

PHY 341/641 Thermodynamics and Statistical Physics

Lecture 27

Chemical potentials and phase equilibria (Chapter 7 in STP)

- Van der Waals equation of state
- Chemical reactions

4/2/2012

PHY 341/641 Spring 2012 -- Lecture 27

1

	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)

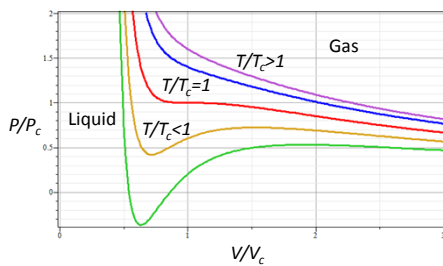
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2

van der Waals equation of state : $P = \frac{NkT}{(V - bN)} - a \frac{N^2}{V^2}$

$$P_c = \frac{a}{27b^2} \quad kT_c = \frac{8a}{27b} \quad V_c = 3bN$$



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3

Behavior of the thermodynamic potentials for the van der Waals equation of state

$$F = -NkT \ln(V - bN) - a \frac{N^2}{V} + NkTw(T)$$

Gibb's free energy :

$$G = F + PV = -NkT \ln(V - bN) - a \frac{N^2}{V} + PV + NkTw(T)$$

$$g = \frac{G}{N} = -kT \ln(V - bN) - a \frac{N}{V} + \frac{PV}{N} + kTw(T)$$

Note : In principle $g = g(P, T)$ so that we should eliminate the N and V dependence using the

$$\text{van der Waals equation of state : } P = \frac{NkT}{(V - bN)} - a \frac{N^2}{V^2}$$

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4

Behavior of the thermodynamic potentials for the van der Waals equation of state

Using scaled variables with

$$\tilde{g} \equiv \frac{G}{N} \frac{8}{3kT_c} = \frac{G}{N} \frac{9b}{a} \quad \tilde{P} \equiv 27 \left(\frac{b^2}{a} \right) P \quad \tilde{T} \equiv \frac{27}{8} \left(\frac{b}{a} \right) kT \quad \tilde{\rho} \equiv 3b \frac{N}{V}$$

$$G = F + PV = -NkT \ln(V - bN) - a \frac{N^2}{V} + PV + NkTw(T)$$

$$\tilde{g} = -\frac{8}{3} \tilde{T} \ln \left(\left(\frac{3}{\tilde{\rho}} - 1 \right) bN \right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w'(\tilde{T})$$

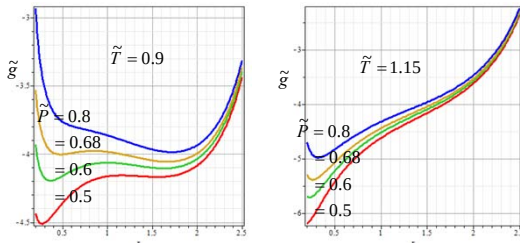
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5

Behavior of Gibbs chemical potential :

$$\begin{aligned} \tilde{g}(\tilde{T}, \tilde{P}, \tilde{\rho}) &= -\frac{8}{3} \tilde{T} \ln \left(\left(\frac{3}{\tilde{\rho}} - 1 \right) bN \right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w'(\tilde{T}) \\ &= -\frac{8}{3} \tilde{T} \ln \left(\frac{3}{\tilde{\rho}} - 1 \right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w''(\tilde{T}, N) \end{aligned}$$

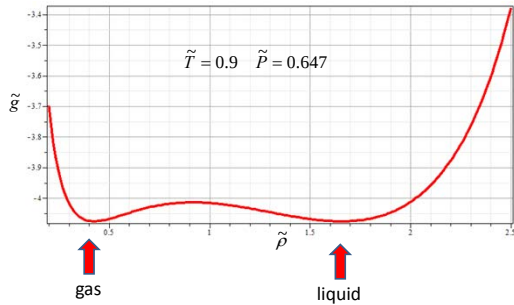


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6

Gibbs chemical potential at coexistence point



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7

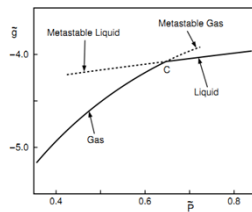


Figure 7.7: Plot of the dimensionless Gibbs free energy per particle $\tilde{g}$ as a function of $\tilde{P}$ at $T = 0.9T_c$ and fixed density. The system is metastable along the dashed curves.

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8

Analysis of gas-liquid coexistence conditions

General conditions on Gibbs free energy

$$dg(P, T) = \left(\frac{\partial g}{\partial P} \right)_T dP + \left(\frac{\partial g}{\partial T} \right)_P dT$$

$$\left(\frac{\partial g}{\partial P} \right)_T = \frac{V}{N} = \frac{1}{\rho}$$

When both liquid and gas phases are present at fixed T :

$$g(P_{liq}, T) - g(P_{gas}, T) = \int_{P_{gas}}^{P_{liq}} \left(\frac{\partial g}{\partial P} \right)_T dP = \int_{P_{gas}}^{P_{liq}} \frac{dP}{\rho}$$

Integrating by parts:

$$\int_{P_{gas}}^{P_{liq}} \frac{dP}{\rho} = \int_{P_{gas}}^{P_{liq}} \left(d \left(\frac{P}{\rho} \right) - P d \left(\frac{1}{\rho} \right) \right) = \frac{P(\rho_{liq}, T)}{\rho_{liq}} - \frac{P(\rho_{gas}, T)}{\rho_{gas}} - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} P dV$$

$$\Rightarrow g(P_{liq}, T) - g(P_{gas}, T) = \frac{P(\rho_{liq}, T)}{\rho_{liq}} - \frac{P(\rho_{gas}, T)}{\rho_{gas}} - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} P dV$$

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9

Analysis of gas-liquid coexistence conditions -- continued

On coexistence curve:

$$g(P_{liq}, T) - g(P_{gas}, T) = 0 \quad \text{and} \quad P = P_{liq} = P_{gas}$$

$$g(P_{liq}, T) - g(P_{gas}, T) = \frac{P(\rho_{liq}, T)}{\rho_{liq}} - \frac{P(\rho_{gas}, T)}{\rho_{gas}} - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} P dV$$

$$\Rightarrow \frac{P}{N} (V_{liq} - V_{gas}) - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} P dV = 0$$

4/2/2012

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10

$$\tilde{P}(\tilde{V}_{liq} - \tilde{V}_{gas}) - \int_{\tilde{V}_{gas}}^{\tilde{V}_{liq}} \tilde{P} d\tilde{V} = 0$$

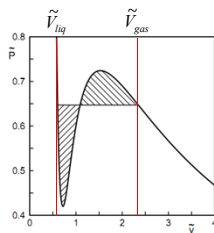


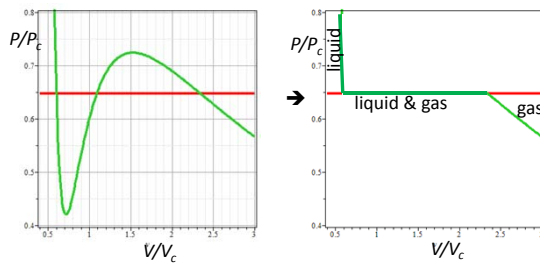
Figure 7.8: Maxwell equal area construction. The pressure $\tilde{P}$ where two phase coexistence begins for $\tilde{T} = 0.9$ is determined so that the areas above and below the horizontal line are equal. In this case $\tilde{P} \approx 0.647$.

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11

P-V diagram for van der Waals material at $T/T_c = 0.9$



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12

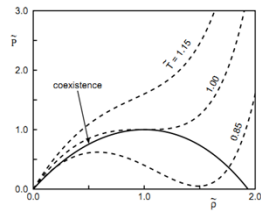


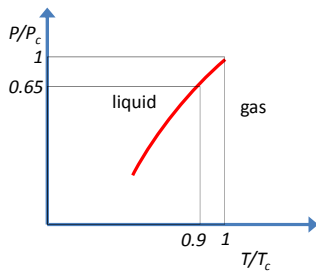
Figure 7.9: The coexistence curve for the van der Waals equation of state as a function of the dimensionless density $\tilde{\rho}$. Also plotted are three isotherms (dashed lines). For $\tilde{T} < 1$ the isotherms intersect the coexistence curve (solid line) at two points whose coordinates give the equilibrium values of $\tilde{P}$, $\tilde{\rho}_{\text{gas}}$, and $\tilde{\rho}_{\text{liq}}$. For $\tilde{T} = 1$ the isotherm intersects the coexistence curve at one point where $\tilde{P} = 1$ and $\tilde{\rho} = \tilde{\rho}_{\text{gas}} = \tilde{\rho}_{\text{liq}} = 1$.

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13

Phase diagram for van der Waals material



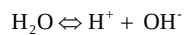
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14

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 : $\sum_i \mu_i dN_i = 0$

4/2/2012

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15