P. Chem I

2/20/23

$$\int_{P^*}^{P^\circ} \frac{\partial \mu_y}{\partial P} dP = \mu_y(P^*) - \underbrace{\mu_x(P^\circ)}_{\mu^\circ_y}$$

Fundamental Theorem of Calculus

$$\frac{\partial \mu_y}{\partial P} = \frac{\partial}{\partial P}\frac{\partial G}{\partial n_y} = \frac{\partial G}{\partial P} = \frac{\partial V}{\partial n_y} = \frac{RT}{P_y}$$

$P_y V = n_y RT$

$V = \frac{n_y RT}{P_y}$

From this, we obtained $\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q$

with $Q = \frac{(P_Y/P^\circ)^{\nu_Y}(P_Z/P^\circ)^{\nu_Z}}{(P_A/P_\circ)^{\nu_A}(P_B/P_\circ)^{\nu_B}}$ for $\nu_A A + \nu_B B \rightleftharpoons \nu_Y Y + \nu_Z Z$

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At equilibrium $\Delta G_{rxn} = 0 \Rightarrow \Delta G^\circ_{rxn} = -RT \ln K$

Get K from $\Delta G^\circ_f$ data which is normally tabulated at 298 K.

ex: $NH_{3(g)} \rightleftharpoons \frac{3}{2} H_{3(g)} + \frac{1}{2} N_{2(g)}$

$\Delta G^\circ_{rxn} = \frac{3}{2}\Delta G^\circ_f(H_{2(g)}) + \frac{1}{2}\Delta G^\circ_f(N_{2(g)}) - \Delta G^\circ_f(NH_{3(g)})$

$= 0 + 0 - (-16.4\ kJ/mol) = 16.4\ kJ/mol$

$\ln K = \frac{-\Delta G^\circ_{rxn}}{RT} = \frac{-16.4\ kJ/mol}{8.31\ J \cdot K^{-1} \cdot mol^{-1} \cdot 298 K} = -6.6$

$K = 1.36 \times 10^{-3}$ equilibrium lies towards $NH_3$

Even with gasses we can use concentration instead of pressure (anticipating solutions)

$P_y V = n_y RT \Rightarrow P_y = \left(\frac{n_y}{V}\right) RT = C_y RT$

$Q_P = P_Y^{d_Y} \ldots = (C_y RT)^{\nu_y} \Rightarrow Q_P = Q_c (RT)^{\nu_y + \nu_z - \nu_A - \nu_B}$

$\frac{(C_Y/C_0)^{\nu_Y}(C_Z/C^\circ)^{\nu_Z}}{(C_A/C_0)^{\nu_A}(C_B/C_0)^{\nu_B}}$

$\left(RT\frac{C^\circ}{P^\circ}\right)^{\nu_y+\nu_z-\nu_A-\nu_B}$

$\Delta G^\circ_{rxn} = -RT \ln K \Rightarrow$

$\Delta G_{rxn} = -RT \ln K + RT \ln Q = RT \ln Q/K$

Say $Q < K$ then $\Delta G^\circ_{rxn} < 0$ forwards direction is spontaneous

$Q > K$ $\Delta G^\circ_{rxn} > 0$ backwards direction is spontaneous

$\Delta G^\circ_{rxn}$ vs $\Delta G_{rxn}$ $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$\Delta G^\circ_{rxn} = 4.73\ kJ/mol$ at 298 K

Put 0.8 bar $N_2O_4$ and 0.2 bar $NO_2$ in flask

$$\Delta G^\circ_{rxn} = 4.73 + (8.31)(298K)\ln\frac{(0.2)^2}{0.8} = -2.7$$

The reaction proceeds in forwards direction.