

26. Chemical Equilibrium

26-1 Chemical Equilibrium Results When the Gibbs Energy is a Minimum with Respect to the Extent of Reaction



Extent of reaction x
$$\begin{aligned} dn_A &= -\nu_A d\xi & dn_Y &= \nu_Y d\xi \\ dn_B &= -\nu_B d\xi & dn_Z &= \nu_Z d\xi \end{aligned}$$

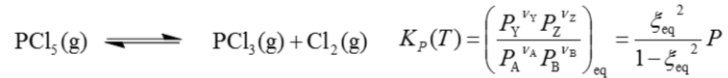
Chemical potential
$$\mu_A = \left(\frac{\partial G}{\partial n_A} \right)_{T, P, n_B, n_Y, n_Z}$$

at constant T, P :
$$\begin{aligned} dG &= \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \\ &= (-\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z) d\xi \\ \left(\frac{\partial G}{\partial \xi} \right)_{T, P} &= -\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z \equiv \Delta_r G \end{aligned}$$

in equilibrium, $\Delta_r G = 0$

$$\Delta_r G^\circ(T) = -RT \ln K_p(T) \quad K_p(T) = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}} \quad \text{(equilibrium constant)}$$

26-2 An Equilibrium Constant is a Function of Temperature Only



Equilibrium constant $K_p(T)$ does not depend on a total pressure P , but P controls ξ_{eq} .
 \Rightarrow Le Chatelier's principle

conversion from P -representation to c -representation: ($P^\circ = 0.1 \text{ MPa}$, $c^\circ = 1 \text{ mol L}^{-1}$)

$$K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^{v_Y + v_Z - v_A - v_B} \quad K_c = \frac{(c_Y / c^\circ)^{v_Y} (c_Z / c^\circ)^{v_Z}}{(c_A / c^\circ)^{v_A} (c_B / c^\circ)^{v_B}}$$

26-3 Standard Gibbs Energies of Formation can be Used to Calculate Equilibrium Constants

$\Delta_r H^\circ$ is calculated from standard enthalpy of formation.

$\Delta_r S^\circ$ is calculated from standard (absolute) entropy.

$$\begin{aligned} \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ \\ &= v_Y \Delta_f G^\circ[Y] + v_Z \Delta_f G^\circ[Z] - v_A \Delta_f G^\circ[A] - v_B \Delta_f G^\circ[B] \end{aligned} \quad \ln K_p(T) = - \frac{\Delta_r G^\circ}{RT}$$

26-4 A Plot of the Gibbs Energy of a Reaction Mixture Against the Extent of Reaction is a Minimum at Equilibrium



$$\begin{aligned} G(\xi) &= (1-\xi)\bar{G}_{\text{N}_2\text{O}_4} + 2\xi\bar{G}_{\text{NO}_2} \\ &= (1-\xi)G^\circ_{\text{N}_2\text{O}_4} + 2\xi G^\circ_{\text{NO}_2} + (1-\xi)RT \ln P_{\text{N}_2\text{O}_4} + 2\xi RT \ln P_{\text{NO}_2} \end{aligned}$$

When a total pressure is 0.1 MPa ,

$$P_{\text{N}_2\text{O}_4} = \frac{1-\xi}{1+\xi}, \quad P_{\text{NO}_2} = \frac{2\xi}{1+\xi}$$

$$\Delta_f G^\circ_{\text{N}_2\text{O}_4} = 97.787 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ_{\text{NO}_2} = 51.258 \text{ kJ mol}^{-1}$$

$$G(\xi) = (1-\xi)\Delta_f G^\circ_{\text{N}_2\text{O}_4} + 2\xi\Delta_f G^\circ_{\text{NO}_2} + (1-\xi)RT \ln \frac{1-\xi}{1+\xi} + 2\xi RT \ln \frac{2\xi}{1+\xi}$$

Under appropriate standard conditions ($RT = 2.4790 \text{ kJ mol}^{-1}$),

$\xi = \xi_{\text{eq}}$ that minimizes $G(\xi)$ leads to the equilibrium constant $\Rightarrow K_p = 0.148$

This value coincides with that obtained from $\ln K_p(T) = -\frac{\Delta_r G^\circ}{RT}$

26-5 The Ratio of the Reaction Quotient to the Equilibrium Constant Determines the Direction in which a Reaction will Proceed



$$\Delta_r G = \Delta_r G^\circ(T) + RT \ln \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \quad (P \text{ is not necessarily equilibrium pressure.})$$

Reaction Quotient: $Q_P = \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \quad \Delta_r G = RT \ln(Q_P / K_P)$

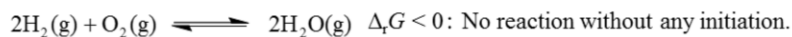
$Q_P < K_P \Rightarrow$ Reaction proceeds from left to right spontaneously.

$(Q_P > K_P \Rightarrow$ right to left)

26-6 The Sign of $\Delta_r G$ and not that of $\Delta_r G^\circ$ Determines the Direction of Reaction Spontaneity

$\Delta_r G^\circ < 0 \Rightarrow K_P > 1$: Reaction proceeds from left to right.

$\Delta_r G^\circ > 0 \Rightarrow K_P < 1$: Reaction proceeds from right to left.



26-7 The Variation of an Equilibrium Constant with Temperature is Given by the Van't Hoff Equation

Gibbs-Helmholtz formula

$$\left(\frac{\partial}{\partial T} \frac{\Delta_r G^\circ}{T} \right)_p = -\frac{\Delta_r H^\circ}{T^2}$$

By representing Gibbs energy with equilibrium constant

$$\left(\frac{\partial \ln K_p}{\partial T} \right)_p = \frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad \begin{array}{l} \Delta_r H^\circ > 0 \text{ (endothermic)} \quad \text{high-}T \rightarrow \text{high-}K_p \\ \Delta_r H^\circ < 0 \text{ (exothermic)} \quad \text{high-}T \rightarrow \text{low-}K_p \end{array}$$

Integration from T_1 to T_2 results:

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2} dT = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$\ln K_p$ is proportional to $1/T$ (cf. Clausius-Clapeyron equation)

Temperature-dependence of $\Delta_r H$

$$\Delta_r H^\circ(T) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \dots$$

→ conversion into temperature-dependence of K_p

$$\ln K_p(T) = A - \frac{\alpha}{RT} + \frac{\beta}{R} \ln T + \frac{\gamma}{R} T + \frac{\delta}{2R} T^2 + \dots$$

26-8 We can Calculate Equilibrium Constants in Terms of Partition Functions

Gas phase reaction under constant V, T



Helmholtz energy: $dA = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$

Condition for chemical equilibrium: $\nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B = 0$

Partition function of a mixed gas is the product of those for each component.

$$\begin{aligned} Q &= Q(N_A, N_B, N_Y, N_Z, V, T) \\ &= Q(N_A, V, T) \times Q(N_B, V, T) \times \dots \\ &= \frac{q_A(V, T)^{N_A}}{N_A!} \times \dots \end{aligned}$$

Chemical potential:

$$\mu_A = -RT \left(\frac{\partial \ln Q}{\partial N_A} \right)_{N_j, V, T} = -RT \ln \frac{q_A(V, T)}{N_A} \quad (\because A = U - TS = -RT \ln Q)$$

With an equilibrium condition, $\frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_Y^{\nu_Y} q_Z^{\nu_Z}}{q_A^{\nu_A} q_B^{\nu_B}} \Rightarrow$ representation of K_c

26-8 We can Calculate Equilibrium Constants in Terms of Partition Functions (cont.)

A. reaction of diatomic molecules



$$K(T) = \frac{q_{\text{HI}}^2}{q_{\text{H}_2} q_{\text{I}_2}}$$

$$= \left(\frac{m_{\text{HI}}^2}{m_{\text{H}_2} m_{\text{I}_2}} \right)^{3/2} \left(\frac{4\theta_{\text{rot}}^{\text{H}_2} \theta_{\text{rot}}^{\text{I}_2}}{(\theta_{\text{rot}}^{\text{HI}})^2} \right) \frac{\{1 - \exp[-\theta_{\text{vib}}^{\text{H}_2}/T]\} \{1 - \exp[-\theta_{\text{vib}}^{\text{I}_2}/T]\}}{\{1 - \exp[-\theta_{\text{vib}}^{\text{HI}}/T]\}^2} \exp \frac{2D_0^{\text{HI}} - D_0^{\text{H}_2} - D_0^{\text{I}_2}}{RT}$$

On calculating K_p based on the right table,

→ to plot against $1/T$

→ to derive ΔH from the line slope

Calcd.: -12.9 kJ / mol

Obsd.: -13.4 kJ / mol

T/K	$K_p(T)$	$\ln K_p(T)$
500	138	4.92
750	51.1	3.93
1000	28.5	3.35
1250	19.1	2.95
1500	14.2	2.65

B. reaction of polyatomic molecules

to use rotation temperature of asymmetric top

to use vibration temperatures of normal modes

Calculated formation constant of $\text{H}_2\text{O}(\text{g}) \rightarrow$

T/K	$\ln K_p(T)$ (calcd.)	$\ln K_p(T)$ exptl.
1000	23.5	23.3
1500	13.1	13.2
2000	8.52	8.15

26-9 Molecular Partition Functions and Related Thermodynamic Data Are Extensively Tabulated (omitted)

26-10 Equilibrium Constants for Real Gases are Expressed in Terms of Partial Fugacities

Chemical potential of non-ideal gas (introduction of fugacity f)

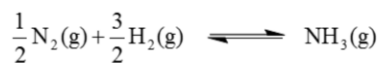
$$\mu(T, P) = \mu^\circ(T) + RT \ln \frac{f}{f^\circ} = \mu^\circ(T) + RT \ln f \quad \text{relative to standard state } f^\circ$$

gas phase reaction



At equilibrium condition ($\Delta_r G = 0$)

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{f_Y^{\nu_Y} f_Z^{\nu_Z}}{f_A^{\nu_A} f_B^{\nu_B}} = 0 \Rightarrow \Delta_r G^\circ = -RT \ln K_f \quad K_f(T) = \left(\frac{f_Y^{\nu_Y} f_Z^{\nu_Z}}{f_A^{\nu_A} f_B^{\nu_B}} \right)_{\text{eq}}$$



K_f : thermodynamical equilibrium constant

$P_{\text{total}}/\text{MPa}$	$K_p/10^{-3}$	$K_f/10^{-3}$
1	6.59	6.55
3	6.76	6.59
5	6.90	6.50
10	7.25	6.36
30	8.84	6.08

26-11 Thermodynamic Equilibrium Constants are Expressed in Terms of Activities

Chemical potential of non-ideal solution (introduction of activity)

$$\mu_j = \mu_j^* + RT \ln a_j \quad \text{solvent of a dilute solution: } a_j \rightarrow x_j \text{ when } x_j \rightarrow 1$$

μ_j^* is a chemical potential of pure solvent (Raoult's standard state)

$$\mu_j = \mu_j^\circ + RT \ln a_j \quad \text{slutes of a dilute solution: } a_j \rightarrow c_j \text{ when } c_j \rightarrow 0$$

μ_j° is a chemical potential of solute in 1 M ideal solution
(Henry's standard state)

General reaction



At equilibrium condition ($\Delta_r G = 0$),

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{a_Y^{\nu_Y} a_Z^{\nu_Z}}{a_A^{\nu_A} a_B^{\nu_B}} = 0 \Rightarrow \Delta_r G^\circ = -RT \ln K_a \quad K_a(T) = \left(\frac{a_Y^{\nu_Y} a_Z^{\nu_Z}}{a_A^{\nu_A} a_B^{\nu_B}} \right)_{\text{eq}}$$

K_a : thermodynamical equilibrium constant

Calculation of activity

$$\ln a = \frac{1}{RT} \int_1^P \bar{V} dP' \quad (\text{gas phase})$$

$$= \frac{\bar{V}}{RT} (P-1) \quad (\text{condensed phase})$$

26-12 The Use of Activities Makes a Significant Difference in Solubility Calculations Involving Ionic Species

Dissociation of aqueous acetic acid (0.100 M)



$$K_a = \frac{a_{\text{H}_3\text{O}^+} a_{\text{CH}_3\text{COO}^-}}{a_{\text{CH}_3\text{COOH}} a_{\text{H}_2\text{O}}} = \frac{a_{\text{H}_3\text{O}^+} a_{\text{CH}_3\text{COO}^-}}{a_{\text{CH}_3\text{COOH}}} = 1.74 \times 10^{-5}$$

$$= \frac{c_{\text{H}_3\text{O}^+} c_{\text{CH}_3\text{COO}^-} \gamma_{\pm}^2}{c_{\text{CH}_3\text{COOH}}} \quad \text{approx. } \gamma_{\pm} = 1 \Rightarrow c_{\text{H}_3\text{O}^+} = 1.31 \text{ mM, pH} = 2.88$$

Calculating γ_{\pm} (by Debye-Hückel's limiting law, I_c is ionic strength)

$$\ln \gamma_{\pm} = -\frac{1.173 |z_+ z_-| (I_c)^{1/2}}{1 + (I_c)^{1/2}} \quad I_c = \frac{1}{2} (c_{\text{H}_3\text{O}^+} + c_{\text{CH}_3\text{COO}^-}) = c_{\text{H}_3\text{O}^+} = c_{\text{CH}_3\text{COO}^-}$$

$\Rightarrow c_{\text{H}_3\text{O}^+} = 1.31 \text{ mM}$ as initial value results γ_{\pm} , which gives new $c_{\text{H}_3\text{O}^+}$ (iteratively).
 $\Rightarrow \gamma_{\pm} = 0.959$, $c_{\text{H}_3\text{O}^+} = 1.37 \text{ mM}$, $\text{pH} = 2.86$

More noticeable error occurs in calculating solubility.

For BaF_2 : approx. $\gamma_{\pm} = 1 \Rightarrow s = 7.52 \times 10^{-3} \text{ M}$
 iterative method $\gamma_{\pm} = 0.700 \Rightarrow s = 0.011 \text{ M}$