PHY 341/641
Thermodynamics and Statistical Physics

Lecture 27

Chemical potentials and phase equilibria (Chapter 7 in STP)

- Phase diagrams
- Clausius-Clapeyron equation

	2/29/2012	APS -- no class; take-home exam			
	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	Phase transformations, continued	7.1-7.3		
	4/02/2012				
	4/04/2012				
	4/06/2012	*Good Friday Holiday*			

Reminder – second exam in April
-- student presentations 4/30, 5/2 (need to pick topics)

Thermodynamic description of the equilibrium between two forms "phases" of a material under conditions of constant *T* and *P*

Review of Gibb's Free energy:

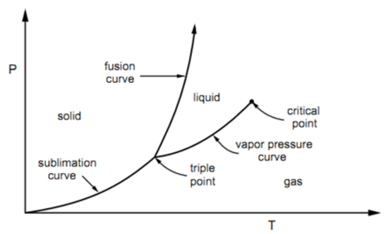
$$G = G(T,P,N) \equiv E - TS + PV = F + PV$$

$$dG = -SdT + VdP + \mu dN$$

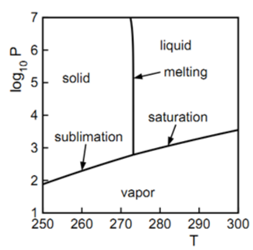
$$\mu = \mu(T,P) = \frac{G}{N} \equiv g(T,P)$$

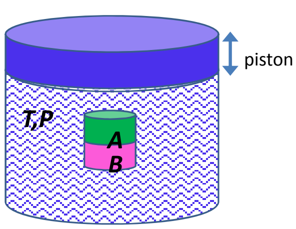
$$\left(\frac{\partial g}{\partial T}\right)_P = -\frac{S}{N} \qquad \left(\frac{\partial g}{\partial P}\right)_T = \frac{V}{N}$$

Example of phase diagram :

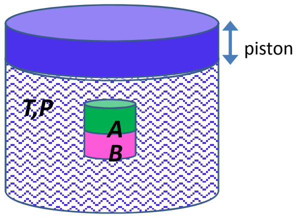


Phase diagram for water:





$$dG_A + dG_B = 0$$
$$-S_A dT + V_A dP + g_A dN_A - S_B dT + V_B dP + g_B dN_B = 0$$
$$\Rightarrow g_A dN_A + g_B dN_B = 0$$

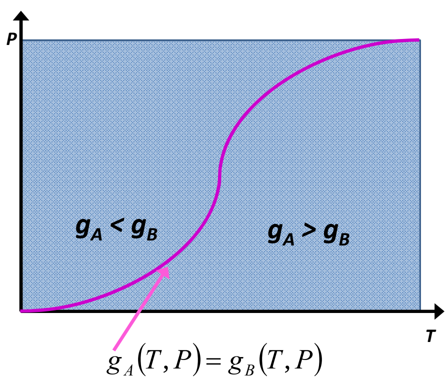


$$g_A dN_A + g_B dN_B = 0$$

Assuming: $N_A + N_B = N$

$$\Rightarrow dN_B = -dN_A$$

$$\Rightarrow (g_A - g_B) dN_A = 0 \quad \Rightarrow g_A = g_B$$



Clausius - Clapeyron Equation

$$g_A(T,P) = g_B(T,P)$$

$$dg_A(T,P) = dg_B(T,P)$$

$$\left\{\left(\frac{\partial g_A}{\partial T}\right)_P - \left(\frac{\partial g_B}{\partial T}\right)_P\right\} dT + \left\{\left(\frac{\partial g_A}{\partial P}\right)_T - \left(\frac{\partial g_B}{\partial P}\right)_T\right\} dP = 0$$

$$-\left\{\frac{S_A}{N_A} - \frac{S_B}{N_B}\right\} dT + \left\{\frac{V_A}{N_A} - \frac{V_B}{N_B}\right\} dP = 0$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta(S/N)}{\Delta(V/N)}$$

MÉMOIRE

SUR LA

PUISSANCE MOTRICE DE LA CHALEUR,

PAR E. CLAPEYRON,

INGÉNIEUR DES MINES.

Journal de l'École polytechnique 23: 153–190 (1834)

II. *Ueber die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen; von R. Clausius*[1].

(Schluſs von S. 397.)

II. Folgerungen aus dem Carnot'schen Grundsatze in Verbindung mit dem Vorigen.

Carnot hat, wie schon oben erwähnt wurde, angenommen, *daſs der Erzeugung von Arbeit als Aequivalent ein bloſser Uebergang von Wärme aus einem warmen in einen kalten Körper entspreche, ohne daſs die Quantität der Wärme dabei verringert werde.*

Der letzte Theil dieser Annahme, nämlich daſs die Quantität der Wärme unverringert bleibe, widerspricht unserem früheren Grundsatze, und muſs daher, wenn wir diesen festhalten wollen, verworfen werden. Der erste Theil dagegen kann seinem Hauptinhalte nach fortbestehen. Denn wenn wir auch eines eigenthümlichen Aequivalentes

1) Zu berichtigen ist:
S. 274 Z. 6 l. nicht nöthig st. nöthig.
S. 506 Z. 8 l. $\left(\frac{dQ}{dv}\right)$ st. $\frac{dQ}{dv}$.

Annalen der Physik Volume 155, Issue 4, pages 500–524, 1850

Clausius - Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta(S/N)}{\Delta(V/N)}$$

For a phase change involving the "Latent Heat":

$$\Delta S = \frac{L_{AB}}{T}$$

$$\frac{dP}{dT} = \frac{L_{AB}}{T(V_A - V_B)}$$

Clausius - Clapeyron Equation

$$\frac{dP}{dT} = \frac{L_{AB}}{T(V_A - V_B)}$$

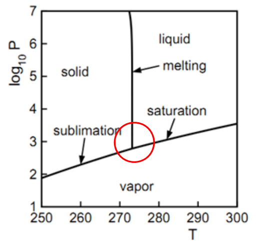
Example : A ≡ ice B ≡ water

$L_{AB} = 3.35 \times 10^5 J/kg$ $\quad T = 273.15K$

$V_A = 1.09070 \times 10^{-3} m^3/kg$

$V_B = 1.00013 \times 10^{-3} m^3/kg$

$$\frac{dP}{dT} = -1.35 \times 10^7 Pa/K$$



Clausius - Clapeyron Equation

$$\frac{dP}{dT} = \frac{L_{AB}}{T(V_A - V_B)}$$

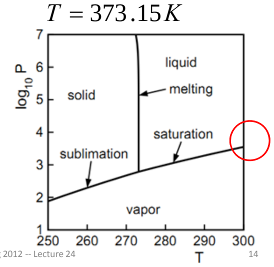
Example : A ≡ vapor B ≡ water

$L_{AB} = 2.257 \times 10^6 J/kg$ $\quad T = 373.15K$

$V_A = 1.673\ m^3/kg$

$V_B = 1.043 \times 10^{-3} m^3/kg$

$$\frac{dP}{dT} = 3.62 \times 10^3 Pa/K$$



Clausius - Clapeyron Equation - - approximate *P(T)* for liquid - gas coexistence

$$\frac{dP}{dT} = \frac{L_{AB}}{T(V_A - V_B)}$$

Example: A ≡ vapor B ≡⟹ water

$L_{AB} = 2.257 \times 10^6 J/kg = 40.7 \times 10^3 J/mole$ $\quad T \geq 373.15K$

$V_A \approx \frac{R_M T}{P}$ (per mole) $\quad R_M = kN_{Avo}$

$V_B \approx 0$

$$\frac{dP}{dT} = \frac{L_{AB}}{R_M} \frac{P}{T^2} \Rightarrow \frac{dP}{P} = \frac{L_{AB}}{R_M} \frac{dT}{T^2}$$

$$\ln(P) = \text{constant} - \frac{L_{AB}}{R_M T} \Rightarrow P(T) = P_0 e^{-L_{AB}/R_M T}$$

Approximate liquid-gas vaporization curve from Clausius-Clapeyron equation:

$$P(T) = P_0 e^{-L_{AB}/R_M T}$$