

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	<i>Spring Break</i>			
	3/14/2012	<i>Spring Break</i>			
	3/16/2012	<i>Spring Break</i>			
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	<i>Good Friday Holiday</i>			

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 :



Constraint on number of molecules of each type :

$$+1N_{\text{H}^+} + 1N_{\text{OH}^-} - 1N_{\text{H}_2\text{O}} = 0 \equiv \sum_i \nu_i N_i$$

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 :

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

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

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

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

Chemical potential – continued:

$$\begin{aligned} -kT \ln \left[\frac{V}{N_i} \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \right] &= -kT \ln \left[\frac{V}{N} \frac{N}{N_i} \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \right] \\ &= -kT \ln \left[\frac{V}{N} \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \right] + kT \ln \left(\frac{N_i}{N} \right) \\ \mu_i &= -kT \ln \left[\frac{kT}{P} \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} \right] + kT \ln \left(\frac{N_i}{N} \right) - kT \ln Z_{\text{internal}}^i \\ &\equiv \mu_i^0(T, P) + kT \ln(n_i) \qquad n_i \equiv \frac{N_i}{N} \end{aligned}$$

Law of “mass action”

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 :



$$K(T, P) = \frac{(n_{\text{H}^+})(n_{\text{OH}^-})}{(n_{\text{H}_2\text{O}})}$$

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From experimental measurement :

$$K' \equiv K(n_{\text{H}_2\text{O}}) = 10^{-14} \text{ moles}^2$$

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

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

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

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

Other examples:
Ionization of H atom



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

For H, $E_I / k = 160000 \text{ K}$

For example at $T = 7000\text{K}$, $[\text{H}] = 2.5 \times 10^{25} \text{ atoms/m}^3$

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