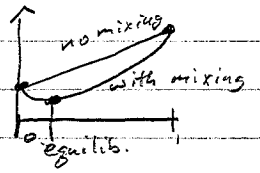
Chap 5.6 Chemical Equilibrium

You have a closed system where reaction can take place $AB \leftrightarrow A + B$
Why don't you see all AB or all $A+B$?

Let x = fraction of AB



Suppose you have a system at fixed P, T, V but number of constituents can change

Equilibrium $dG = 0 = \mu_1 dN_1 + \mu_2 dN_2 + \mu_3 dN_3 + \dots$

However IMPORTANT $dN_1, dN_2, \dots$ are NOT independent

Example $N_2 + 3H_2 \leftrightarrow 2NH_3 \Rightarrow dN_{N_2} = -1,\ dN_{H_2} = -3,\ dN_{NH_3} = 2$

$\Rightarrow \quad \mu_{N_2} + 3\mu_{H_2} = 2\mu_{NH_3}$

General $\nu_1 X_1 + \nu_2 X_2 + \dots \leftrightarrow \nu_3 X_3 + \nu_4 X_4 + \dots$

$\nu_1 \mu_{X_1} + \nu_2 \mu_{X_2} + \dots = \nu_3 \mu_{X_3} + \nu_4 \mu_{X_4} + \dots$

The different cases play out differently due to how the chemical potentials behave in each circumstance.

EXAMPLE ALL GASES

From Eq. 5.39 $\mu(T,P) = \mu(T,P_0) + k_B T \ln\left(\frac{P}{P_0}\right)$

Example $N_2 + 3H_2 \leftrightarrow 2NH_3$

$$\mu^\circ_{N_2} + k_B T \ln\left(\frac{P_{N_2}}{P_0}\right) + 3\mu^\circ_{H_2} + 3k_B T \ln\left(\frac{P_{H_2}}{P_0}\right) = 2\mu^\circ_{N_2} + 2k_B T \ln\left(\frac{P_{NH_2}}{P_0}\right)$$

$$\Rightarrow \ln\left(\frac{P_{N_2} P_{H_2}^3}{P_{NH_2}^2 P_0^2}\right) = \frac{(2\mu^\circ_{NH_3} - \mu^\circ_{N_2} - 3\mu^\circ_{H_2})N_A}{RT} = \frac{\Delta G_0}{RT}$$

$$\Rightarrow \frac{P_{NH_2}^2 P_0^2}{P_{N_2} P_{H_2}^3} = e^{-\frac{\Delta G}{RT}} \equiv K \qquad \text{Law of mass action}$$

In this equation P_{NH_3} is the partial pressure

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$$\ln K = -\frac{\Delta G_0}{RT} \Rightarrow \frac{d\ln K}{dT} = \frac{\Delta G_0}{RT^2} - \frac{1}{RT}\frac{d\Delta G_0}{dT} = \frac{\Delta G_0}{RT^2} + \frac{S}{RT}$$

$$= \frac{\Delta G_0 + ST}{RT^2} = \frac{\Delta H_0}{RT^2}$$

If ΔH_0 has little T dep $\quad \ln K(T_2) - \ln K(T_1) = \frac{\Delta H_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow K(T) e^{\frac{\Delta H_0}{RT}} = \text{const}$

EXAMPLE Dissociation of solvent

Even a pure molecular substance is not "pure". The molecules can dissociate to give "solvent" particles.

$$H_2O \leftrightarrow H^+ + OH^-$$

$$\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \qquad N_{H^+} = N_{OH^-}$$

assuming dilute

Eq. 5.69 $\mu_{H_2O} = \mu_{o,H_2O} - \frac{2N_{H^+}}{N_{H_2O}} k_B T$

Eq 5.72 $\mu_{H^+} + \mu_{OH^-} = \mu_{o,H^+} + k_B T \ln(M_{H^+}) + \mu_{o,OH^-} + k_B T \ln(M_{OH^-})$

If dilute $\frac{N_{H^+}}{N_{H_2O}} << 1$

$$\Rightarrow \mu_{o,H_2O} = \mu_{o,H^+} + \mu_{o,OH^-} + k_B T \ln(M_{H^+} M_{OH^-})$$

$$\Rightarrow RT \ln(M_{H^+} M_{OH^-}) = -[N_A(\mu_{o,H^+} + \mu_{o,OH^-} - \mu_{o,H_2O})] = -\Delta G_o$$

$$M_{H^+} M_{OH^-} = e^{-\Delta G_o/RT} \equiv K$$

$\Delta G_o = (0 - 157.24 + 237.13)\,kJ = 79{,}900\,J$

$$M_{H^+} M_{OH^-} = e^{\frac{-79{,}900\,J}{8.315\,J/K \cdot 298\,K}} = e^{-32.3} = 1.0 \times 10^{-14}$$

Since $M_{H^+} = M_{OH^-} \Rightarrow M_{H^+} = 10^{-7}$ the 7 is called pH

From previous problem $K(T_2) = K(T_1)\, e^{\left(\frac{\Delta H_o}{RT_1} - \frac{\Delta H_o}{RT_2}\right)}$

At 35°C $T_2 = 308\,K$ $\Delta H_o = (0 - 229.99 + 285.83)\,kJ = 55{,}800\,J$

$$K(35°C) = 1.0 \times 10^{-14}\, e^{\frac{55{,}800\,J}{8.315\,J/K \cdot 298K} - \frac{55800\,J}{8.315\,J/K \cdot 308K}}$$

$$= 1.0 \times 10^{-14}\, e^{0.73} = 2.1 \times 10^{-14} \Rightarrow \sim 1.4\times \text{ more } H^+$$

At 45°C $K(45°C) = 1.0 \times 10^{-14}\, e^{1.42} \simeq 4.1 \times 10^{-14} \Rightarrow \sim 2\times$ more H^+

See Book about O_2 dissolving in H_2O and Ionizing H