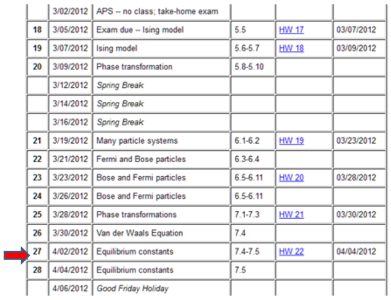
PHY 341/641
Thermodynamics and Statistical Physics

Lecture 28

Chemical potentials and phase equilibria (Chapter 7 in STP)

- Chemical reactions
- Equilibrium constants



	3/02/2012	APS -- no class; take-home exam			
18	3/05/2012	Exam due -- Ising model	5.5	HW 17	03/07/2012
19	3/07/2012	Ising model	5.6-5.7	HW 18	03/09/2012
20	3/09/2012	Phase transformation	5.8-5.10		
	3/12/2012	*Spring Break*			
	3/14/2012	*Spring Break*			
	3/16/2012	*Spring Break*			
21	3/19/2012	Many particle systems	6.1-6.2	HW 19	03/23/2012
22	3/21/2012	Fermi and Bose particles	6.3-6.4		
23	3/23/2012	Bose and Fermi particles	6.5-6.11	HW 20	03/28/2012
24	3/26/2012	Bose and Fermi particles	6.5-6.11		
25	3/28/2012	Phase transformations	7.1-7.3	HW 21	03/30/2012
26	3/30/2012	Van der Waals Equation	7.4		
27	4/02/2012	Equilibrium constants	7.4-7.5	HW 22	04/04/2012
28	4/04/2012	Equilibrium constants	7.5		
	4/06/2012	*Good Friday Holiday*			

Second exam: April 9-13

-- student presentations 4/30, 5/2 (need to pick topics)

Extension of analysis of Gibbs Free energy to analyze chemical equilibria:

Consider the following example:

$$\mathrm{H_2O} \Leftrightarrow \mathrm{H^+} + \mathrm{OH^-}$$

Constraint on number of molecules of each type:

$$+1N_{H^+} + 1N_{OH^-} - 1N_{H_2O} = 0 \equiv \sum_i \nu_i N_i$$

Change in Gibbs Free energy for this system:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

At equilibrium: $dG = 0$

At equilibrium with constant T and P: $\sum_i \mu_i dN_i = 0$

Extension of analysis of Gibbs Free energy to analyze chemical equilibria -- continued:

At equilibrium with constant T and P: $\sum_i \mu_i dN_i = 0$

Let R denote the number of times the chemical reaction occurs and recall that the reaction controls the number of each particle type according to: $\sum_i \nu_i N_i = 0.$

$$\Rightarrow dN_i = \nu_i R$$

$$\sum_i \mu_i dN_i = \sum_i \mu_i \nu_i R = 0$$

Determination of the chemical potential

In terms of the canonical partition function Z and the Helmholtz free energy :

$$F = -kT \ln Z \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$Z = Z_{trans} Z_{rot} Z_{vib} Z_{elec} \equiv Z_{trans} Z_{\text{internal}}$$

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] - kT \ln Z_{\text{internal}}$$

$$\Rightarrow \mu_i = -kT \ln\left[\frac{V}{N_i}\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2}\right] - kT \ln Z^i_{\text{internal}}$$

Chemical potential – continued:

$$-kT \ln\left[\frac{V}{N_i}\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2}\right] = -kT \ln\left[\frac{V}{N}\frac{N}{N_i}\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2}\right]$$

$$-kT \ln\left[\frac{V}{N}\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2}\right] + kT \ln\left(\frac{N_i}{N}\right)$$

$$\mu_i = -kT \ln\left[\frac{kT}{P}\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2}\right] + kT \ln\left(\frac{N_i}{N}\right) - kT \ln Z^i_{\text{internal}}$$

$$\equiv \mu_i^0(T,P) + kT \ln(n_i) \qquad n_i \equiv \frac{N_i}{N}$$

Law of "mass action"

$$\text{Equilibrium condition:}$$

$$\sum_i \mu_i \nu_i = 0$$

$$\sum_i \left[\mu_i^0(T,P) + kT\ln(n_i)\ \right]\nu_i = 0$$

$$\text{Let: } -kT\ln K(T,P) \equiv \sum_i \mu_i^0(T,P)\nu_i$$

$$\Rightarrow K(T,P) = \prod_i (n_i)^{\nu_i}$$

Example:

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

$$K(T,P) = \frac{(n_{H^+})(n_{OH^-})}{(n_{H_2O})}$$

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From experimental measurement:

$$K' \equiv K(n_{H_2O}) = 10^{-14}\ \text{moles}^2$$

$$\Rightarrow \text{For neutral water: } (n_{H^+}) = (n_{HO^-}) = 10^{-7}\ \text{moles}$$

$$pH \equiv -\ln_{10}(n_{H^+}) = 7$$

If you had a solution with $(n_{HO^-}) = 0.1\,\text{moles}$

$$pH = -\ln_{10}(n_{H^+}) = -\ln_{10}\left(\frac{10^{-14}}{10^{-1}}\right) = 13$$

Other examples:

Ionization of H atom

$$H \leftrightarrow H^+ + e^-$$

$$K = \frac{[H^+][e^-]}{[H]} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{-E_I/kT}$$

For H, $E_I/k = 160000\,K$

For example at $T = 7000K$, $[H] = 2.5\times10^{25}$ atoms/m^3

$$\frac{[H^+]}{[H]} = \left(\frac{K}{[H]}\right)^{1/2} \approx 0.1$$