

McQuarrie – Chapter 9 – Chemical Equilibrium



$$\nu_C C + \nu_D D - \nu_A A - \nu_B B = 0$$

$$\text{Define } \lambda: \quad dN_j = \nu_j d\lambda, \quad j = A, B, C, D$$

measures extent of
the reaction

$$\nu_j \begin{cases} + \text{ products} \\ - \text{ reactants} \end{cases}$$

$$dA = -SdT - pdV + \sum \mu_j dN_j$$



$$dA = \sum \mu_j dN_j = \sum \mu_j \nu_j d\lambda$$

if vol, T are fixed

equil. $\frac{dA}{d\lambda} = 0 \Rightarrow \sum \mu_j \nu_j = 0$

$$Q(N_A, N_B, N_C, N_D, V, T) = Q(N_A, V, T) Q(N_B, V, T) Q(N_C, V, T) Q(N_D, V, T)$$

$$= \frac{q_A^{N_A} q_B^{N_B} q_C^{N_C} q_D^{N_D}}{N_A! N_B! N_C! N_D!}$$

Assuming ideal
gas behavior

$$\mu_A = -kT \left(\frac{\partial \ln Q}{\partial N_A} \right)_{N_j, V, T} = -kT \ln \frac{q_A}{N_A}$$

chemical potential of each species is
calculated ignoring other species

$$\nu_C \left[-kT \ln \frac{q_C}{N_C} \right] + \nu_D \left[-kT \ln \frac{q_D}{N_D} \right] - \nu_A \left[-kT \ln \frac{q_A}{N_A} \right] - \nu_B \left[-kT \ln \frac{q_B}{N_B} \right] = 0$$

$$\ln \left(\frac{q_C}{N_C} \right)^{\nu_C} + \ln \left(\frac{q_D}{N_D} \right)^{\nu_D} - \ln \left(\frac{q_A}{N_A} \right)^{\nu_A} - \ln \left(\frac{q_B}{N_B} \right)^{\nu_B} = 0$$

$$\ln \left[\frac{\left(\frac{q_C}{N_C} \right)^{\nu_C} \left(\frac{q_D}{N_D} \right)^{\nu_D}}{\left(\frac{q_A}{N_A} \right)^{\nu_A} \left(\frac{q_B}{N_B} \right)^{\nu_B}} \right] = 0$$

$$\frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}}$$

$q = f(T)V \Rightarrow \frac{q}{V}$ is a function of T alone
 holds for ideal gas

$$\frac{(q_C/V)^{\nu_C} (q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}} = \frac{\rho_C^{\nu_C} \rho_D^{\nu_D}}{\rho_A^{\nu_A} \rho_B^{\nu_B}} = K_c(T)$$

also
$$K_p(T) = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} = (kT)^{\nu_C + \nu_D - \nu_A - \nu_B} K_c(T)$$

Example $2Na \rightleftharpoons Na_2$

$$K_p = \frac{p_{Na_2}}{p_{Na}^2} = \frac{1}{kT} \frac{q_{Na_2}/V}{(q_{Na}/V)^2}$$

$$q_{Na} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V q_{el} \quad m = m_{Na}$$

$$q_{Na_2} = \left(\frac{2\pi MkT}{h^2} \right)^{3/2} V \left(\frac{T}{2\theta_r} \right) (1 - e^{-\theta_v/T})^{-1} e^{D_0/kT}$$

$$M = 2m_{Na}$$

$$D_o = D_e - \frac{h\nu}{2}$$

at $T = 1000\text{ K}$

$$\frac{q_{Na}}{V} = 1.31 \times 10^{27}$$

accounts for degeneracy of ground state

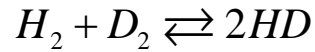
$$\frac{q_{Na_2}}{V} = 1.22 \times 10^{35}$$

$$K_p = \frac{1}{kT} \frac{q_{Na_2}/V}{(q_{Na}/V)^2} = \frac{1.22 \times 10^{35}}{(1.38 \times 10^{-16})(1000)(1.72 \times 10^{54})}$$
$$= 0.50 \times 10^{-6} (\text{dyne/cm}^2)^{-1} = 0.50 \text{ atm.}$$

expt. measurements give 0.475 atm.

dimer favored by energy
atoms favored by entropy

Isotope exchange



$$K = \frac{P_{HD}^2}{P_{H_2} P_{D_2}} = \frac{q_{HD}^2}{q_{H_2} q_{D_2}}$$

$$= \frac{M_{HD}^3}{(M_{H_2} M_{D_2})^{3/2}} \frac{4\theta_{r,H_2} \theta_{r,D_2}}{\theta_{r,HD}^2} \frac{\left(1 - e^{-\theta_{v,H_2}/T}\right) \left(1 - e^{-\theta_{v,D_2}/T}\right)}{\left(1 - e^{-\theta_{v,HD}/T}\right)^2} e^{-(2\theta_{v,HD} - \theta_{v,H_2} - \theta_{v,D_2})/2T}$$

$$\theta_{r,H_2} = 85.3 \text{ K}$$

$$\theta_{r,D_2} = 42.7 \text{ K}$$

$$\theta_{v,H_2} = 6215 \text{ K}$$

$$\theta_{v,D_2} = 4394 \text{ K}$$

Can set = 1

From difference of zero-point energies

$$\theta_{r,HD} = 3/4 \theta_{r,H_2}$$

$$\theta_{v,HD} = \sqrt{3/4} \theta_{v,H_2}$$

$$K(T) = 4 \left(\frac{9}{8}\right)^{3/2} \left(\frac{8}{9}\right) e^{-77.7/T}$$

4 is from symm #'s

Next two factors from translation, rotation, respectively

Recall, translation uses total mass, and rotation, reduced mass

H-exchange reaction

T	K (calc)	K (expt)
195	2.84	2.92
298	3.26	3.28
670	3.77	3.80

general $A_2 + B_2 \rightleftharpoons 2AB$ (where A, B are isotopes)

Δ = difference in mass of 2 isotopes

M = atomic mass of heavier isotope

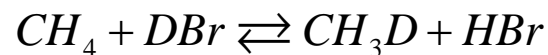
$$K(T) = 4 \left(1 + \frac{\Delta^2}{8M^2} \right) e^{-\Delta^2 \theta_{M,vib} / 32M^2 T}$$

for $N_2^{14} + N_2^{15} \rightleftharpoons 2N^{14}N^{15}$

$$K(T) = 4(1.0005)e^{-.44/T}$$

mainly dominated by
symmetry numbers





$$K(T) = \frac{\rho(\text{CH}_3\text{D})\rho(\text{HBr})}{\rho(\text{CH}_4)\rho(\text{DBr})} = \frac{q(\text{CH}_3\text{D})q(\text{HBr})}{q(\text{CH}_4)q(\text{DBr})}$$

$$= \frac{\sigma_{\text{CH}_4}\sigma_{\text{DBr}}}{\sigma_{\text{CH}_3\text{D}}\sigma_{\text{HBr}}} \left(\frac{M_{\text{CH}_3\text{D}}M_{\text{HBr}}}{M_{\text{CH}_4}M_{\text{DBr}}} \right)^{3/2} \frac{I_{\text{HBr}}}{I_{\text{DBr}}} \frac{(I_A I_B I_C)_{\text{CH}_3\text{D}}^{1/2}}{(I_A I_B I_C)_{\text{CH}_4}^{1/2}} \frac{q_{\text{vib,CH}_3\text{D}}q_{\text{vib,HBr}}}{q_{\text{vib,CH}_4}q_{\text{vib,DBr}}}$$

$$(1 - e^{-\theta_v/T}) \sim 1 \quad \text{at room temperature}$$

In this case, vibration part has only ZPE terms = $e^{200\text{cm}^{-1}/kT}$

$$\text{ratio of symmetry numbers } \frac{12 \cdot 1}{3 \cdot 1} = 4$$

to get needed moments of inertia
use the [Teller-Redlich product rule](#)

$A \rightarrow A'$ differ only by isotopic substitution

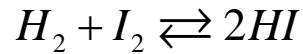
$$\text{(linear)} \quad \left(\frac{M'}{M}\right)^{3/2} \frac{I'}{I} = \prod_{i=1}^n \left(\frac{m'_i}{m_i}\right)^{3/2} \prod_{j=1}^{3n-5} \frac{v'_j}{v_j}$$

$$\text{(nonlinear)} \quad \left(\frac{M'}{M}\right)^{3/2} \sqrt{\frac{I'_A I'_B I'_C}{I_A I_B I_C}} = \prod_{i=1}^n \left(\frac{m'_i}{m_i}\right)^{3/2} \prod_{j=1}^{3n-6} \frac{v'_j}{v_j}$$

M = total mass of molecule A
 m_j is the mass of the j^{th} atom

$$\begin{aligned} K(T) &= 4e^{317/T} \frac{v_{HBr}}{v_{DBr}} \prod_{j=1}^9 \left(\frac{v_{j,CH_3D}}{v_{j,CH_4}} \right) \\ &= 2.99e^{317/T} \\ &= 8.65 \text{ @ } T = 298K \end{aligned}$$

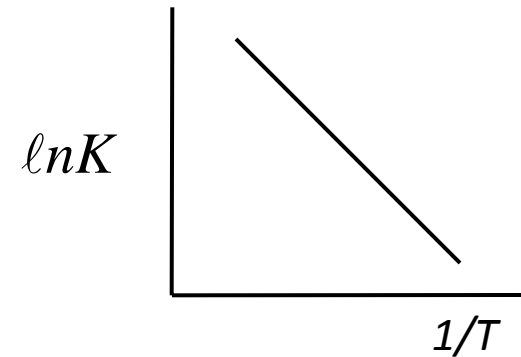
A chemical reaction

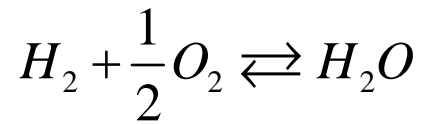


$$K(T) = \frac{(q_{HI}/V)^2}{(q_{H_2}/V)(q_{I_2}/V)} = \frac{q_{HI}^2}{q_{H_2} q_{I_2}}$$

$$= \left(\frac{M_{HI}^2}{M_{H_2} M_{I_2}} \right)^{3/2} \frac{4\theta_r^{H_2} \theta_r^{I_2} (1 - e^{-\theta_{v,H_2}/T})(1 - e^{-\theta_{v,I_2}/T})}{(\theta_r^{HI})^2 (1 - e^{-\theta_{v,HI}/T})^2} e^{(2D_0^{HI} - D_0^{H_2} - D_0^{I_2})/RT}$$

$$\Delta d(\ln K) = -\frac{\Delta H}{R} d\left(\frac{1}{T}\right), \quad \Delta H = \text{heat of reaction}$$



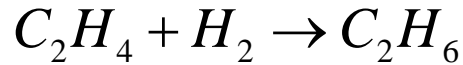


$$K_p(T) = \frac{(q_{H_2O}/V)}{(q_{H_2}/V)(q_{O_2}/V)^{1/2}}$$

Recall factor of 3 in q_{O_2} due to triplet state

T	log K (calc)	log K (expt)
1000	10.2	10.1
1500	5.7	5.7
2000	3.7	3.5

small difference at high T –
assumptions of rigid-rotor and
decoupling of vibrations/rotations
beginning to break down



The new feature here is the presence of hindered rotation in C_2H_6 .

Before it was possible to calculate accurate torsion barriers, one approach was to choose a simple functional form for the torsion potential with a guessed barrier, calculate the vibrational levels and then K , adjusting the barrier height to reproduce the experimental K value.

Best fit $V_0 = 3.1 \text{ kcal/mol}$

Arbitrariness of the zero of energy

$$q(V, T) = \frac{q^0(V, T) e^{-\varepsilon_0^0/kT}}{\quad}$$

← ground state of molecule
taken to be the zero of energy

$$\mu - \varepsilon_0^0 = -kT \ln \left[\left(\frac{q^0}{V} \right) \frac{kT}{1.01 \times 10^6} \right] + kT \ln p(\text{atm})$$

In using thermodynamic tables

energy of element = 0 at $T = 0^\circ K$
if element is in same physical state that
exists at $T = 25^\circ C, P = 1 atm$

standard state

$$G^0 - E_0^0 = -RT \ln \left\{ \left(\frac{q^0}{V} \right) \frac{kT}{1.06 \times 10^6} \right\}$$

↑
convert to per mol

↑
Gibbs free energy per mol at $P = 1 atm$

$$G^0 \rightarrow E_0^0 \text{ as } T \rightarrow 0$$

$$-R \ln K_p = \frac{\Delta E_0^0}{T} + \Delta \frac{(G^0 - E_0^0)}{T}$$

Given the results in Table 9-6 and similar tables, one can readily calculate the entropy as a function of T