Estimating the Energy Profile for Elementary Reactions

Recall the relation between the Gibbs free energy and the equilibrium constant K.

$$\Delta G^o = -RT\ln K \quad \text{so} \quad \ln K = \frac{-\Delta G^o}{RT}$$

$$\therefore \quad K = e^{-\left(\frac{\Delta G^o}{RT}\right)}$$

The equilibrium constant K is equal to the fraction of molecules with kinetic energy $E_k \geq \Delta G^o$ (the change in the free energy of the equilibrium process).

Taking the natural logarithm of both sides gives

$$\ln K = -\left(\frac{\Delta G^o}{RT}\right)$$

$$-\ln K = \left(\frac{\Delta G^o}{RT}\right)$$

$$-RT\ln K = \Delta G^o$$

$$-2.303RT\log K = \Delta G^o$$

$$2.303RT(-\log K) = \Delta G^o$$

$$2.303RT(pK) = \Delta G^o$$

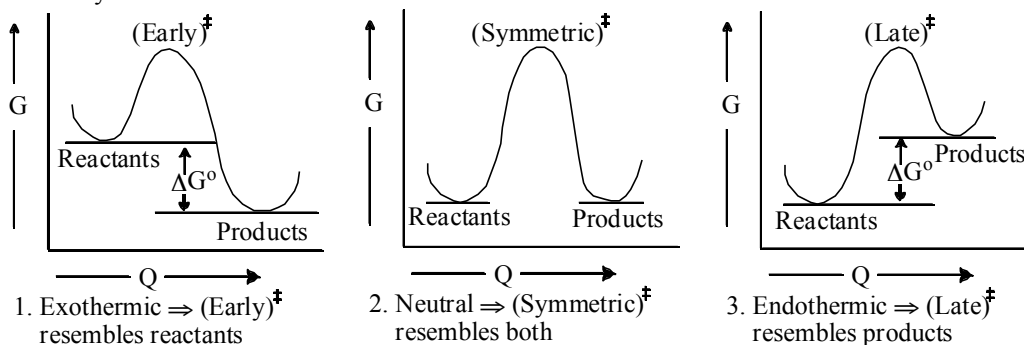$$\therefore \quad \text{@ 25}^o\text{C this expression is}$$

$$\Delta G^o = 5.7 \text{kJmol}^{-1}(pK)$$

The pK scale provides a measure of how a process is favored thermodynamically. The change in the Gibbs free energy (ΔG) corresponds to the maximum work available from the process. Since G is a state function it is path independent and therefore can be calculated from available thermodynamic data.

Energy Profile (Hammond' s postulate):

For every elementary reaction the transition state looks like the side of the reaction that it is closest to in energy (This is Hammonds Postulate).Thus the shape of the transition state is predicted from thermodynamic data.

1. Exothermic $\Rightarrow$ (Early)‡ resembles reactants
2. Neutral $\Rightarrow$ (Symmetric)‡ resembles both
3. Endothermic $\Rightarrow$ (Late)‡ resembles products

Case 1. Draw Reactants 1st , Case 2. Draw Reactants and Products 1st, Case 3. Draw Products 1st

Consider the dissociation of bromic acid in water.

$$HBrO_3(aq) + H_2O(l) \rightleftharpoons BrO_3^-(aq) + H_3O^+(aq)$$
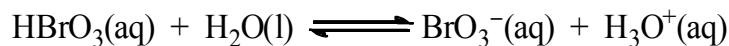
The pKa can be estimated from the Pauling rules for this acid. There are two oxo groups and one hydroxy group in the formula O_2BrOH so p = 2 and q = 1.
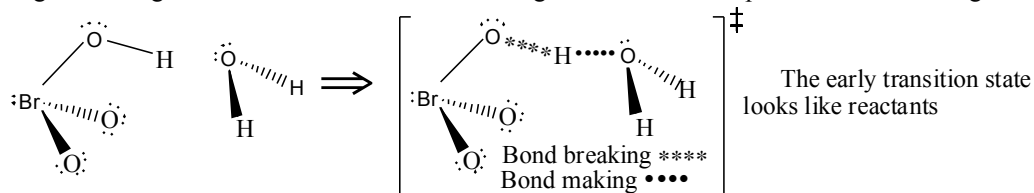
The pKa is approximately

pKa $\approx$ 8 – 2(5) = -2

$\Delta G^o \approx 5.7\text{kJmol}^{-1}(-2) = -11.4\text{kJmol}^{-1}$

Exothermic $\therefore$ ∃ Early Transition state (resembles reactants)

First draw the Lewis structures of the reactants with the proper geometry. Next combine the two reactants together using dotted lines to denote bond making and asterisks to represent bond breaking.

The early transition state looks like reactants

Now Consider the dissociation of bromous acid in water.

$$HBrO_2(aq) + H_2O(l) \rightleftharpoons BrO_2^-(aq) + H_3O^+(aq)$$

There is one oxo groups and one hydroxy group in the formula OBrOH so p = 1 and
q = 1.

The pKa is approximately

$$pKa \approx 8 - 1(5) = 3$$
$$\Delta G^o \approx 5.7 kJmol^{-1}(3) = 17.1 kJmol^{-1}$$

Endothermic $\therefore \exists$ Late Transition state (resembles products)

First draw the Lewis structures of the products with the proper geometry. Then combine the two products together using dotted lines to denote bond making and asterisks to represent bond breaking.

The late transition state looks like products

Bond breaking ∗∗∗∗
Bond making ••••
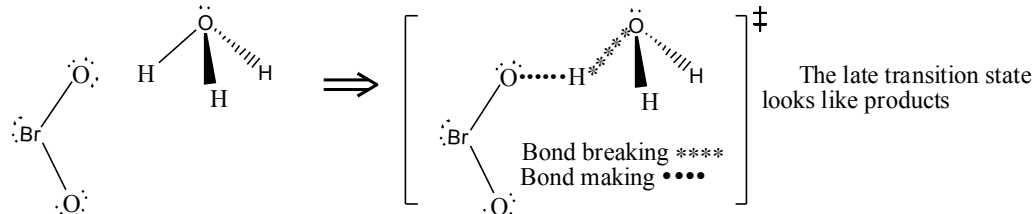
Now consider the exchange of a proton between a hydronium ion and a water molecule.

$$H_2O(l) + H_3O^+(aq) \rightleftharpoons H_3O^+(aq) + H_2O(l)$$
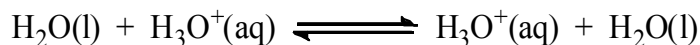
This process is thermally neutral ($\Delta G^o = 0$) so the transition state must be symmetric. First draw the whole reaction with the acceptor molecules (H_2O in this case) disposed on the outside and the donor molecules (H_3O^+ in this case) on the inside. The products should look like the mirror image of the reactants. For the transition state draw the two acceptor molecules and connect them together with the exchanged atom so that they look like the donor molecules that share the exchanged atom.

Bond breaking ∗∗∗∗
Bond making ••••
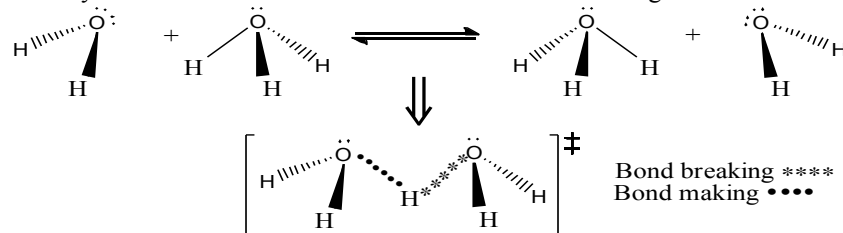
The resulting transition state is symmetrical.

Exercise 1:

Consider the dissociation of hypobromous acid in water

(a) Estimate the pKa for the acid and ΔG^o for the process.

(b) Draw the energy profile.

(c) Draw the transition state.

Consider the dissociation of perbromic acid in water

(d) Estimate the pKa for the acid and ΔG^o for the process.

(e) Draw the energy profile.

(f) **Draw the transition state.**

Consider the exchange of a proton between hypobromous acid and hypobromite ion

(g) Estimate ΔG^o for the process.

(h) Draw the energy profile.

(i) **Draw the transition state.**

Again consider the expression for K
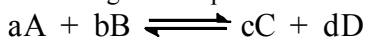
$$K = e^{-\left(\frac{\Delta G^o}{RT}\right)}$$

Substitution of $\Delta H^o - T\Delta S^o$ for ΔG^o in the expression
gives

$$K = e^{-\left(\frac{\Delta H^o - T\Delta S^o}{RT}\right)} = e^{-\left(\frac{\Delta H^o}{RT}\right)}e^{\left(\frac{\Delta S^o}{R}\right)}$$

$$K = e^{\left(\frac{\Delta S^o}{R}\right)}e^{-\left(\frac{\Delta H^o}{RT}\right)}$$

Recall that for the general equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

In the special case where $(c + d) = (a + b)$, K_c has no units and K can be shown to have the following relation to the molecular partition functions.

$$K = \left(\frac{q_C{}^c q_D{}^d}{q_A{}^a q_B{}^b}\right) e^{\left(\frac{-\Delta H^o}{RT}\right)} = Ze^{-\left(\frac{\Delta H^o}{RT}\right)}$$

Where Z represents the total partition function for the equilibrium. Comparison with result derived previously reveals the relation between Z and the change in entropy for this process.

$$Z = e^{\left(\frac{\Delta S^o}{R}\right)} \quad so \quad lnZ = \left(\frac{\Delta S^o}{R}\right) \quad and \quad \therefore \quad \Delta S^o = Rln(Z)$$

In fact all of the state functions of thermodynamics can be expressed in terms of the partition function. The partition function is the "super function" of thermodynamics.

The partition function for a translational degree of freedom of a molecule (q_{tr}) corresponds to the kinetic energy that arises from the motion of the molecule. The thanslational partition function in one dimension depends on distance so the three-dimensional case ($q_{tr}{}^3$) depends on volume (the partition functions for the rotational motion q_r and vibrational motion q_v of the molecule do not depend on distance so they are independent of the volume). If a distance of 1dm is used in q_{tr} the volume in $q_{tr}{}^3$ is one liter (V = 1L). This is the form of q_{tr} that is needed to obtain units of molarity. Then concentration in molL^{-1} of the molecule B ([B]) is equal to the partition function for B (q_B) divided by the product of Avogadros' number and 1 liter (N_oL).

$$[B] = \frac{q_B}{N_oL}$$

Then for the general equilibrium

$$aA + bB \rightleftharpoons cC + dD$$
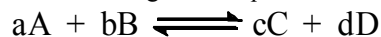
The expression for the equilibrium constant K_C is

$$K_c = (N_oV)^{(a + b - c - d)}\left(\frac{q_C{}^c q_D{}^d}{q_A{}^a q_B{}^b}\right) e^{\left(\frac{-\Delta H^o}{RT}\right)}$$

Kinetic Considerations:

The Ahrreneous equation for the rate constant k in terms of Boltzmann's law is

$$k = Ae^{-\left(\frac{E_a}{RT}\right)}$$

If a system is at thermal equilibrium at temperature T, then the fraction of the molecules with kinetic energy $E_k \geq Ea$ is equal to the ratio of the rate constant k to the frequency factor A.

$$\frac{k}{A} = e^{-\left(\frac{E_a}{RT}\right)}$$

In other words the observed rate constant k is a fraction of the frequency factor A (the maximum possible rate). That fraction is equal to the fraction of the molecules with $E_k \geq Ea$ when there is a Boltzmann disribution (when the system is at thermal equilibrium).

Taking the natural log of both sides of the above expression gives

$$\ln(\frac{k}{A}) = -\left(\frac{Ea}{RT}\right)$$

$$- RT\ln(\frac{k}{A}) = Ea$$

$$- 2.303RT\log(\frac{k}{A}) = Ea$$

$$2.303RT(- \log(\frac{k}{A})) = Ea$$

$$2.303RT(p(\frac{k}{A})) = Ea$$

Thus at the standard temperature (25°C)

$$5.7 kJmol^{-1}(p(\frac{k}{A})) = Ea$$

Processes with low activation energy are called **labile** while those with a high activation energy are called **inert**. The ratio of k to A provides a measure of the lability or inertness of a process. Both k and A depend upon the path of the reaction so they do not correspond to state functions. The rate constant k cannot be predicted and has to be measured experimentally. The frequency factor A is measured experimentally but can also be calculated in terms of Boltzmann's law.

If the partition functions of the molecules are known then the frequency factor for an elementary process is easy to calculate. The details of calculating the partition functions for the various degrees of freedom will not be needed or considered here. The magnitude of q_t , q_r , and q_v does not vary significantly for different small molecules so typical values for q_t , q_r , and q_v provide good order of magnitude estimates. Estimation of the frequency factor for an elementary reaction reveals the relationship between the degrees of freedom available to the molecules, the partition functions for the molecules, and the partition function for the elementary process.

Molecular Motion and Degrees of Freedom:

For every N-atom molecule there exists

3 – Translational degrees of freedom   (in 3–dimensional space)

and

2 – Rotational degrees of freedom   For Linear Molecules
3 – Rotational degrees of freedom   For Nonlinear Molecules
3N – 5 – Vibrational degrees of freedom   For Linear Molecules
3N – 6 – Vibrational degrees of freedom   For Nonlinear Molecules

Molecular Partition Functions:

For every molecule B, q_B is the product of q_t , q_r , and q_v for that molecule.

$$q_B = q_t^{\,3} \bullet q_r^{\,2} \bullet q_v^{\,3N-5} \qquad \forall \text{ linear molecule B}$$

and

$$q_B = q_t^{\,3} \bullet q_r^{\,3} \bullet q_v^{\,3N-6} \qquad \forall \text{ non-linear molecule B}$$

For example

Consider a water molecule H_2O. Water is a nonlinear molecule with N = 3 atoms
∴ ∃ 3 Translational, 3 rotational, and 3(3) – 6 = 3 vibrational degrees of freedom

$$q_{H2O} = q_t^{\,3} q_r^{\,3} q_v^{\,3}$$

Consider carbon dioxide CO_2. Carbon dioxide is a linear molecule with N = 3 atoms
∴ ∃ 3 Translational, 2 rotational, and 3(3) – 5 = 4 vibrational degrees of freedom

$$q_{CO2} = q_t^{\,3} q_r^{\,2} q_v^{\,4}$$
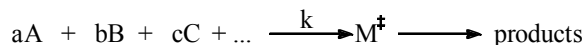
Consider the iodide ion I^-. This is an atomic ion ∴ N = 1 atom
∴ ∃ 3 Translational, 0 rotational, and 0 vibrational degrees of freedom

$$q_{I^-} = q_t^{\,3}$$

Exercise 2: Find q_B for

(a) **Hydronium ion (H_3O^+)**
(b) **Bromic acid ($HBrO_3$)**
(c) **Bromite ion (BrO_2^-)**
(d) **Hypobromous acid (HBrO)**
(e) **Bromous acid ($HBrO_2$)**

Consider the elementary process

$$aA \ + \ bB \ + \ cC \ + ... \ \xrightarrow{\ k\ } M^{\ddagger} \ \longrightarrow \ products$$

Where $M^{\ddagger}$ denotes the activated complex

The activated complex decomposes to products at the maximum possible rate. The maximum possible rate is the universal frequency factor $\upsilon^{\ddagger}$. The rate constant k of the elementary process is equal to the universal frequency factor $\upsilon^{\ddagger}$ times the equilibrium constant for the activated complex $K^{\ddagger}$.

$$k = \upsilon^{\ddagger} K^{\ddagger}$$

The equilibrium constant (the mass action constant) for the activated complex is described by the expression.

$$K^{\ddagger} = (N_oV)^{(a+b+c+...-1)} \left(\frac{q_{\ddagger}}{q_A^a q_B^b q_C^c ...} \right) e^{-\ Ea/RT}$$

Where $N_o \equiv$ Avogadro's number, V is the volume (1L), q_A is the partition function for reactant A, q_B for reactant B etc. etc., and $q^{\ddagger}$ is the partition function for the activated complex.

The activated complex is the "supermolecule" that corresponds to the arrangement of atoms in the transition state. **The activated complex has 3N − 7 vibrational degrees of freedom since one vibrational degree of freedom is lost to the reaction**. The reaction coordinate Q corresponds to the lost vibrational degree of freedom of the activated complex

The universal frequency factor is the ratio of Boltzmann's constant to Planck's constant multiplied by the absolute temperature. The resulting units are s^{-1}. The value at room temperature (300K) is

$$\upsilon^{\ddagger} \equiv \left(\frac{k_BT}{h} \right) \qquad \text{for } T = 300K$$

$$\upsilon^{\ddagger} = \left(\frac{k_BT}{h} \right) = \left(\frac{(1.38 \text{X} 10^{-23} JK^{-1})(3.0 \text{X} 10^2 K)}{(6.626 \text{X} 10^{-34} Js)} \right) = 6.248 \text{X} 10^{12} s^{-1}$$

**Estimating The Frequency Factor:**

The procedure for estimating frequency factors is described (better and more completely) in Kinetics and Mechanism 3rd Edition; John W. Moore and Ralph G. Pearson; Wiley Interscience Publications.

Approximate values for the partition functions for each type of degree of freedom have been calculated using typical values for the molecular constants and a length of 1dm for calculating the translational degree of freedom (this provides a value appropriate for a volume of 1L = 1dm³). These approximate values are given in the table below.

Degree of freedom	Designation	Order of magnitude (300K – 500K)	Temperature dependence
Translation	f_t	$10^9 - 10^{10}$	$T^{1/2}$
Rotation	f_r	$10^1 - 10^2$	$T^{1/2}$
Vibration	f_v	$10^0 - 10^1$	$T^0 - T^1$

For example consider the mechanism the class proposed for the oxidation of iodide ions by bromate ions in acid. The rate determining step (step 3) is

$$(3) \qquad I^-(aq) \ + \ H_2BrO_3^+(aq) \ \xrightarrow{\ k_3\ } \ IBrO_2(aq) \ + \ H_2O(l)$$
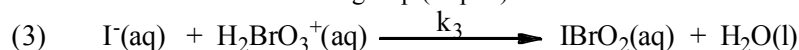
The fundamental assumption of kinetics is that the activated complex must contain all of the reactants in the elementary reaction. Therefore the activated complex must have the form

$$(I \bullet H_2BrO_3)^{\ddagger}$$

Iodide is a mono-atomic ion so there are only three translational degrees of freedom
$$q_{I^-} = q_t^{\ 3} \approx f_t^{\ 3}$$
$H_2BrO_3^+$ is a nonlinear molecule with N = 6 atoms
$\therefore \exists$ 3 Translational, 3 rotational, and 3(6) − 6 = 12 vibrational degrees of freedom
$$q_{H2BrO3} = q_t^{\ 3} q_r^{\ 3} q_v^{\ 12} \approx f_t^{\ 3} f_r^{\ 3} f_v^{\ 12}$$

$(I \bullet H_2BrO_3)^{\ddagger}$ is a nonlinear molecule with $N = 7$ atoms.

$\therefore \exists$ 3 – translational, 3 – rotational, and $3(7) - 7 = 14$ vibrational degrees of freedom

$$q_{\ddagger} = q_t^3 q_r^3 q_v^{14} \approx f_t^3 f_r^3 f_v^{14}$$

The approximate partition function for the process is

$$\frac{q_{\ddagger}}{q_I \cdot q_{H2BrO3}} \approx \frac{f_t^3 f_r^3 f_v^{14}}{f_t^3 f_t^3 f_r^3 f_v^{12}} = \frac{f_v^2}{f_t^3} = \frac{(10^0)^2}{(10^9)^3} = 10^{-27}$$

The mass action for the activated process is

$$K^{\ddagger} = (N_o V)^{(1+1-1)} \left(\frac{q_{\ddagger}}{q_I q_{H2BrO3}} \right) e^{-E_a/RT}$$

$$K^{\ddagger} \approx (6.022 \times 10^{23} \text{mol}^{-1}\text{L})(10^{-27})e^{-E_a/RT} = (6.022 \times 10^{-4} \text{mol}^{-1}\text{L})e^{-E_a/RT}$$

The rate constant k_3 is approximately

$$k_3 = \upsilon^{\ddagger} K^{\ddagger} = (6.246 \times 10^{12} \text{s}^{-1})(6.022 \times 10^{-4} \text{mol}^{-1}\text{L})e^{-E_a/RT}$$

$$k_3 = 3.76 \times 10^9 \text{mol}^{-1}\text{Ls}^{-1} e^{-E_a/RT}$$

The frequency factor for (3) is $\sim 10^9 \text{Lmol}^{-1}\text{s}^{-1}$

This is consistent with our experimentally measured frequency factor.

Exercise 3:

Estimate the frequency factor @ 300K for

(a) The proposed rate determining step

$$I^-(aq) + H_2BrO_3^+(aq) \rightleftharpoons IBrO_2(aq) + H_2O(l)$$

(b) The dissociation of bromic acid in water.

(c) The dissociation of bromous acid in water.

(d) The dissociation of hypobromous acid in water.

(e) The exchange of a proton between two hpobromite ions.