles L$^{-1}$ to number density in molec m$^{-3}$.
- This may be diffentiated to give an expression for $\partial^2 n_B/\partial r^2$ which can be substituted into Fick's Second Law:
$$\frac{\partial n_B(r,t)}{\partial t} = D\frac{\partial^2 n_B}{\partial r^2}$$
- Thus:
$$\frac{\partial n_B(r,t)}{\partial t} = -\frac{\partial J_B}{\partial r}$$
  - But if there is a steady state, $\partial n_B/\partial t = 0$, then $\partial J_B/\partial r = 0$ and the flux is the same through a spherical shell at any distance $r$ about A.
  - Total radial flow through a sphere of radius $r$ is the radial flux times the surface area $4\pi r^2$
- Thus the inward flow is:
$$I_r = -4\pi r^2 J_{B,r} = 4\pi r^2 D_B N_A(1000 \text{ L m}^{-3})\frac{d[B]}{dr})$$
- Because the number of B molecules is conserved, $I_r$ must be a constant and independent of $r$. Therefore:
$$r^2\frac{d[B]}{dr} = \frac{I_r}{4\pi D_B N_A(1000 \text{ L m}^{-3})}$$
which has the solution:
$$[B] = [B]_\infty - \frac{I_r}{4\pi r D_B N_A(1000 \text{ L m}^{-3})}$$
where $[B]_\infty$ is the bulk concentration of B in the large distance limit.
- Since $[B] = 0$ at $r = R^*$,
$$[B]_\infty = \frac{I_r}{4\pi R^* D_B N_A(1000 \text{ L m}^{-3})}$$
or
$$I_r = [B]_\infty 4\pi R^* D_B N_A(1000 \text{ L m}^{-3})$$
- Thus for $r > R^*$, the concentration profile for [B] becomes:
$$[B] = [B]_\infty\left(1 - \frac{R^*}{r}\right)$$
- As indicated in figure 27.3, the gradient can be quite long range.
- Recall that all of the above is with respect to B diffusing toward A.
- Now consider the diffusion of A and B toward each other:
  - This entails replacing $D_B$ with $D_A + D_B$.
- The total radial flow is the rate of formation of $A\cdots B$ per A molecule.
- Thus the reaction rate is:
$$\Re = \frac{d[A\cdots B]}{dt} = -\frac{d[B]}{dt} = k_2[A][B]$$
- Recalling that [B] in the above refers the bulk concentration, called $[B]_\infty$ in the derivation of radial diffusion, the rate becomes:
$$\Re = [A]I_r$$

  - With the correct diffusion coefficient, this becomes:

    $$\begin{aligned}\Re &= k_2[A][B]\\ &= \left[4\pi R^*(D_A+D_B)N_A(1000 \text{ L m}^{-3})\right][A][B]\end{aligned}$$

    and the diffusion rate coefficient $k_2$ can be identified:

    $$k_2 = \left[4\pi R^*(D_A+D_B)N_A(1000 \text{ L m}^{-3})\right]$$

- Thus a maximum rate of reaction is solution in the diffusion controlled regime may be estimated.
  - Assuming that $R^* = 5$ Å and $D_A + D_B = 10^{-9}$ m$^2$ s$^{-1}$ yields a rate coefficient $k_2 = 4 \times 10^9$ M$^{-1}$ s$^{-1}$.
- When this is compared with the gas phase bimolecular rate coefficient, it may be noted that:
  - The gas phase rate coefficient is proportional to the relative speed times a cross section.
  - The solution rate coefficient is proportional to a diffusion coefficient times a length.
  - The gas phase rate coefficient is proportional to the square of a characteristic reaction radius.
  - The solution rate coefficient appears as a linear function of a characteristic reaction radius.
  - But the diffusion coefficient depends on viscosity and molecular size.
- The dependence of the solution rate coefficient on molecular size can be further explored by the consideration of viscosity.
  - Recall the Stokes-Einstein relation:

    $$D = \frac{k_B T}{6\pi\eta R}$$

  - Applying this to $D_A + D_B$ gives:

    $$D_A + D_B = \frac{k_B T}{6\pi\eta}\left(\frac{1}{R_A} + \frac{1}{R_B}\right)$$

  - If it is assumed that $R^* = R_A + R_B$, the sum of the hydrodynamic radii of A and B, then

    $$k_2 = \frac{2k_B T}{3\eta}\frac{(R_A+R_B)^2}{R_A R_B}N_A(1000 \text{ L m}^{-3})$$

  - If it is further assumed that $R_A = R_B$ and noting that the universal gas constant is $R = kN_A$ then:

    $$k_2 = \frac{8RT}{3\eta}(1000 \text{ L m}^{-3})$$

- Thus $k_2$ is independent of the size of the molecule.
  - Two effects cancel each other out.
  - Large molecules diffuse more slowly.
  - Large molecules present a larger target.
- A value for $k_2$ may be estimated based on viscosity.
  - Water has a viscosity of $10^{-3}$ Pa s at 300 K.
  - This predicts $k_2 = 7 \times 10^9$ M$^{-1}$ s$^{-1}$ which is in reasonable agreement with the previous estimate.

  - The viscosity dependence of diffusion controlled rate coefficients has been confirmed by studies of mixed solvent systems of varying viscosity.
- The above expressions apply to neutral-neutral interactions and were first derived by Smoluchowski in the context of colloidal particle growth.
- Additional factors must be considered in the case of ionic reactants.
  - Electrostatic interactions, whether ion-ion or ion-neutral, are longer ranged than neutral-neutral interactions.
- Ion-ion interactions of like charge will diffuse more slowly than neutral-neutral.
- Ion-ion interactions of unlike charge will diffuse more quickly than neutral-neutral.
- Therefore, Fick's First Law needs to be modified to account for the electrostatic potential energy gradient in addition to the concentration gradient, since the chemical potential gradients will be a function of the two gradients.
- Thus the rate coefficient becomes:

  $$k_2 = 4\pi R^*(D_A + D_B)N_A(1000 \text{ L m}^{-3})f$$

  where $f$ is the electrostatic factor:

  $$f = \frac{R_0}{R^*(e^{R_0/R^*} - 1)}$$

  and $R_0$ is the distance at which the electrostatic energy is $k_BT$, the characteristic thermal energy.
- Recall that the Colomb energy is:

  $$\mathcal{E} = \frac{z_A z_B e^2}{4\pi\epsilon_0\epsilon_r R}$$

  where
  - $z_A$ and $z_B$ are the charge numbers of A and B
  - $\epsilon_0$ is the permittivity of free space
  - $\epsilon_r$ is the relative permittivity of the solvent.
- Since this energy is equal to $k_BT$ at $R_0$,

  $$R_0 = \frac{z_A z_B e^2}{4\pi\epsilon_0\epsilon_r k_B T}$$

- For water at 25°C:
  - $\epsilon_r = 78.3$
  - $R_0 = z_A z_B(7.16 \times 10^{-10})$ m.

  Thus at $R^* = 5$ Å:
  - $f = 1.88$ for $z_A z_B = -1$.
  - $f = 0.45$ for $z_A z_B = 1$.
  - $f = 5.7$ for $z_A z_B = -4$.
  - $f = 0.019$ for $z_A z_B = 4$.
- This does not take into account the possibility of other ions affecting A and B as they diffuse toward each other.

  - If the total ion concentration is $10^{-4}$ M or greater, then corrections must be applied to account for the primary salt effect.
  - The Debye-Hückel expression for ionic activity coefficients are useful.

## The Transition State

- Consider the potential energy surface for the reaction
  - in particular, the forces among the atoms at various geometries along the way from reactants to products.
  - Rigourously, one should consider all spatial coordinates
  - In practice only a few geometric variables change as the reaction proceeds.
- Consider a case with only three spatial variables, the $H + H_2 \rightarrow H_2 + H$ reaction.
  - May be studied through isotopic substitution, $D + H_2 \rightarrow HD + H$
  - Only three geometric parameters need to be considered, either three atom-atom separations or two atom-atom separations and an angle.
  - If one of these is fixed, then there are only two coordinates required.
  - If the angle is fixed, then the distances from one atom to each of the other atoms are all that is required to completely describe the system.
- The full dimensional potential energy surface for $H + H_2$ is very well known.
  - In the ground electronic state, $H_3$ is not a stable electronic species.
  - In the course of the exchange reaction, the three atoms will be close together.
  - The forces are such as to push the atoms toward a linear conformation.
- The transition state of a reaction is ill-defined in terms of configuration.
  - Represents an arrangement of atoms that is neither isolated reactants nor isolated products.
  - The concept of transition state is widely used in interpreting reactions.
- Accurate chemical potentials may be determined quantum mechanically for systems with few electrons.
  - It is difficult to perform accurate calculations for many electron systems.
  - Therefore approximate methods are used.
- These approximate methods includes.
  - LEPS (London, Eyring, Polanyi, and Sato, 1928) combines diatomic Morse potentials with adjustable “interaction terms” which match empirical energies.
- The existence of a potential energy barrier along the path from reactants to product suggests the microscopic origin of activation energy.
  - Barrier height is not equal to the activation energy.
- The classical reaction coordinate may be defined by the minimum energy path between reactants and products.
  - This path will go through the saddle point, if it exists for that potential.
  - It is classical in that it does not take into account quantum effects such as tunnelling or zero point energy.
- Consider the saddle point, which is sometimes identified as the transition state.

  - A saddle point, by definition, is a maximum in one direction and a minimum in the other.
  - It sits on the classical reaction coordinate.
  - Motion along $q_1$, a line tangential to the classical reaction coordinate corresponds assymmetric stretch ( $R_1 + R_2 =$ constant).
  - Motion perpendicular to the reaction coordinate along $q_2$ (i.e. along the $R_1 = R_2$ line) corresponds to symmetric stretch.
- Motion in the $q_1$ direction is not bound.
  - Because the potential has a maximum along $q_1$, the second derivative is negative.

$$\frac{\partial^2 U}{\partial q_1^2} < 0$$

  - This means that the corresponding harmonic force constant is negative, which in turn corresponds to a negative force constant.
  - This means that the harmonic oscillator (or normal mode) frequency is an imaginary number.

$$\omega_i = \sqrt{\frac{\text{normal mode force constant}}{\text{normal mode reduced mass}}}$$

- Note that the potential energy surface is specific to the atoms and the electronic state involved.
  - For example the $H^+ + H_2 \rightarrow H_2 + H^+$ potential has a local minimum when the three atoms are close together.
  - The energy of the "transition state" is at the local minimum when the atoms are in a triangular configuration.
- The existence of a local minimum is associated with a potentially stable intermediate that can exist as a distinct species.
  - Examples include $O + CO \rightarrow CO + O$ (stable $CO_2$), $O + N_2 + ON + N$ (stable $N_2O$).
- Potential energy surfaces for different electronic configurations of the same atoms are not always well separated.
  - Each potential energy surface will have its own transition state and reaction coordinate.
  - Surfaces can intersect and a reaction can cross intersections of the potentials.
  - It is the intersections of these potential energy surfaces that gives rise to branching of chemical reactions.
- Minima associated with transition states cannot be the absolute minimum of the potential energy surface.
  - If it were, it would be a stable compound and would be classified as an intermediate rather than a transition state.

## Activated Complex Theory

- A transition state is often identified as an activated complex.
- In 1935, Eyring and, independently Evans and Polanyi, published theory about bimolecular rate coefficients.
- This theory is known as:

  - Transition state theory
  - Absolute rate theory
  - Activated complex theory
- This theory considers
  - the reaction potential energy surface
  - the transition state
  - the thermal distribution of collision energies.
  - statistical mechanics and partition functions
- Results have
  - reasonable accuracy
  - important physical insights
  - opportunities for improvement
- Consider activated complex theory (ACT) in the context of the exchange reaction A + BC → AB + C.
  - The activated complex is $\mathrm{ABC}^{\dagger}$.
  - The rate coefficient is $k_2$ at temperature T.
  - Assume classical mechanics describes the reaction.
  - Quantum effects will be considered later.
- The assumption of constant T allows the use of equilibrium distribution functions for reactants and activated complex.
- Assume that every activated complex goes to products.
  - This violates microscopic reversibility so this will have to be reexamined later.
- Start with the system's Hamiltonian, $H$, which describes the total kinetic and potential energy of the system.
  - The potential energy may be considered in terms of the intermolecular potential for the system and the intramolecular potential within the molecules.
  - The Hamiltonian is written in terms of coordinates $q_i$ and momenta $p_i$.
  - The potential energy depends on the coordinates $q_i$.
  - The kinetic energy depends on the momenta $p_i$.
  - For a three atom system there will be 18 variables, 9 momenta $p_i$ and 9 coordinates $q_i$.
- Imagine the associated 18 dimensional cartesian space:
  - Coordinates and momenta selected to be orthogonal
  - This 18 dimensional cartesian space is known as phase space.
  - A volume element, d$\tau$, in phase space is 18 dimensional:

$$d\tau = dq_1 \dots dq_9 dp_1 \dots dp_9$$

  - Generally for N particles, the associated phase space is 6N dimensional.
- The reaction coordinate is denoted $q_1$.
  - A surface perpendicular to this coordinate is constructed in phase space.

  - This surface is known as a dividing surface.
  - At this point your text, like many other treatments of transition state theory, stops referring to the momenta and continues to refer to coordinates.
  - All coordinates far to one side of the dividing surface are clearly reactants.
  - All coordinates far to the other side of the dividing surface are clearly products.
  - The dividing surface is through the transition state on the potential.
- Consider the fraction of the total of N systems in a volume element $d\tau$:

$$\frac{d^{18}N}{N} = \frac{\text{(Boltzmann Factor)(Volume Element)}}{\text{Partition Function}}$$
$$= \frac{e^{-\beta H} d\tau / h^9}{\int e^{-\beta H} d\tau / h^9}$$

  where $\beta = 1/kT$.

  - This is exact at equilibrium.
  - It is assumed that the reacting system does not deviate significantly from equilibrium.
  - $h^9$ may be thought of as a scaling factor for the volume element since $dq_i dp_i$ has units of kg $\text{m}^2$ $\text{s}^{-1}$ or J s.
- The expression is now integrated over the positive values of $p_i$ to find the rate at which systems cross the dividing surface from reactants to products.
  - When integrating the denominator, take note that most of the time A is far from BC and thus their interaction potential may be ignored. Thus the demoninator may be treated as the product of the partition functions for A and for BC.
  - When integrating the numerator, integrate over all the coordinates and momenta, except the reaction coordinate.
  - The numerator is in the form of a partition function for the activated complex, $\text{ABC}^\dagger$, corrected for the fact that the internal energy of $\text{ABC}^\dagger$ is measured from the energy at the barrier height.
- This yields:
  where $q^\dagger$ is the partition function for the activated complex with the reaction coordinate removed.
  - This represents the rate at which reactants approach the dividing surface.
  - Since it is assumed that all systems which reach the dividing surface go on to products, this leads directly to the rate of reaction:

$$\Re = k_2[A][BC] = d\frac{[ABC^\dagger]}{dt}$$
$$= \frac{dN}{dt}\frac{1}{VN_A(1000 \text{ L m}^{-3})}$$

    where V is the volume of the system.
- Must now consider exactly what N means in these equations.
  - In this context, let the number of A atoms be represented by $\text{N}_A$ and the number of BC molecules be represented by $\text{N}_{BC}$.

$$\frac{d^{18}N}{N} = \frac{d^6 N_A}{N_A}\frac{d^{12}N_{BC}}{N_{BC}}$$

    Thus $N = N_A N_{BC}$ and is the number of ABC complexes possible.

- Expressing N's in terms of concentration:

$$\Re = k_2[A][BC] =$$

$$[A][BC]\frac{k_BT}{h}\left(\frac{q^\dagger}{q_A q_{BC}}e^{-U^\dagger/k_BT}\right)VN_A(10^3 \text{ L m}^{-3})$$

where $N_A$ now represents Avogadro's number.

- Thus the rate coefficient is:

$$k_2 = \frac{k_BT}{h}\left(\frac{q^\dagger}{q_A q_{BC}}e^{-U^\dagger/k_BT}\right)VN_A(10^3 \text{ L m}^{-3})$$