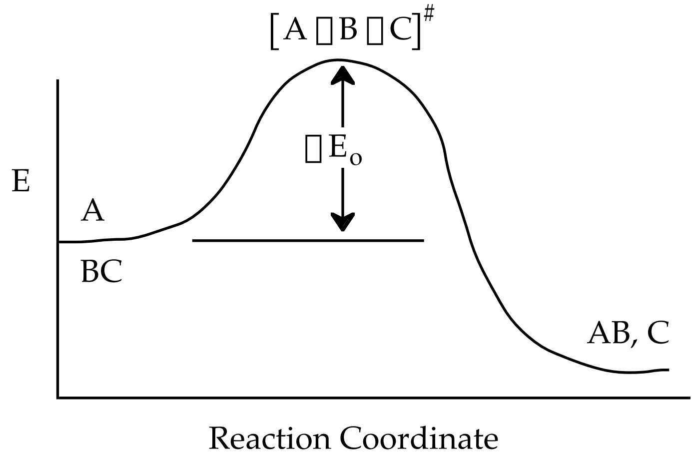
Transition Theory

Abbreviated Derivation

$$A + BC \longrightarrow AB + C$$



$$A + BC \rightleftarrows [A \cdots B \cdots C]^{\#} \longrightarrow A - B + C$$

The rate of reaction is the frequency of the complex crossing the barrier

$$-r_A = r_{AB} = \nu_I C_{ABC}^{\#} \tag{1}$$

where the frequency ν_I can be thought of as a loose vibration. We are going to assume that the activated complex is in virtual equilibrium with the reactants

$$K_C^{\#} = \frac{C_{ABC}^{\#}}{C_A C_{BC}} \tag{2}$$

Then

$$\boxed{-r_A = \nu_I K_C^{\#} C_A C_{BC}} \tag{3}$$

From thermodynamics we know

$$\Delta G = -RT \ln K \tag{4}$$

Then

$$K = e^{-\Delta G/RT} \tag{5}$$

where K is the dimensionless true equilibrium constant and related to the concentration equilibrium constant K_C by

$$K = K_{\gamma} K_C V_m^{\delta} = K_C V_m^{\delta} = e^{-\Delta G/RT} \tag{6}$$

Then for the equilibrium between the reactants and the transition state

$$K_C^{\#} = V_m^{-\delta} e^{-\Delta G^{\#}/RT}$$

Part I Relate $K_C^{\#}$ to Partition Functions

We are now going use statistical mechanics to derive the equation for $K_C^{\#}$. We start by recalling that the number of ways, W, of arranging N particles among m energy states is

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

where n_i is the number of particles in the ith state.

For **a fixed total number of molecules $N = \sum n_i$** and **a fixed total energy $E = \sum n_i \varepsilon_i$** the most probable distribution, the one that overwhelms all the others, is found by setting dW = 0. The result is

$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q} \qquad (7)$$

where

$$q = \sum e^{-\beta\varepsilon_i}, \quad \beta = \frac{1}{k_B T} \qquad (8)$$

$$\frac{n_i}{N} = \text{fraction of molecules that occupy energy state } \varepsilon_i \qquad (9)$$

q = molecular partition function

The molecular partition function, q, gives a measure of how the molecules are distributed (partitioned) among the energy states. It gives an indication of the average number of states that are accessible at a particular temperature for non interacting molecules.

Fundamental postulate relating $\tilde{S}$ and W

$$\tilde{S} = k \ln W = k\left[\ln N! - \sum \ln n_i!\right] \qquad (10)$$

Sterling's approximation

$$\ln X! = X \ln X - X \qquad (11)$$

Using Sterling's approximation, Equation (10) becomes

$$\boxed{\tilde{S} = -k \sum \ln \frac{n_i}{N}} \qquad (12)$$

Substituting for $\left(\frac{n_i}{N}\right)$ using Equation (8)

$$\tilde{S} = k\beta\overbrace{\sum n_i\varepsilon_i}^{U-U_o} + k\overbrace{\sum n_i}^{N}\ln q$$

The sum $\sum n_i\varepsilon_i$ is the internal energy relative to the ground state, i.e. $(U - U_o)$

$$\boxed{\tilde{S} = \frac{U - U_o}{T} + kN\ln q} \tag{13}$$

This result is for non interacting particles. For interacting particles, the result is

$$\boxed{\tilde{S} = \frac{U - U_o}{T} + k\ln\frac{q^N}{N!}} \tag{14}$$

From thermodynamic we know the relationship between

$$\tilde{G} = \tilde{U} - T\tilde{S} + PV = U - T\tilde{S} + nRT \tag{15}$$

Combining Equations (14) and (15)

$$\boxed{\tilde{G} = \tilde{U}_o - nRT\ln\frac{q}{N}} \tag{16}$$

We now define molar partition function, q_m

$$\frac{q}{N} = \frac{q}{n\cdot N_{Avo}} = \frac{q_m}{N_{Avo}}$$

$$q_m = \frac{q}{n} \tag{17}$$

Dividing Equation (16) by the number of moles n

$$\boxed{G = U_o - RT\ln\frac{q_m}{N_{Avo}}} \tag{18}$$

when

$$G = \frac{\tilde{G}}{n}\ ,\quad U_o = \frac{\tilde{U}}{n}$$

Typical units of G and U are (J/mol).

We now will apply Equation (18) to each species in the reaction

$$aA + bB \rightleftharpoons cC + dD \tag{19}$$

$$G_i = U_{oi} - RT\ln\frac{q_{mi}}{N_{Avo}} \tag{20}$$

The change in Gibbs free energy for reaction (19) is

$$\Delta G = cG_C + dG_D - bG_B - aG_A \tag{21}$$

Using Equation (18) we obtain

$$\Delta G = \Delta E_0 - RT\ln\left(\frac{q_{mC}^{c}\,q_{mD}^{d}}{q_{mA}^{a}\,q_{mB}^{b}}\right)N_{Avo}^{-\nu} \qquad (22)$$

where

$$\Delta E_0 = cU_C + dU_{Do} - bU_{Bo} - aU_{Ao} \qquad (23)$$

and

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

using Equation (22)

$$K = e^{-\Delta E_0/RT}\left(\frac{q_{mC}^{c}\,q_{mD}^{d}}{q_{mB}^{b}\,q_{mA}^{a}}\right)N_{Avo}^{-\nu} \qquad (24)$$

The molar partition function is

$$q_{mi} = q_i/n$$

and the partition function per unit volume is

$$q_i' = q_i/V$$

then

$$q_{mi} = q_i'\frac{V}{n} = q_i'V_m \qquad (25)$$

$$K = e^{-\Delta E_0/RT}\left(\frac{(q_C')^{c}(q_D')^{d}}{(q_B')^{b}(q_A')^{a}}\right)V_m^{\nu}N_{Avo}^{-\nu} \qquad (26)$$

Recalling Equation (6) and equating it to Equation (26)

$$K_C K_\gamma V_m^{\nu} = K = e^{-\Delta E_0/RT}\left(\frac{(q_C')^{c}(q_D')^{d}}{(q_B')^{b}(q_A')^{a}}\right)V_m^{\nu}N_{Avo}^{-\nu} \qquad (27)$$

For ideal mixtures $K_\gamma = 1$ and canceling the molar volumes we arrive at the main result we have been looking for

$$\boxed{K_C = e^{-\Delta E_0/RT}\left(\frac{(q_C')^{c}(q_D')^{d}}{(q_B')^{b}(q_A')^{a}}\right)N_{Avo}^{-\nu}} \qquad (28)$$

We now apply Equation (28) to our transition state reaction ($\nu = -1$)

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

$$\boxed{K_C^{\#} = e^{-(\Delta E_0/RT)}\,\frac{q_{ABC}'^{\#}}{q_A'\,q_{BC}'}\,N_{Avo}^{-1}} \qquad (29)$$

Part II Partition Function

We now focus on the partition function per unit volume

$$q = \sum e^{-\beta\varepsilon_i} = \sum e^{-\beta(\varepsilon_{el}+\varepsilon_T+\varepsilon_V+\varepsilon_{Rot})_i} = \sum e^{-\beta\varepsilon_{el}} \sum e^{-\beta\varepsilon_T} \sum e^{-\beta\varepsilon_V} \sum e^{-\beta\varepsilon_{Rot}}$$

$$= q_{el} \bullet q_T \bullet q_V \bullet q_R \tag{30}$$

$$q_T = q'_T V \tag{31}$$

Dividing by V

$$\boxed{q' = q_{el} \bullet q'_T \bullet q_V \bullet q_R} \tag{32}$$

The Transitional Partition Function, q_T

The translational partition function is obtained by solving the wave equation for a particle in a box.

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

$$q'_T = \frac{1}{\Lambda^3} = \left[\frac{(2\pi mkT)^{1/2}}{h}\right]^3 \tag{33}$$

Where Λ is the thermal wave length, h is Plank's constant, m = mass of the molecule and k is Boltzmann's constant. Substituting for k and h and simplifying

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

The Vibrational Partition Function, q_V

$$q_V = q_{V1} q_{V2} q_{V3} \cdots \tag{34}$$

For the harmonic oscillator

$$q_{Vi} = \frac{1}{\left[1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right]} \tag{35}$$

For small arguments of $\left(\frac{h\nu_i}{kT}\right)$

$$q_{vi} = \frac{kT}{h\nu_i} \tag{36}$$

Evaluating

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

c = speed of light

The Rotational Partition Function, q_R

For linear molecules we solve the wave equation for the rigid rotator model to find the rotational partition function to be

$$q_R = \frac{kT}{2hcB} \tag{37}$$

where B = Rotational Constant

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

where I = moment of inertia

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

c = speed of light

Evaluating k, h, c, and simplifying

$$\boxed{q_R = 12.4\left(\frac{T}{300\mathrm{K}}\right)\left(\frac{I_{AB}}{1\ \mathrm{amu}\ \ \mathrm{Ang}^2}\right)\left(\frac{1}{S_y}\right)}$$

The overall or total partition function for the activated complex is

$$q_{ABC}^{\#} = q_e^{\#} q_T^{\#} q_V^{\#} q_R^{\#} \tag{38}$$

We now consider the loose imaginary vibration ν_I. The total vibrational partition function is the product of the partition functions for each vibrational mode, i.e.,

$$q_V^{\#} = q_{Vi}^{\#} q_{V1}^{\#} q_{V2}^{\#} = \frac{kT}{h\nu_I} q_{V1}^{\#} q_{V2}^{\#} = \frac{kT}{h\nu_I} q_{V\#} \tag{39}$$

where $q_{V\#}$ is the partition function that includes the loose vibration and $q_{V\#}$ is the vibrational partition function without the loose vibration. Similarly for the total partition function

$$q_{ABC}^{\#} = \frac{kT}{h\nu_I} q_{ABC\#} \tag{40}$$

substituting into Equation (39)

$$K_C^{\#} = \frac{kT}{h\nu_I} e^{-\Delta E_o/RT} \frac{q_{ABC\#}}{q_A q_{BC}} N_{Avo} \tag{41}$$

Substituting Equation (41) into Equation (3) we note that the loose vibration frequency cancels and we obtain

$$\boxed{-r_A = \left(\frac{kT}{h}\right)\underbrace{e^{-\Delta E_o/RT}\frac{q'_{ABC\#}N_{Avo}}{q'_A q'_{BC}}}_{K_{C\#}}C_A C_{BC}} \tag{42}$$

$$\frac{k_B T}{h} = \frac{6.25\times 10^{12}}{\text{molecules}\cdot \text{s}}\left(\frac{T}{300\text{K}}\right)$$

$$N_{Avo} = 6.023\times 10^{23}\,\frac{\text{molecules}}{\text{mol}}$$

$$A = \left(\frac{kT}{h}\right)\left(\frac{q'_{ABC\#}}{q'_A q'_{BC}}\right)N_{Avo} \tag{43}$$

Note: If B and C are the same molecule, B_2, in the reaction

$$A + B_1 - B_2 \to AB + B$$

There will be a factor of 2 $(2kT/h)$ in the rate constant because A can attach either B molecule, B_1 or B_2. It's sometimes easier to make TST calculations by taking ratios

$$\frac{q'_{A-B-C}}{q'_A q'_{BC}} = \left(\frac{q'_{A-B-C}}{q'_A q'_{BC}}\right)_{Tran} \bullet \left(\frac{q_{A-B-C}}{q_A q_{BC}}\right)_{Vib} \bullet \left(\frac{q_{A-B-C}}{q_A q_{BC}}\right)_{Rot}$$

The Eyring Equation

Letting $K_{C\#}$ represent the equilibrium constant with the loose vibration removed we have

$$-r_A = \frac{k_B T}{h}K_{C\#}C_A C_{BC}$$

the true dimensionless equilibrium constant is

$$K = K_{\varphi} K_C V_m^{\Delta n}$$

then

$$K_{C\#} = K_{\#} V_m^{-\Delta n} = K_{\#} V_m = K_{\#}/C_T$$

where C_T is the total concentration

$$\Delta G^{\#} = -RT \ln K_{\#}$$

$$K_{\#} = e^{-\Delta G/RT}$$

$$\Delta G = \Delta H - T\Delta S$$

$$K_{C\#} = K_{C\#} = \frac{\left(e^{-\Delta G^{\#}/RT}\right)}{C_T} = \frac{\left(e^{\Delta S^{\#}/R}\right)\left(e^{-\Delta H^{\#}/RT}\right)}{C_T}$$

$$\boxed{-r_A = \left(\frac{k_B T}{h}\right)\left(\frac{1}{C_T}\right)\left(e^{\Delta S^{\#}/R}\right)\left(e^{-\Delta H^{\#}/RT}\right)C_A C_{BC}} \qquad (44)$$

$\Delta S^{\#} = S^{\#}_{ABC} - S_A - S_B =$ a negative number because we are going from a less ordered state to a more ordered state.

$\Delta H^{\#} = H_{ABC-\#} - H_A - H_{BC} =$ a positive number

$$e^{\Delta S^{\#}/R} = \frac{\text{Configurations Leading to Reactions}}{\text{Total Number of Configurations}} \qquad (45)$$

Definitions

$q =$ overall partition function $= \sum e^{-\beta \varepsilon_i}$, $\beta = \dfrac{1}{kT}$

$q_m = \dfrac{q}{n} =$ molar partition function

$q = q_e \bullet q_{Tr} \bullet q_{Vib} \bullet q_{Rot}$

$q_T = q_T' V$

$q_V = q_{Vi} q_{V1} q_{V2}$

$q^{\#}_V =$ vibrational partition for activated state including loose vibration

$q_{V\#} =$ vibrational partition function with loose vibration removed

$q'_{\#} =$ overall partition function per unit volume with loose vibration removed