Professional Reference Shelf

B. Transition State Theory

Overview

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

$$A + BC \rightarrow AB + C$$

The rate law is

$$-r_A = kC_A C_{BC} = Ae^{-E_A/RT} C_A C_{BC}$$

For simple reactions, transition state theory 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 products from reactants.

$$A + BC \rightleftarrows A \cdots B \cdots C^{\#} \rightarrow AB + C$$

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

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

The transition state molecule $(A \cdots B \cdots C^{\#})$ and the reactants are in pseudo equilibrium at the top of the energy barrier.

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

Combining gives

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

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

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

where q' is overall the partition function per unit volume and is the product of translational, vibration, rotational, and electric partition functions, that is,

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

The individual partition functions to be evaluated are

Translation

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

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

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

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

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

The Eyring Equation

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

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

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  - J. The Loose Vibration, v_I
  - K. Evaluating the Partition Functions
- III. The Eyring Equation

References for Collision Theory, Transition State Theory and Molecular Dynamics

P. W. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998)
P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994).
G. D. Billing and K. V. Mikkelsen, *Introduction to Molecular Dynamics and Chemical Kinetics* (New York: Wiley, 1996).
P.W. Atkins, *The Elements of Physical Chemistry*, 2nd ed. (Oxford: Oxford Press, 1996).
K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987).
G. Odian, *Principles of Polymerization*, 3rd ed. (New York: Wiley 1991).
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.

I. INTRODUCTION

While the idea of an activated complex has been postulated for years, the first real definitive observation was made by Nobel Prize Laureate, Ahmed Zewail. He used femtosecond spectroscopy to study the formation of ethylene from cyclobutane.[1] The reaction is shown schematically in Figure R3.B-1.

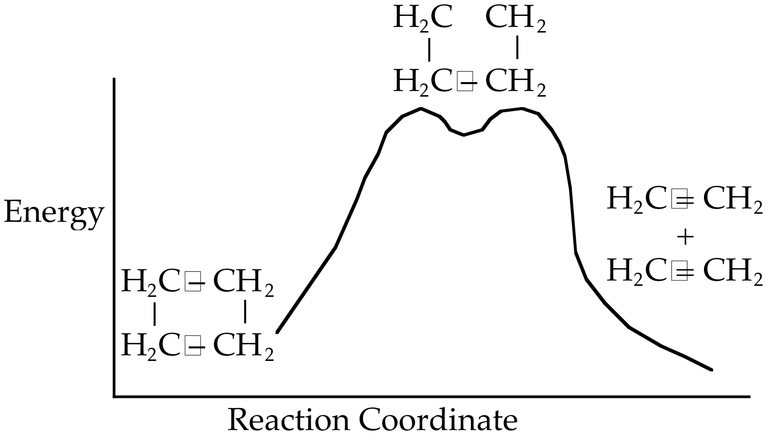


Figure R3.B-1 Evidence of active intermediate.

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.

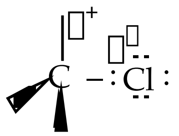
A. The Transition State

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.

$$\mathrm{Nu}:^{-} + \boxed{\mathrm{R}}\ \mathrm{X} \longrightarrow \mathrm{Nu}:\ \mathrm{R}\ \boxed{+}\ \mathrm{X}^{-}$$

An example is the exchange of Cl for OH^-, that is,

$$OH^{-} + CH_3Cl \longrightarrow HOCH_3 + Cl^{-}$$



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.[2]

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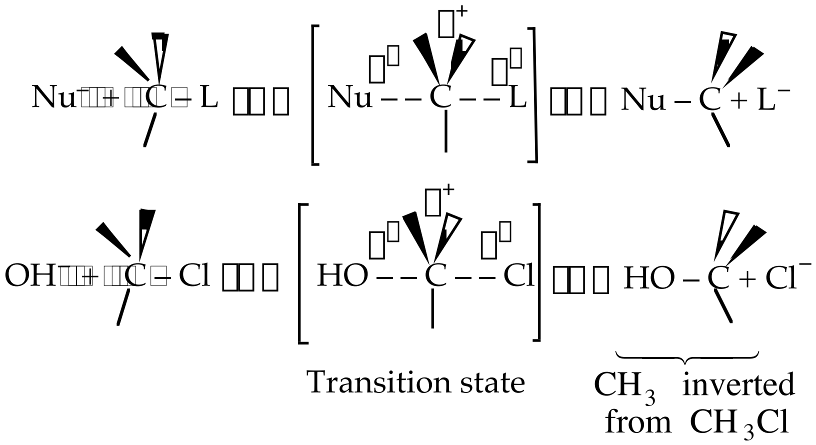
[1] *Science News*, Vol. 156, p. 247.

[2] T. W. G. Solomon, *Organic Chemistry*, 6th ed. (New York: Wiley, 1996) p.233.



$$\text{rate} = k\left[CH_3Cl\right]\left[OH^-\right]$$

Figure R3.B-1 shows the energy of the molecules along the reaction coordinate which measures the progress of the reaction. One measure of this progress might be the distance between the CH_3 group and the Cl atom.

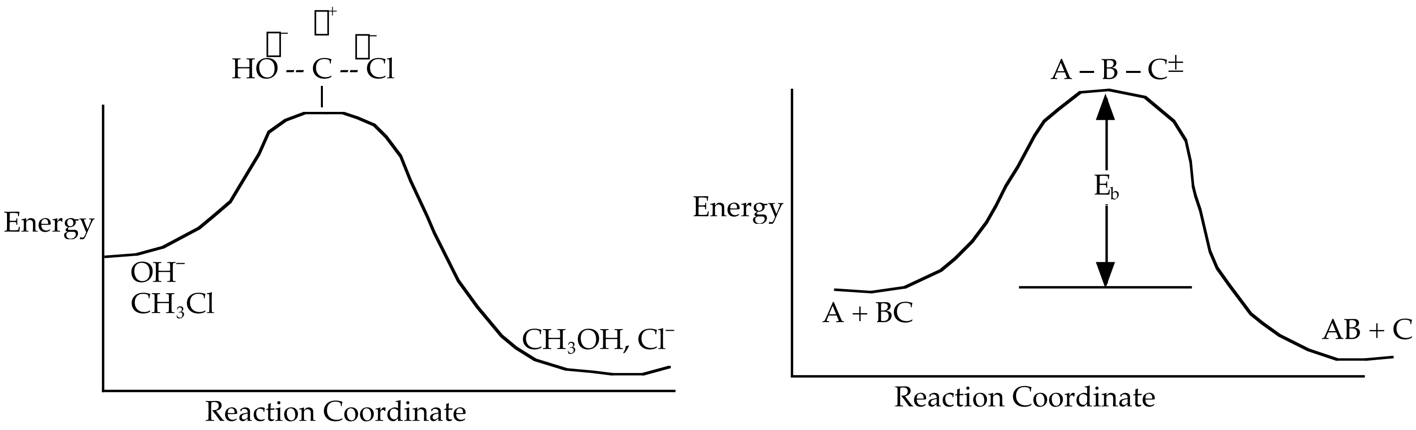


Figure R3.B-2 Reaction coordinate for (a) S_{N2} reaction, and (b) generalized reaction.

We now generalize

$$A + BC \to ABC^{\#} \to AB + C$$

with the reaction coordinate given in terms of the distance between the B and C molecules. The reaction coordinate for this reaction was discussed in R.3-A Collision Theory–D Polyani Equations when discussing the Polanyi equation.

The energy barrier shown in Figure R3.B-2 is the shallowest barrier along the reaction coordinate. The entire energy diagram for the A–B–C system is shown in three dimensions in Figure R3.B-3. To obtain Figure R3.B-2 from Figure R3.B-3, we start from the initial state (A + BC) and move through the valley up over the barrier, E_b (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 R3.B-3, we arrive at Figure R3.B-2.

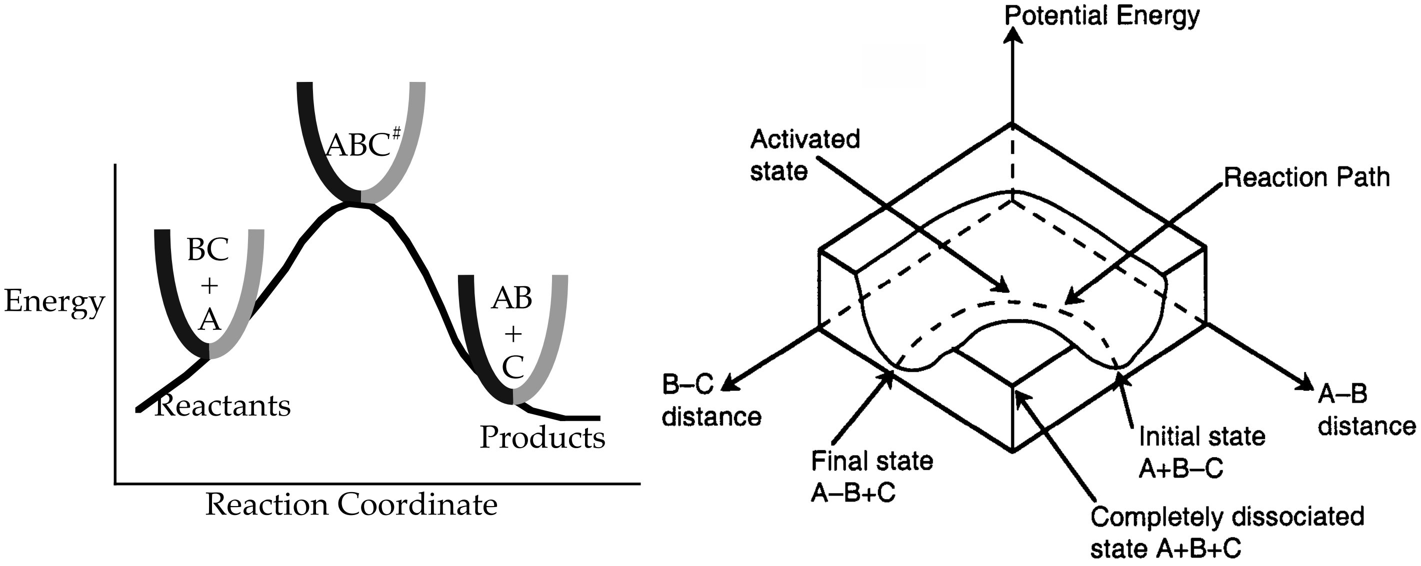


Figure R3.B-3 3-D energy surface for generalized reaction.

The rate of reaction for the general reaction[3] is the rate of crossing the energy barrier

$$A + BC \rightleftarrows A \cdots B \cdots C^{\#} \xrightarrow{v_I} AB + C$$

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

$$-r_A = v_I \ C_{ABC^{\#}} \tag{R3.B-1}$$

We assume the activated complex $ABC^{\#}$ is in virtual equilibrium with the reactants A and BC. Consequently, we can use the equilibrium concentration constant $K_C^{\#}$ to relate these concentrations, that is,

$$K_C^{\#} = \frac{\left(ABC^{\#}\right)}{(A)(B)} \equiv \frac{C_{ABC^{\#}}}{C_A C_{BC}} \tag{R3.B-2}$$

Combining Equations (A) and (B), we obtain

$$\boxed{-r_A = v_I \ K_C^{\#} \ C_A C_{BC}} \tag{R3.B-3}$$

The procedure to evaluate v_I and $K_C^{\#}$ is shown in Table R.3B-1.

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[3] K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987) p. 90.

B. Procedure to Calculate the Frequency Factor

Table R3.B-1 Transition State Procedure to Calculate v_I and $K_C^{\#}$

Step 1. **Molecular partition function**. The number of ways, W, of arranging N molecules in m energy states, with n_i molecules in the ε_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.

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

Step 2. **Relating $\tilde{S}$, n_i, and N.** The entropy or 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. **Relate $\tilde{S}$ and q.** Starting with the total energy of the system $E = \tilde{U} - \tilde{U}_0 = \sum n_i\varepsilon_i$, relative to the ground state, substitute for the number of molecules, n_i, in energy state, ε_i, using the Boltzmann distribution in the last equation of Step 3

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

and then sum to arrive at

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

for noninteracting molecules. $\tilde{U}_0$ is the ground state energy.

Step 4. **Canonical partition function for interacting molecules**. We need to consider interacting molecules. To do this, we have to use the canonical partition function

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

The probability of finding a system with energy, E_i, is

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

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 preceding equation, we can arrive at

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

Step 5. **Thermodynamic relationship to relate $\tilde{G}$, $\tilde{U}$ and q_i, the molecular partition function.** We begin by combining the Maxwell relationship, that is,

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

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 equation. We next use the relationship between Q and q, that is,

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

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

$$\boxed{\tilde{G} = \tilde{U}_0 - nRT \ \ln \frac{q}{N}}$$

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

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

and then substitute in the last equation in Step 5.

$$\boxed{G = U_0 - RT \ \ln \frac{q_m}{N_{Avo}}}$$

(Note: The tilde's have been removed.)

where n = Number of moles, N_{Avo} = Avogadro's number, and G and U_0 are on a per mole basis (e.g., kJ/mole).

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

$$aA + bB \rightleftarrows cC + dD$$

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

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

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

Combining the last equation in Step 6 and the preceding equations give

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

where

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

Step 8. **Relate the partition function on a per unit volume basis, q′, 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

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

Step 9. **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. In other words, for the transition state $A - B - C^{\#}$, with $\delta = -1$,

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

we also know

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

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

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

The prime (e.g., q′) denotes the partition functions are per unit volume.

Step 10. **The loose vibration.** The rate of reaction is the frequency, v_I, of crossing the barrier times the concentration of the activated complex $C_{ABC^{\#}}$:

$$r_{ABC} = v_I C_{ABC^{\#}}$$

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:

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

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.

$$q'^{\#}_{ABC} = q^{\#}_E\ q^{\#}_R\ q^{\#}_V\ q'^{\#}_T$$

$$q'^{\#}_{ABC} = q'_{ABC\#}\ \frac{k_BT}{hv_I}$$

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

$$\boxed{-r_A = \underbrace{\frac{k_BT}{h}\ N_{Avo}\ \frac{q'_{ABC\#}}{q'_A q'_{BC}}}_{A}\ e^{-\Delta E_o/RT}\ C_A C_{BC}}$$

where A is the frequency factor.

Step11. **Evaluate the partition functions (q'_T, q_V, q_R).** Evaluate the molecular partition functions using the Schrödenger equation

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

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

$$q'_T = \frac{\left(2\pi m k_B T\right)^{3/2}}{h^3} = \left(\frac{9.84\times10^{29}}{m^3}\right)\left(\frac{m_{AB}}{1\ \text{amu}}\right)^{2/3}\left(\frac{T}{300K}\right)^{3/2}$$

Vibration

$$q_V = \frac{1}{1-\exp\left(-\frac{hv}{k_BT}\right)}$$

$$\frac{hv}{k_BT} = \frac{hc\tilde{\nu}}{k_BT} = 4.8\times10^{-3}\left(\frac{\tilde{\nu}}{1\ \text{cm}^{-1}}\right)\left(\frac{300K}{T}\right)$$

Rotation

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

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

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

$$\boxed{-r_A = \underbrace{\frac{k_BT}{h}\ N_{Avo}\ \frac{q'_{ABC\#}}{q'_A q'_{BC}}}_{A}\ e^{-\Delta E_o/RT}\ C_A C_{BC}}$$

We can use computational software packages such as Cerius^2 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 R3.B-1: Calculating the Frequency Factor Using Transition State Theory

Use transition state theory to calculate the frequency factor A at 300 K for the reaction

$$H + HBr \rightarrow H_2 + Br$$

Additional Information. Literature values.[4] (Note: Most of this information can be obtained from computational chemistry software packages such as Cerius^2, Spartan, or Cache.)

Reactants – H, HBr

H atom (mass)	1 amu
HBr (mass)	80.9 amu
HBr vibration wave number	2650 cm^{-1}
H–Br separation distance	142 pm

Transition State Complex – H–H–Br

Vibration wave numbers

2340 cm^{-1}

460 cm^{-1} (degenerate)

Separation distances

$$H \xleftrightarrow{150\text{ pm}} H \xleftrightarrow{142\text{ pm}} Br$$

Solution

The reaction is

$$H + HBr \rightleftharpoons H\text{–}H\text{–}Br \rightarrow H_2 + Br$$

The specific reaction rate is

$$k = \underbrace{\left[\left(\frac{k_B T}{h}\right)\left(\frac{q'_{HHBr^{\#}} N_{avo}}{q'_H q'_{HBr}}\right)\right]}_{A} e^{-\frac{E_o}{RT}}$$

Reactants

Hydrogen

Translation

$$q'_T = \frac{(2\pi m k_B T)^{3/2}}{h^3} = \left[\frac{9.88\times 10^{29}}{m^3}\right]\left(\frac{m_H}{1\text{ amu}}\right)^{2/3}\left(\frac{T}{300\text{ K}}\right)^{3/2} = \frac{9.88\times 10^{29}}{m^3}\left(\frac{1\text{ amu}}{1\text{ amu}}\right)^{3/2}\left(\frac{300\text{ K}}{300\text{ K}}\right.$$

$$q'_{T,H} = 9.88\times 10^{29}\,m^{-3}$$

Hydrogen Bromide

Translation

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[4] K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987).

$$q_T = \frac{(2\pi m k_B T)^{3/2}}{h^3} = \left(\frac{9.88\times10^{29}}{m^3}\right)\left(\frac{m_{HBr}}{1\ \text{amu}}\right)^{3/2}\left(\frac{T}{300\ \text{K}}\right)^{3/2} = \frac{9.84\times10^{29}}{m^3}\left(\frac{80.9\ \text{amu}}{1\ \text{amu}}\right)^{3/2}\left(\frac{300\ \text{K}}{300\ \text{K}}\right.$$

$$\boxed{q_{T,HBr} = 7189\times10^{29}\,m^{-3}}$$

Vibration

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

$$\frac{h\nu}{k_B T} = \frac{hc\tilde{\nu}}{k_B T} = 4.8\times10^{-3}\left(\frac{\tilde{\nu}}{1\ \text{cm}^{-1}}\right)\left(\frac{300\ \text{K}}{T}\right) = 4.8\times10^{-3}\left(\frac{2650\ \text{cm}^{-1}}{1\ \text{cm}^{-1}}\right)\left(\frac{300\ \text{K}}{300\ \text{K}}\right)$$

$$\frac{h\nu}{k_B T} = 4.8\times10^{-3}\bullet 2650 = 12.7$$

$$\boxed{q_{V,HBr} = \frac{1}{1-\exp(-12.7)} = 1.0}$$

Rotation

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

$$I_{HBr} = \sum m_i r_i^2 = \mu_{HBr} d_{HBr}^2$$

$$I = \mu_{HBr} d_{HBr}^2 = \frac{(79.9)(1)}{79.9+1}(1.42\text{Å})^2 = 1.99\ \text{amu}\ \text{Å}^2$$

$$S_y = 1$$

$$q_r = 12.4\left(\frac{300\text{K}}{300\text{K}}\right)\left(\frac{1.99\ \text{amu}\ \text{Å}^2}{1\ \text{amu}\ \text{Å}^2}\right)$$

$$\boxed{q_r = 24.6}$$

The total partition function is

$$q_{HBr} = q_T q_V q_r = \left(\frac{7189\times10^{29}}{m^3}\right)(1)(24.6)$$

$$q_{HBr} = 1.76\times10^{34}/m^3$$

Transition State Complex

Translation

$$q_T^{\#} = \frac{(2\pi m k_B T)^{3/2}}{h^3} = \left(\frac{9.88\times10^{29}}{m^3}\right)\left(\frac{m_{H-H-Br}}{1\ \text{amu}}\right)^{3/2}\left(\frac{T}{300\ \text{K}}\right)^{3/2} = \frac{9.88\times10^{29}}{m^3}\left(\frac{81.9\ \text{amu}}{1\ \text{amu}}\right)^{3/2}\left(\frac{300\ \text{K}}{300\ \text{K}}\right.$$

$$\boxed{q^{\#}_{T,1} = 7322\times10^{29}\,m^{-3}}$$

Vibration

$$q_V^{\#} = q_{V1} q_{V2}^2$$

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

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

1. $\tilde{\nu} = 2{,}340\ \text{cm}^{-1}$

$$\frac{h\nu}{k_B T} = 11.2$$

$$q_{V1} = \frac{1}{1 - e^{-11.2}} = 1.0$$

2. $\tilde{\nu} = 460\ \text{cm}^{2}$

$$\frac{h\nu}{k_B T} = 2.2$$

$$q_{V2} = \frac{1}{1 - e^{-2.2}} = 1.235$$

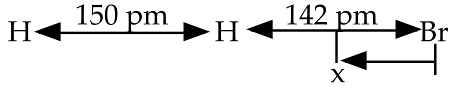
$$q_V^{\#} q_{V1} q_{V2}^2 = (1)(1.1235)^2 = 1.26$$

Rotation

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

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

Calculate the rotational partition function, $q_r^{\#}$, for the following transition state.



First, we find the center of mass at x.

$$m_{Br} \bullet x = (292 - x)m_H + (142 - x)m_H$$

$$79.9x = (292 - x)(1) + (142 - x)(1)$$

$$x = 5.34\ \text{pm} = 0.0534\ \text{Å}$$

The moment of inertia

$$I = m_{H1}r_1^2 + m_{H2}r_2^2 + m_{Br}r_3^2$$

$$r_1 = 292 - 5.34 = 286.6\text{pm} = 2.866\ \text{Å}$$

$$r_2 = 142 - 5.34 = 136.6\text{pm} = 1.366\ \text{Å}$$

$$r_3 = 0.0534\ \text{Å}$$

$$I = (1\ \text{amu})(2.866\ \text{Å})^2 + (1\ \text{amu})(1.366\ \text{Å})^2 + (79.9\ \text{amu})(0.0534\ \text{Å})^2$$

$$I = 8.21\ \text{amu Å}^2 + 1.866\ \text{amu Å}^2 + 0.228\ \text{amu Å}^2$$

$$I = 10.3\ \text{amu Å}^2$$

The rotational partition function is

$$q_r^{\#} = (12.4)(10.3) = 127.8$$

The total partition function for the transition state is

$$q_{HHBr}^{\#} = q_T^{\#} q_v^{\#} q_r^{\#} = \left(7322 \times 10^{29}\right)(1.26)(127.8)$$

$$= 1.17 \times 10^{35}/\mathrm{m}^3$$

We now calculate the frequency factoring A.

$$A = \left[\frac{k_B T}{h}\right]\left[\frac{q_{HHBr}^{\#}}{q_H q_{HBr}}\right] N_{Avo}$$

$$= \left[\frac{1.38 \times 10^{-23}\,\mathrm{kg\ m^2/s^2/molecule/K}\ \ 300\ \mathrm{K}}{h = 6.626 \times 10^{-34}\,\mathrm{kg} \cdot \mathrm{m^2/s}}\right]\left[\frac{1.17 \times 10^{35}/\mathrm{m}^3}{\left(9.88 \times 10^{29}/\mathrm{m}^3\right)\left(1.76 \times 10^{34}/\mathrm{m}^3\right)}\right] N_{Avo}$$

$$A = \left(62.5 \times 10^{11}/\mathrm{s}\right)\left[\frac{6.78 \times 10^{-30}\,\mathrm{m}^3}{\mathrm{molecule}}\right]\left[6.02 \times 10^{23}\,\frac{\mathrm{molecules}}{\mathrm{mol}}\right]$$

$$= 253 \times 10^5\,\frac{\mathrm{m}^3}{\mathrm{mol} \bullet \mathrm{s}} \times \frac{1000\ \mathrm{dm}^3}{\mathrm{m}^3} = 2.53 \times 10^{10}\,\frac{\mathrm{dm}^3}{\mathrm{mol} \bullet \mathrm{s}}$$

$$\boxed{A = 2.53 \times 10^{10}\,\frac{\mathrm{dm}^3}{\mathrm{mol} \bullet \mathrm{s}}}$$

Data From Computational Chemistry

Now let's calculate A and E using the parameters from cache.

For the reaction:

$$H + HBr \rightarrow H_2 + Br$$

The three dimensional potential energy surfaces of the reacting particles along the reaction coordinates was calculated using the MOPAC PM3 method:

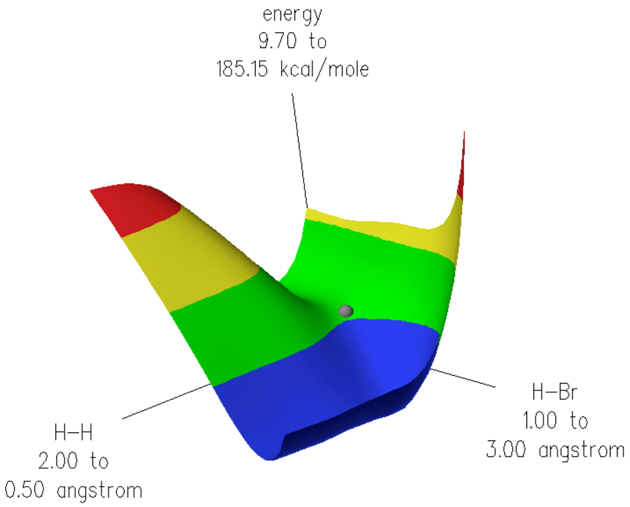


Figure R3.B-4 Potential energy surface.

The transition state structure was found at the saddle point, refined by using the DFT/B88-PW91 method as

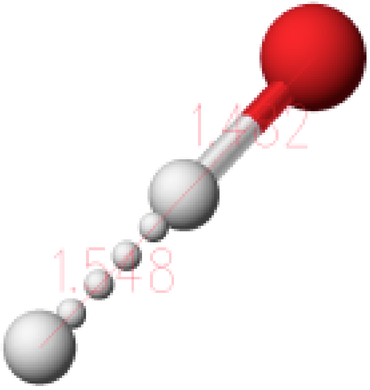


Figure R3.B-5 H–H–Br transition state.

In the transition state, the three atoms are linear, and the H-Br distance is 1.48 Å while the H-H distance is 1.55 Å.

The transition state was further proved by vibrational analysis (PM3 FORCE), showing one and only one negative vibration (imaginary frequency of crossing the barrier). Moreover, the negative vibration corresponds to the movement of the atoms on the two reaction coordinates.

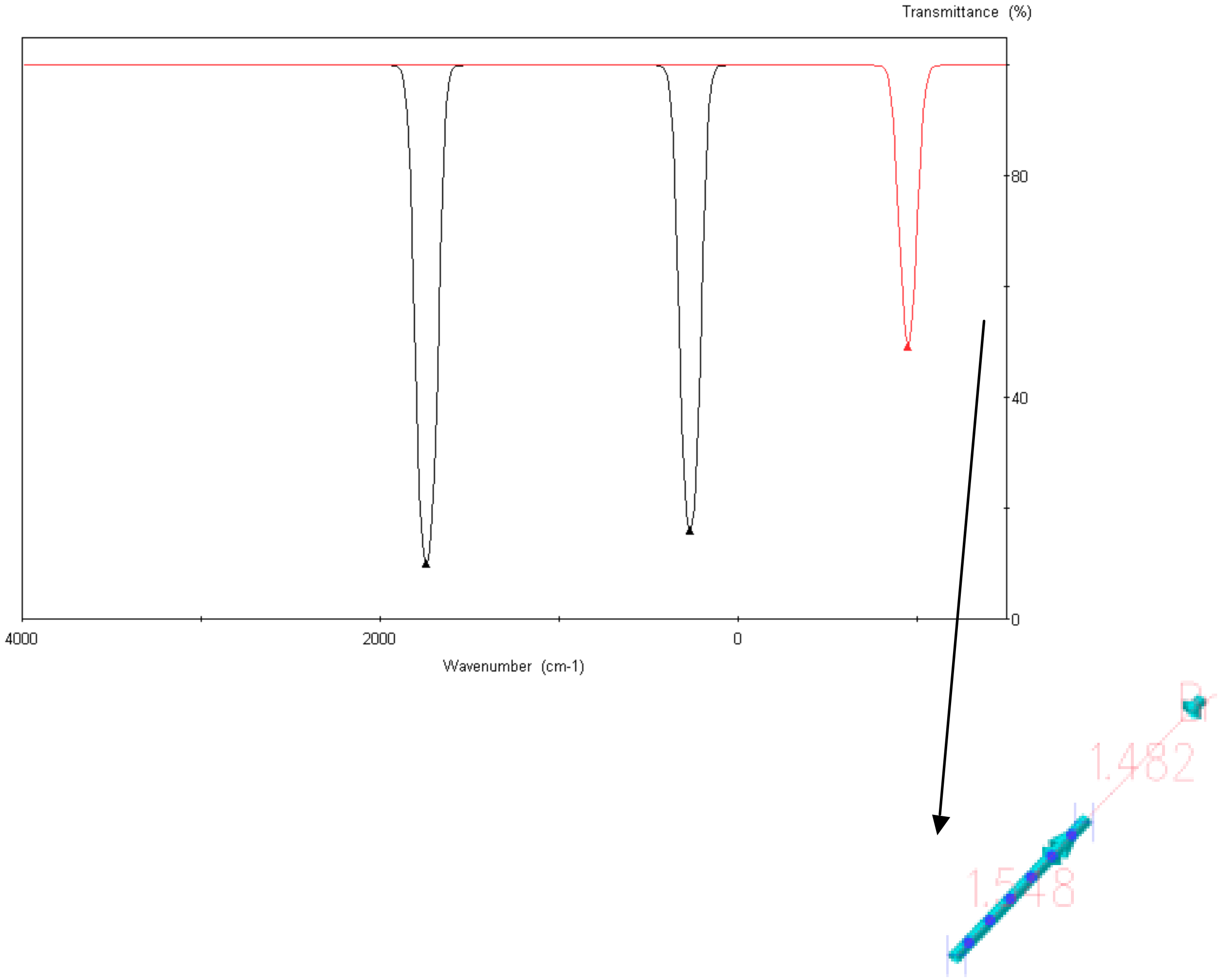


Figure R3.B-6 ______________________________.

Example R3.B-2: Summary of Information from Cache Software

Reactants – H, HBr

H atom (mass)	1 amu
HBr (mass)	80.9 amu
HBr vibration wave number	2,122 cm^{-1}
H–Br separation distance	147 pm

Transition State Complex – H–H–Br

Vibration wave numbers

1,736 cm^{-1}

289 cm^{-1}

Separation distances

$$H \xleftrightarrow{155\ pm} H \xleftrightarrow{148\ pm} Br$$

The translational partition functions remain the same:

$$q'_H = 9.88 \times 10^{29} m^{-3}$$

$$q_{HBr} = 7189 \times 10^{29} m^{-3}$$

$$q_{HHBr} = 7322 \times 10^{29} m^{-3}$$

HBr

Vibration

$$\frac{hv}{k_B T} = 10.19$$

$$q_v = 1$$

Rotation

$$I_{HBr} = \frac{(79.9)(1)}{79.9+1}\left(1.47 Å\right)^2 = 2.13 \ \text{amu} \ \ Å^2$$

$$q_r = (12.4)(2.13) = 26.46$$

$$q'_{HBr} = \left(7{,}189 \times 10^{29}\right)(1)(26.46) = 1.90 \times 10^{34}/m^3$$

HHBr

Vibration

1. $\frac{hv}{k_B T} = (1736)\left(4.8 \times 10^{-3}\right) = 8.33$

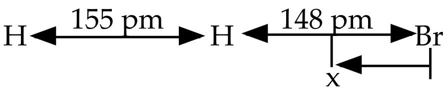
   $q_{v1} = 1.0002$

2. $\frac{hv}{k_B T} = (289)\left(4.8 \times 10^{-3}\right) = 1.387$

   $q_{v2} = 1.33$

Rotation

Calculate the rotational partition function, $q_r^{\#}$, for the followingtransition state.



First, we find the center of mass at x:

$$m_{Br} \bullet x = (303 - x)m_H + (148 - x)m_H$$

$$79.9x = (303 - x)(1) + (148 - x)(1)$$

$$x = 5.51 \text{ pm} = 0.0551 \text{ Å}$$

$$r_1 = 303 - 5.51 = 2.97 \text{ pm} = 2.97 \text{ Å}$$

$$r_2 = 148 - 5.51 = 142.5 \text{ pm} = 1.425 \text{ Å}$$

$$r_3 = 0.0551 \text{ Å}$$

$$I = (1)(2.97)^2 + (1)(1.425)^2 + (79.9)(0.0551)$$

$$I = 8.82 + 2.03 + 0.24 = 11.1$$

$$q_r = 137.5$$

$$q^{\#}_{HHBr} = \left(7322 \times 10^{29}\right)(1.0002)(1.33)(137.5)/m^3$$

$$q^{\#}_{HHBr} = 1.339 \times 10^{35} m^{-3}$$

$$A = \left(62.5 \times 10^{11}/s\right)\frac{1.339 \times 10^{35} m^3}{\left(1.9 \times 10^{34}\right)\left(9.88 \times 10^{29}\right)}\left(6.02 \times 10^{23}\right)$$

$$= \left(62.5 \times 10^{11}/s\right)\left(7.13 \times 10^{-30} m^3\right)\left(6.02 \times 10^{23}\right)$$

$$\boxed{A = 2.66 \times 10^{10} \frac{dm^3}{mol \bullet s}}$$

Chemical	Heat of formation at 298 K (kcal/mol)		Energy of zero point level (au)
	MOPAC PM3 method	Experiments	DFT/B88-PW91 method
HBr	5.3	-8.71	-2574.451933
H	52.1	52.1	-0.502437858
H-H-Br Transition state	59.6	N/A	-2574.953345

Therefore, the standard enthalpy of activation is:

$$\Delta H^{\ddagger}_{298} = 59.6 - 5.3 - 52.1 = 2.2 \text{ kcal/mol} = 9.2 \text{ kJ/mol}$$

The intrinsic Arrhenius activation energy is

$$E_a^{intrinsic} = \Delta H^{\ddagger}_{298} + 298R = 2.8 \text{ kcal/mol} = 11.7 \text{ kJ/mol}$$

Barrier height E_0 (difference between zero-point levels of activated complexes and reactants) (because the conversion between the au and the kcal/mol units is very large, we need to maintain a high number of decimal points):

$E_0 = 627.5 * ((-2574.953345) - (-2574.451933) - (-0.502437858)) = 0.64$ kcal/mol = 2.7 kJ/mol

II. 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, ε_i.

Total Energy of System

Total number of molecules, N, is

$$\boxed{N = \sum n_i} \qquad \text{(R3.B-4)}$$

where n_i = Number of molecules with energy ε_i.

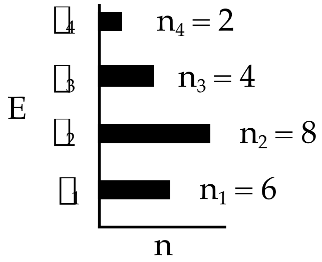
The total energy, E, is

$$\boxed{E = \sum n_i \varepsilon_i} \qquad \text{(R3.B-5)}$$

The number of ways, W, arranging N molecules among m energy states ($\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_m$) is

$$W = \frac{N!}{n_1!n_2! \ldots n_m!} \qquad \text{(R3.B-6)}$$

For example, if we have $N = 20$ molecules shared in four energy levels (ε_1, ε_2, ε_3, ε_4) as shown here



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

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

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 almost always be found in that arrangement. Differentiating Equation (R3.B-3) and setting $dW = 0$, we find the distribution that gives this maximum.[5] The fraction of molecules in energy state, ε_i, is

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[5] See P. W. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998) p. 571.

Boltzmann distribution

$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum e^{-\beta\varepsilon_i}} = \frac{e^{-\beta\varepsilon_i}}{q}, \quad \beta = 1/k_B T \qquad \text{(R3.B-7)}$$

$$q = \sum e^{-\beta\varepsilon_i} \qquad \text{(R3.B-8)}$$

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

Equation (R3.B-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.

Total energy

$$\boxed{E = \sum n_i \varepsilon_i} \qquad \text{(R3.B-5)}$$

This energy, $E = \sum n_i \varepsilon_i$, 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,[6] to obtain the total internal energy

$$\tilde{U} = \tilde{U}_0 + \sum n_i \varepsilon_i \qquad \text{(R3.B-9)}$$

The tildes, $\tilde{U}$, represent that this is the total energy <u>not</u> the energy per mole.

Comments on the Partition Function q

The <u>molecular partition function</u> 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 ($kT \geq\geq \varepsilon$), almost all states are accessible.

$$q = \sum e^{-\beta\varepsilon_i} = \sum e^{-\varepsilon_i/kT} = e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT} + e^{-\varepsilon_3/kT} + \ldots$$

Now as $T \to \infty$, $e^{-\varepsilon_i/kT} \to 1$ are $q \to \infty$ because $\beta \to 0$, that is, $q = 1 + 1 + 1 + 1 + 1 + \ldots$, and we see the partition function goes to infinity as all energy states are accessible.

(b) At the other extreme, very very low temperatures ($kT << \varepsilon_i$),

as $T \to 0$ and $e^{-\varepsilon_i/kT} \to 0$

then $q \to g_0$

and we see that none of the states are accessible with one exception, namely degeneracy in the ground state (i.e., $q \to g_o$ for $\varepsilon_o = 0$).

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

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

$$E = \varepsilon_1 n_1 + \varepsilon_2 n_2 + \varepsilon_3 n_3 + \ldots$$

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[6] P. W. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998) p. 579.

$$W = \frac{N!}{n_1!n_2! \;\ldots\; n_i!} \tag{R3.B-6}$$

Boltzmann formula for entropy

Ludwig Boltzmann 1896

Recall n_i = number of particles in energy level ε_i. The Basic Postulate is

$$\boxed{\tilde{S} = k \ln W = k \ln \frac{N!}{n_1!n_2! \;\ldots\; n_i!}} \tag{R3.B-10}$$

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

$$\ln W = \ln N! - \ln n_1!n_2!$$

$$= \ln N! - \left[\ln n_0! + \ln n_1! + \ldots\right]$$

$$\boxed{\ln W = \ln N! - \sum \ln(n_i!)} \tag{R3.B-11}$$

Stirling's approximation for the natural lag of factorials is

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

or approximately

$$\ln X! = X \ln X - X \tag{R3.B-12}$$

Stirling's approximation

For our system this approximation becomes

$$\ln W = N \ln N - N - \left[\sum n_i \ln n_i - \underbrace{\sum n_i}_{N}\right] \tag{R3.B-13}$$

$$N = \sum n_i \tag{R3.B-4}$$

Recall substituting Equation (R3.B-4) in Equation (R3.B-13). We find

$$\ln W = N \ln N - \sum n_i \ln n_i$$

$$= \sum n_i \ln N - \sum n_i \ln n_i$$

$$\ln W = -\sum \left(n_i \ln n_i - n_i \ln N\right)$$

Further rearrangement gives

$$\ln W = -\sum n_i \ln \frac{n_i}{N} \tag{R3.B-14}$$

combining Equations (R3.B-10) and (R3.B-14)

$$\boxed{\tilde{S} = -k \sum n_i \ln \frac{n_i}{N}} \tag{R3.B-15}$$

C. Relate $\tilde{S}$ and q

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

$$\boxed{\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q}} \qquad \text{(R3.B-8)}$$

Taking the natural log of Equation (R3.B-5) gives

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

Substituting for $\ln\left(\frac{n_i}{N}\right)$ in Equation (R3.B-13) gives

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

Rearranging gives

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

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

Recall from Equation (R3.B-9) for $\sum n_i\varepsilon_i = E = \tilde{U} - U_0$, where U_0 is the ground state energy in kcal.

$$\boxed{\tilde{S} = \frac{\tilde{U} - \tilde{U}_0}{T} + kN\ln q} \qquad \text{(R3.B-16)}$$

This result is for noninteracting 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 state, we must consider the canonical partition function, Q.

D. Canonical Partition Function for Interacting Molecules

Canonical Ensemble (Collection)[7]

We now will consider interacting molecules. 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.

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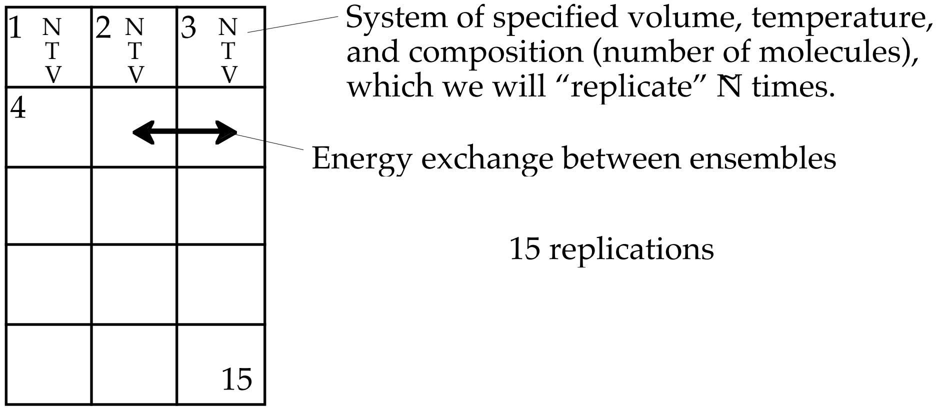
[7] P. W. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998) p. 583.



Let

E_i = Energy of ensemble i

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

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

$$Q = \sum e^{-\beta E_i} \qquad \text{(R3.B-17)}$$

Q is the canonical partition function.

We now rate the canonical partition function the molecular partition function.[8] The energy of ensemble i, E_i, is the sum of the energies of each of the molecules in the ensembles

$$E_i = \varepsilon_i(1) + \varepsilon_N(2) + \ \dots \ + \varepsilon_N(N)$$

Energy of molecule 1 when it is in state i

Energy of molecule N when it is in state N

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

Expanding the i = 1 and i = 2 terms,

$$Q = e^{-\beta\varepsilon_1(1) - \beta\varepsilon_1(2)} + \ \dots + e^{-\beta\varepsilon_2(1)} + e^{-\beta\varepsilon_2(2)} + \ \dots + \sum_{i=3} e^{-\beta E_i}$$

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, and so on.

---

[8] P. W. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998) p. 858

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

$$Q = q^N$$

This result (Equation (R3.B-17)) is for *distinguishable* molecules. However, for *indistinguishable* molecules, it doesn't matter which molecule is in which state, that is, whether molecule 1 is in state (a) or (b) or (c)[9]

$$\begin{array}{llll} (1) \to (a) & (1) \to (b) & (1) \to (c) & \\ (2) \to (b) & (2) \to (c) & (2) \to (a) & \qquad E = \varepsilon_a + \varepsilon_b + \varepsilon_c \\ (3) \to (c) & (3) \to (a) & (3) \to (b) & \text{(etc.)} \end{array}$$

Consequently, we have to divide by N!

$$\boxed{Q = \frac{q^N}{N!}} \qquad \text{(R3.B-18)}$$

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.

$$\boxed{q = q^T q^V q^R q^E} \qquad \text{(R3.B-19)}$$

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[10]

$$\boxed{\tilde{S} = \frac{\tilde{U} - \tilde{U}_o}{T} + k \ln Q} \qquad \text{(R3.B-20)}$$

Combining Equations (R3.B-17) and (R3.B-20) thus gives

Which is a result we have been looking for.

$$\boxed{\tilde{S} = \frac{\tilde{U} - \tilde{U}_o}{T} + k \ln\left(\frac{q^N}{N!}\right)} \qquad \text{(R3.B-22)}$$

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

$$\tilde{G} = \tilde{U} - T\tilde{S} + PV \qquad \text{(R3.B-23)}$$

For an ideal gas with n total moles,

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[9] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994) p. 605. P. W. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998) p. 585.

[10] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994) p. 684.

$$\tilde{G} = \tilde{U} - T\tilde{S} + nRT \qquad \text{(R3.B-24)}$$

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 (R3.B-20) and (R3.B-24) for $\tilde{S}$ and $\tilde{G}$, we obtain

$$\tilde{G} = \tilde{U}_0 - kT \ \ln Q + nRT \qquad \text{(R3.B-25)}$$

Recalling the relationship of Q to the molecular partition function

$$Q = q^N / N! \qquad \text{(R3.B-18)}$$

$$\tilde{G} = \tilde{U}_0 - NkT \ln q + kT \ln N! + \ nRT \qquad \text{(R3.B-26)}$$

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

$$\tilde{G} = \tilde{U}_0 - N_{avo}n \ \ kT \ln q + kT\left(N \ln N - N\right) + nRT \qquad \text{(R3.B-27)}$$

Now

$$kTN = kTN_{avo}n = RTn$$

$$= \tilde{U}_0 - nRT \ln q + nRT \ln N - nRT + nRT$$

$$\boxed{\tilde{G} = \tilde{U}_0 - nRT \ln \frac{q}{N}} \qquad \text{(R3.B-28)}$$

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

F. Relate G and the Molar Partition Function, q_m

We divide by the number of moles, n, to get

$$\boxed{q_m = \frac{q}{n}} \qquad \text{(R3.B-29)}$$

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

Substituting for (q/N) in Equation (R3.B-28) gives

$$\tilde{G} = \tilde{U}_0 - nRT \ln \frac{q_m}{N_{avo}} \qquad \text{(R3.B-30)}$$

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.

$$\frac{\tilde{G}}{n} = G \ \text{ and } \ \frac{\tilde{U}_0}{n} = U_0$$

This is a result we have been looking for.

$$\boxed{G = U_0 - RT \ \ln \frac{q_m}{N_{avo}}} \qquad \text{(R3.B-31)}$$

where G and U_0 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 Equation (R3.B-31) to species i gives

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

For the reaction

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

the change in Gibbs free energy is

$$\Delta G = cG_C + dG_D - bG_B - aG_A \qquad \text{(R3.B-32)}$$

Combining Equations (R3.B-31) and (R3.B-32) gives

$$\Delta G = \underbrace{cU_{C0} + dU_{D0} - bU_{B0} - aU_{A0}}_{\Delta E_0}$$

$$-\left[cRT\ \ln\left(\frac{q_{cm}}{N_{Avo}}\right) + dRT\ \ln\left(\frac{q_{dm}}{N_{Avo}}\right) - bRT\ \ln\left(\frac{q_{bm}}{N_{Avo}}\right) - aRT\ \ln\left(\frac{q_{am}}{N_{Avo}}\right)\right]$$

$$\boxed{\Delta G = \Delta E_0 - RT\ \ln\left(\frac{q_{Cm}^{c}q_{Dm}^{d}}{q_{Am}^{a}q_{Bm}^{b}} \bullet N_{avo}^{-\delta}\right)} \qquad \text{(R3.B-33)}$$

where again

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

From thermodynamics and Appendix C, we know

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

Dividing by RT and taking the antilog, we get

$$\boxed{K = e^{-\frac{\Delta E_0}{RT}}\frac{q_{Cm}^{c}q_{Dm}^{d}}{q_{Am}^{a}q_{Bm}^{b}}N_{Avo}^{-\delta}} \qquad \text{(R3.B-34)}$$

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

$$q = \sum e^{-\beta\varepsilon_i} = \sum e^{-\beta\left[\varepsilon_{E_i} + \varepsilon_{T_i} + \varepsilon_{V_i} + \varepsilon_{R_i}\right]} = \sum e^{-\beta\varepsilon_{E_i}} \sum e^{-\beta\varepsilon_{T_i}} \sum e^{-\beta\varepsilon_{V_i}} \sum e^{-\beta\varepsilon_{R_i}}$$

$$q = q_E q_T q_V q_R \qquad \text{(R3.B-19)}$$

Equations for each of these partition functions $(q_E,\ q_T,\ \ldots)$ 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

$$q_T = q'_T V \tag{R3.B-35}$$

therefore,

$$q = q'_T V q_E q_V q_R = q' V \tag{R3.B-36}$$

and

$$q_m = \frac{q}{n} = q'\frac{V}{n} = q' V_m \tag{R3.B-37}$$

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

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

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

$$\boxed{K = e^{-\frac{\Delta E_o}{RT}} \frac{(q'_C)^c (q'_D)^d}{(q'_A)^a (q'_B)^b}\left(\frac{RT}{1 \text{ atm}}\right)^{\delta}} \tag{R3.B-38}$$

(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

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

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{\left(\frac{f_C}{f_{C0}}\right)^c \left(\frac{f_D}{f_{D0}}\right)^d}{\left(\frac{f_A}{f_{A0}}\right)^a \left(\frac{f_B}{f_{B0}}\right)^b} \tag{R3.B-39}$$

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

$$K = \underbrace{\frac{a_C^c a_D^d}{a_A^a a_B^b}}_{K_a} = \underbrace{\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}}_{K_\gamma} \bullet \underbrace{\frac{P_C^c P_D^d}{P_A^a P_B^b}}_{K_p} \left(1 \ f_{i0}^\circ\right)^{-\delta}, \quad \delta = d + c - a - b \tag{R3.B-40}$$

$$P_i = C_i RT$$

$$\boxed{K = K_\gamma K_C \left(\frac{RT}{1 \ f^\circ}\right)^{\delta} = K_\gamma \left(1 \text{ atm}\right)^{-\delta} \frac{C_C^c C_D^d}{C_A^a C_B^b}\left(\frac{RT}{f_{i0}^\circ}\right)^{\delta}} \tag{R3.B-41}$$

For an ideal gas $K_\gamma = 1$

Equating Equations (R3.B-40) and (R3.B-41) and canceling $\left(RT/f_i^\circ\right)^{\delta}$ on both sides gives

$$\boxed{K_C = e^{-\frac{\Delta E_0}{RT}} \frac{(q'_C)^c (q'_D)^d}{(q'_A)^a (q'_B)^b} N_{avo}^{-\delta}} \qquad \text{(R3.B-42)}$$

Now back to our transition state reaction

$$\underbrace{A + BC \rightleftarrows ABC^{\#}}_{\delta=1-1-1=-1} \longrightarrow AB + C$$

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

$$K_C^{\#} = \frac{\left[C_{ABC^{\#}}\right]}{\left[C_A\right]\left[C_{BC}\right]} = e^{-\frac{\Delta E_0}{RT}} \frac{q'^{\#}_{ABC}}{q'_A q'_{BC}} N_{avo} \qquad \text{(R3.B-43)}$$

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

$$q'^{\#}_{ABC} = q_E^{\#} q_V^{\#} q_R^{\#} q'^{\#}_T \qquad \text{(R3.B-44)}$$

Rearranging Equation (R3.B-43), we solve for the concentration of the activated complex $C_{ABC\#}$

$$\boxed{C_{ABC\#} = v_I C_A C_B e^{-\frac{\Delta E_0}{RT}} \frac{q'^{\#}_{ABC} N_{avo}}{q'_A q'_{BC}}} \qquad \text{(R3.B-45)}$$

J. The Loose Vibration, v_I

We consider the dissociation of A–B–C$^{\#}$ as a loose vibration with frequency v_I in that the transition state molecule A–B–C$^{\#}$ 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$^{\#}$[11]

$$-r_{ABC} = v_I C_{ABC^{\#}} \qquad \text{(R3.B-46)}$$

Substituting Equation (R3.B-45) into Equation (R3.B-46) yields

$$-r_{ABC} = v_I C_A C_B \; e^{-\Delta E_0/RT} \; \frac{q'^{\#}_{ABC}}{q'_A q'_{BC}} \; N_{Avo}$$

Where q' 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

$$q_v^{\#} = q_{vI} q_{v1} q_{v2} \qquad \text{(R3.B-47)}$$

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

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[11] K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987), p. 208.

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

$$q_v^{\#} = q_{vI}q_{v\#} \qquad \text{(R3.B-48)}$$

$$q'_{ABC\#} = q_E^{\#}q_{vI}q_{v\#}q_R^{\#}q_T'^{\#} \qquad \text{(R3.B-49)}$$

Note that 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.[12]

$$q_{vI} = \frac{1}{1-e^{-\frac{hv_I}{k_BT}}} = \frac{1}{1-\left(1-\frac{hv_I}{kT}\right)} = \frac{k_BT}{hv_I} \qquad \text{(R3.B-50)}$$

$$q'^{\#}_{ABC} = q'_{ABC\#}\frac{kT}{h\ v_I} \qquad \text{(R3.B-51)}$$

Substituting for $q^{\#}_{ABC}$ in Equation (R3.B-45) and canceling v_I

This is the result we have been looking for!

$$\boxed{-r_{ABC} = -r_A = \left[\left(\frac{k_BT}{h}\right)e^{-\frac{E_0}{RT}}\frac{q'_{ABC\#}N_{avo}}{q'_Aq'_{BC}}\right]C_AC_{BC}} \qquad \text{(R3.B-52)}$$

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

Nomenclature Notes:

q = molecular partition function = $q_Eq_Tq_Vq_R$

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 v_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?

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[12] K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987), p. 96.

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[13]

$$\left[\frac{-h^2}{2\pi^2 m}\nabla^2+V(x,y,z)\right]\psi=E\psi(x,y,z) \qquad \text{(R3.B-53)}$$

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). "h" is Planck's constant. The one-dimensional form is

$$\frac{d^2\psi}{dx^2}=\frac{2m}{\hbar^2}\left[E-V(x)\right]\psi=0 \qquad \text{(R3.B-54)}$$

$$\hbar=h/2\pi=1.05\times10^{-34}\,\text{J}\bullet\text{s}$$

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.[14]

Molecular Partition Function

We shall use this equation to obtain the translational, vibrational, and rotational energies, (ε_T, ε_V, and ε_R) used in the partition function q. The equation is solved for three special cases

1. Translational energy, ε_T. Particle in a Box.
2. Vibrational energy, ε_V. Harmonic Oscillator.
3. Rotational Energy, ε_R. Rigid Rotator.
4. Electronic Energy, ε_E.

Recall $\boxed{q' = q_E q_V q_R q_T}$

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

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[13] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 370.

[14] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 373.

Table R3.B-2 Overview of Q

Parameter Values

$$1\ \text{atomic mass unit} \equiv 1\ \text{amu} = 1.67 \times 10^{-27}\ \text{kg},\ h = 6.626 \times 10^{-34}\ \text{kg}\bullet\text{m}^2/\text{s},$$

$$k_B = 1.38 \times 10^{-23}\ \text{kg}\bullet\text{m}/\text{s}^2/\text{K}/\text{molecule}$$

1. Transitional Partition Function q_T Derive

$$q_T = \frac{(2\pi m k_B T)^{3/2}}{h^3} = \frac{1}{\Lambda^3} = \text{the order of } 10^{30}\ \text{m}^{-3} \qquad \text{(R3.B-55)}$$

$$\Lambda = \text{Thermal wavelength} = \frac{h}{(2\pi m k_B T)^{1/2}} \qquad \text{(Derive)}$$

$$q_T = \left(\frac{2\pi k_B}{h^2}\right)^{3/2} (m)^{3/2} \left(\frac{1\ \text{amu}}{1\ \text{amu}}\right)^{3/2} T^{3/2} \times \frac{300}{300}$$

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

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

$$\boxed{q_T = \left(\frac{9.84 \times 10^{29}}{m^2}\right)\left(\frac{m_{AB}}{1\ \text{amu}}\right)^{3/2} \left(\frac{T}{300}\right)^{3/2}} \qquad \text{(R3.B-56)}$$

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

2. Vibrational Partition Function q_v Derive

$$q_v = \frac{1}{1 - e^{-h\nu/k_B T}} \qquad \text{(R3.B-57)}$$

Expanding in a Taylor series

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

$$\boxed{\frac{h\nu}{k_B T} = \frac{hc\tilde{\nu}}{k_B T} = 4.8 \times 10^{-3} \left(\frac{\tilde{\nu}}{1\ \text{cm}^{-1}}\right)\left(\frac{300}{T}\right)} \qquad \text{(R3.B-58)}$$

3. Electronic Partition Function

$$q_E = q_E \quad (q_E = 1) \qquad \text{(Derive)}$$

4. Rotational Partition Function q_R Derive

For linear molecules,

$$q_R = \frac{8\pi^2 I k_B T}{S_y h^2} = \frac{k_B T}{S_y hcB} \qquad \text{(R3.B-59)}$$

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

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

For nonlinear molecules,

$$q_R \frac{1}{S_y} = \left(\frac{k_B T}{hc}\right)^{3/2} \left(\frac{\pi}{ABC}\right) = \text{the order of 10 to 1,000} \qquad \text{(Derive)}$$

where ABC are the rotational constants for a nonlinear molecule about the three axes at right angles to one another

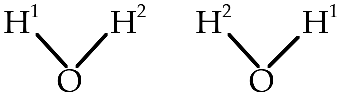
$$I = \sum \mu_i r_i^2$$

For a linear molecule,

$$\boxed{q_R = 12.4\left(\frac{T}{300}\right)\left(\frac{I_{AB}}{1\ \text{amu} \bullet \text{Å}^2}\right)\left(\frac{1}{S_y}\right)} \qquad \text{(R3.B-60)}$$

S_y = symmetry number of different but equivalent arrangements that can be made by rotating the molecule.[15]

For the water and hydrogen molecule, $S_y = 2$,



, $H^1 - H^2$, $H^2 - H_1$

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.

$$-r_A = \underbrace{\frac{k_B T}{h} N_{Avo} \frac{q'_{ABC^\#}}{q'_A q'_{BC}}}_{A\ \left(m^3/\text{mol}\bullet\text{s}\right)} \ e^{-\Delta E/RT} C_A C_B$$

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

Let's first calculate the quantity

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[15] K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987), p. 99.

$$\left(\frac{k_BT}{h}\right)\approx 10^{13}$$

at 300°K

$$\frac{k_BT}{h}=\frac{1.38\times10^{-23}\ \text{J/K}\cdot\text{molecule}\cdot 300\ \text{K}}{6.62\times10^{-34}\ \text{J}\cdot\text{s}}=6.25\times10^{12}\ \text{s}^{-1}\big/\text{molecule}$$

$$\frac{k_BT}{h}\approx 10^{13}\ \text{s}^{-1}\big/\text{molecule}$$

$$\boxed{\begin{gathered}-r_A=kC_AC_{BC}\\ k=\left[\left(\frac{k_BT}{h}\right)e^{-\frac{E_o}{RT}}\left(\frac{q'_{ABC^\#}}{q'_Aq'_{BC}}\right)N_{avo}\right]\end{gathered}}\qquad\text{(R3.B-61)}$$

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

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

$$N_{Avo}=6.02\times10^{23}\ \frac{\text{molecules}}{\text{mole}}$$

At 300 K

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

$$q'_T\approx10^{32}\ \text{m}^{-3}$$

$$q_v\approx6$$

$$q_R\approx100$$

$$A=\frac{k_BT}{h}N_{Avo}\frac{q'_{ABC^\#}}{q'_Aq'_{BC}}$$

$$-r_A=Ae^{-E/RT}C_AC_B$$

	A	BC	ABC
q'_T	$6\times10^{32}\ \text{m}^{-3}$	6×10^{32}	6×10^{32}
q_v		5	5
q_R		20	200
q'	$6\times10^{32}\ \text{m}^{-3}$	$600\times10^{32}\ \text{m}^{-3}$	$6000\times10^{32}\ \text{m}^{-3}$

$$\frac{q'_{ABC^{\#}}}{q'_A q'_{BC}} = \frac{6000 \times 10^{32}}{6 \times 10^{32} \times 600 \times 10^{32}} = 1.7 \times 10^{-32}\ m^{-3}$$

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

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

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

which compares with A predicted by collision theory.

Derivation of the equation for q'_T, q_V, q_E, and q_R

CLICK BACKS

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1. Translational Partition Function, q_T

(Click Back 1)

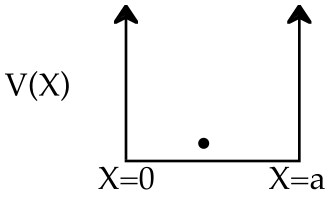
HOT BUTTON

To show

$$q'_T = \left(\frac{2\pi k_B T m}{h^2}\right)^{3/2}\left(m^{-3}\right) \qquad \text{(T1)}$$

Translational Energy

We solve the Schrödinger equation for the energy of a molecule trapped in an infinite potential well. This situation is called "a particle in a box." For a particle in a box of length a,



The potential energy is zero everywhere except at the walls where it is infinite so that the particle cannot escape the box. Inside the box

$$-\frac{\hbar}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad \text{(T2)}$$

The box is a square well potential where the potential is zero between x = 0 and x = a but infinite at x = 0 and x = a.[16] The solution to the Equation (T2) is

$$\psi = A\ \sin(kx) + B\ \cos(kx) \qquad \text{(T3)}$$

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[16] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 392.

where $$E = \frac{k^2\hbar^2}{2m} \qquad \text{(T4)}$$

$$\left(\text{from } k = \sqrt{\frac{2mE}{\hbar^2}}\right)$$

We now use the boundary conditions

At $x = 0$: $\psi = 0$, $\sin 0 = 0$, and $\cos 0 = 1$

$\therefore$ $B = 0$

The wave equation is now

$\psi = A \sin kx$

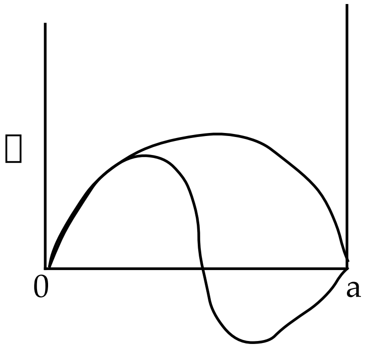
At $x = a$, $\psi = 0$,

ψ will be zero provided

$\therefore$ $ka = n\pi$

where n is an integer, 1, 2, 3

$$k = \frac{n\pi}{a} \qquad \text{(T5)}$$



Substituting (T5) into (T4), we see that only certain energy states are allowed

$$\boxed{E_n = \frac{n^2h^2}{8ma^2}} \qquad \text{(T6)}$$

For particle in a three-dimensional box of sides a, b, and c

$$E_n = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

<u>Back to one dimension</u>

$$E_n = \frac{n^2h^2}{8m\ a^2}$$

Therefore relative to the lowest energy level $n = 1$, the energy is

$$\varepsilon_n = \left(E_n - E_1\right) = \left(n^2 - 1\right)\varepsilon, \text{ where } \varepsilon = \frac{h^2}{8ma^2} \qquad \text{(T7)}$$

Then

$$q_{Tx} = \sum_{n=1} e^{-\left(n^2-1\right)\varepsilon\beta} \qquad \text{(T8)}$$

$$q_{Tx} = \left(\frac{2\pi kTm}{h^2}\right)a \qquad \text{(T9)}$$

Derive

(Click Back within a Click Back) – Hot Button within a Hot Button

We will assume that the energy states are sufficiently close together, such that there is a continuous distribution of energies. Replace Σ by $\int$

$$q_{Tx} = \int_1^\infty e^{-(n^2-1)\alpha}\,dn \approx \int_0^\infty e^{-n^2\alpha}\,dn$$

Let: $x^2 = n^2\alpha$, $dn = dx/(\alpha)^{1/2}$

$$q_{Tx} = \left(\frac{1}{\alpha}\right)^{1/2}\int_0^\infty e^{-x^2}dx = \left(\frac{1}{\alpha}\right)^{1/2}\frac{\pi^{1/2}}{2}$$

$$= \left(\frac{2\pi m}{h^2\beta}\right)^{1/2} a = \left(\frac{2\pi kTm}{h^2}\right)^{1/2} a \qquad \text{(T10)}$$

For Three Dimensions

The translation partition function for y and z directions are similar to that for q_{Tx}

This is the result we have been looking for!

$$\boxed{\begin{aligned} q_{Txyz} = q_{Tx}q_{Ty}q_{Tz} &= \left[\left(\frac{2\pi kTm}{h^2}\right)^{1/2}\right]^3 \underbrace{abc}_{V} \\ &= q_T' V \\ q_T' &= \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \end{aligned}} \qquad \text{(T11)}$$

We define Λ as thermal wave length

$$\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2} \text{(m)} \qquad \text{(T12)}$$

$$q_T' = \frac{1}{\Lambda^3}$$

Order of Magnitude and Representative Values

For O_2 @25°C $q_T' = 2\times10^{28}\ m^{-3}$

at 25°C for H_2 : Λ = 71 pm, for O_2 : Λ = 18 pm (pm = picometer)

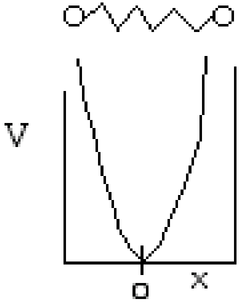
2. Vibration Partition Function q_v (Click Back 2)

To show

$$\boxed{q_v = \frac{1}{1-e^{-\beta h\nu}}} \qquad \text{Derive} \quad \text{(A12)}$$

(Click Back)

Again we solve the wave equation for two molecules undergoing oscillation about an equilibrium position x = 0. The potential energy is shown here as a function of the displacement from the equilibrium position x = 0[17]



The uncertainty principle says that we cannot know exactly where the particle is located. Therefore, zero frequency of vibration in the ground state (i.e., $v = 0$ is not an option.[18] When v_0 is the frequency of vibration, the ground state energy is

$$E_0 = \frac{1}{2}hv \qquad \text{(V1)}$$

<u>Harmonic oscillator</u>[19]

Spring Force $F = -kx$, potential energy from equilibrium position x = 0

$$m\frac{dx^2}{dt^2} = kx$$

the solution is of the form for $t = 0$ then $x = 0$

$$x = A \sin \omega t$$

where

$$\omega = \sqrt{\frac{k}{m}}$$

$$\underbrace{\omega = \left(\frac{\text{Spring contant}}{\text{Mass}}\right) = (k/m)^{1/2}}_{\text{Classical vibration}}, \quad \omega = 2\pi v$$

The potential energy is

$$V = \frac{1}{2}kx^2 \qquad \text{(V2)}$$

We now want to show

$$E_v = \left(v + \frac{1}{2}\right)hv \qquad \text{(V3)}$$

and solve the wave equation

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[17] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 402.
[18] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), pp. 22, 402.
[19] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 402.

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right)\psi = E\psi \tag{V4}$$

to find the allowable energies, ε.

Let $y=\frac{x}{\alpha}$, $\varepsilon=\frac{E}{\frac{1}{2}\hbar\omega}$, where $\alpha=\left(\frac{\hbar^2}{mk}\right)^{1/4}$, $\omega=\frac{k}{m}$, and $w=2\pi v$.

With these changes of variables Equation (A15) becomes

$$\frac{d^2\psi}{dy^2}+\left(\varepsilon-y^2\right)\psi=0 \tag{V5}$$

The solutions to this equation[20] will go to infinity unless

$$\varepsilon = 2v+1$$

$$v = 0, 1, 2, 3, \ldots$$

$$E_v=\left(v+\frac{1}{2}\right)h\nu, \quad \nu=\frac{\omega}{2\pi}=\frac{c}{\lambda} \qquad [c = \text{speed of light}]^{21}$$

$$\text{Wave number}=\tilde{v}=\frac{\nu}{c}=\frac{1}{\lambda} \qquad \left[\tilde{v}=\frac{s^{-1}}{cm/s}=\frac{1}{cm}\right]$$

λ = wave length

$$E_v=\left(v+\frac{1}{2}\right)h\nu=\left(v+\frac{1}{2}\right)hc\tilde{v} \tag{V6}$$

Measuring energy <u>relative</u> to the zero point vibration frequency (i.e., $v = 0$) gives

$$Ev=h\nu\left(v+\frac{1}{2}\right)-\frac{1}{2}h\nu$$

$$E_v=\frac{h\nu v}{kT}$$

Substituting for E_v in the partition function summation $\sum e^{-\beta E_v}$ yields

$$q_v=\sum_{v=0}^{\infty}e^{-\beta h\nu v}=\sum_{v=0}^{\infty}\left(e^{-\beta h\nu}\right)^v$$

$$\sum_{i=0}^{\infty}X^i=\frac{1}{1-X}$$

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[20] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 22, Appendix 8.

This is the result we have been looking for!

$$\boxed{q_v = \frac{1}{1 - e^{-\beta h\nu}}} \qquad (V7)$$

For $\beta hc\tilde{\nu} << 1$, then $\left[\left(1 - e^{-X}\right) = 1 - \left(1 - X\right)\right] = X$. We can make the approximation

$$\boxed{q_v = \frac{kT}{h\nu} = \frac{kT}{hc\tilde{\nu}}} \qquad (V8)$$

For m multiple frequencies of vibration

$$q_v = q_{v1} q_{v2} \cdots q_{vm}$$

Order of Magnitude and Representative Values

For H_2O we have three vibrational frequencies with corresponding wave numbers, $\tilde{\nu}_i$, $\tilde{\nu}_2$ and $\tilde{\nu}_3$.

$$\tilde{\nu}_1 = 3656 \text{ cm}^{-1} \rightarrow q_{v1} = 1.03$$

$$\tilde{\nu}_2 = 1594.8 \text{ cm}^{-1} \rightarrow q_{v2} = 1.27$$

and

$$\tilde{\nu}_3 = 3755.8 \text{ cm}^{-1} \rightarrow q_{v3} = 1.028$$

$$q_v = (1.03)(1.27)(1.028) = 1.353$$

3. **Electronic Partition Function**[22] (Click Back 3)

From the ground state, electronic energy separation is very large.

$$q_E \cong g_E$$

where g_E is the degeneracy of the ground state.

For most cases, $q_E \cong 1$ (E1)

4. **Rotational Partition Function** (Click Back 4)

$$q_R = \frac{k_B T}{\sigma hcB}$$

Rigid Rotation[23]

To show

$$q_R = \frac{k_B T}{\sigma hcB} \qquad (R1)$$

where

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[21] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 541.

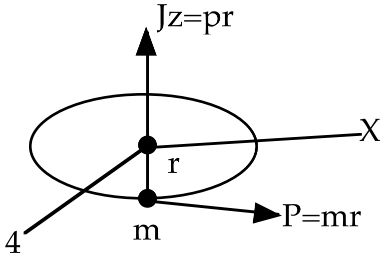
[22] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 701.

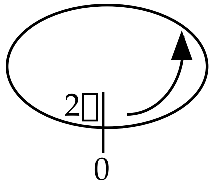
[23] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), pp. 409, 413, 557, A24.

$$B = \frac{h}{8\pi^2 cI} = \text{Rotational constant} \qquad (R2)$$

Consider a particle of mass m rotating about the z-axis a distance r from the origin.

$$\lambda = \frac{2\pi r}{m_\ell} \qquad (R3)$$





This time we convert the wave equation to spherical coordinate to obtain[24]

$$\frac{d^2\Phi}{d\phi^2} = -\frac{2IE}{\hbar^2} \qquad (R4)$$

Classical energy of a rigid rotator is

$$E = \frac{1}{2}\omega^2 I \qquad (R5)$$

where w is the angular velocity (rod/s) and I is the
moment of inertia[25]

$$I = \sum m_i r_i^2 \qquad (R6)$$

where m_i is the mass located and distance r_i from the center of mass.
Quantum mechanics solutions to the wave equation gives two quantum numbers, ℓ and m.

$$\text{Magnitude of angular momentum} = \left[\ell(\ell+1)\right]^{1/2}\hbar$$

$$z\text{-component of angular momentum} = mh$$

$$\boxed{E = \ell(\ell+1)\frac{\hbar^2}{2I}} \qquad (R7)^{26}$$

$$m = 0,\ \pm\ell \ \text{ with } \begin{cases} +\ell & \text{clockwise rotation} \\ -\ell & \text{counter clockwise rotation} \end{cases}$$

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[24] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 410.

[25] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 555.

[26] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), pp. 408, 413.

Let J ≡ ℓ

For a linear rigid rotator

$$E = \frac{J(J+1)\hbar^2}{2I} = hcB\,J\,(J+1) \qquad \text{(R8)}$$

Where B is the rotation constant:

$$B = \frac{\hbar}{4\pi Ic} = \frac{h}{8\pi^2 cI} \qquad \text{(R2)}^{27}$$

with

c = Speed of light

I = Moment of inertia about the center of mass $= \sum m_i r_i^2$

The rotational partition function is

$$q_R = \sum_{J=0}^{\infty} (2J+1)\, e^{-hcB(J)(J+1)\beta} \qquad \text{(R9)}^{28}$$

Replacing the $\sum_{J=0}$ by an integral from 0 to ∞ and integrating, we obtain the rotational partition function q_R for a <u>linear</u> molecule[29]

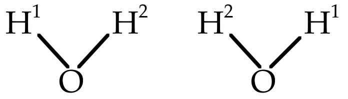
This is the result we have been looking for!

$$\boxed{q_R = \frac{k_B T}{S_y hcB} = \frac{8\pi^2 I k_B T}{S_y h^2}} \qquad \text{(R10)}$$

where S_y is the symmetry number, which is the number of different but equivalent arrangements that can be made by rotating the molecules.

For HCl $\quad S_y = 1$

For H_2O $\quad S_y = 2$



For a nonlinear molecule,

$$\boxed{q_R = \left(\frac{1}{S_y}\right)\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}}$$

where $\quad A = \frac{h}{8\pi^2 cI_A}, \quad B = \frac{h}{8\pi^2 cI_B}, \quad C = \frac{h}{8\pi^2 cI_C}$

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[27] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 557.

[28] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), pp. 414, 563, 671.

[29] P. W. Atkins, *Physical Chemistry*, 5th ed. (New York: Freeman, 1994), p. 694.

S_y = symmetry number.[30] For a hetronuclear molecule, $\sigma = 1$ and for a homonuclear diatomic molecule or a symmetrical linear molecule (e.g., H_2), then $\sigma = 2$.

Order of Magnitude and Representative Values

For HCl @ 25°C,[31] $B = 10.591\ \text{cm}^{-1}$ then $q_R = 19.9$ and at 0°C $q_R = 18.26$.

For ethylene at 25°C, then $q_R = 661$.

III. THE EYRING EQUATION

For the reaction

$$A + BC \rightarrow AB + C$$

The rate law is

$$-r_A = kC_AC_{BC} \tag{R3.B-62}$$

$$k = Ae^{-E_A/RT} \tag{R3.B-63}$$

$$\ln k = A\ln - E_A/RT \tag{R3.B-64}$$

$$\frac{d\ln k}{dT} = \frac{E_A}{RT^2} \tag{R3.B-65}$$

Now let's compare this with transition state theory.

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

$$A + BC \rightleftarrows ABC^{\#} \rightarrow AB + C$$

$$-r_A = v_I C_{ABC^{\#}} \tag{R3.B-1}$$

$$K_C^{\#} = \frac{\left(ABC^{\#}\right)}{(A)(B)} \equiv \frac{C_{ABC^{\#}}}{C_AC_{BC}} \tag{R3.B-2}$$

$$-r_A = v_I K_C^{\#} C_A C_{BC} \tag{R3.B-3}$$

Factoring out partition function for the loose vibration frequency, v_I, from the vibrational partition function, $q_v^{\#}$, gives

$$q_v^{\#} = \frac{k_BT}{hv_I}q_{v\#} \tag{R3.B-66}$$

Then from Equation (R3.B-43), we can obtain

$$K_C^{\#} = K_{C\#}\frac{k_BT}{hv_I} \tag{R3.B-67}$$

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[30] For discussion of σ, see K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987), p. 99.

[31] P. W. Atkins, *Physical Chemistry*, 6th ed. (New York: Freeman, 1998), p. 695.

$$\boxed{-r_A = \left(\frac{k_B T}{h}\right) K_{C\#} C_A C_B} \qquad \text{(R3.B-68)}$$

which is referred to as the Eyring equation.

From thermodynamics

$$\Delta G = \Delta H - T\Delta S \qquad \text{(R3.B-69)}$$

$$K^{\#} = e^{-\Delta G^{\#}/RT} = e^{\Delta S^{\#}/R} e^{-\Delta H^{\#}_{Rx}/RT} \qquad \text{(R3.B-70)}$$

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

$$K^{\#} = K_{\gamma} K_C^{\#} V_m^{-1} = K_{\gamma} K_C^{\#} C_T \qquad \text{(R3.B-71)}$$

$$K_C^{\#} = \frac{K^{\#}}{K_{\gamma} C_T} \qquad \text{(R3.B-72)}$$

$$K_{C^{\#}} = \frac{K}{K_{\gamma} C_T} = \frac{e^{-\Delta G^{\#}/RT}}{K_{\gamma} C_T} = \frac{e^{\Delta S^{\#}/R} \quad e^{-\Delta H/RT}}{K_{\gamma} C_T} \qquad \text{(R3.B-73)}$$

$\Delta S^{\#}$ 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,

$$\frac{\text{Number of configurations leading to reaction}}{\text{Total number of configurations}} = e^{\Delta S^{\#}/R}$$

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

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

Case I Liquid

For liquid $C_T \cong$ a constant $\cong C_{T0}$. Recall for water that $C_w \cong 55.5$ mol/dm^3

$$\boxed{k = \left(\frac{k_B T}{h}\right) \bullet \frac{e^{\Delta S^{\#}/R} \quad e^{-\Delta H/RT}}{K_{\gamma} C_{T0}}} \qquad \text{(R3.B-74)}$$

$$\Delta S^{\#} = \left(S_{ABC^{\#}} - S_A - S_{BC}\right) \qquad \text{(R3.B-75)}$$

Here we see the temperature dependence as

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

Case II Gases

For gases

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

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

Here we see the temperature dependence as

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

As with liquids, $\Delta S^{\#}$ is negative, and $\Delta H^{\#}_{Rx}$ is positive.

Relating E_A and ΔH_{Rx}

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 R3.B-2.

$$k=\left(\frac{k_B}{h}\right)\left(\frac{R}{P}\right)T^2 e^{\Delta S^{\#}/R} e^{-\Delta H^{\#}_{Rx}/RT} \tag{R3.B-76}$$

$$\ln k=\ln\left(\frac{k_B R}{hP}\right)+\ln T^2+\frac{\Delta S^{\#}}{R}-\frac{\Delta H^{\#}_{Rx}}{RT} \tag{R3.B-77}$$

$$\frac{d(\ln k)}{dT}=\frac{2}{T}+\frac{\Delta H^{\#}_{Rx}}{RT^2}=\frac{E_A}{RT^2} \tag{R3.B-78}$$

Comparing Equations (R3.B-1) and (R3.B-16), the activation energy the Erying equation is

$$\boxed{E_A=2RT+\Delta H^{\#}_{Rx}} \tag{R3.B-79}$$

with the frequency factor

$$A=\left(\frac{k_B}{h}\right)\left(\frac{R}{P}\right)e^{\Delta S^{\#}/R} \tag{R3.B-80}$$

Some Generalizations May Be Eliminated

Table R3.B-3 Equations for Reaction Rate Constant Using Partition Functions

For reactants where there are N atoms[32]

Atoms

$$q = q_T^3$$

Linear polyatomic molecules

$$q = q_T^3 q_R^2 q_v^{3N-5}$$

Nonlinear polyatomic molecules

$$q = q_T^3 q_R^3 q_v^{3N-6}$$

Let $q_T \cong 10^{-8}\ \text{cm}^{-1}$ for each degree of transitional freedom, $q_R = 10$, $q_v = 1$ and $(kT/h) \cong 10^{13}\ \text{s}^{-1}$ with $N_A = 6.02 \times 10^{23}$ molecules/mol.

Case 1 Atom + Atom $\rightleftharpoons$ Diatomic Activated Complex

$$k = \overbrace{N_{avo}\left(\frac{kT}{h}\right)\frac{q_T^3 q_R^2}{q_T^3 q_T^3}}^{A_{calc}} e^{-E_0^{+}/RT}$$

Assuming all translational partition functions are approximately the same

$$k_R = \underbrace{N_A\left(\frac{kT}{h}\right)\left(\frac{q_R^2}{q_T^3}\right)}_{A_{calc}=6\times 10^{14}\ \text{cm}^3/\text{mol}/\text{s}} e^{-E_0^{+}/RT}$$

Case 2 Atom + Linear Molecule $\rightleftharpoons$ Linear Complex

$$k = N_A\left(\frac{kT}{h}\right)\frac{q_T^3 q_R^2 q_v^{3(N+1)-6}}{q_T^3\left(q_T^3 q_R^2 q_v^{3N-5}\right)} e^{-E_0/RT}$$

$$k = \underbrace{N_A\left(\frac{kT}{h}\right)\left(\frac{q_R^2}{q_T^3}\right)}_{A_{calc}=6\times 10^{12}\ \text{m}^3/\text{mol}\cdot\text{s}} e^{-E_0^{+}/RT}$$

Case 3 Atom + Nonlinear Molecule

Same results as for a linear molecule

Case 4 Linear Molecule + Linear Molecule $\rightleftharpoons$ Linear Complex

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[32] K. J. Laidler, *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987), p. 108.

$$k = \underbrace{N_A \left(\frac{kT}{h}\right) \frac{q_v^4}{q_R^2 q_T^3}}_{A_{calc} = 6\times10^{10}\ cm^3/mol\cdot s} e^{-E_0/RT}$$

Case 5 Linear Molecule + Nonlinear Molecule $\rightleftarrows$ Nonlinear Complex

$$k = \underbrace{N_A \left(\frac{kT}{h}\right) \frac{q_v^5}{q_R^3 q_T^3}}_{A_{calc} = 6\times10^{9}\ cm^3/mol\cdot s} e^{-E_0^{+}/RT}$$

For the general reaction

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

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

$$= \ln b_1^{a_1} \ b_2^{a_2} \ b_N^{a_N} = \ln \prod_{i=1}^{N} b_i^{a_i}$$

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

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

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

$$\sum v_i \tilde{G}_o = \sum \tilde{U}_0 v_i - nRT \ln \prod \left(\frac{q_{mi}}{N_A}\right)^{v_i}$$

$\div$ by n $\quad \tilde{G}/n = G \quad \tilde{U}/n = U_0$

$$\Delta G = -RT \ln K = \sum U_{io} v_i - RT \prod \left(\frac{q_{mi}}{N_{Avo}}\right)^{v_i}$$

$$A + BC \rightleftharpoons ABC$$

$$K_C = \frac{C_{ABC}}{C_A C_{BC}} \bullet e^{-\Delta E_0/RT} = \frac{q'_{ABC}}{q'_A q'_{BC}} N_{Avo}^{-\Delta n}$$

$$\Delta n = 1 - 1 - 1 = -1$$

$$K_C = \frac{q'_{ABC} N_{Avo}}{q'_A q'_{BC}} e^{-\Delta E_0/RT} = \frac{C_{ABC}}{C_A C_{BC}} \left[\left(\frac{mol}{dm^3}\right) \Big/ \left(\frac{mol}{dm^3}\right)^2\right]$$

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

$$C_{ABC} = C_A C_{BC} \ e^{-\Delta E_0/RT} \ \frac{q'_{ABC} N_{Avo}}{q'_A q'_{BC}}$$

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

$$r_A = vC_{ABC}\frac{kT}{h}\, e^{-\Delta E_0/RT}\,\frac{q'_{ABC}N_{Avo}}{q'_A q'_{BC}} \Big/ OK$$

Molar partition function

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

$$q_m = \frac{q}{h} = q'\frac{V}{n} = \left(\frac{q_m}{dm^3}\right)\left(\frac{dm^3}{mol}\right) = q_m(1/mol)$$

$$\Delta\nu = c + d - b - a$$

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

$$K = K_\gamma K_P\left(f^\circ\right)^{-\Delta\nu}, \qquad P_A = C_A RT$$

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

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

$$\Delta E_0 = \sum v_i U_{io}$$

$$-RT\ln K = \Delta E_0 - RT\ln\prod\frac{q_{mi}^{v_i}}{N_{Avo}}$$

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

$$K = e^{-\Delta E_0/RT}\prod\left(\frac{q_{mi}}{N_{Avo}}\right)^{v_i}$$

$$K_\gamma K_C\left(\frac{RT}{f^\circ}\right)^{\Delta\nu} = e^{-\Delta E_0/RT}\,\frac{q_C^c q_D^d}{q_A^a q_B^b}\,N_{avg}^{-\Delta\nu}, \qquad q'V = q$$

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

$$K = K_\gamma\left(\frac{RT}{f^\circ}\right)^{\Delta\nu}K_C = e^{-\Delta E_0/RT}\,\frac{q'^c_C q'^d_D}{q'^a_A q'^b_B}\left(\frac{V}{n}\right)^{c+d-a-d}N_{Avo}^{-\Delta\nu}$$

However,

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

$$K_C = e^{\square\square E_0/RT} \frac{q_C^{\square c} q_D^{\square d}}{q_A^{\square a} q_B^{\square b}} N_{Avo}^{\square\square}$$