

6. THEORY OF ELEMENTARY REACTIONS

6.1 Collision Theory

Collision theory is the extension of the kinetic theory of gases in predicting reaction rates of a bimolecular gas phase reaction of the type:



It is assumed that the reaction rate expressed in terms of disappearance of molecules of A is given by:

$$-\tilde{r}_A \left(\frac{\text{molecules}}{\text{cm}^3 \text{ s}} \right) = 2f Z_{AA} \quad \text{for reaction (1)}$$

A factor two appears on the right hand side of eq (1) because for each collision two molecules of A disappear.

$$-\tilde{r}_A = -\tilde{r}_B \left(\frac{\text{molecules}}{\text{cm}^3 \text{ s}} \right) = f Z_{AB} \quad \text{for reaction (2)}$$

where

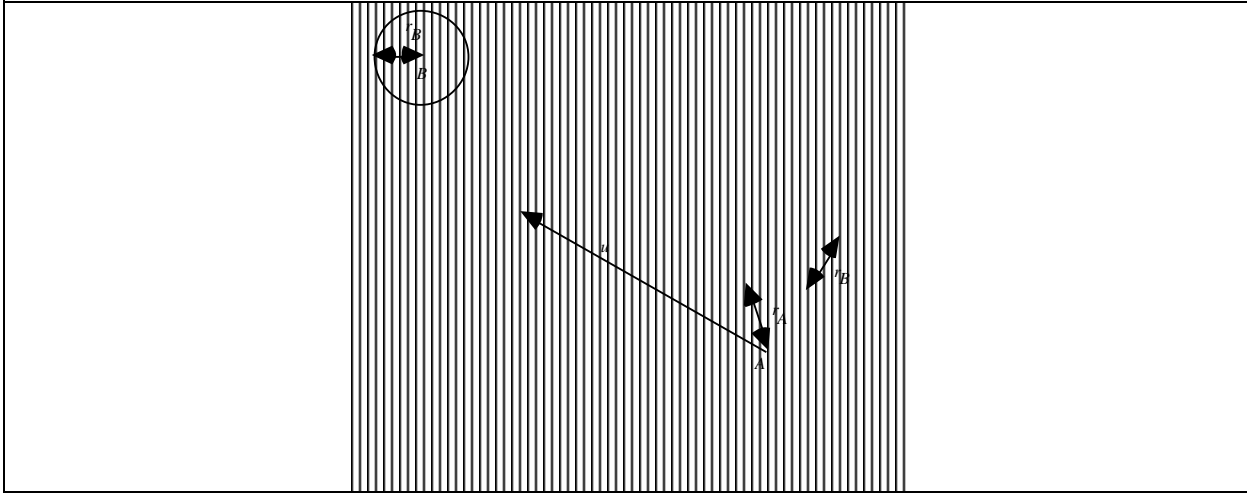
Z_{AB} - is the total number of collisions between molecules A and B in 1 cm^3 of reaction mixture per second (frequency of collision per 1 cm^3)

Z_{AA} - is the total number of collisions among the molecules A in 1 cm^3 per second

f - the fraction of molecules that possess the required excess energy for reaction i.e. the fraction of molecules that upon collision will react.

The kinetic theory of gases postulates that the collision frequency Z_{AB} is proportional to the size of the "target", to the relative mean velocity \bar{u}_{AB} , and to the number concentrations of both molecular species. The size of the "target" is interpreted as the maximum area perpendicular to the trajectory of the moving A (or B) molecule which when it contains a B (or A) molecule will lead to an inevitable collision of the two. (See Figure 1).

FIGURE 1: Frequency of collisions: molecule A is moving with speed u relative to B. In unit time the sphere of radius $r_A + r_B$ has swept out a volume $\pi(r_A + r_B)^2 u$ and has encountered $\pi(r_A + r_B)^2 u N_B$ molecules of B.



Thus

$$\text{"target area"} = \pi d_{AB}^2 = \pi \sigma_{AB}^2$$

$$\text{where } d_{AB} = \frac{d_A + d_B}{2} = d_{AB} \text{ is the radius of collision area}$$

d_A , d_B can be interpreted as equivalent molecular diameter of molecule A and B , respectively, if the molecules are viewed as hard spheres according to the classical collision theory. d_A , d_B can also be viewed as diameters in space of the sphere within which the attraction forces of A or B would force a collision.

The mean relative velocity is given by the kinetic theory as

$$\bar{u}_{AB} = \left(\frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} \quad (3)$$

where $k_B = 1.38062 \times 10^{-23} \text{JK}^{-1}$ is the Boltzmann's constant.

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} - \text{reduced molecular mass} \quad (4)$$

with $m_A \left(\frac{\text{g}}{\text{molecule}} \right)$ being the molecular mass of A , m_B the molecular mass of B .

The number concentrations are:

$$N_A \left(\frac{\text{number of molecules of } A}{\text{cm}^3} \right) ; N_B \left(\frac{\text{number of molecules of } B}{\text{cm}^3} \right)$$

The fraction of molecules having sufficient energy levels to react are given by the Boltzmann factor

$$f = e^{-E_m/k_B T}$$

where E_m is the difference in energy of an "excited" and "base" molecule.

The rate then becomes:

$$-\tilde{r}_A \left(\frac{\text{molecules}}{\text{cm}^3 \text{ s}} \right) = \pi \sigma_{AB}^2 \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} e^{-E_m/k_B T} N_A N_B \quad (5)$$

We want to express the rate in $\left(\frac{\text{mol}}{\text{lit s}} \right)$ and the concentrations in $\left(\frac{\text{mol}}{\text{lit}} \right)$. Then:

$$\frac{N_a}{10^3} C_A = N_A ; \quad \frac{N_a}{10^3} C_B = N_B$$

$$-r_A \left(\frac{\text{moles}}{\text{lit s}} \right) \times \frac{N_a}{10^3} = -\tilde{r}_A \left(\frac{\text{molecules}}{\text{cm}^3 \text{ s}} \right)$$

Also

$$k_B N_a = R ; \quad \mu_{AB} N_a = M_{AB} = \left(\frac{M_A + M_B}{M_A M_B} \right)^{-1}$$

where N_a is the Avogadro's constant

$$N_a = 6.02217 \times 10^{23} \frac{\text{molecules}}{\text{mole}}$$

M_A, M_B – molecularweights

The expression for the rate finally becomes

$$-r_A \left(\frac{\text{mole}}{\text{lit s}} \right) = \underbrace{\sigma_{AB}^2 \sqrt{\frac{8\pi R T}{M_{AB}}}}_k e^{-E/RT} \frac{N_a}{10^3} C_A C_B \quad (6)$$

Thus

$$k = k_o T^{1/2} e^{-E/RT} \quad (7a)$$

$$k_o = \sigma_{AB}^2 \sqrt{\frac{8\pi R}{M_{AB}}} \frac{N_a}{10^3} \quad (7b)$$

Collision theory predicts the dependence of the rate constant on temperature of the type $T^{1/2} e^{-E/RT}$ and allows actual prediction of the values for the frequency factor from tabulated data.

For reaction of type (1)

$$Z_{AA} = \frac{1}{2} \pi \sigma_A^2 \left(\frac{8k_B T}{\pi \mu_{AA}} \right)^{1/2} N_A^2 \quad (8)$$

Factor $\frac{1}{2}$ is there since all the molecules are the same and otherwise the collisions would have been counted twice. This factor is offset by the 2 in the rate expression which simply indicates that in every collision two molecules of A react.

$$\text{Now } \mu_{AA} = \frac{m_A}{2}$$

$$-\tilde{r}_A \left(\frac{\text{molecules}}{cm^3 s} \right) = \sigma_A^2 \left(\frac{16\pi k_B T}{m_a} \right)^{1/2} e^{-E_m/k_B T} N_A^2 \quad (9a)$$

$$-r_A \left(\frac{\text{moles}}{\text{lit s}} \right) = \underbrace{4\sigma_A^2 \sqrt{\frac{\pi R}{M_A}} \frac{N_a}{10^3} T^{1/2}}_{k_{o\ coll}} e^{-E/RT} C_A^2 \quad (9b)$$

Some predictions of the collision theory will be compared later to transition state theory.

Note: $T^{1/2}$ dependence is almost entirely masked by the much stronger $e^{-E/RT}$ dependence. Thus Arrhenius form is a good approximation.

The relationship to Arrhenius parameters is:

$$k_{o\ Arr} = k_{o\ coll} (e\bar{T})^{1/2} \quad (10a)$$

$$E_{Arr} = E_{coll} + \frac{1}{2} R\bar{T} \quad (10b)$$

Original comparison of the collision theory prediction with experimental values for the reaction $2HI \rightarrow H_2 + I_2$ resulted at 556K in $k_{\text{predicted}} = 3.50 \times 10^{-7}$ (L/mol s) as opposed to $k_{\text{exp}} = 3.52 \times 10^{-7}$ (l/mol s). This proved to be an unfortunate coincidence as later it became evident that predictions based on collision theory can lead to gross discrepancies with data. For example, for more complex gas molecules predicted pre-exponential factors are often order of magnitude higher than experimental values and severe problems arise for reactions of ions or dipolar substances.

The modifications to the collision theory recognize that the collision cross-sectional area is not a

constant, but a function of energy, introduce a steric factor and acknowledge that molecules do not travel at the same speed but with a Maxwell-Boltzmann distribution of velocity! If one considers just the translational energy, ε_t , one can argue that the rate constant can be predicted from

$$k(T) = \left(\frac{8}{\pi \mu (kT)^3} \right)^{1/2} \int_0^{\infty} \varepsilon_t \sigma(\varepsilon_t) e^{-\varepsilon_t/kT} d\varepsilon_t \quad (11)$$

Similar but more complex expressions can be derived accounting for rotational and vibrational energies. Modern analytical tools allow measurement of effective reaction cross-section when reactant molecules are in prescribed vibrational and rotational states. When such information is available collision theory in principle leads to the 'a priori' prediction of the rate constant.

Example 1. Using collision theory estimate the specific rate constant for the decomposition of HI at 321°C, $\sigma_{HI} = 3.5 \text{ \AA}$, $E = 44000 \frac{\text{cal}}{\text{mol}}$. Experimentally the rate constant is found to be

$$k = 2.0 \times 10^{-6} \left(\frac{\text{lit}}{\text{mols}} \right). \text{ Collision theory prediction is:}$$

$$k = 4 \sigma_{HI}^2 \sqrt{\frac{\pi RT}{M_{HI}}} \frac{N_a}{10^3} e^{-E/RT}$$

$$k = 4 \times (3.5 \times 10^{-8})^2 \sqrt{\frac{\pi \times 8.314 \times 10^7 \times (273 + 321)}{127.9}} e^{-\frac{44000}{1.987 \times 594}} \times \frac{6.023 \times 10^{23}}{10^3}$$

$$\sigma_{HI} = 3.51 \times 10^{-8} \text{ cm} ; R = 8.314 \times 10^7 \text{ erg/molK}$$

$$T = 273 + 321 = 594 \text{ K} , M_{HI} = 127.9$$

$$N_a = 6.023 \times 10^{23} \text{ molecules/mol}$$

$$k = 6.63 \times 10^{-6} \frac{\text{lit}}{\text{mols}} \leftarrow \text{collision theory estimate}$$

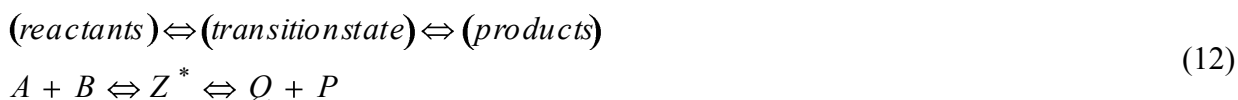
$$k = 2.0 \times 10^{-6} \frac{\text{lit}}{\text{mols}} \leftarrow \text{experimental value}$$

Collision theory usually gives the upper bound of the rate constant.

6.2 Classical Transition State Theory (CTST)

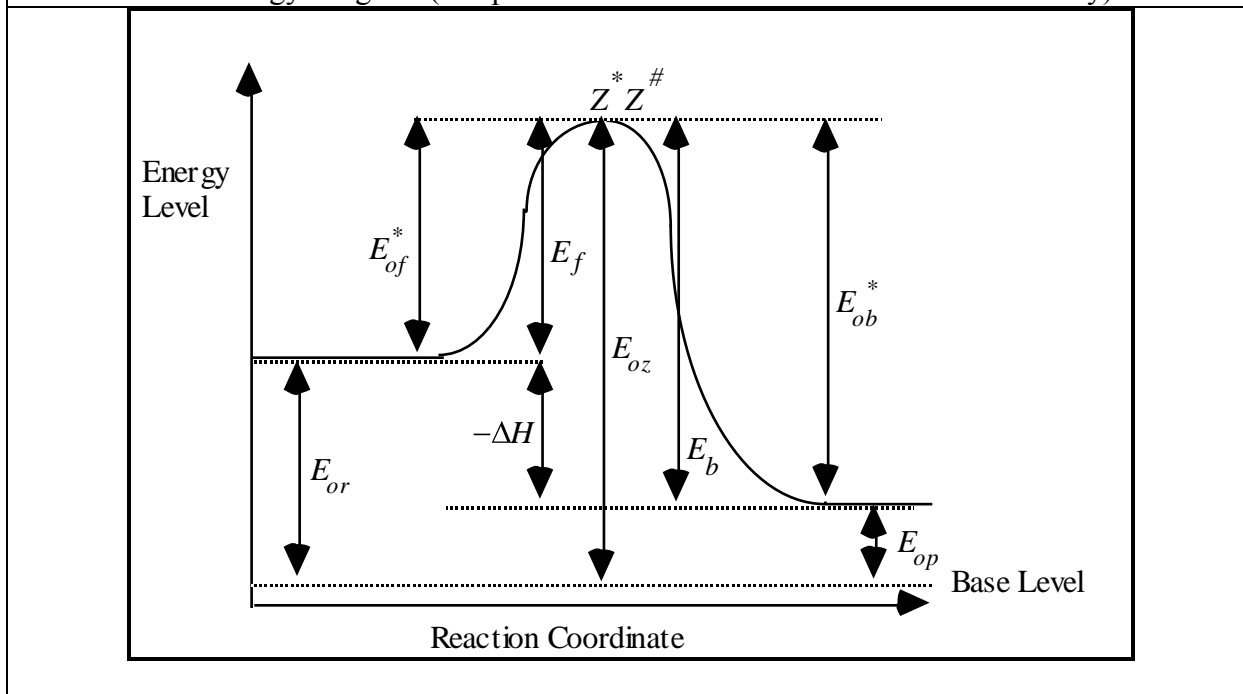
This is the most promising of the rate theories and deals again with elementary reactions. However, even an elementary reaction is not viewed any more to occur exactly in one step (this shows how flexible the definition of elementary reactions has become since they are supposed to occur in one step).

According to transition state theory every elementary reaction proceeds through an activated complex - a transition state.



The transition state is a little more than the fraction of excited (energized) reactant molecules as in Arrhenius or collision theory. Its structure is neither that of the reactants nor of products, it is someplace in between and its concentration is always orders of magnitude lower than that of reactants or products. The transition state can either be formed starting solely with reactant molecules from the left or with product molecules from the right. The energy picture is as shown in Figure 2.

FIGURE 2: Energy Diagram (Simplified for the Classical Transition State Theory)



- E_{or} - energy level of reactants
- E_{op} - energy level of products
- E_{oz} - energy level of transition state
- E_{of}^* - activation barrier for forward reaction
- E_{ob}^* - activation barrier for reverse reaction
- ΔH° - heat of reaction

$$|E_{of}^* = E_f = E_{oz} - E_{or}|$$

$$|E_{ob}^* = E_b = E_{oz} - E_{op}|$$

$$|\Delta H = E_{op} - E_{or} = (E_{oz} - E_b) - (E_{oz} - E_f)|$$

$$|\Delta H = E_f - E_b|$$

When the overall system, i.e reactants and products, is in equilibrium, clearly the net rate of reaction is zero, i.e

$$r = r_f - r_b = 0$$

However, even in overall equilibrium a certain number of reactant molecules gets transformed per unit

time into the transition state, and the same number gets transformed from transition state to reactants as required by the principle of microscopic balancing. At the same time a certain rate of exchange exists between transition state and products which is balanced by the exchange between products and transition state. That exchange rate at overall equilibrium is proportional to νC_z where ν is the frequency of occurrence of exchange $\left(\frac{1}{s}\right)$ and C_z the number concentration of the transition state.

The three fundamental assumptions of transition state theory are:

1. The rate of reaction is given by

$$r = \nu C_z \quad (13)$$

even when the system is removed from equilibrium i.e when there are no products, or products are being removed, or they are present in amount less than required by equilibrium. This is equivalent to assuming that the equilibrium between the transition states and reactants is always established.

2. The frequency ν involved is a universal frequency, it does not depend on the nature of the molecular system and is given by

$$\nu = \frac{k_B T}{h_p} \quad (14)$$

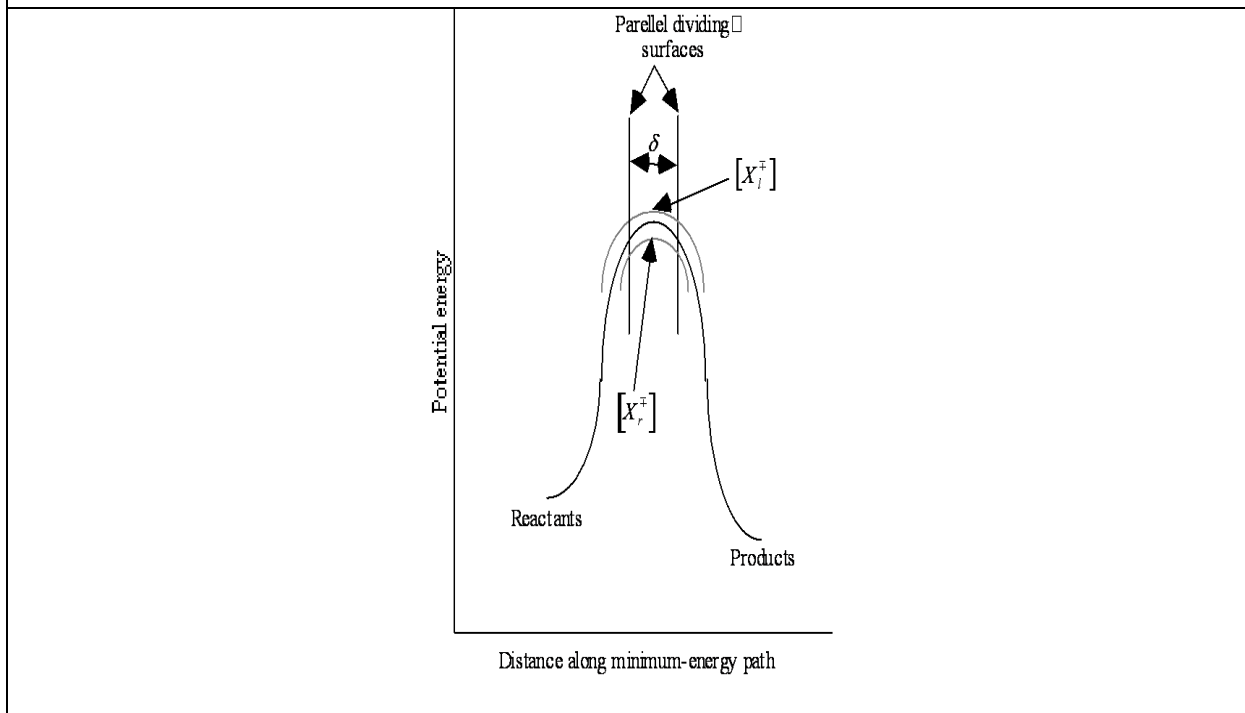
where $k_b = 1.38062 \times 10^{-23} \text{ JK}^{-1}$ Boltzmann's constant

$h_p = 6.6262 \times 10^{-34} \text{ Js}$ Planck's constant

T (K) - absolute temperature

3. The reaction system is "symmetric" with respect to the transition state and the above is also true when starting from products to make reactants (from right to left). A more rigorous treatment is outlined in appropriate textbooks on kinetics (e.g. see Laidler, Chemical Kinetics). This is a very bold assumption asserting that the equilibrium rate of exchange is equal to the rate for the system out of equilibrium. If we refer to Figure 3, the above assumptions indicate that once reactant molecules have reached the col of the activated complex (transition state) from the left there is no going back and they get converted to products. Similarly, the product molecules that reach the col from the right cannot turn back and do get transformed to reactants.

FIGURE 3: Profile through the minimum-energy path, showing two-dividing surfaces at the col separated by a small distance δ .



Let us look at the forward reaction (from left to right)

$$r_f = \nu C_z$$

Reactants and transition state are at equilibrium

$$K^* = \frac{a_z}{a_A a_B} = \frac{\gamma_z C_z}{\gamma_A \gamma_B C_A C_B} = K_\gamma K_c$$

$$C_z = K^* K_\gamma^{-1} C_A C_B \quad \nu = \frac{k_B T}{h_p} \quad (15)$$

$$r_f = \frac{k_B T K^*}{h_p \gamma_z} \gamma_A \gamma_B C_A C_B = \frac{k_B T}{h_p \gamma_z} K^* a_A a_B$$

Now we can define a rate constant for the forward reaction that is a function of temperature only

$$k_{f_i}(T) = \frac{k_B T}{h_p} K^*. \quad \text{This yields}$$

$$r_f = \frac{k_{f_i}(T)}{\gamma_z} a_A a_B \quad \text{and} \quad K^* = e^{-\frac{\Delta G^*}{RT}} = e^{-\frac{\Delta H^*}{RT}} e^{\frac{\Delta S^*}{R}} \quad (16)$$

Similarly for the reverse reaction $r_b = \nu C_z$, and the equilibrium between transition states and products is always established.

$$K^\ddagger = \frac{\gamma_z C_z}{\gamma_Q \gamma_P C_Q C_P} \quad C_z = \frac{a_Q a_P}{\gamma_z} K^\ddagger$$

$$K^\ddagger = e^{-\frac{\Delta G^\ddagger}{RT}} = e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$$

The reverse rate is now expressed by

$$r_b = \frac{k_{bi}(T)}{\gamma_z} a_Q a_P \quad \text{where} \quad k_{bi}(T) = \frac{k_B T}{h_p} K^\ddagger \quad (17)$$

In the above ΔG^* , ΔH^* , ΔS^* and ΔG^\ddagger , ΔH^\ddagger , ΔS^\ddagger are the Gibbs free energy, heat of reaction, and change in entropy for formation of the transition state starting from reactants and products, respectively.

The net rate of reaction then is

$$r = r_f - r_b = \frac{1}{\gamma_z} [k_{fi} a_A a_B - k_{bi} a_Q a_P]$$

or

$$r = \frac{k_B T}{h_p \gamma_z} [K^* a_A a_B - K^\ddagger a_Q a_P] = \frac{k_B T}{h_p \gamma_z} \left[e^{-\frac{\Delta H^*}{RT}} e^{\frac{\Delta S^*}{R}} a_A a_B - e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} a_Q a_P \right] \quad (18)$$

At equilibrium $r = 0$ so that the equilibrium constant K for the reaction is recovered:

$$K = \frac{a_Q a_P}{a_A a_B} = e^{-\frac{\Delta H^* - \Delta H^\ddagger}{RT}} e^{\frac{\Delta S^* - \Delta S^\ddagger}{R}} = e^{-\frac{\Delta G^* - \Delta G^\ddagger}{RT}}$$

Therefore, the following equations hold:

$$\Delta H^* - \Delta H^\ddagger = \Delta H^\circ \quad - \text{heat of reaction}$$

$$\Delta S^* - \Delta S^\ddagger = \Delta S^\circ \quad - \text{entropy due to reaction}$$

$$\Delta G^* - \Delta G^\ddagger = \Delta G^\circ \quad - \text{Gibbs free energy change due to reaction}$$

$$\Delta H^* = E_f \quad \Delta H^\ddagger = E_b$$

Let us call $k_f(T) = k_{fi}$, $k_b(T) = k_{bi}$, rate constants which are functions of T only.

$$r = \frac{1}{\lambda_z} [k_f a_A a_B - k_b a_Q a_P] \quad (19)$$

We usually express the rate in the form:

$$r = k_f C_A C_B - k_b C_Q C_P \quad (20)$$

This gives the relationship:

$$k_f = k_{f_i} \frac{\gamma_A \gamma_B}{\gamma_z} \quad k_b = k_{b_i} \frac{\gamma_Q \gamma_P}{\gamma_z} \quad (21)$$

This is a very important result of the transition state theory. It tells us that whenever we write and evaluate a rate expression with its driving force being expressed in molar concentrations the rate constants, k_f , k_b , etc. that appear in such expressions are not only functions of temperature but also could be functions of pressure and concentration. This is obvious from the above since k_{f_i} , k_{b_i} are functions of temperature only but $\gamma_A, \gamma_B, \gamma_Q, \gamma_P, \gamma_z$ can also be functions of pressure or concentration.

The above relationship between rate constants k_f, k_b in nonideal systems for rates whose driving force is as usual expressed in concentrations, and the ideal rate constants k_{f_i}, k_{b_i} which would be observed in a system with all activity coefficients of unity, is frequently used to correct the constants for pressure effects in gas reactions or for concentration effects in ionic solutions.

Relationship to Arrhenius parameters $k_{o_Arr} e^{-E_{Arr}/RT}$ is:

$$k_{o_Arr} = \left(e \frac{k_B \bar{T}}{\gamma_z h_p} \right) e^{\Delta S^\circ/R} \quad ; \quad E_{Arr} = \Delta H^* + R\bar{T} \quad (22)$$

Note: Sometimes transition state theory is interpreted by asserting that the rate is proportional to the product of the universal frequency and the activity of the transition state (rather than to its concentration). This would lead essentially to the same expressions as shown above except that γ_z would not appear, i.e wherever it appears it would be replaced by unity.

Example.2

Estimate the rate constant for decomposition of methyl azide CH_3N_3 by transition state theory at 500K, given $\Delta H^* = 42,500 \text{ cal/mol}$, $\Delta S^* = 8.2 \text{ cal/molK}$.

$$k = \frac{k_B T}{h_p} e^{-\frac{\Delta H^*}{RT}} e^{\frac{\Delta S^*}{R}}$$

$$k = \frac{1.38062 \times 10^{-23} \times 500}{6.6262 \times 10^{-34}} e^{-\frac{42500}{1.987 \times 500}} e^{\frac{8.2}{1.987}}$$

$$k = 1.705 \times 10^{-4} \text{ s}^{-1}$$

When we use transition state theory to calculate the rate constant for reaction of the type $A = B$ there is no ambiguity as to the units of the rate constant. However, when we deal with bimolecular reactions of the type $A + B \rightleftharpoons P + Q$ and

$$k_f = \frac{\overline{k_B T}^\nu}{h_p} K_d^* \quad ; \quad k_h = \frac{\overline{k_B T}^\nu}{h_p} K_d^\ddagger$$

the units of the rate constants are not governed by the kinetic factor $\nu \left(\frac{1}{s} \right)$ but rather by the thermodynamic factor K_d^* and K_d^\ddagger , i.e. by the choice of standard states for calculation of ΔG^* and ΔG^\ddagger upon which the calculation of these parameters K_d^*, K_d^\ddagger are based. If concentration is chosen for the driving force in the rate expression then $d = c$ and $K_d^* = K_c^* = C_z^* / C_A C_B$, if pressure is chosen then $d = p$ and $K_p^* = P_z^* / P_A P_B$. Similarly,

$$K_c^\ddagger = C_z^* / C_p C_q, \text{ and } K_p^\ddagger = P_z^* / P_p P_q.$$

It is useful therefore to review the use of standard states and relationships between thermodynamic quantities at this point.

For a general reaction

$$\sum_{j=1}^s \nu_j A_j = 0$$

The thermodynamic quantities $K, \Delta H^\circ, \Delta G^\circ, \Delta S^\circ, C_p^\circ$ are generally tabulated for standard states of 1 atm and ideal gas. Frequently we want to transform these to standard states expressed in concentration units, generally $1 \frac{\text{mol}}{\text{lit}}$ (1 M).

Example. 3

When using transition state theory for a bimolar reaction for which $\sum_{j=1}^s \nu_j = -1$, since two moles of reactant give one mole of transition complex, and when the quantities $K^*, \Delta H^*, \Delta S^*$ are based on standard states at 1 atm of ideal gases, then from transition theory

$$\Delta H_p^* = \Delta H_c^* - RT.$$

$$k_p = \frac{k_B T}{h_p} e^{\frac{\Delta S_p^*}{R}} e^{-\frac{\Delta H_p^*}{RT}} \quad (\text{atm}^{-1}, \text{s}^{-1})$$

Compared with Arrhenius equation

$$k_{p_{f, Arr}} = k'_{p_o} e^{-E'_p/RT} (\text{atm}^{-1}, \text{s}^{-1})$$

yields the frequency factor

$$k'_{p_o} = e \frac{k_B \bar{T}}{h_p} e^{\frac{\Delta S_p^*}{RT}} (\text{atm}^{-1}, \text{s}^{-1})$$

and activation energy $E'_p = \Delta H^* + R\bar{T} = \Delta U^*$

Compared with Arrhenius equation in concentration units

$$k_c = k_{c_o} e^{-E_c/RT} \left(\frac{\text{lit}}{\text{mol}} \text{s}^{-1} \right)$$

it gives the frequency factor:

$$\begin{aligned} k_{c_o} &= k'_{p_o} (R'T) e = e^2 \frac{k_B \bar{T}}{h_p} R'T e^{\frac{\Delta S_p^*}{R}} \\ &= e^2 \frac{k_B \bar{T}}{h_p} e^{\frac{\Delta S_p^* + R \ln R'T}{R}} = e^2 \frac{k_B \bar{T}}{h_p} e^{\Delta S_c^*/R} \end{aligned}$$

since $\sum \nu_j = -1$ going from two reactant molecules to one molecule of the transition state

The activation energy is

$$E_c = E'_p + RT = \Delta H_p^* + 2R\bar{T} = \Delta U^* + RT$$

Example. 4. The homogeneous dimerization of butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) has been studied extensively. An experimental rate constant based on disappearance of butadiene was found as:

$$k = \underbrace{9.2 \times 10^9}_{k_o} e^{-23960/RT} \left(\frac{\text{cm}^3}{\text{mols}} \right)$$

- a) Use collision theory to predict a value of k_o at 600 K and compare with experimental value of 9.2×10^9 . Assume effective collision diameter 5×10^{-8} cm.

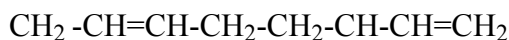
$$k_o \left(\frac{\text{cm}^3}{\text{mols}} \right) = 4 \sigma_B^2 \sqrt{\frac{\pi RT}{M_B}} N_a e$$

$$k_o = 4 \times (5 \times 10^{-8})^2 \sqrt{\frac{\pi \times 8.314 \times 10^7 \times 600}{54}} \times 6.023 \times 10^{23} e$$

$$k_o = 8.81 \times 10^{14} \left(\frac{\text{cm}^3}{\text{gmols}} \right) \leftarrow \text{collision theory prediction}$$

$$k_o = 9.2 \times 10^9 \left(\frac{\text{cm}^3}{\text{gmols}} \right) \leftarrow \text{experimental value}$$

- b) Use transition-state theory to predict k_o at 600 K and compare to experimental value. Assume the following form of the transition state (a hint from a friendly chemist!)



$$k_o = e^2 \frac{k_B T}{h_p} R' T e^{\frac{\Delta S_p^*}{R}} = e^2 \frac{k_B T}{h_p} e^{\Delta S_c^*/R}$$

$$\Delta S_c^* = \Delta S_p^* + R \ln R' T$$

We have to calculate the change of entropy for the formation of transition state from reactants. To do this the group contribution method and appropriate tables are used. [D.A. Hougen and K.M. Watson "Chemical Process Principles" Vol. II: pp 759-764 Wiley, NY, 1947; or S.W. Benson "Thermochemical KInetics, 2nd ed. - Methods for the Estimation of Thermochemical Data and Rate Parameters", Wiley, NY 1976].

Using Benson's Tables (attached) we get for $\text{CH}_2=\text{CH-CH=CH}_2$

$$S^\circ = 2 \times 27.61 + 2 \times 7.97 = 71.16 \frac{\text{cal}}{\text{mol K}}$$

| | | | | |
|----------------|-------|-------|-------|-------|
| T | 300 | 400 | 500 | 600 |
| C _p | 18.52 | 22.78 | 26.64 | 30.00 |

For $\text{CH}_2\text{-CH=CH-CH}_2\text{-CH}_2\text{-CH-CH=CH}_2$

using the contributions of CH_2 to be between those for $-\text{CH}_3$ and $-\text{CH}_2$ radical we get $S^\circ = 110.995$ cal/mol K.

| | | | | |
|----------------|------|-------|-------|-------|
| T | 300 | 400 | 500 | 600 |
| C _p | 40.0 | 49.42 | 57.82 | 65.02 |

Then

$$\Delta S_T^* = \Delta S_o^* + \int_{T_o}^T \frac{\Delta C_p}{T} dT$$

$$\Delta S_T^* = \Delta S_o^* + \left[\frac{1}{2} \frac{\Delta C_p(T_o)}{T_o} + \frac{\Delta C_p(T_1)}{T_1} + \frac{\Delta C_p(T_2)}{T_2} + \frac{1}{2} \frac{\Delta C_p(T_3)}{T_3} \right] \Delta T$$

$$\Delta S_T^* = (110995 - 2 \times 7116) + \left[\frac{1}{2} \frac{40.00 - 2 \times 18.52}{300} + \frac{49.42 - 2 \times 22.78}{400} + \frac{57.82 - 2 \times 26.64}{500} + \frac{1}{2} \frac{65.02 - 2 \times 30.00}{600} \right] \times 100$$

$$\Delta S_T^* = -31.325 + 2.785 = -28.54 \frac{\text{cal}}{\text{molK}}$$

$$k_{c_o} = e^2 \frac{1.38062 \times 10^{23} \times 600}{6.6262 \times 10^{34}} e^{-\frac{28.54 + 1.987 \ln(0.0821 \times 600)}{1.987}} \times 10^3$$

$$k_{c_o} = 2.63 \times 10^{12} \left(\frac{\text{cm}^3}{\text{gmols}} \right) \leftarrow \text{transition state theory prediction}$$

$$k_{c_o} = 9.2 \times 10^9 \left(\frac{\text{cm}^3}{\text{gmols}} \right) \leftarrow \text{experimental value}$$

A closer prediction but still an upper bound. Remember the structure of the transition state was only hypothesized and all thermodynamic quantities only estimated.

Table 1: Some useful orders of magnitude

| Quantity | Expression | Order of Magnitude | Units |
|-------------------------------|--|--------------------|---------------------------------|
| mean molecular velocity | $\left(\frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2}$ | 5×10^4 | (cm/s) |
| universal frequency | $\frac{k_B T}{h_p}$ | 10^{13} | (1/s) |
| collision frequency gas-gas | $\pi \sigma_{AB}^2 u_{AB}$ | 10^{-10} | (cm ³ /s - molecule) |
| collision frequency gas-solid | $\frac{\bar{u}}{4}$ | 10^4 | (cm/s) |

It is instructive to gain an insight into the order of magnitude of some important quantities by examining Table 1 above, and to learn a little more about the comparison in prediction of the TST and collision theory from Table 2.

Table 2: Comparison of Theories

| Reaction | Logarithm of k_{CO} | | |
|--------------------------------------|-----------------------|-------------------------|------------------|
| | Observed | Transition State Theory | Collision Theory |
| $NO + O_3 \rightarrow NO_2 + O_2$ | 11.9 | 11.6 | 13.7 |
| $NO_2 + O_3 \rightarrow NO_3 + O_2$ | 12.8 | 11.1 | 13.8 |
| $NO_2 + F_2 \rightarrow NO_2 F + F$ | 12.2 | 11.1 | 13.8 |
| $NO_2 + CO \rightarrow NO + CO_2$ | 13.1 | 12.8 | 13.6 |
| $F_2 + ClO_2 \rightarrow FClO_2 + F$ | 10.5 | 10.9 | 13.7 |
| $2ClO \rightarrow Cl_2 + O_2$ | 10.8 | 10.0 | 13.4 |

Transition theory seems to give consistently better predictions.

6.3. Transition State Theory explained by Statistical Mechanics

In this section, we will investigate the relationship between molecular level concepts and thermodynamic properties. In order to be able to start looking at molecular level, we will introduce partition functions that describe a specific system using statistical mechanics.

Let's start with a few definitions.

An **ensemble** is a collection of subsystems that make up the thermodynamic state. Different ensembles are obtained depending on the intensive (e.g. temperature (T)) or extensive (e.g. volume (V)) variables that define the thermodynamic state. Figure 4 shows an example of an ensemble that has 16 states. If there is no material exchange between the states, composition (N) is constant for each state. In a **microcanonical** ensemble, V, energy (E) and N are kept constant.

| | | | |
|--------|--------|--------|--------|
| 1 NVE | 2 NVE | 3 NVE | 4 NVE |
| 5 NVE | 6 NVE | 7 NVE | 8 NVE |
| 9 NVE | 10 NVE | 11 NVE | 12 NVE |
| 13 NVE | 14 NVE | 15 NVE | 16 NVE |

FIGURE 4. An example of a microcanonical ensemble with 16 states each at constant N, V and E

Microcanonical ensemble is therefore isolated since each state is at the same energy and no energy transfer occurs between the states. In a **canonical** ensemble, the states are not isolated and T is fixed instead of E. By this way, E may be transferred as heat.

If the states are not closed but open to material exchange and chemical potential (μ), V and T are fixed, the ensemble is defined as **grand canonical ensemble**.

Finally, the ensemble is called **isothermal-isobaric** for states with constant N, T, and pressure (P).

In statistical mechanics, each ensemble can be connected to the classical thermodynamical information using partition functions. The derivation for the connectivity equations are explained in detail in statistical mechanics books (e.g. Donald A. McQuarrie, "Statistical Mechanics", Harper Collins Publishers, NY, 1976 and M.P. Allen, D.J. Tildesley, "Computer Simulation of Liquids", Clarendon Press, Oxford, 1997) Table 3 summarizes the connectivity equations between the micro-level partition functions and the macro-level classical thermodynamic equations.

Table 3. Connectivity equations

| Ensemble | Thermodynamic Quantity | Equation |
|---------------------|------------------------|----------------------------------|
| microcanonical | S | $S = k_B Q_{NVE}$ |
| canonical | A | $\frac{A}{k_B T} = -\ln Q_{NVT}$ |
| grand canonical | pV | $pV = k_B T \ln Q_{\mu NT}$ |
| isothermal-isobaric | G | $G = -k_B T \ln Q_{NPT}$ |

In the table Q represents the partition function for the ensemble. (e.g. Q_{NVE} represents partition function for the microcanonical ensemble where N, V, and E are constant.)

If the molecules that make up the system are independent of each other as in an ideal gas at the canonical ensemble, the partition function, Q can further be divided into individual molecular partition functions as:

$$Q = \frac{q^N}{N!} \quad (23)$$

The molecular partition function itself consists of different contributing partition functions of different contributing partition functions arising from different modes of motion, mainly translational, rotational, vibrational, electronic and nuclear.

In other words,

$$q = q_{\text{translational}} q_{\text{rotational}} q_{\text{vibrational}} q_{\text{nuclear}} q_{\text{electronic}} \quad (24)$$

Let's focus on the individual contributions:

Translational contribution:

$$q_{\text{translational}} = V \left(\frac{2\pi mk_B T}{h_p^2} \right)^{3/2} \quad (25)$$

with m being the molecular mass and h_p being the Plank constant = 6.62608×10^{-34} Js

Rotational contribution:

$$q_{\text{rotational}} = \frac{1}{\sigma} \sum_J (2J + 1) e^{-\frac{J(J+1)hcB}{k_B T}} \quad (26)$$

with $J = 0, 1, 2, \dots$,

σ = symmetry number, 1 for heteroatomic molecules and 2 for homoatomic molecules

c = speed of light

B = rotational constant for each molecule (cm^{-1})

Rotational contribution is usually approximated by Eq. 27.

$$q_{\text{rotational}} \approx \frac{k_B T}{\sigma hc B} \quad (27)$$

Vibrational contribution:

$$q_{\text{vibrational}} = \frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}} \quad (28)$$

$$\text{where } \nu = \left(\frac{k}{\mu} \right)^{1/2} \frac{1}{2\pi} \quad (29)$$

with k being the force constant of the molecule and μ being the reduced mass.

Nuclear contribution:

$q_{nuclear}$ is taken as the degeneracy of the ground nuclear state. It is usually omitted in the calculations because for most cases, nuclear state is not altered for states of interest.

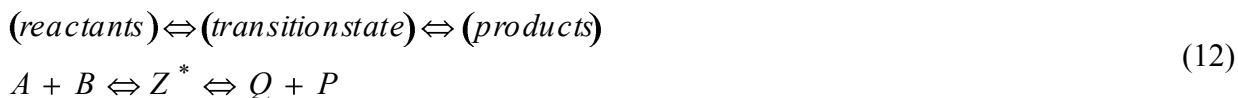
Electronic contribution:

$$q_{electronic} = f(e) \quad (30)$$

The electronic partition function is basically given as a function of degeneracy of the electronic ground state and is equal to 1 for most cases.

Rate Constant Related to Molecular Partition Functions

If we look at our reaction Eq (12) and express the equilibrium constant, K using partial pressures, we can see how molecular partition functions correlate with transition state theory.



From classical thermodynamics:

$$G = A + pV \quad (31)$$

$$\text{Combining and keeping in mind that } nRT = k_B NT \quad (32)$$

$$\begin{aligned} G &= -k_B T \ln \frac{q^N}{N!} + nRT = -k_B T (N \ln q - \ln N!) + nRT = -k_B TN \ln q + k_B T (N \ln N - N) + nRT = \\ &-k_B TN \ln \left(\frac{q}{N} \right) = -nRT \ln \left(\frac{q}{N} \right) \end{aligned} \quad (33)$$

We also know that

$$\Delta G_r = \sum_{j=1}^s \nu_j \Delta G_{fj} \quad (34)$$

Then combining with Eq. 33

$$\Delta G_{fj} = G_j + G_{T_0} = -RT \ln \left(\frac{q_j}{N} \right) + U_{T_0} \quad (35)$$

Note that we lost the n factor of Eqn (35) since G is in terms of molar quantity. If we select our reference system as $T = 0$, then $G = U$.

Combining Eqs (34) and (35) gives

$$\Delta G_r = -RT \sum_{j=1}^s \ln \left(\frac{q_j}{N} \right)^{\nu_j} + \Delta E_0 \quad (36)$$

We also know that

$$\Delta G_r = -RT \ln K \quad (37)$$

Finally we have K in terms of q by

$$K = \prod_j \left(\frac{q_j}{N} \right)^{\nu_j} e^{-\Delta E_0 / RT} \quad (38)$$

6.4 Some Consequences of TST

6.4.1 Rate Constants in Dilute Strong Electrolytes

Debye-Hückel theory relates the activity coefficient of dilute strong electrolytes with the ionic strength I of solution and with the charge of the ion in question:

$$\ln \gamma_j = -AZ_j^2 \sqrt{I} \quad (39)$$

Where

Z_j – charge of j ion

γ_j - activity coefficient of ion

$$I = \frac{1}{2} \sum_{j=1}^s C_j Z_j^2 \text{ - ionic strength} \quad (40)$$

C_j - molar concentration of j ion

A - constant ($A \approx 0.51$ for water at 25°C)

For reaction of



the transition state theory predicts:

$$k_{1c} = k_1 \frac{\gamma_A \gamma_B}{\gamma_Z^*} \quad (42)$$

Clearly the transition state must have a charge of $Z_A + Z_B$ in order to satisfy the law of conservation of charge.

Taking logarithms

$$\begin{aligned}
 \ln k_{1c} &= \ln k_1 + \ln \gamma_A + \ln \gamma_B - \ln \gamma_Z^* \\
 &= \ln k_1 - A\sqrt{I} \left[Z_A^2 + Z_B^2 - (Z_A + Z_B)^2 \right] \\
 \ln k_{1c} &= \ln k_1 + 2AZ_A Z_B \sqrt{I}
 \end{aligned}
 \tag{43}$$

This equation gives excellent agreement with experimental data and is very useful for correlating liquid phase reaction data.

3.2.2 Pressure Effects in Gas Phase Reactions

For gases

$$a_j = f_j = \phi_j P_j = \gamma_j C_j = \frac{\gamma_j P_j}{Z_j RT}$$

Z_j – compressibility factor of j
 γ_j – activity coefficient of j
 P_j – partial pressure of j
 C_j – molar concentration of j
 ϕ_j – fugacity coefficient of j
 f_j – fugacity of j

(44)

From the above

$$\gamma_j = \phi_j Z_j RT
 \tag{45}$$

For a reaction $A + B \rightarrow Z^*$

$$k_c = k \frac{\gamma_A \gamma_B}{\gamma_Z^*} = k \frac{\phi_A Z_A (RT) \phi_B Z_B}{\phi_Z Z_Z}$$

$$k_c = k \frac{\phi_A \phi_B}{\phi_Z} \frac{Z_A Z_B}{Z_Z} RT$$
(46)

$$\phi_j \rightarrow 1, Z_j \rightarrow 1$$

At sufficiently low pressures $\left(\frac{k_c}{k} \right)_{\text{low pressure}} = RT$ (47)

At high pressure

$$\left(\frac{k_c}{k} \right)_{\text{high P}} = RT \frac{\phi_A \phi_B}{\phi_Z} \frac{Z_A Z_B}{Z_Z}
 \tag{48}$$

Thus the ratio

$$\left(\frac{k_c \text{ high } P}{k_c \text{ low } P} \right) = \frac{\phi_A \phi_B}{\phi_Z} \frac{Z_A Z_B}{Z_Z} \quad (49)$$

In the case of a reaction $2A \rightarrow$

$$\left(\frac{k_c \text{ high } P}{k_c \text{ low } P} \right) = \frac{\phi_A^2}{\phi_Z} Z_Z \quad \text{assuming } Z_A \approx Z_Z \quad (50)$$

The variation of the thermodynamic properties with pressure was calculated for HI decomposition ($2HI \rightarrow I_2 + H_2$). The above equation agreed excellently with all experimental data up to 250 atm which led to density variations of 300.

6.4.3 Dependence of Rate Constants on Temperature and Pressure In Chain Reactions

So far we have treated only simple reactions (often elementary ones) and their rate constants. Let us take a look at more complex overall reactions - say in free radical polymerization:

$$r_{pol} = \underbrace{k_p}_{k} \sqrt{\frac{k_d f}{k_t}} C_M C_I \quad (51)$$

using Arrhenius form for k and each other constant k_p, k_d, k_t we get

$$\ln k = \ln \left[k_{p_o} \left(\frac{k_{d_o}}{k_{t_o}} \right)^{1/2} \right] + \frac{1}{2} \ln f - \frac{E_p + \frac{1}{2} E_d - \frac{1}{2} E_t}{RT} \quad (52)$$

$$k_o = k_{p_o} \left(\frac{k_{d_o}}{k_{t_o}} \right)^{1/2} \quad E = E_p + \frac{1}{2} (E_d - E_t) \quad (53)$$

Range of values $30 < E_d < 35$ kcal/mol

$$5 < E_p < 10 \text{ kcal/mol}$$

$$2 < E_t < 5 \text{ kcal/mol}$$

$$17 < E < 26$$

$$E \approx 20 \frac{\text{kcal}}{\text{mol}}$$

Polymerization rate increases with temperature. However the degree of polymerization X_n is proportional to the following group that depends on temperature:

$$X_n \propto \frac{k_p}{(k_d k_t)^{1/2}} \quad (54)$$

The activation energy for the degree of polymerization is then given by

$$X_n = X_{n_o} e^{-\frac{E_{x_n}}{RT}} \quad (55)$$

$$E_{x_n} = E_p - \frac{1}{2}(E_d + E_t) \quad (56)$$

$$-15 < E_{x_n} < -6 \text{ kcal/mol}$$

Thus, degree of polymerization decreases rapidly with increasing temperature.

The dependence on pressure is

$$\frac{d \ln k}{dP} = \frac{-\Delta V^*}{RT} \quad (57)$$

ΔV^* - volume of activation, i.e change in volume in going from reactants to transition state.

$$\Delta V_R^* = \frac{\Delta V_d^*}{2} + \Delta V_P^* + \frac{\Delta V_t^*}{2} \quad (58)$$

$$-20 < \Delta V_R^* < 15 \text{ (cm}^3/\text{gmol)}$$

Polymerization rate increases with pressure.

$$\Delta V_{X_n}^* = \Delta V_P^* - \frac{1}{2}(\Delta V_d^* + \Delta V_t^*) \quad (59)$$

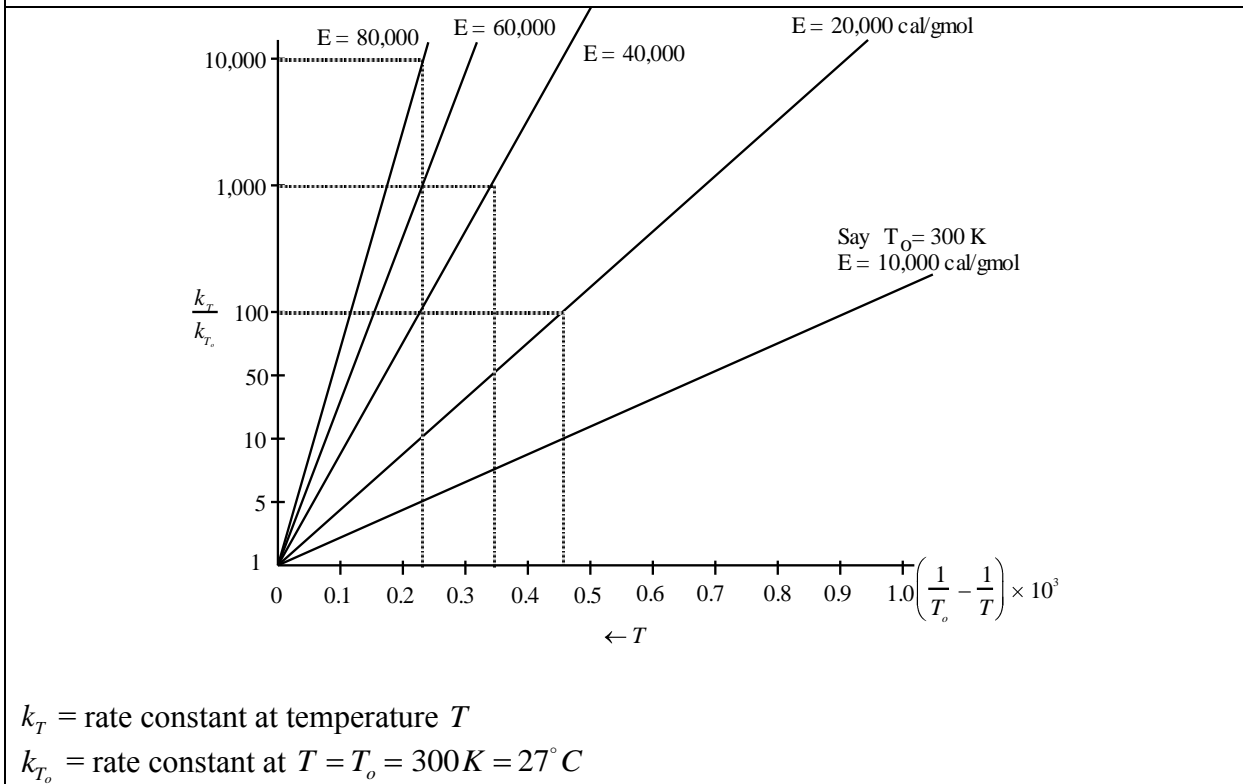
$$-25 < \Delta V_{X_n}^* < -20 \text{ (cm}^3/\text{gmol)}$$

Degree of polymerization increases with pressure $\frac{d \ln X_n}{dP} = \frac{-\Delta V_{X_n}}{RT}$ (60)

6.5 Summary

1. Temperature dependence of rate constants can be represented over a limited range of temperature in a satisfactory manner by the Arrhenius equation
 $k = k_o e^{-E/RT}$
2. E, k_o usually are constant within a narrow temperature range but may become functions of T in a broader temperature range $E \propto \alpha + \beta T, k_o \propto T^m$.
3. In case of high E ($E \gg 20,000$ cal) and moderate temperatures ($T < 600$ K) the value of E is not affected by the choice of units for the driving force i.e C_A (mol/lit) or P_A (atm), etc.

- In case of low E ($E < 10,000$ cal) and high and moderate temperatures the value of E is greatly affected by the choice of variables for the driving force i.e. C_A (mol/lit) or P_A (atm) etc.
- The reaction rate can increase dramatically with temperature. The larger the E the more rapidly the rate increases with T .

FIGURE 5: Effect of Temperature on the Rate Constant

The above figure (Figure 5) demonstrates the possible rapid rise in reaction constants and rates if activation energy is sufficiently high.

The rate increases 10 times for $E = 10,000$ cal for a ΔT of 50K. For the same rise in temperature the rate with $E = 20,000$ cal will increase 100 times.

It takes only 35°K to raise a rate constant 1000 times for $E = 40,000$. 25°K temperature increase gives a 1000 times larger rate for $E = 60,000$ cal and a staggering 10,000 times larger rate for $E = 80,000$ cal!

- $E_f - E_b = \Delta H^\circ$ reaction for elementary reactors.

For exothermic reactions ($\Delta H^\circ < 0$)

$E_f < E_b$ and a rise in temperature will promote more the reverse reaction and thus reduce equilibrium conversion. This is obvious also from $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} < 0$.

$\Delta H < 0 \quad \frac{d \ln K}{dT} < 0$ as $T \uparrow K \downarrow$. However, forward rate rises also with T to some extent. There always is a T_{optimal} which balances the increased rate with more unfavorable equilibrium.

7. For endothermic reactions $E_f > E_b$, and for irreversible reactions, the higher the temperature the higher the rate and the higher conversion is obtainable.
8. A temperature excursion of 10-20°C can cause dramatic increases in the rate and lead to runaways and explosion.
9. The reaction rate is so much more sensitive to temperature than to concentration. For a first order reaction with $E = 20,000$ cal a rise of 50°C in T leads to an increase of 100 times in the rate. To accomplish the same augmentation of the rate by changing concentrations we would have to increase concentration 100 times. For a 2nd order reaction with the same activation energy we would have to increase concentration 10 times. For higher activation energies the difference between temperature and concentration sensitivity of the rate is even more pronounced.