PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 18:

Thermodynamics of dilute solutions

Reading: Chapter 5.5

1. **Gibbs free energy of a dilute solution**
2. **Osmotic pressure**
3. **Solute effects on temperature of phase transitions**

Course schedule for Spring 2021

Reading assignments are for the **An Introduction to Thermal Physics** by Daniel V. Schroeder.

' assignment numbers refer to problems in that text if written in black and to original problems as describe

	Lecture date	Reading	Topic	HW	Due date
1	Wed: 01/27/2021	Chap. 1.1-1.3	Introduction and ideal gas equations	1.21	01/29/2021
2	Fri: 01/29/2021	Chap. 1.2-1.4	First law of thermodynamics	1.17	02/03/2021
3	Mon: 02/01/2021	Chap. 1.5-1.6	Work and heat for an ideal gas		
4	Wed: 02/03/2021	Chap. 1.1-1.6	Review of energy, heat, and work	1.45	02/05/2021
5	Fri: 02/05/2021	Chap. 2.1-2.2	Aspects of entropy		
6	Mon: 02/08/2021	Chap. 2.3-2.4	Multiplicity distributions	2.24	02/10/2021
7	Wed: 02/10/2021	Chap. 2.5-2.6	Entropy and macrostate multiplicity	2.26	02/12/2021
8	Fri: 02/12/2021	Chap. 2.1-2.6	Review of entropy and macrostates	2.32	02/15/2021
9	Mon: 02/15/2021	Chap. 3.1-3.2	Temperature, entropy, heat	3.10a-b	02/17/2021
10	Wed: 02/17/2021	Chap. 3.3-3.4	Temperature, entropy, heat	3.23	02/19/2021
11	Fri: 02/19/2021	Chap. 3.5-3.6	Temperature, entropy, heat	3.28	02/22/2021
12	Mon: 02/22/2021	Chap. 4.1-4.3	Ideal engines and refrigerators	4.1	02/24/2021
13	Wed: 02/24/2021	Chap. 4.3-4.4	Real engines and refrigerators	4.20	02/26/2021
14	Fri: 02/26/2021	Chap. 5.1	Free energy	5.5	03/01/2021
15	Mon: 03/01/2021	Chap. 5.1-5.2	Thermodynamic relations	1.46c-e	03/03/2021
16	Wed: 03/03/2021	Chap. 5.3	Phase transformations	3.33	03/05/2021
17	Fri: 03/05/2021	Chap. 5.4	Multicomponent systems	5.14a-e	03/08/2021
18	Mon: 03/08/2021	5.5	Dilute solutions	#16	03/10/2021
19	Wed: 03/10/2021	5.6	Chemical equilibria		
20	Fri: 03/12/2021	Chap. 1-5	Review		
	Mon: 03/15/2021	No class	*APS March Meeting*	Take Home Exam	

PHY 341/641 -- Assignment #16

March 8, 2021

Continue reading Chapter 5 in **Schroeder** .

1. Suppose you desolve 0.1 kilograms of KCl salt into 10 liters of pure water. Estimate the boiling point and freezing point of the solution measured at atmospheric pressure.

Your questions –

From Michael – Why do particles tend to flow towards lower chemical potentials?

From Kristen – 1. Does each type of solute have its own chemical potential (equation 5.72) that is independent of the solvent, or is it dependent? 2. I'm a bit confused about the derivations to obtain equations 5.86 and 5.9, could we go over them?

From Rich -- How would equation 5.72 (the one relating chemical potential to molality) change if we wanted to use molarity instead? -What approximation is used to move from 5.73 to 5.74?

From Chao -- When deriving formulas for entropy, why can we write microstate with only Avegadoro's Number, instead of a factorial expression?

From Parker -- how do you explain Raoult's Law?

Consider a system with N_A solvent particles and N_B solute particles with $N_A \gg N_B$.

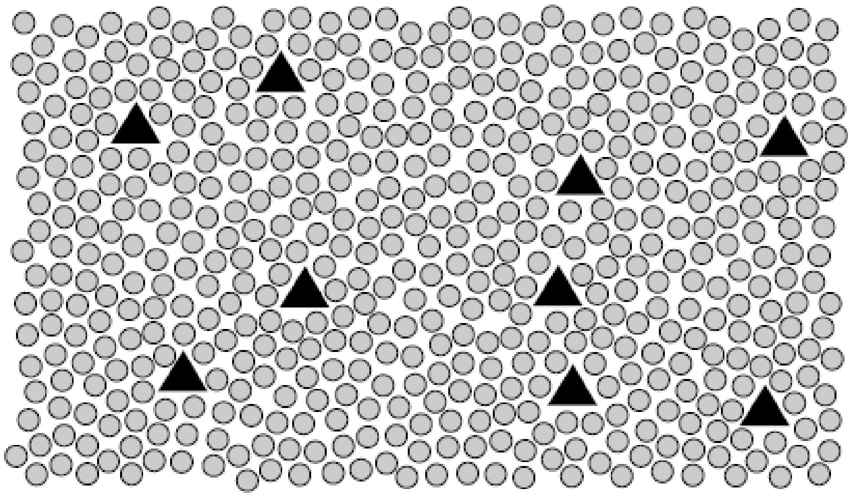


Figure 5.36. A dilute solution, in which the solute is much less abundant than the solvent. Copyright ©2000, Addison-Wesley.

Deduce the form of the Gibbs free energy of this system

$$G(T,P,N_A,N_B) = N_A \mu_{0A}(T,P) + N_B f(T,P) - TS_{solution}(N_A,N_B)$$

$$S_{solution}(N_A,N_B) \approx k_B \ln\left(\frac{N_A^{N_B}}{N_B!}\right) \approx k_B N_B \ln(N_A) - k_B N_B \left(\ln(N_B) - 1\right)$$

Gibbs free energy of dilute solution

$$G(T,P,N_A,N_B) = N_A\mu_{0A}(T,P) + N_B f(T,P) - TS_{solution}(N_A,N_B)$$

$$S_{solution}(N_A,N_B) \approx k_B N_B \ln(N_A) - k_B N_B \left(\ln(N_B) - 1\right)$$

Chemical potential of solvent:

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P,N_B} = \mu_{0A}(T,P) - k_B T \frac{N_B}{N_A}$$

Chemical potential of solute:

$$\mu_B = \left(\frac{\partial G}{\partial N_B}\right)_{T,P,N_A} = f(T,P) + k_B T \ln\left(\frac{N_B}{N_A}\right)$$

Consider the situation where a semi-permeable membrane separates pure solvent (left) from the dilute solution (right). Solvent can flow through membrane but solute cannot.

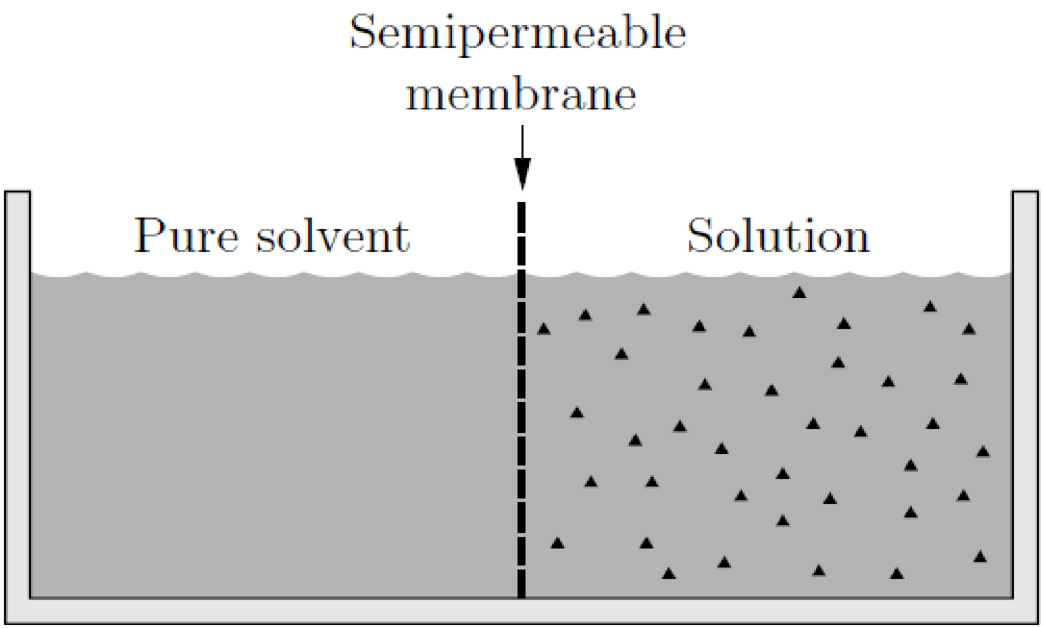


Figure 5.37. When a solution is separated by a semipermeable membrane from pure solvent at the same temperature and pressure, solvent will spontaneously flow into the solution. Copyright ©2000, Addison-Wesley.

What is the reason for solvent flowing?
When will it stop flowing?

Osmotic pressure

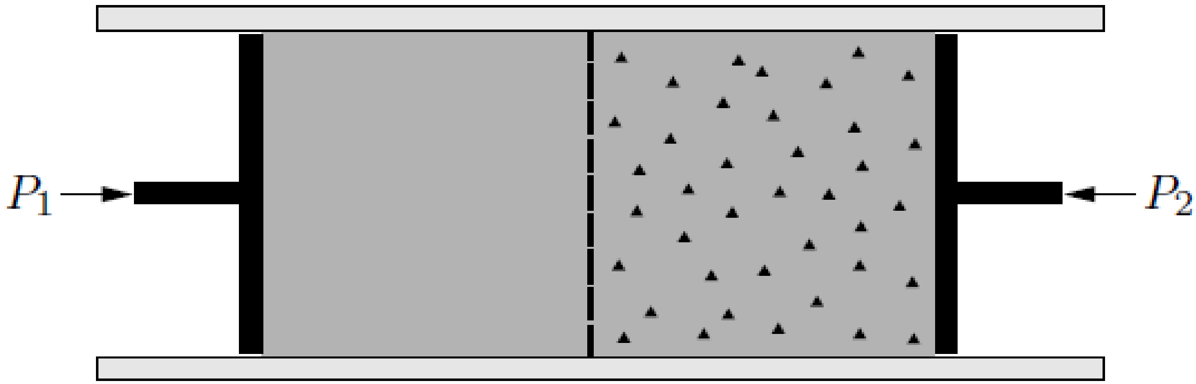


Figure 5.38. To prevent osmosis, P_2 must exceed P_1 by an amount called the **osmotic pressure**. Copyright ©2000, Addison-Wesley.

$$\mu_{0A}(T,P_1) = \mu_{0A}(T,P_2) - k_B T \frac{N_B}{N_A}$$

Approximately, $\mu_{0A}(T,P_2) \approx \mu_{0A}(T,P_1) + (P_2 - P_1)\dfrac{\partial \mu_{0A}}{\partial P}$

$$\Rightarrow (P_2 - P_1)\frac{\partial \mu_{0A}}{\partial P} \approx k_B T \frac{N_B}{N_A}$$

According to the Gibbs-Dunham relation: $\dfrac{\partial \mu_{0A}}{\partial P} = \dfrac{V_A}{N_A}$

$$\Rightarrow P_2 - P_1 \approx \frac{k_B T}{V_A / N_A}\frac{N_B}{N_A}$$

van't Hoff formula

Practical evaluations –

$Nk_B \rightarrow nR$

particles x Boltzmann constant → moles x Gas constant

van't Hoff formula --

$$P_2 - P_1 = \frac{n_B}{V_A} RT$$

Estimate from your textbook for cell stuff as a dilute solution:

$$\frac{n_B}{V_A} \approx 278 \text{ mol/m}^3$$

$$\Rightarrow P_2 - P_1 \approx 278 \text{ mol/m}^3 \times 8.3 \text{ J/(mol K)} \times 300 \text{ K} = 6.9 \times 10^5 \text{ Pa}$$

Liquid solutions and vapor pressure

Gas

Dilute solution

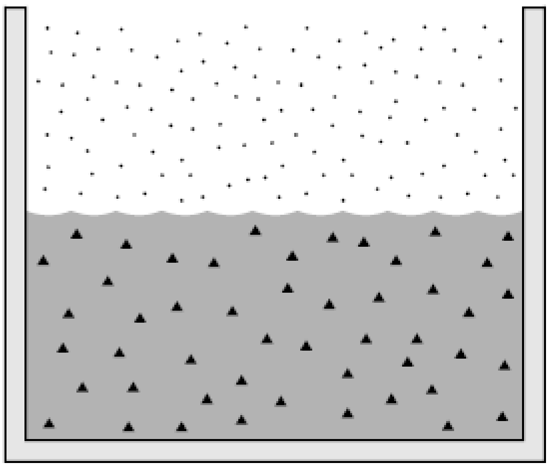
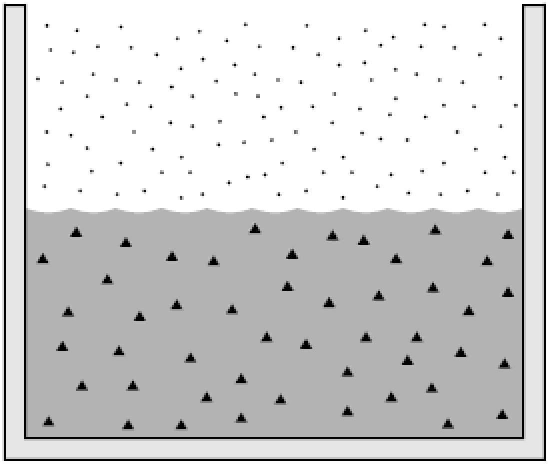


Figure 5.40. The presence of a solute reduces the tendency of a solvent to evaporate. Copyright ©2000, Addison-Wesley.

Assume that only A particles vaporize; compare the vapor composition above the dilute solution of B into A to that above pure A

Liquid solutions and vapor pressure



Focusing on A at equilibrium:

$$\mu_{A,liq}(T,P) = \mu_{A,gas}(T,P)$$

Dilute solution — Ideal gas

$$\mu_{0A}(T,P) - k_B T \frac{N_B}{N_A} \qquad \mu_{A,gas}(T,P)$$

Taylor expansion of both phases about a reference pressure P_0 and fixed T at which $\mu_{A,liq}(T,P_0) = \mu_{A,gas}(T,P_0)$

$$\mu_{0A}(T,P_0) + (P-P_0)\left(\frac{\partial \mu_{0A}}{\partial P}\right)_{liq} - k_B T \frac{N_B}{N_A} = \mu_{A,gas}(T,P_0) + (P-P_0)\left(\frac{\partial \mu_{A,gas}}{\partial P}\right)_{gas}$$

Liquid solutions and vapor pressure

$$\mu_{0A}(T,P_0)+(P-P_0)\left(\frac{\partial \mu_{0A}}{\partial P}\right)_{liq}-k_BT\frac{N_B}{N_A}=\mu_{A,gas}(T,P_0)+(P-P_0)\left(\frac{\partial \mu_{A,gas}}{\partial P}\right)_{gas}$$

Recall the Gibbs-Dunham relation for the liquid phase:

$$\frac{\partial \mu_{0\mathrm{A}}}{\partial P}=\frac{V}{N}$$

Recall the expression for the Gibbs free energy of a monoatomic ideal gas:

$$\mu_{\text{ideal gas}}=-k_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi M k_BT}{h^2}\right)^{3/2}\right)\right)$$

$$\frac{\partial \mu_{\text{ideal gas}}}{\partial P}=\frac{k_BT}{P}=\frac{V}{N}$$

$$(P-P_0)\left(\frac{V}{N}\right)_{liq}-k_BT\frac{N_B}{N_A}=(P-P_0)\left(\frac{V}{N}\right)_{gas}$$

$$\approx 0 \qquad\qquad =\frac{k_BT}{P_0}$$

Liquid solutions and vapor pressure

$$-k_B T \frac{N_B}{N_A} = (P - P_0)\left(\frac{k_B T}{P_0}\right)_{gas}$$

$$\Rightarrow P = P_0\left(1 - \frac{N_B}{N_A}\right)$$

Raoult's law
vapor pressure changes at constant T

Now consider temperature changes at constant P

$$\mu_{0A}(T_0, P) + (T - T_0)\left(\frac{\partial \mu_{0A}}{\partial T}\right)_{liq} - k_B T \frac{N_B}{N_A} = \mu_{A,gas}(T_0, P) + (T - T_0)\left(\frac{\partial \mu_{A,gas}}{\partial T}\right)_{gas}$$

Gibbs-Dunham relation: $\left(\frac{\partial \mu}{\partial T}\right)_{P,N} = -\frac{S}{N}$

$$-(T - T_0)\left(\frac{S}{N}\right)_{liq} - k_B T \frac{N_B}{N_A} = -(T - T_0)\left(\frac{S}{N}\right)_{gas}$$

Liquid solutions and vapor pressure – effects on phase change temperature

From previous slide:

$$\mu_{0A}(T_0,P)+(T-T_0)\left(\frac{\partial\mu_{0A}}{\partial T}\right)_{liq}-k_BT\frac{N_B}{N_A}=\mu_{A,gas}(T_0,P)+(T-T_0)\left(\frac{\partial\mu_{A,gas}}{\partial T}\right)_{gas}$$

Gibbs-Dunham relation: $\left(\frac{\partial\mu}{\partial T}\right)_{P,N}=-\frac{S}{N}$

$$-(T-T_0)\left(\frac{S}{N}\right)_{liq}-k_BT\frac{N_B}{N_A}=-(T-T_0)\left(\frac{S}{N}\right)_{gas}$$

Now suppose that $N\to N_A$ for both phases

$$(T-T_0)\left(S_{gas}-S_{liq}\right)=k_BT_0N_B$$

Latent heat: $L=T_0\left(S_{gas}-S_{liq}\right)$

$$\Rightarrow T=T_0+\frac{k_BT_0^2N_B}{L}$$

Liquid solutions and vapor pressure – effects on phase change temperature

In terms of Latent heat: $L = T_0 \left(S_{gas} - S_{liq} \right)$

$$\Rightarrow T = T_0 + \frac{k_B T_0^2 N_B}{L} = T_0 + \frac{R T_0^2 n_B}{L}$$

Example: Boiling temperature of sea water

$T_0 = 373K$

$L = 2260 \text{ kJ/kg} \qquad n_B \approx 1.2 \text{ moles/kg}$

$T \approx 373.6K$