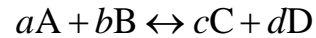


Thermodynamics and Chemical Equilibrium

- Consider a differential amount of the following chemical reaction in a closed system:



Define one **mole of reaction** as a moles of A and b moles of B forming c moles of C and d moles of D. Moles of reaction occurring in a given system is $\Delta\eta$.

$$dn_A = -a\Delta\eta; \quad dn_B = -b\Delta\eta; \quad dn_C = +c\Delta\eta; \quad dn_D = +d\Delta\eta$$

- Like in physical systems, the change (reaction) will occur if it decreases PE_{sys} (in this case, G_{sys}).

$$G_{\text{sys},1} = n_{A,1}\bar{G}_A + n_{B,1}\bar{G}_B + n_{C,1}\bar{G}_C + n_{D,1}\bar{G}_D$$

$$G_{\text{sys},2} = (n_{A,1} + dn_A)\bar{G}_A + (n_{B,1} + dn_B)\bar{G}_B + (n_{C,1} + dn_C)\bar{G}_C + (n_{D,1} + dn_D)\bar{G}_D$$

$$\begin{aligned} dG_{\text{sys}} &= dn_A\bar{G}_A + dn_B\bar{G}_B + dn_C\bar{G}_C + dn_D\bar{G}_D \\ &= -a d\eta(\bar{G}_A) - b d\eta(\bar{G}_B) + c d\eta(\bar{G}_C) + d d\eta(\bar{G}_D) \end{aligned}$$

$$\frac{dG_{\text{sys}}}{d\eta} = -a\bar{G}_A - b\bar{G}_B + c\bar{G}_C + d\bar{G}_D \equiv \Delta\bar{G}_r$$

$$\begin{aligned} \Delta\bar{G}_r &= -a(\bar{G}_A^\circ + RT \ln\{A\}) - b(\bar{G}_B^\circ + RT \ln\{B\}) \\ &\quad + c(\bar{G}_C^\circ + RT \ln\{C\}) + d(\bar{G}_D^\circ + RT \ln\{D\}) \end{aligned}$$

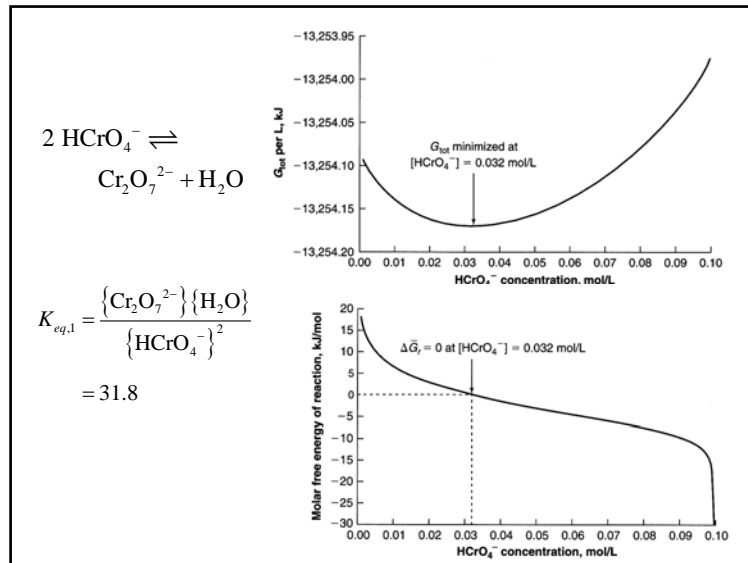
$$\Delta\bar{G}_r = -a\bar{G}_A^\circ - b\bar{G}_B^\circ + c\bar{G}_C^\circ + d\bar{G}_D^\circ + RT \ln \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

$$\Delta\bar{G}_r = \Delta\bar{G}_r^\circ + RT \ln Q = \Delta\bar{G}_r^\circ + \left(5.71 \frac{\text{kJ}}{\text{mol}}\right) \log Q$$

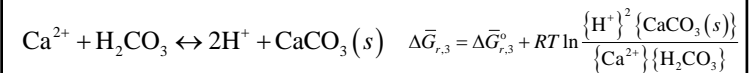
- At equilibrium, G_{sys} will be minimized, so $dG_{\text{sys}}/d\eta=0$:

$$0 = \left(\Delta\bar{G}_r^\circ + RT \ln Q\right)_{eq} = \Delta\bar{G}_r^\circ + RT \ln K_{eq}$$

$$\Delta\bar{G}_r^\circ = -RT \ln K_{eq}; \quad K_{eq} = \exp\left(-\frac{\Delta\bar{G}_r^\circ}{RT}\right)$$



- Additive (Sequential) Reactions



- Additive (Sequential) Reactions

$$\Delta \bar{G}_{r,3}^{\circ} = \Delta \bar{G}_{r,1}^{\circ} + \Delta \bar{G}_{r,2}^{\circ}$$

$$RT \ln Q_1 + RT \ln Q_2 = RT \ln Q_1 Q_2 = RT \ln Q_3$$

$$\Delta \bar{G}_{r,3} = \Delta \bar{G}_{r,1} + \Delta \bar{G}_{r,2}$$

- Molar Gibbs energy of Additive (Sequential) Reactions
 - Equal to the sum of the molar Gibbs energy of constituent reactions

Dependence of K_{eq} on Temperature

Note: The relationship $\ln K_{eq} = -\Delta \bar{G}_r^{\circ} / RT$ is valid for any standard state T . How does K_{eq} change when $T_{std.state}$ changes?

$$d \ln K_{eq} = -d \frac{\Delta \bar{G}_r^{\circ}}{RT} = -d \frac{\Delta \bar{H}_r^{\circ} - T \Delta \bar{S}_r^{\circ}}{RT} = -d \frac{\Delta \bar{H}_r^{\circ}}{RT} + d \frac{\Delta \bar{S}_r^{\circ}}{R}$$

If $\Delta \bar{H}_r^{\circ}$ and $\Delta \bar{S}_r^{\circ}$ are insensitive to T over the range of interest:

$$d \ln K_{eq} = -\frac{\Delta \bar{H}_r^{\circ}}{R} d \left(\frac{1}{T} \right)$$

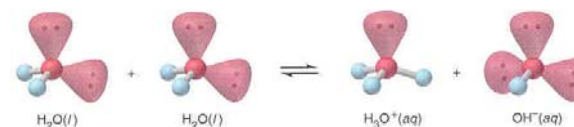
$$\ln \frac{K_{eq}|_{T_2}}{K_{eq}|_{T_1}} = \frac{\Delta \bar{H}_r^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Acids and Bases

- An **acid** is a chemical that increases the H^+ activity in solution. A **base** is a chemical that decreases that activity.
- An H^+ ion is a proton, which is very unstable in water; it becomes hydrated to form H_3O^+ (**hydronium ion**) or other $H_{2n+1}O_n^+$ species.
- The simplest way that an acid can increase H^+ activity is to release an H^+ ion into solution (i.e., give it to an H_2O to form H_3O^+). Similarly, the simplest way to decrease H^+ activity is to acquire an H^+ from solution. Therefore, acids and bases are sometimes referred to as **proton donors** and **proton acceptors**, respectively.
- Everyday examples include citric acid, ammonia, phosphoric acid and other phosphate species, sodium benzoate, carbonic acid/ bicarbonate/ carbonate, amino acids, and many, many others.

Acid/Base Properties of Water

- Water molecules react with one another, to a small extent, to donate and accept protons:



$$K_{eq} = \frac{\{H^+\}\{OH^-\}}{\{H_2O\}^2} \equiv K_w$$

$$K_w = 10^{-14.0}; \quad pK_w = 14.0$$

Acid/Base Properties of Water

- Water dissociation reaction is fast, so assumption is made that it is always at equilibrium
- Activity of H_2O is ~ 1.0 , so:

$$K_w = \{H^+\}\{OH^-\} = 10^{-14.0}$$

$$\log\{H^+\} + \log\{OH^-\} = -14.0$$

$$pH + pOH = 14.0$$

where it is understood that pH and pOH are $-\log_{10}\{H^+\}$ and $-\log_{10}\{OH^-\}$, respectively

Acid/Base Properties of Water

