

3. RATE LAW AND STOICHIOMETRY

Professional Reference Shelf

R3.2 Transition State Theory

Abbreviated Lecture Notes

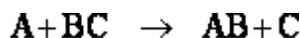
Transition State Theory

Full Lecture Notes

- I. Overview
- II. Introduction
 - A. The Transition State
 - B. Procedure to Calculate the Frequency Factor
- III. Background
 - A. Molecular Partition Function
 - B. Relating $\sum n_i$ and N
 - C. Relate $\sum n_i$ and q
 - D. Canonical Partition Function for Interacting Molecules
 - E. Thermodynamic relationships to relate $\sum n_i$ and q
 - F. Relate G, the molar partition function q_m
 - G. Relating the dimensionless equilibrium constant K and the molar partition function q_m
 - H. Relate the molecular partition function on a basis of per unit volume, q' and the equilibrium constant K
 - I. Recall the relationship between K and KC from Appendix C.
 - J. The Loose Vibration, ν_I
 - K. Evaluating the Partition Functions
- IV. The Eyring Equation
- V. Problems

I. Overview

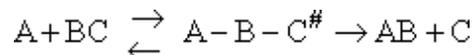
Transition state theory provides an approach to explain the temperature and concentration dependence of the rate law. For example, for the elementary reaction



The rate law is

$$-r_A = k C_A C_{BC} = A e^{-E_A/RT} C_A C_{BC}$$

For simple reactions transition state can predict E and A in concert with computational chemistry. In transition state theory (TST) an activated molecule is formed during the reaction at the transition state between forming products from reactants.



The rate of reaction is equal to the product of the frequency, ν_I , of the activated complex crossing the barrier and the concentration of the transition state complex

$$-r_A = \nu_I C_{ABC^{\#}}$$

The transition state molecule (**A – B – C[#]**) and the reactants are in pseudo equilibrium at the top of the energy barrier.

$$K_C^{\#} = \frac{C_{ABC^{\#}}}{C_A C_{BC}}$$

Combining

$$-r_A = \nu_I K_C^{\#} C_A C_{BC}$$

We will now use statistical and quantum mechanics to evaluate $K_C^{\#}$ to arrive at the equation

$$-r_A = \left(\frac{k_B T}{h} \right) e^{-\frac{\Delta E_0}{kT}} \frac{q'_{ABC^{\#}}}{q'_A q'_{BC}} C_A C_{BC}$$

where $q\phi$ is overall the partition function per unit volume and is the product of translational, vibration, rotational and electric partition functions, i.e.,

$$q' = q'_T q'_V q'_R q'_E$$

The individual partition functions to be evaluated are:

Translation

$$q'_T = \frac{(2\pi m k_B T)^{3/2}}{h^3} = \left(\frac{9.84 \times 10^{29}}{m^3} \right) \left(\frac{m_{AB}}{1 \text{ amu}} \right)^{3/2} \left(\frac{T}{300K} \right)^{3/2}$$

Vibration

$$q_v = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)}$$

$$\frac{h\nu}{k_B T} = \frac{hc\tilde{\nu}}{k_B T} = 4.8 \times 10^{-3} \left(\frac{\tilde{\nu}}{1 \text{ cm}^{-1}} \right) \left(\frac{300\text{K}}{T} \right)$$

Rotation

$$q_R = \frac{8\pi^2 I k_B T}{S_y h^2} = 12.4 \left(\frac{T}{300\text{K}} \right) \left(\frac{I_{AB}}{1 \bullet \text{amu} \bullet \text{\AA}^2} \right) \left(\frac{1}{S_y} \right)$$

$$I_{AB} = \sum m_i r_i^2$$

$$I_{AB} = \mu_{AB} d^2 \text{ for diatomic molecules}$$

The Eyring Equation

$$\text{Liquids } k = \left(\frac{k_B T}{h} \right) \frac{e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}}{K_\gamma C_{T0}}$$

$$\text{Gases } k = \left(\frac{k_B T}{h} \right) \left(\frac{RT}{P} \right) \frac{e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}}{K_\gamma}$$

R. I. Masel, *Chemical Kinetics and Catalysis*, Wiley Interscience, New York, 2001.

References Nomenclature

A5p403 Means Atkins, P. W. *Physical Chemistry*, 5th ed. (1994) page 403.

A6p701 Means Atkins, P. W. *Physical Chemistry*, 6th ed. (1998) page 701.

L3p208 Means Laidler, K. J., *Chemical Kinetics*, 3rd ed. (1987) page 208.

M1p304 Means Masel, R.I., 1st Edition (2001) page 304.

II. Introduction

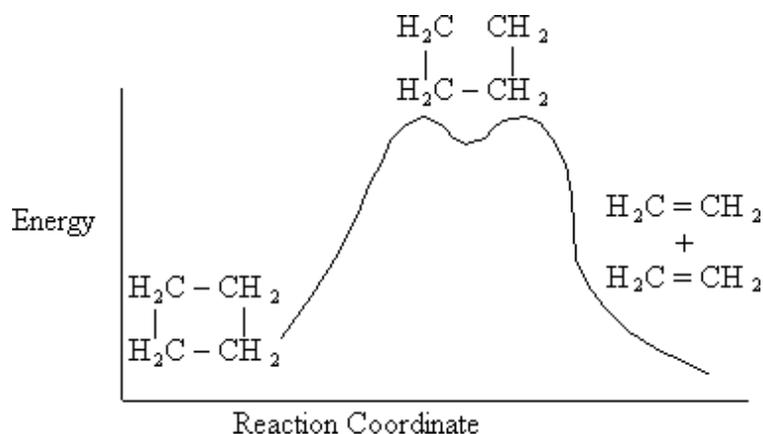
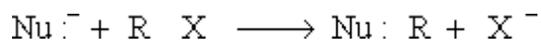


Figure PRS.3B-1 Evidence of Active Intermediate.

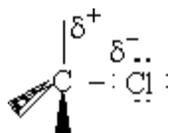
The active intermediate is shown in transition state at the top of the energy barrier. A class of reactions that also goes through a transition state is the S_N2 reaction.

A. The Transition State

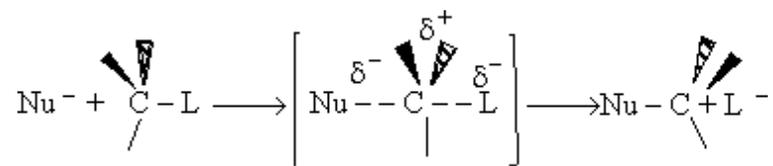
We shall first consider **S_N2 reactions** [Substitution, Nucleophilic, 2nd order] because many of these reactions can be described by transition state theory. A Nucleophile is a substance (species) with an unshared electron. It is a species that seeks a positive center.

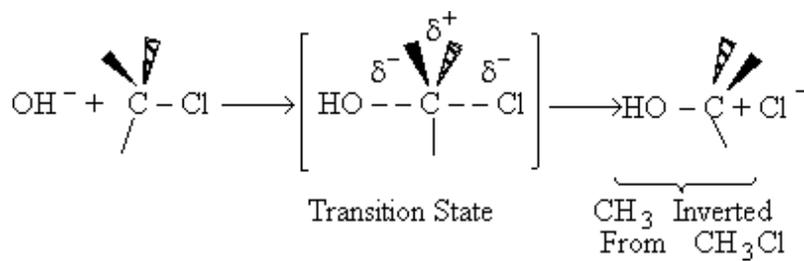


, i.e.,



The nucleophile seeks the carbon atom that contains the halogen. The nucleophile always approaches from the backside, directly opposite the leaving group. As the nucleophile approaches the orbital that contains the nucleophile electron pairs, it begins to overlap the empty antibonding orbital of the carbon atom bearing the leaving group (Solomon, T.W.G, *Organic Chemistry*, 6/e Wiley 1996, p.233).





$$\text{rate} = k [\text{CH}_3\text{Cl}] [\text{OH}^-]$$

The Figure PRS.3B-1 shows the energy of the molecules along the reaction coordinate which measures the progress of the reaction. [See PRS.A Collision theory-D Polyani Equations]. One measure of this progress might be the distance between the CH₃ group and the Cl atom.

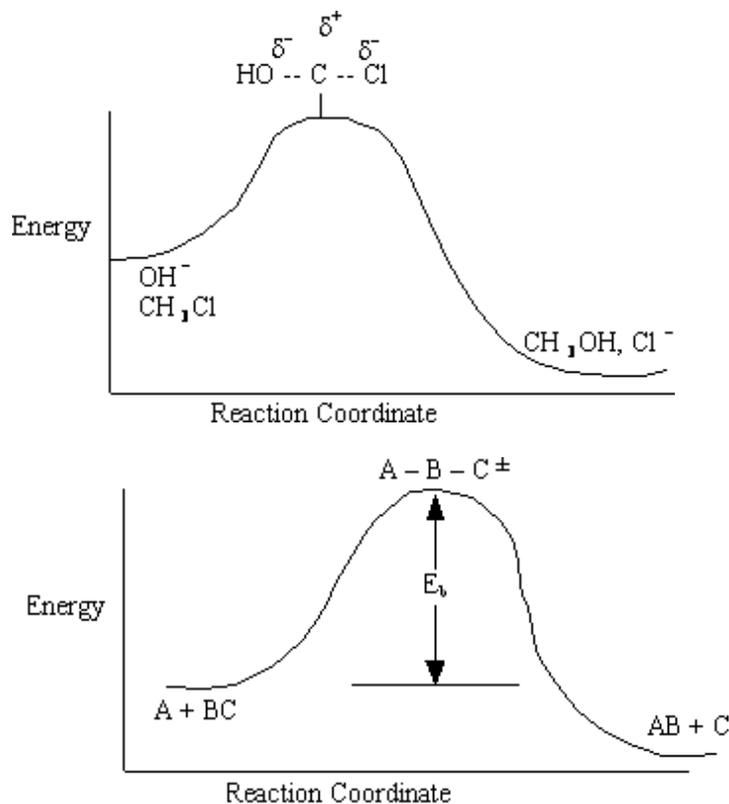


Figure PRS.3B-2 Reaction coordinate for (a) S_{N2} reaction, and (b) generalized reaction

Collision Theory when discussing the Polyani Equation.

The energy barrier shown in Figure PRS.3B-2 is the shallowest barrier along the reaction coordinate. The entire energy diagram for the ABC system is shown in 3-D in Figure PRS.3B-3. To obtain Figure PRS.3B-2 from Figure PRS.3B-3 we start from the initial state (A + BC) and move through the valley up over the barrier, E_a, (which is also in a valley) over to the valley on the other side of the barrier to the final state

(A + BC). If we plot the energy along the dashed line pathway through the valley of Figure PRS.3B-3 we arrive at Figure PRS.3B-2.

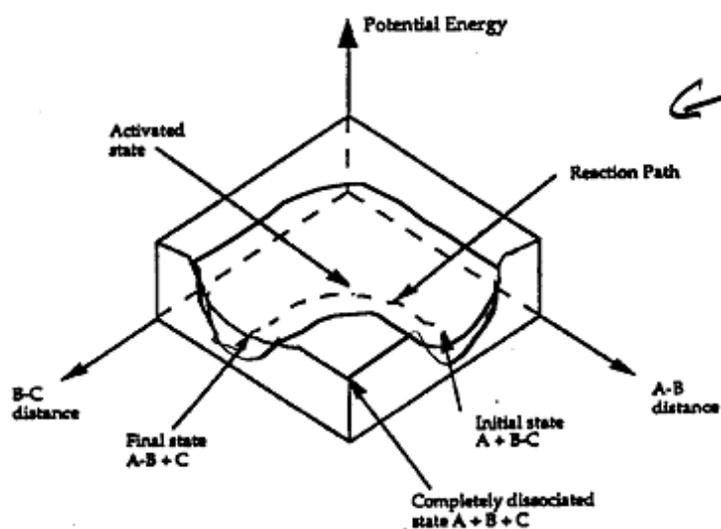
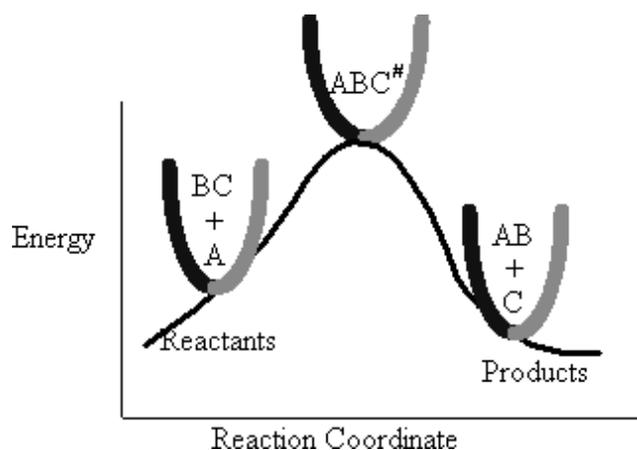
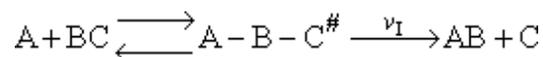


Figure PRS.3B-3 3-D energy surface for generalized reaction.

The rate of reaction for the general reaction (Lp90) is the rate of crossing the energy barrier



We consider the dissociation of the activated complex $A - B - C^{\#}$ as a loose vibration of frequency ν_I , (s^{-1}). The rate of crossing the energy barrier is just the vibrational frequency, ν_I , times the concentration of the activated complex, $C_{ABC^{\#}}$

$$-r_A = \nu_I C_{ABC^{\#}} \quad (1)$$

We assume the activated complex $ABC^{\#}$ is in virtual equilibrium with the reactants A

and BC so we can use the equilibrium concentration constant $K_C^\#$ to relate these concentrations, i.e.,

$$K_C^\# = \frac{(ABC^\#)}{(A)(B)} \equiv \frac{C_{ABC^\#}}{C_A C_{BC}} \quad (2)$$

Combining Eqns. (A) and (B) we obtain

$$\boxed{-r_A = v_I K_C^\# C_A C_{BC}} \quad (3)$$

The procedure to evaluate v_I and $K_C^\#$ is shown in the table T.S.1

B. Procedure to Calculate the Frequency Factor

Table PRS.3B-1 Transition State Procedure to Calculate v_I and $K_C^\#$

Step 1)A. **Molecular partition function.** The number of ways, W , of arranging N molecules in m energy states, with n_i molecules in the e_i energy state is

$$W = \frac{N!}{n_1! n_2! \dots n_m!}$$

The distribution that gives a maximum in W is the Boltzmann distribution from which we obtain the molecular partition function, q .

$$\frac{n_i}{N} = \frac{e^{-\beta \epsilon_i}}{q}, \quad q = \sum e^{-\beta \epsilon_i}, \quad \beta = \frac{1}{kT}$$

Step 2)B. **Relating \tilde{S} , n_i and N .**

The entropy of the system is given by the fundamental postulate

$$\tilde{S} = k \ln W = k \ln \frac{N!}{n_1! n_2! \dots n_m!}$$

Next we manipulate the Boltzmann equation for N molecules distributed in m energy states using Stirling's approximation to arrive at

$$\tilde{S} = -k \left[\sum n_i \ln \frac{n_i}{N} \right]$$

Step 3)C. **Relate \tilde{S} and q .** Starting with the total energy of the system $E = \tilde{U} - \tilde{U}_0 = \sum n_i e_i$, relative to the ground state, substitute for the number of molecules, n_i , in energy state e_i , using the Boltzmann distribution in the last equation of Step 3

$$\ln \frac{n_i}{N} = -\beta e_i - \ln q$$

and then sum to arrive at

$$\tilde{S} = \frac{\tilde{U} - \tilde{U}_0}{T} + kN \ln q$$

for non-interacting molecules. \tilde{U}_0 is the ground state energy.

Step 4)D. **Canonical partition function for interacting molecules.** We need to consider interacting molecules and to do this we have to use Canonical partition function

$$Q = \sum_{i=1}^k e^{-\beta_i E_i}$$

with the probability of finding a system with energy E_i is

$$P_i = \frac{e^{-\beta_i E_i}}{Q}$$

These relationships are developed with the same procedure as that used for the molecular partition function. For indistinguishable molecules, the canonical and molecular partition functions are related by

$$Q = \frac{q^N}{N!}$$

using the above equation we can arrive at

$$\tilde{S} = \frac{\tilde{U} - \tilde{U}_0}{T} + kN \ln \left(\frac{q}{N!} \right)$$

Step 5)E. **Thermodynamic relationship to relate \tilde{G} , \tilde{U} and q_i , the molecular partition function**

We begin by combining the Maxwell relationship, i.e.,

$$\tilde{G} = \tilde{U} - T\tilde{S} + PV$$

with the last equation in Step 4 where the tilde (e.g. \tilde{G}) represents the symbols are in units of kcal or kJ without the tilde is in units per mole, e.g., kJ/mol. We first use the last equation for S in Step 4 to substitute in the Maxwell Eqn. We next use the relationship between Q and q, i.e.,

$$Q = \frac{q^N}{N!}$$

To relate \tilde{G} to q, the molecular partition function. For N indistinguishable molecules of an ideal gas

$$\tilde{G} = \tilde{U}_o - nRT \ln \frac{q}{N}$$

Step 6)F. **Relate G to the molar partition function q_m .** We define q_m as

$$q_m = \frac{q}{n}, \text{ where } N = n N_{\text{Avo}}$$

and then substitute in the last equation in Step 5.

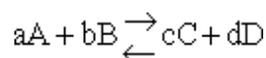
$$G = U_o - RT \ln \frac{q_m}{N_{\text{Avo}}}$$

Note: The tilde's have been removed.

where n = Number of moles, and N_{Avo} = Avogadro's number and where G and U_o are on a per mole basis, e.g. (kJ/mole).

Step 7)G. **Relate the dimensionless equilibrium constant K and the molar partition function q_{mi}**

For the reaction



the change in the Gibb's free energies is related to K by

$$\sum v_i G_i = \Delta G = -RT \ln K$$

$$G_i = U_{i0} - RT \ln q_{mi}/N_{\text{Avo}}$$

Combining the last equation in Step 6 and the above equations

$$K = e^{-\Delta E_o/RT} \frac{q_{mC}^c q_{mD}^d}{q_{mA}^a q_{mB}^b} N_{Avo}^{-\delta}$$

where

$$\delta = \mathbf{d + c - b - a}$$

Step 8)H. Relate the partition function on a per unit volume basis, $q\Phi$, and the equilibrium constant K

$$q_m = \frac{q}{n} = q' \left(\frac{V}{n} \right) = q' V_m$$

Where V_m is the molar volume (dm^3/mol). Substituting for q_{mi} in the equation for K in Step 7 we obtain

$$K = e^{-\frac{\Delta E_o}{RT}} \frac{(q'_C)^c (q'_D)^d}{(q'_A)^a (q'_B)^b} V_m^\delta N_{Avo}^{-\delta}$$

Step 9)I. Recall the relationship between K and K_C from Appendix C

$$K = K_\gamma K_C \left(\frac{RT}{f^\circ} \right)^\delta = K_\gamma K_C V_m^\delta$$

Equate the equilibrium constant K given in the last equation of Step 8 to the thermodynamic K for an ideal gas, ($K_\gamma = 1$) to obtain K_C in terms the partition functions, i.e.,

For the transition state A B C[#], with $d = 1$,

$$K_C^\# = e^{-\Delta E_o/RT} \frac{q_{ABC}^\#}{q'_A q'_{BC}} N_{Avo}$$

we also know

$$K_C^\# = \frac{C_{ABC^\#}}{C_A C_{BC}}$$

Equating the two equations and solving for $C_{ABC^\#}$

$$C_{ABC^\#} = e^{-\Delta E_o/RT} \frac{q_{ABC}^\#}{q'_A q'_{BC}} N_{Avo} C_A C_{BC}$$

The prime, e.g., q' , denotes the partition functions are per unit volume.

Step 10) **J. The loose vibration.**

The rate of reaction is the frequency, ν_I , of crossing the barrier times the concentration of the activated complex $C_{ABC\#}$

$$r_{ABC} = \nu_I C_{ABC\#}$$

This frequency of crossing is referred to as a loose (imaginary) vibration. Expand the vibrational partition function to factor out the partition function for the crossing frequency.

$$q_v^\# = q_{v\#} \quad q_{vI} = \frac{k_B T}{h \nu_I} \quad q_{v\#}$$

Note that # has moved from a superscript to a subscript to denote the imaginary frequency of crossing the barrier has been factored out of both the vibrational, $q_v^\#$ and overall partition functions, $q^\#$, of the activated complex.

$$q_{ABC}^{\prime\#} = q_E^\# \quad q_R^\# \quad q_v^\# \quad q_T^{\prime\#}$$

$$q_{ABC}^{\prime\#} = q'_{ABC\#} \quad \frac{k_B T}{h \nu_I}$$

Combine with rate equation, $-r_{ABC} = \nu_I C_{ABC\#}$ noting that ν_I cancels out, we obtain

$$-r_A = \frac{k_B T}{h} \underbrace{N_{Avo} \frac{q'_{ABC\#}}{q'_A q'_{BC}}}_{A} e^{-\Delta E_o/RT} C_A C_{BC}$$

where A is the frequency factor.

Step 11) **K. Evaluate the partition functions (q'_T , q'_v , q'_R)**

Evaluate the molecular partition functions.

Using the Schrödinger Equation

$$\frac{d^2 \psi}{dx^2} - \frac{2m}{h} [E - V(x)] \psi = 0$$

we can solve for the partition function for a particle in a box, a harmonic oscillator and a rigid rotator to obtain the following partition functions

Translation:

$$q'_T = \frac{(2\pi mk_B T)^{3/2}}{h^3} = \left(\frac{9.84 \times 10^{29}}{m^3} \right) \left(\frac{m_{AB}}{1 \text{ amu}} \right)^{2/3} \left(\frac{T}{300K} \right)^{3/2}$$

Vibration:

$$q_V = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)}$$

$$\frac{h\nu}{k_B T} = \frac{hc\tilde{\nu}}{k_B T} = 4.8 \times 10^{-3} \left(\frac{\tilde{\nu}}{1 \text{ cm}^{-1}} \right) \left(\frac{300K}{T} \right)$$

Rotation:

$$q_R = \frac{8\pi^2 I k_B T}{S_y h^2} = 12.4 \left(\frac{T}{300K} \right) \left(\frac{I_{AB}}{1 \bullet \text{amu} \bullet \text{\AA}^2} \right) \left(\frac{1}{S_y} \right)$$

$$I_{AB} = \sum m_i r_i^2$$

The end result is to evaluate the rate constant and the activation energy in the equation

$$-r_A = \underbrace{\frac{k_B T}{h} N_{\text{Avo}} \frac{q'_{\text{ABC}\#}}{q'_A q'_{\text{BC}}}}_A e^{-\Delta E_o/RT} C_A C_{\text{BC}}$$

We can use computational software packages such as Cerius² or Spartan to calculate the partition functions of the transition state and to get the vibrational frequencies of the reactant and product molecules. To calculate the activation energy one can either use the barrier height as E_A or use the **Polyani Equation**.

Example

III. Background

A. Molecular Partition Function

In this section we will develop and discuss the molecular partition function for N molecules with a fixed total energy E in which molecules can occupy different energy states, e_i .

Total Energy of System

Total number of molecules, N ,

$$\boxed{N = \sum n_i} \quad (4)$$

n_i = Number of molecules with energy e_i

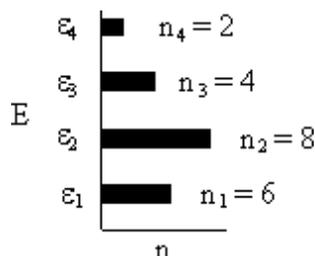
The total Energy E is

$$\boxed{E = \sum n_i \varepsilon_i} \quad (5)$$

The number of ways, W , arranging N molecules among m energy states (e_1, e_2, \dots, e_m) is

$$W = \frac{N!}{n_1! n_2! \dots n_m!} \quad (6)$$

For example, if we have $N=20$ molecules shared in four energy levels (e_1, e_2, e_3, e_4) as shown below



$$W = \frac{N!}{n_1! n_2! n_3! n_4!} = \frac{20!}{6! 8! 4! 2!}$$

$$W = 1.75 \times 10^9$$

there are 1.75×10^9 ways to arrange the 20 molecules among the four energy levels shown. There are better ways to put the 20 molecules in the four energy states to arrive at a number of arrangements greater than 1.75×10^9 . What are they?

For a constant total energy, E , there will be a maximum in W , the number of possible arrangements and this arrangement will overwhelm the rest. Consequently, the system will most always be found in that arrangement. Differentiating Eqn. (3) and setting $dW = 0$, we find the distribution that gives this maximum [see A6p571]. The fraction of molecules in energy state e_i is

Boltzmann

Distribution

$$\frac{n_i}{N} = \frac{e^{-\beta \epsilon_i}}{\sum e^{-\beta \epsilon_i}} = \frac{e^{-\beta \epsilon_i}}{q}, \quad \beta = 1/k_B T \quad (7)$$

$$q = \sum e^{-\beta \epsilon_i} \quad (8)$$

The molecular partition function q , measures how the molecules are distributed (i.e. **partitioned**) over the available energy states.

Total Energy

Equation (7) is the Boltzmann Distribution. It is the most probable distribution of N molecules among all energy states ϵ_i from $i=0$ to $i=\infty$ subject to the constraints that the total number of molecules N and the total energy, E are constant.

$$\boxed{E = \sum n_i \epsilon_i} \quad (5)$$

This energy $E = \sum n_i \epsilon_i$ is relative to the lowest energy, U_0 , (the ground state) the value at $T=0$. To this internal energy, E , we must add the energy at zero degrees Kelvin, U_0 (A6p579) to obtain the total internal energy

$$\tilde{U} = \bar{U}_0 + \sum n_i \epsilon_i \quad (9)$$

The tildes, \tilde{U} , represent that this is the total energy not the energy per mole.

Comments on the Partition Function q

The molecular partition function gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. At low temperatures only the ground state is accessible. Consider what happens as we go to the extremes of temperature.

(a) At high temperatures, ($kT \gg \epsilon_i$), most all states are accessible.

$$\begin{aligned} q &= \sum e^{-\beta \epsilon_i} = \sum e^{-\epsilon_i/kT} = e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + e^{-\epsilon_3/kT} \dots \\ &= 1 + e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + \dots \end{aligned}$$

Now as $T \rightarrow \infty$, $e^{-\epsilon_i/kT} \rightarrow 1$, $q \rightarrow \infty$ because $\sum \rightarrow \infty$

i.e. $q = 1 + 1 + 1 + 1 + 1 + \dots$

and we see the partition function goes to infinity as all energy states are accessible.

(b) At the other extreme, very very low temperatures ($kT \ll \epsilon_i$).

as $T \rightarrow 0, e^{-\epsilon_i/kT} \rightarrow 0$

then $q \rightarrow g_0$

and we see that none of the states are accessible with one exception, namely degeneracy in the ground state, i.e., $q \rightarrow g_0$ for $\epsilon_0 = 0$

B. Relating \tilde{S} , n_i and N

W is the number of ways of realizing a distribution for N particles distributed on e_i levels for a total energy E

$$E = \epsilon_1 n_1 + \epsilon_2 n_2 + \epsilon_3 n_3 + \dots$$

$$W = \frac{N!}{n_1! n_2! \dots n_i!} \quad (6)$$

e_i

The Basic Postulate is

$$\tilde{S} = k \ln W = k \ln \frac{N!}{n_1! n_2! \dots n_i!} \quad (10)$$

Next we relate \tilde{S} and q through W

$$\begin{aligned} \ln W &= \ln N! - \ln n_1! n_2! \\ &= \ln N! - [\ln n_0! + \ln n_1! + \dots] \end{aligned}$$

$$\ln W = \ln N! - \sum \ln(n_i!) \quad (11)$$

Stirling's approximation for the ln of factorials is

$$X! = (2\pi)^{1/2} X^{X+1/2} e^{-X}$$

or approximately

Stirling's

Approximation

$$\ln X! = X \ln X - X, \quad (12)$$

For our system this approximation becomes

$$\ln W = N \ln N - N - \left(\sum n_i \ln n_i - \sum \frac{n_i}{N} \right) \quad (13)$$

$$N = \sum n_i \quad (4)$$

Recall substituting Eqn. (4) in Eqn. (13) we find

$$\begin{aligned} \ln W &= N \ln N - \sum n_i \ln n_i \\ &= \sum n_i \ln N - \sum n_i \ln n_i \\ \ln W &= -\sum (n_i \ln n_i - n_i \ln N) \end{aligned}$$

Further rearrangement gives

$$\ln W = -\sum n_i \ln \frac{n_i}{N} \quad (14)$$

combining Eqns. (10) and (14)

$$\boxed{\tilde{S} = -k \sum n_i \ln \frac{n_i}{N}} \quad (15)$$

C. Relate \tilde{S} and q

Recall that the fraction of molecules in the i th energy state is

$$\boxed{\frac{n_i}{N} = \frac{e^{-\beta\epsilon_i}}{q}} \quad (8)$$

Taking the natural log of Eqn. (5)

$$\ln \frac{n_i}{N} = -\beta\epsilon_i - \ln q$$

Substituting for $\ln\left(\frac{n_i}{N}\right)$ in Eqn. (13)

$$\tilde{S} = -k \sum n_i [-\beta\epsilon_i - \ln q]$$

Rearranging

$$= k\beta \sum n_i \epsilon_i + k \sum n_i \ln q$$

$$\tilde{S} = \frac{\sum n_i \epsilon_i}{T} + kN \ln q$$

Recall from Eqn. (9) for $E = U_0$, where U_0 is the ground state energy in kcal.

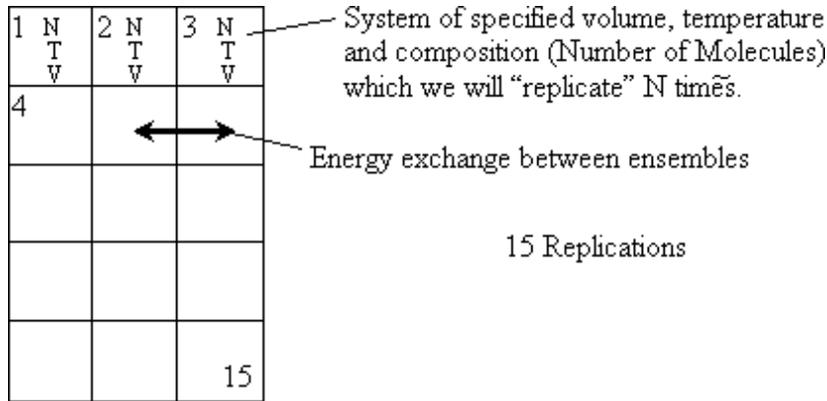
$$\boxed{\tilde{S} = \frac{\tilde{U} - \tilde{U}_0}{T} + kN \ln q} \quad (16)$$

This result is for non interacting molecules. We now must extend/generalize our conclusion to include systems of interacting molecules. The molecular partition function, q , is based on the assumption the molecules are independent and don't interact. To account for interacting molecules distributed in different energy states we must consider the Canonical partition function, Q .

D. Canonical Partition Function for Interacting Molecules

Canonical ensemble (collection) (A6p583)

We now will consider interacting molecules and to do this we must use the Canonical ensemble which is a collection of systems at the same temperature T , volume V , and number of molecules N . These systems can exchange energy with each other.



Let

E_i = Energy of ensemble i

\hat{E} = Total energy of all the systems $\sum \hat{n}_i E_i = \text{a constant}$

\hat{n}_i = Number of members of the ensemble with energy E_i

\tilde{N} = Total number of ensembles

Let P_i be the probability of occurrence that a member of the ensemble has an energy E_i . The fraction of members of the ensemble with energy E_i can be derived in a manner similar to the molecular partition function.

$$P_i = \frac{\hat{n}_i}{\tilde{N}} = \frac{e^{-\beta E_i}}{Q}$$

$$Q = \sum e^{-\beta E_i} \tag{17}$$

Q is the Canonical Partition Function.

We now relate the Canonical partition function to the molecular partition function (A6p858). The energy of ensemble i , E_i , is the sum of the energies of each of the molecules in the ensembles

$$E_i = \epsilon_i(1) + \epsilon_N(2) + \dots + \epsilon_N(N)$$



Energy of molecule (1) when it is in



Energy of molecule (N) when it is in state N

$$Q = \sum e^{-\beta E_i} = \sum_{i=1}^{\infty} e^{-\beta \epsilon_i(1) - \beta \epsilon_i(2) \dots - \beta \epsilon_i(N)}$$

Expanding the $i=1$ and $i=2$ terms

$$Q = e^{-\beta \epsilon_1(1) - \beta \epsilon_1(2)} + \dots + e^{-\beta \epsilon_2(1)} + e^{-\beta \epsilon_2(2)} \dots + \sum_{i=3}^{\infty} e^{-\beta \epsilon_i}$$

Each molecule, e.g. molecule (1), is likely to occupy all the states available to it. Consequently, instead of summing over the states i of the system we can sum over the states i of molecule 1, molecule 2, etc.

$$Q = \left(\frac{\sum e^{-\beta \epsilon_i}}{\text{molecule 1}} \right) \left(\frac{\sum e^{-\beta \epsilon_i}}{\text{molecule 2}} \right) \dots = \left(\sum e^{-\beta \epsilon_i} \right)^N$$

$$Q = q^N$$

This result (Eqn. (17)) is for *distinguishable* molecules.

However, for *indistinguishable* molecules it doesn't matter which molecule is in which state, i.e., whether molecule (1) is in state (a) or (b) or (c)

(A5p605)
(A6p585)

$$= \epsilon_a + \epsilon_b + \epsilon_c$$

(1) → (a)	(1) → (b)	(1) → (c)	
(2) → (b)	(2) → (c)	(2) → (a)	E
(3) → (c)	(3) → (a)	(3) → (b)	(etc)

Consequently we have to divide by $N!$

$$Q = \frac{q^N}{N!} \quad (18)$$

The molecular partition function is just the product of the partition functions for

translational (q_T), vibrational (q_V), rotational (q_R) and electronic energy (q_E) partition functions.

$$q = q^T q^V q^R q^E \quad (19)$$

This molecular partition function, q , describes molecules that are not interacting. For interacting particles we have to use the canonical ensemble. We can do a similar analysis on the canonical ensemble [collection] to obtain [A5p684]

$$\tilde{S} = \frac{\tilde{U} - \tilde{U}_o}{T} + k \ln Q \quad (20)$$

Combining Equations (17) and (20) thus

Which is a result we have been looking for.

$$\tilde{S} = \frac{\tilde{U} - \tilde{U}_o}{T} + k \ln \left(\frac{q^N}{N!} \right) \quad (22)$$

E. Thermodynamic relationships to relate \tilde{G} , \tilde{S} and q

We now are going to use the various thermodynamic relationships to relate the molecular partition function to change in free energy ΔG . Then we can finally relate the molecular partition function to the equilibrium constant K . From thermodynamic relationships we know that the Gibbs Free Energy, \tilde{G} , can be written as

$$\tilde{G} = \tilde{U} - T\tilde{S} + PV \quad (23)$$

For an ideal gas with n total moles

$$\tilde{G} = \tilde{U} - T\tilde{S} + nRT \quad (24)$$

Again we note the dimensions of \tilde{G} are energy (e.g. kcal or kJ) and not energy/mol (e.g. kcal/mol). Combining Equations (20) and (24) for \tilde{S} and \tilde{G} we obtain

$$\tilde{G} = \tilde{U}_o - kT \ln Q + nRT \quad (25)$$

Recalling the relationship of Q to the molecular partition function

$$Q = q^N / N! \quad (18)$$

$$\tilde{G} = \tilde{U}_o - NkT \ln q + kT \ln N! + nRT \quad (26)$$

We use Avogadro's number to relate the number of molecules N and moles n , i.e., $N = nN_{\text{avo}}$, along with the Stirling approximation to obtain

$$\tilde{G} = \tilde{U}_o - N_{\text{avo}} n kT \ln q + kT (N \ln N - N) + nRT \quad (27)$$

$$\text{Now : } kTN = kTN_{\text{avo}} n = RTn$$

$$= \tilde{U}_o - nRT \ln q + nRT \ln N - nRT + nRT$$

$$\tilde{G} = \tilde{U}_o - nRT \ln \frac{q}{N} \quad (28)$$

$$N = nN_{\text{avo}}, \text{ where } N_{\text{avo}} = 6.032 \times 10^{23} \text{ molecules/mole}$$

F. Relate G , the molar partition function q_m

We divide by the number of moles, n to get

$$q_m = \frac{q}{n} \quad (29)$$

$$\frac{q}{N} = \frac{q}{nN_{\text{avo}}} = \frac{q_m}{N_{\text{avo}}}$$

Substituting for (q/N) in Eqn. (28)

$$\tilde{G} = \tilde{U}_o - nRT \ln \frac{q_m}{N_{\text{avo}}} \quad (30)$$

To put our thermodynamic variables on a per mole basis (i.e., the Gibbs free energy and the internal energy) we divide by n , the number of moles.

This is a result we have been looking for

$$\frac{\tilde{G}}{n} = G \quad \text{and} \quad \frac{\tilde{U}_o}{n} = U_o$$

$$\boxed{G = U_o - RT \ln \frac{q_m}{N_{\text{avo}}}} \quad (31)$$

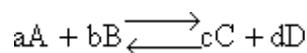
where G and U_o are on a per mole basis and are in units such as (kJ/mol) or (kcal/mol).

G. Relating the dimensionless equilibrium constant K and the molar partition function q_m

Applying Eqn. (31) to species i

$$G_i = U_{i0} - RT \ln \left(\frac{q_{im}}{N_{\text{Avo}}} \right)$$

For the reaction



the change in Gibbs free energy is

$$\Delta G = cG_C + dG_D - bG_B - aG_A \quad (32)$$

Combining Eqns. (31) and (32)

$$\Delta G = \underbrace{cU_{C0} + dU_{D0} - bU_{B0} - aU_{A0}}_{\Delta E_o} - \left[cRT \ln \left(\frac{q_{cm}}{N_{\text{Avo}}} \right) + dRT \ln \left(\frac{q_{dm}}{N_{\text{Avo}}} \right) - bRT \ln \left(\frac{q_{bm}}{N_{\text{Avo}}} \right) - aRT \ln \left(\frac{q_{am}}{N_{\text{Avo}}} \right) \right]$$

$$\Delta G = \Delta E_0 - RT \ln \left(\frac{q_{Cm}^c q_{Dm}^d}{q_{Am}^a q_{Bm}^b} \cdot N_{avo}^{-\delta} \right) \quad (33)$$

where again

$$\delta = c + d - b - a$$

From thermodynamic and Appendix C we know

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

Dividing by RT and taking the antilog

$$K = e^{-\frac{\Delta E_0}{RT}} \frac{q_{Cm}^c q_{Dm}^d}{q_{Am}^a q_{Bm}^b} N_{Avo}^{-\delta} \quad (34)$$

H. Relate the molecular partition function on a basis of per unit volume, q' and the equilibrium constant K

The molecular partition function q is just the product of the electronic, q_E , translational, q_T , vibrational, q_V , and rotational, q_R partition functions

$$q = \sum e^{-\beta \epsilon_i} = \sum e^{-\beta [\epsilon_{E_i} + \epsilon_{T_i} + \epsilon_{V_i} + \epsilon_{R_i}]} = \sum e^{-\beta \epsilon_{E_i}} \sum e^{-\beta \epsilon_{T_i}} \sum e^{-\beta \epsilon_{V_i}} \sum e^{-\beta \epsilon_{R_i}}$$

$$q = q_E q_T q_V q_R \quad (19)$$

Equations for each of these partition functions (q_E, q_T, \dots) will be given later. We now want to put the molecular partition function on a per unit volume basis. We will do this by putting the translational partition function on a per unit volume basis. This result comes naturally when we write the equation for q_T

$$q_T = q'_T V \quad (35)$$

therefore

$$q = q'_T V q_E q_V q_R = q' V \quad (36)$$

and

$$q_m = \frac{q}{n} = q' \frac{V}{n} = q' V_m \quad (37)$$

By putting q'_T on a per unit volume basis we put the product $q' = q'_T q'_E q'_R q'_V$ on a per unit volume basis. The prime again denotes the fact that the transitional partition function, and hence the overall molecular partition function, is on per unit volume.

The molar volume is

$$V_m = \frac{RT}{f^\circ}, \quad f^\circ = 1 \text{ atm}$$

where f° is the fugacity of the standard state of a gas and is equal to 1 atm.

$$K = e^{-\frac{\Delta E_0}{RT}} \frac{(q'_C)^c (q'_D)^d}{(q'_A)^a (q'_B)^b} \left(\frac{RT}{1 \text{ atm}} \right)^\delta \quad (38)$$

(See Appendix TS2 page 29 of Transition State Theory Notes for derivation)

I. Recall the relationship between K and K_C from Appendix C.

The equilibrium constant and free energy are related by

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

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{\left(\frac{f_C}{f_{C0}}\right)^c \left(\frac{f_D}{f_{D0}}\right)^d}{\left(\frac{f_A}{f_{A0}}\right)^a \left(\frac{f_B}{f_{B0}}\right)^b} \quad (39)$$

The standard state is $f_{i0} = 1 \text{ atm}$. The fugacity is given by $f_A = g_A P_A$ [See Appendix C of text]

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \cdot \frac{P_C^c P_D^d}{P_A^a P_B^b} (1 f_{i0})^{-\delta}, \quad \delta = d + c - a - b \quad (40)$$

$$P_i = C_i RT$$

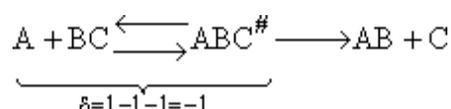
$$K = K_\gamma K_C \left(\frac{RT}{1 f^\circ} \right)^\delta = K_\gamma (1 \text{ atm})^{-\delta} \frac{C_C^c C_D^d}{C_A^a C_B^b} \left(\frac{RT}{f_{i0}^\circ} \right)^\delta \quad (41)$$

For an ideal gas $K_\gamma = 1$

Equating Eqns. (40) and (41) and canceling $\left(\frac{RT}{f_i^\infty}\right)^\delta$ on both sides

$$K_C = e^{-\frac{\Delta E_0}{RT}} \frac{(q_C)^f (q_D)^d}{(q_A)^a (q_B)^b} N_{\text{avo}}^{-\delta} \quad (42)$$

Now back to our transition state reaction



$$-r_A = v_I C_{ABC^\#} = v_I K_c^\# C_A C_B \quad (c)$$

$$K_C^\# = \frac{[C_{ABC^\#}]}{[C_A][C_{BC}]} = e^{-\frac{\Delta E_0}{RT}} \frac{q_{ABC^\#}^\#}{q_A' q_{BC}'} N_{\text{avo}} \quad (43)$$

where $q_{ABC^\#}^\#$ is the molecular partition function per unit volume for the activated complex.

$$q_{ABC^\#}^\# = q_E^\# q_V^\# q_R^\# q_T^\# \quad (44)$$

Rearranging Eqn. (43), we solve for the concentration of the activated complex $C_{ABC^\#}$

$$C_{ABC^\#} = v_I C_A C_B e^{-\frac{\Delta E_0}{RT}} \frac{q_{ABC^\#}^\# N_{\text{avo}}}{q_A' q_{BC}'} \quad (45)$$

J. The Loose Vibration, v_I

We consider the dissociation of $ABC^\#$ as a loose vibration with frequency v_I in that the transition state molecule $ABC^\#$ dissociates when it crosses the barrier. Therefore the rate of dissociation is just the vibrational frequency at which it dissociates times the concentration of $ABC^\#$ (Lp96)

$$-r_{ABC} = v_I C_{ABC\#} \quad (46)$$

Substituting Eqn. (45) into Eqn. (46)

$$-r_{ABC} = v_I C_A C_B e^{-\Delta E_o/RT} \frac{q'_{ABC\#}}{q'_A q'_{BC}} N_{Av0}$$

Where $q\phi$ is the partition function per unit volume. Where v_I is the "imaginary" dissociation frequency of crossing the barrier

The vibrational partition, $q_{v\#}^{\#}$, function is the product of the partition function for all vibrations

$$q_{v\#}^{\#} = q_{vI} q_{v1} q_{v2} \quad (47)$$

Factoring out q_{vI} for the frequency of crossing the barrier

$$q_{v\#}^{\#} = q_{vI} \overbrace{q_{v1} q_{v2}}^{q_{v\#}}$$

$$q_{v\#}^{\#} = q_{vI} q_{v\#} \quad (48)$$

$$q'_{ABC\#} = q_E^{\#} q_{vI} q_{v\#}^{\#} q_R^{\#} q_T^{\#} \quad (49)$$

Note we have moved the # from a superscript to subscript to denote that $q_{v\#}$ is the vibrational partition function less the imaginary mode v_I . $q_{v\#}^{\#}$ is the vibrational partition function for all modes of vibration, including the imaginary dissociation frequency (Lp96).

$$q_{vI} = \frac{1}{1 - e^{-\frac{hv_I}{k_B T}}} = \frac{1}{1 - \left(1 - \frac{hv_I}{kT}\right)} = \frac{k_B T}{hv_I} \quad (50)$$

$$q'_{ABC\#} = q'_{ABC\#} \frac{kT}{h v_I} \quad (51)$$

*This is the result
we have been
looking for!*

Substituting for $q_{ABC}^{\#}$ in Eqn. (45) and canceling v_I

$$-r_{ABC} = -r_A = \left[\left(\frac{k_B T}{h} \right) e^{-\frac{\Delta E_o}{RT}} \frac{q'_{ABC}{}^{\#} N_{avo}}{q'_A q'_{BC}} \right] C_A C_{BC}$$

(52)

where $q'_{ABC}{}^{\#}$ is the partition function per unit volume with the partition function for the vibration frequency for crossing removed.

q = molecular partition function = $q_E q_T q_V q_R$

q' = molecular partition function per unit volume

$q = q' V$

$q_m = \frac{q}{n} = q' V_m$ molar partition function

$q^{\#}$ = Partition function (per unit volume) of activated complex that includes partition function of the vibration frequency ν_I , the frequency of crossing

$q'_{\#}$ = Partition function (per unit volume) of the activated complex but does not include the partition function of the loose vibration for crossing the barrier

What are the Equations for q'_T , q'_V , q'_E , and q'_R

K. Evaluating the Partition Functions

Schrödinger Wave Equation

We will use the Schrödinger wave equation to obtain the molecular partition functions. The energy of the molecule can be obtained from solutions to the Schrödinger wave equation (A5p370)

$$\left[\frac{-\hbar^2}{2\pi^2 m} \nabla^2 + V(x, y, z) \right] \psi = E \psi(x, y, z) \quad (53)$$

This equation describes the wave function, ψ , for a particle (molecule) of mass m and energy E traveling in a potential energy surface $V(x, y, z)$. " \hbar " is Planck's constant. The one dimensional form is

$$-\frac{d^2 \psi}{dx^2} = \frac{2m}{\hbar^2} [E - V(x)] \psi = 0 \quad (54)$$

$$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J} \cdot \text{s}$$

The probability of finding a particle in a region between x and $x+dx$ is

$$\text{Probability} = \psi^2 dx$$

ψ^2 is the probability density (A5p373)

e_t , e_v , and e_r) used in the partition function q . The equation is solved for three special cases

1. Translational energy, e_t . Particle in a Box.
2. Vibrational energy, e_v . Harmonic Oscillator.
3. Rotational Energy, e_r . Rigid Rotator.
4. Electronic Energy, e_e .

Recall $q^r = q_E q_V q_R q_T^r$

The electronic partition functions q_E , is most always close to one.

Table PRS.3B-2 Overview of q^r

Parameter Values

1 atomic mass unit \circ 1 amu = 1.67×10^{-27} kg, $h = 6.626 \times 10^{-34}$ kg \cdot m²/s,

$k_B = 1.38 \times 10^{-23}$ kg \cdot m/s²/K/molecule

1. Transitional Partition Function q_T^r

$$q'_T = \frac{(2\pi mk_B T)^{3/2}}{h^3} = \frac{1}{\Lambda^3} = \text{the order of } 10^{30} \text{ m}^{-3} \quad (55)$$

$$\Lambda = \text{Thermal wavelength} = \frac{h}{(2\pi mk_B T)^{1/2}}$$

Derive

$$q'_T = \left(\frac{2\pi k_B}{h^2}\right)^{3/2} (\text{m})^{3/2} \left(\frac{1 \text{ amu}}{1 \text{ amu}}\right)^{3/2} T^{3/2} \times \frac{300}{300}$$

$$= \left(\frac{2\pi k_B \cdot 300 \cdot 1 \text{ amu}}{h^2}\right)^{3/2} \cdot \left(\frac{m_{AB}}{1 \text{ amu}}\right)^{3/2} \left(\frac{T}{300}\right)^{3/2}$$

Substituting for k_B , 1 amu and Plank's constant h

$$q'_T = \left(\frac{9.84 \times 10^{29}}{\text{m}^2}\right) \left(\frac{m_{AB}}{1 \text{ amu}}\right)^{3/2} \left(\frac{T}{300}\right)^{3/2} \quad (56)$$

$$\text{for } H_2 \text{ at } 25^\circ C \quad \Lambda = 7.12 \times 10^{-11} \text{ m}$$

2. Vibrational Partition Function q_v

$$q_v = \frac{1}{1 - e^{-h\nu/k_B T}}, \quad (57)$$

Derive

Expanding in a Taylor series

$$q_v = \left(\frac{1}{1 - e^{-\frac{h\nu}{k_B T}}}\right) \cong \frac{k_B T}{h\nu} = \text{the order of } 1 \text{ to } 10$$

$$\frac{h\nu}{k_B T} = \frac{hc\tilde{\nu}}{k_B T} = 4.8 \times 10^{-3} \left(\frac{\tilde{\nu}}{1 \text{ cm}^{-1}}\right) \left(\frac{300}{T}\right) \quad (58)$$

3. Electronic Partition Function

$$q_E = q_E \quad (q_E = 1)$$

Derive

4. Rotational Partition Function q_R

For linear molecules

$$q_R = \frac{8\pi^2 I k_B T}{S_y h^2} = \frac{k_B T}{S_y h c B} \quad (59)$$

$$B = \text{Rotational constant} = \frac{h}{8\pi^2 c I}$$

$$I = \sum m_i r_i^2$$

Derive

where ABC are the rotational constants (Eqn. 57) for a nonlinear molecule about the three axes at right angles to one another

$$I = \sum \mu_i r_i^2$$

For a linear molecule

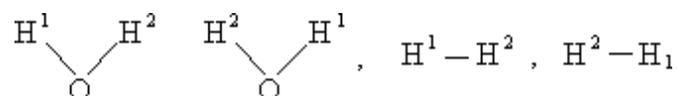
$$q_R = 12.4 \left(\frac{T}{300} \right) \left(\frac{I_{AB}}{1 \text{ amu} \cdot \text{\AA}^2} \right) \left(\frac{1}{S_y} \right) \quad (60)$$

For non-linear molecules

$$q_R \frac{1}{S_y} = \left(\frac{k_B T}{hc} \right)^{3/2} \left(\frac{\pi}{ABC} \right) = \text{the order of 10 to 1000}$$

S_y = symmetry number of different but equivalent arrangements that can be made by rotating the molecule. (See Laidler p. 99)

For the water and hydrogen molecule $S_y = 2$



For HCl $S_y = 1$

Estimate A from Transition State Theory

Let's do an order of magnitude calculation to find the frequency factor A.

$$-r_A = \frac{k_B T}{h} N_{\text{Avo}} \frac{q'_{\text{ABC}\#}}{q'_A q'_{\text{BC}}} e^{-\Delta E/RT} C_A C_B$$

$A \text{ (m}^3/\text{mol}\cdot\text{s)}$

Let's first calculate the quantity

$$-r_A = A e^{-\Delta E/RT} C_A C_B$$

$$\left(\frac{k_B T}{h} \right) \cong 10^{13}$$

at 300K

$$\frac{k_B T}{h} = \frac{1.38 \times 10^{-23} \text{ J/K} \cdot \text{molecule} \cdot 300\text{K}}{6.62 \times 10^{-34} \text{ J} \cdot \text{s}} = 6.25 \times 10^{12} \text{ s}^{-1}/\text{molecule}$$

$$\frac{k_B T}{h} \cong 10^{13} \text{ s}^{-1}/\text{molecule}$$

$$\boxed{-r_A = k C_A C_{\text{BC}}}$$

$$k = \left[\left(\frac{k_B T}{h} \right) e^{-\frac{\Delta E_o}{RT}} \left(\frac{q'_{\text{ABC}\#}}{q'_A q'_{\text{BC}}} \right) N_{\text{avo}} \right]$$

(61)

$$\text{Units } [k] = \left(\frac{1}{\text{s} \cdot \text{molecule}} \right) \times \left(\frac{\left(\frac{1}{\text{dm}^3} \right)}{\left(\frac{1}{\text{dm}^3} \right) \left(\frac{1}{\text{dm}^3} \right)} \right) \times \frac{\text{molecules}}{\text{mole}}$$

$$[k] = \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$$

$$N_{\text{Avo}} = 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}}$$

At 300K

$$\frac{k_B T}{h} = 10^{13} \text{ s}^{-1} \text{ molecule}^{-1}$$

$$q'_T \cong 10^{32} \text{ m}^{-3}$$

$$q_V \cong 6$$

$$q_R \cong 100$$

$$A = \frac{k_B T}{h} N_{\text{Avo}} \frac{q'_{\text{ABC}\#}}{q'_A q'_{\text{BC}}}$$

$$-r_A = A e^{-\Delta E/RT} C_A C_B$$

A	BC	ABC
$q'_T 6 \times 10^{32} \text{ m}^3$	$6 \times 10^{32} \text{ m}^3$	6×10^{32}
$q_V \text{ --}$	5	5
$q_R \text{ --}$	20	200
$q' 6 \times 10^{32} \text{ m}^3$	$600 \times 10^{32} \text{ m}^3$	$6000 \times 10^{32} \text{ m}^3$

$$\frac{q'_{\text{ABC}\#}}{q'_A q'_{\text{BC}}} = \frac{6000 \times 10^{32}}{6 \times 10^{32} \times 600 \times 10^{32}} = 1.710^{-32} \text{ m}^{-3}$$

$$A = \left(\frac{q'_{\text{ABC}\#}}{q'_A q'_{\text{BC}}} \right) \cdot (N_{\text{Avo}}) \cdot \left(\frac{k_B T}{h} \right)$$

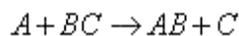
$$A = \left(1.7 \times 10^{-32} \text{ m}^{-3} \right) \left(6 \times 10^{23} \frac{\text{molecule}}{\text{mole}} \right) \left(10^{13} \frac{1}{\text{molecule} \cdot \text{s}} \right)$$

$$A \cong 10 \times 10^4 \text{ m}^3 / \text{mole} \cdot \text{s} = 10^8 \text{ dm}^3 / \text{mole} \cdot \text{s}$$

which compares with A predicted by collision theory

IV. The Eyring Equation

For the reaction



The rate law is

$$-r_A = k C_A C_{BC} \quad (62)$$

$$k = A e^{-E_A / RT} \quad (63)$$

$$\ln k = A \ln - E_A / RT \quad (64)$$

$$\frac{d \ln k}{dT} = \frac{E_A}{RT^2} \quad (65)$$

Now let's compare this with transition state theory.

The rate of reaction is the rate at which the activated complex crosses the barrier.



$$-r_A = v_I C_{ABC^\ddagger} \quad (1)$$

$$K_C^\ddagger = \frac{(ABC^\ddagger)}{(A)(B)} \equiv \frac{C_{ABC^\ddagger}}{C_A C_{BC}} \quad (2)$$

$$\boxed{-r_A = v_I K_C^\ddagger C_A C_{BC}} \quad (3)$$

Factoring out partition function for loose vibrational frequency, v_I , from the vibrational partition function, gives q_v^\ddagger

$$q_v^\ddagger = \frac{k_B T}{h v_I} q_{v^\ddagger} \quad (66)$$

then from Eqn. (43) we can obtain

$$K_C^\ddagger = K_{C^\ddagger} \frac{k_B T}{h v_I} \quad (67)$$

$$\boxed{-r_A = \left(\frac{k_B T}{h} \right) K_{C^\ddagger} C_A C_B} \quad (68)$$

which is referred to as the Eyring Equation.

From thermodynamics

$$\Delta G = \Delta H - T\Delta S \quad (69)$$

$$K^\# = e^{-\Delta G^\#/RT} = e^{\frac{\Delta S^\#}{R}} e^{-\frac{\Delta H^\#}{RT}} \quad (70)$$

The overall dimensionless terms of mole fraction x_i and the activity coefficients g_i

$$K = \frac{\gamma_{ABC} x_{ABC^\#}}{\gamma_A x_A \gamma_{BC} x_{BC}} = K_\gamma \frac{x_{ABC^\#}}{x_A x_{BC}} \cdot \frac{C_T^2}{C_T^2} \quad (71)$$

$$K = K_\gamma C_T \frac{C_{ABC^\#}}{C_A C_{BC}} = K_\gamma C_T K_{C^\#} \quad (72)$$

$$K_{C^\#} = \frac{K}{K_\gamma C_T} = \frac{e^{-\Delta G^\#/RT}}{K_\gamma C_T} = \frac{e^{-\Delta S^\#/R} e^{-\Delta H/RT}}{K_\gamma C_T^2} \quad (73)$$

$\Delta S^\#$ will be negative because we are going from a less ordered system of A, BC moving independently as reactants to a more ordered system of A, B and C being connected in the transition state. The entropy can be thought of as the number of configurations/orientations available for reactions. That is

$$\frac{\text{Number of Configurations Leading to Reaction}}{\text{Total Number of Configurations}} = e^{\Delta S^\#/R}$$

$$\Delta H^\# = (H_{ABC^\#} - H_A - H_{BC})$$

will be positive because the energy of the transition state is greater than that of the reactant state.

Case I Liquid

For liquid $C_T = \text{a constant} = C_{T0}$ (Recall for water that $C_w = 55.5 \text{ mol/dm}^3$)

$$k = \left(\frac{k_B T}{h} \right) \cdot \frac{e^{-\Delta S^\#/R} e^{-\Delta H/RT}}{K_\gamma C_{T0}} \quad (74)$$

$$\Delta S^\ddagger = (S_{ABC^\ddagger} - S_A - S_{BC}) \quad (75)$$

Here we see the temperature dependence as

$$k(T) \sim T e^{-\Delta H^\ddagger/RT}$$

Case II Gases

For gases

$$C_T = \frac{P}{RT}$$

$$k = \left(\frac{k_B R}{hP} \right) \frac{T^2 e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}}{K_\gamma}$$

Here we see the temperature dependence as

$$k(T) \sim T^2 e^{-\Delta H^\ddagger/RT}$$

As with liquids ΔS^\ddagger is negative and $\Delta H_{R_x}^\ddagger$ is positive.

A and ΔH_{R_x}

Now let's compare the temperature dependent terms. The heat of reaction will be positive because the activated state is at a higher energy level than the reactants. See figure PRS.3B-2.

$$k = \left(\frac{k_B}{h} \right) \left(\frac{R}{P} \right) T^2 e^{\Delta S^\ddagger/R} e^{-\Delta H_{R_x}^\ddagger/RT} \quad (76)$$

$$\ln k = \ln \left(\frac{k_B R}{hP} \right) + \ln T^2 + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H_{R_x}^\ddagger}{RT} \quad (77)$$

$$\frac{d(\ln k)}{dT} = \frac{2}{T} + \frac{\Delta H_{R_x}^\ddagger}{RT^2} = \frac{E_A}{RT^2} \quad (78)$$

Comparing Eqns (1) and (16), the activation energy the Eyring Equation is

$$E_A = 2RT + \Delta H_{R_x}^\ddagger \quad (79)$$

with the frequency factor

$$A = \left(\frac{k_B}{h} \right) \left(\frac{R}{P} \right) e^{\Delta S^\ddagger / R} \quad (80)$$

Appendix

For the general reaction

$$\Delta G = \sum_{i=1}^M v_i G_i = \sum U_{io} v_i - RT \sum v_i \ln \frac{q_{im}}{N_A}$$

$$\sum_{i=1} a_i \ln b_i = \sum \ln b_i^{a_i} = \ln b_1^{a_1} + \ln b_2^{a_2} + \ln b_3^{a_3} \dots$$

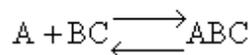
$$= \ln b_1^{a_1} b_2^{a_2} b_3^{a_3} \dots = \ln \prod_{i=1}^N b_i^{a_i}$$

$$\Delta G = \Delta E_o - RT \ln \prod_{i=1}^M \left(\frac{q_{im}}{N_A} \right)^{v_i}$$

$$-RT \ln K = \Delta E_o - RT \ln \prod_{i=1}^m \left(\frac{q_{mi}}{N_{avg}} \right)^{v_i}$$

$$\sum v_i nRT \ln \frac{q_{mi}}{N_A} = nRT \left[\sum v_i \ln \frac{q_{mi}}{N_A} = v_1 \ln \frac{q_{m1}}{N_A} + v_2 \ln \frac{q_{m2}}{N_A} + \dots = nRT \prod \left(\frac{q_{mi}}{N_A} \right)^{v_i} \right]$$

$$\begin{aligned}\sum v_i \tilde{G}_o &= \sum \tilde{U}_o v_i - nRT \ln \prod \left(\frac{q_{mi}}{N_A} \right)^{v_i} \\ &+ \text{by } n \quad \tilde{G}/n = G \quad \tilde{U}/n = U_o \\ \Delta G &= -RT \ln K = \sum U_{io} v_i - RT \ln \prod \left(\frac{q_{mi}}{N_{\text{Avo}}} \right)^{v_i}\end{aligned}$$



$$K_C = \frac{C_{ABC}}{C_A C_{BC}} \bullet e^{-\frac{\Delta E_o}{RT}} = \frac{q'_{ABC}}{q'_A q'_{BC}} N_{\text{Avo}}^{-\delta}$$

$$\delta = 1 - 1 - 1 = -1$$

$$K_C = \frac{q'_{ABC} N_{\text{Avo}}}{q'_A q'_{BC}} e^{-\frac{\Delta E_o}{RT}} = \frac{C_{ABC}}{C_A C_{BC}} \left[\frac{\text{mol}}{\text{dm}^3} / \left(\frac{\text{mol}}{\text{dm}^3} \right)^2 \right]$$

$$[K_C] = \frac{\text{dm}^3}{\text{mol}} \left[\frac{q'_{ABC} N_{\text{Avo}}}{q'_A q'_{BC}} \right]$$

$$C_{ABC} = C_A C_{BC} e^{-\frac{\Delta E_o}{RT}} \frac{q'_{ABC} N_{\text{Avo}}}{q'_A q'_{BC}}$$

$$q'_{ABC} = q_{ABC\#} \frac{kT}{h}$$

$$r_A = v C_{ABC} \frac{kT}{h} e^{-\frac{\Delta E_o}{RT}} \frac{q'_{ABC} N_{\text{Avo}}}{q'_A q'_{BC}} / \text{OK}$$

Molar partition function

$$q_m = \frac{q}{n} = (q/\text{mol})$$

$$q_m = \frac{q}{h} = q' \frac{V}{n} = \left(\frac{q_m}{\text{dm}^3} \right) \left(\frac{\text{dm}^3}{\text{mol}} \right) = q_m (\text{l/mol})$$

$$\delta = c + d - b - a$$

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{\frac{f_C^c}{f_C^\circ} \frac{f_D^d}{f_D^\circ}}{\frac{f_A^a}{f_A^\circ} \frac{f_B^b}{f_B^\circ}} = (f^\circ)^{-\delta} \frac{f_C^c f_D^d}{f_A^a f_B^b} = \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \frac{P_C^c P_D^d}{P_A^a P_B^b} (f^\circ)^{-\delta}$$

$$K = K_\gamma K_P (f^\circ)^{-\delta}, \quad P_A = C_A RT$$

$$K = K_\gamma K_P = K_\gamma \frac{P_C^c P_D^d}{P_A^a P_B^b} (f^\circ)^{-\delta} = K_\gamma \frac{C_C^c C_D^d}{C_A^a C_B^b} \left(\frac{RT}{f^\circ} \right)^{c+d-a-b} = K_\gamma K_C \left(\frac{RT}{f^\circ} \right)^{c+d-a-b}$$

$$K = K_\gamma K_C \left(\frac{RT}{f^\circ} \right)^{c+d-a-b}$$

$$\Delta E_o = \sum v_i U_{io}$$

$$-RT \ln K = \Delta E_o - RT \ln \prod \frac{q_{mi}^{v_i}}{N_{\text{Avo}}}$$

$$\ln K = -\frac{\Delta E}{RT} + \ln \prod \left(\frac{q_{mi}}{N_{\text{Avo}}} \right)^{v_i} \quad q_m = \text{mol}^{-1}$$

$$K = e^{-\frac{\Delta E_o}{RT}} \prod \left(\frac{q_{mi}}{N_{\text{Avo}}} \right)^{v_i}$$

$$K_\gamma K_C \left(\frac{RT}{f^\circ} \right)^\delta = e^{-\frac{\Delta E_o}{RT}} \frac{q_C^c q_D^d}{q_A^a q_B^b} N_{\text{avg}}^{-\delta}, \quad q^{\text{V}} = q$$

$$q_m = q'_m \frac{V}{n} = q^{\text{V}} q_m =$$

$$K = K_\gamma \left(\frac{RT}{f^\circ} \right)^\delta K_C = e^{-\frac{\Delta E_o}{RT}} \frac{q_C^c q_D^d}{q_A^a q_B^b} \left(\frac{V}{n} \right)^{c+d-a-b} N_{\text{Avo}}^{-\delta}$$

However,

$$\frac{V}{n} = \frac{RT}{f^\circ}$$

$$K_C = e^{-\frac{\Delta E_o}{RT}} \frac{q_C^c q_D^d}{q_A^a q_B^b} N_{\text{Avo}}^{-\delta}$$

Problems

Problems for Transition State Theory

Fogler & Gurmen
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