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

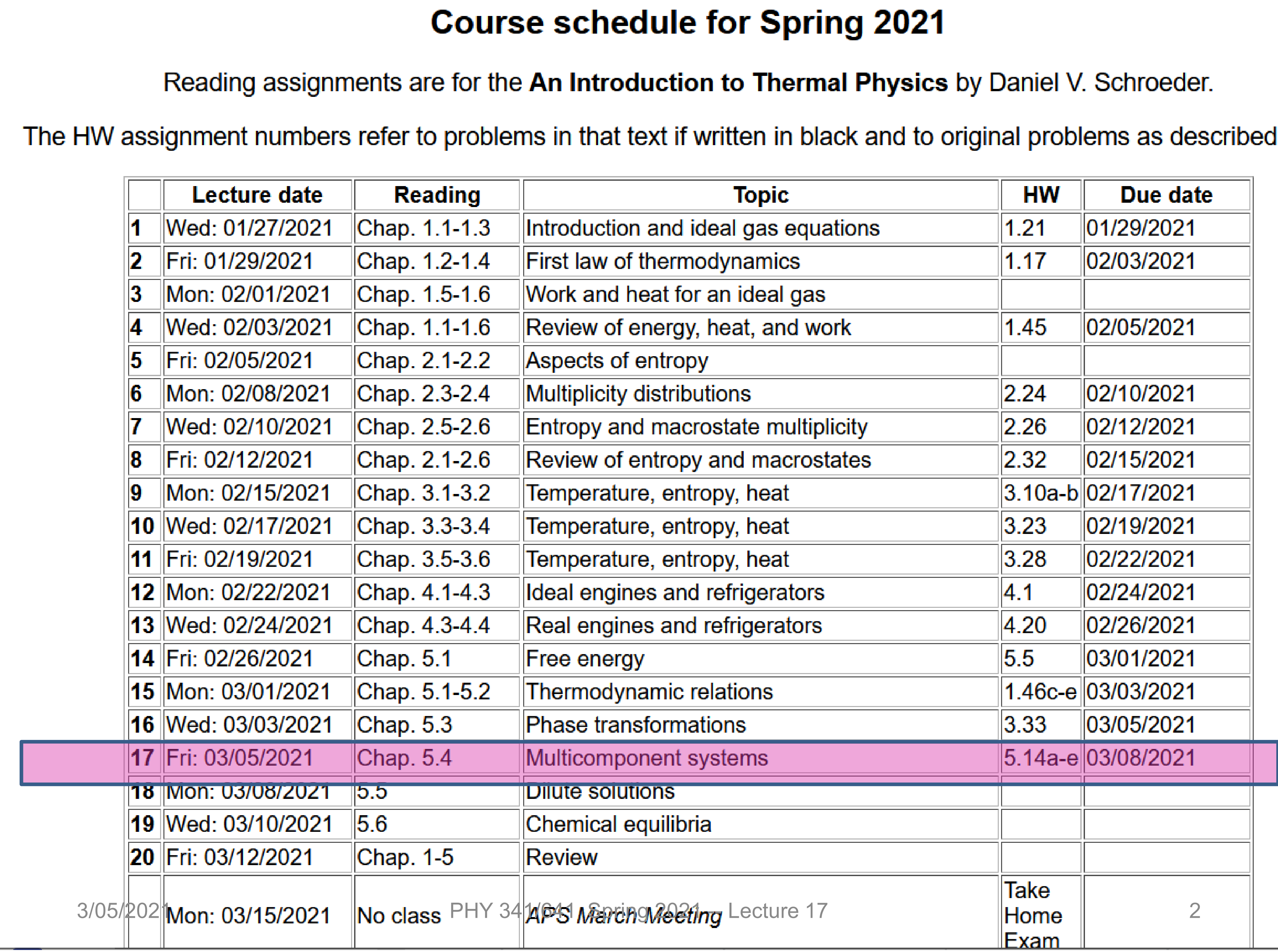
Record!!!

Discussion for Lecture 17:

Thermodynamics multicomponent systems

Reading: Chapter 5.4

1. **Thermodynamic energies for multicomponent systems**
2. **Thermodynamics of mixing**
3. **Some phase diagrams**



Course schedule for Spring 2021

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

The HW assignment numbers refer to problems in that text if written in black and to original problems as described

	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		
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	

Your questions –

From Parker – What is a Eutectic System?

From Kristen – 1. Could you explain in more detail the "competition in G" as shown in figure 5.26? 2. What exactly is an "impurity molecule"? 3. I'm a bit confused about what happens in the center of a phase diagram with two curves, such as figure 5.31.

From Michael – Can you please expand on the solubility gap and what exactly this means, specifically on a graph? Do all mixtures of two substances have a solubility gap?

From Noah – Can you explain eutectic points? I am confused because the book initially says the stable configuration is the unmixed solids, but then goes on to say that a liquid near the eutectic point is stable because it has more mixing entropy than unmixed solids.

Generalizing the thermodynamic functions for a single component system --

Internal energy $U = U(S, V, N)$ $dU = TdS - PdV + \mu dN$

Entropy $S = S(U, V, N)$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

Enthalpy $H = H(S, P, N) = U + PV$ $dH = TdS + VdP + \mu dN$

Helmholtz energy $F = F(T, V, N) = U - ST$ $dF = -SdT - PdV + \mu dN$

Gibbs free energy $G = G(T, P, N) = F + PV$ $dG = -SdT + VdP + \mu dN$

It is useful to consider systems containing several components $N \rightarrow N_1, N_2, ...$ where N_i denotes particles of type "i". For the moment, we are assuming that no reactions (chemical, nuclear, etc.) occur.

Generalizing thermodynamic functions to multi-component systems --

It is useful to consider systems containing several components $N \rightarrow N_1, N_2, \ldots$ where N_i denotes particles of type "i". For the moment, we are assuming that no reactions (chemical, nuclear, etc.) occur.

Entropy: $S(U, V, N_1, N_2, \ldots)$ $\quad dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dN_i$ where $T\left(\frac{\partial S}{\partial N_i}\right)_{U,V,\{N_j j\neq i\}} = \mu_i$

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,\{N_j j\neq i\}} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,\{N_j j\neq i\}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,\{N_j j\neq i\}} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,\{N_j j\neq i\}}$$

Internal energy $\quad U = U(S, V, \{N_i\}) \quad dU = TdS - PdV + \sum_i \mu_i dN_i$

Enthalpy $\quad H = H(S, P, \{N_i\}) = U + PV \quad dH = TdS + VdP + \sum_i \mu_i dN_i$

Helmholtz energy $\quad F = F(T, V, \{N_i\}) = U - ST \quad dF = -SdT - PdV + \sum_i \mu_i dN_i$

Gibbs free energy $\quad G = G(T, P, \{N_i\}) = F + PV \quad dG = -SdT + VdP + \sum_i \mu_i dN_i$

Thermodynamics of mixing -- first consider a two-component (binary) system $N_A=N(1-x)$ $N_B=xN$

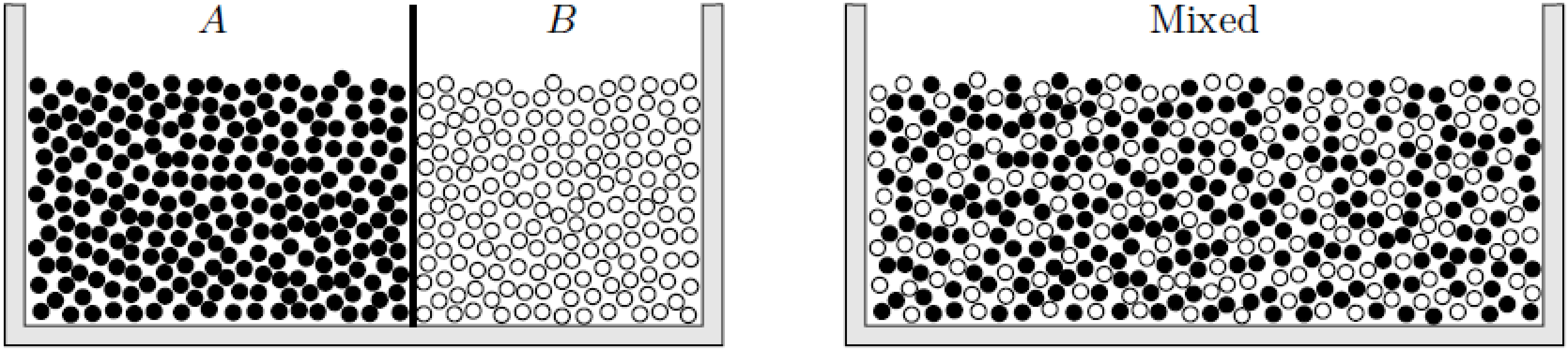


Figure 5.24. A collection of two types of molecules, before and after mixing. Copyright ©2000, Addison-Wesley.

Separated system

$$G(T,P,N,x)=(1-x)G_A(T,P,(1-x)N)+xG_B(T,P,xN)$$

Mixed system depends on details of system even if no chemical reactions occur.

Possible mixing behaviors.

Consider the case of the monoatomic ideal gas for which we derived the Gibbs free energy expression:

$$G(T,P,N) = -Nk_BT\left(\ln\left(\frac{k_BT}{P}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)\right) = -Nk_BT\ln\left(\frac{T^{5/2}}{P}\right) + G_0$$

T and P independent constant

For binary example --

For the case of separated gases, both at pressure P:

$$G_{separated} = -Nk_BT\ln\left(\frac{T^{5/2}}{P}\right) + (1-x)G_{0A} + xG_{0B}$$

Notion of partial pressure when the gases are mixed -- $P_A + P_B = P$

$P_A = (1-x)P \qquad P_B = xP$

$$G_{mixed} = -(1-x)Nk_BT\ln\left(\frac{T^{5/2}}{(1-x)P}\right) - xNk_BT\ln\left(\frac{T^{5/2}}{xP}\right) + (1-x)G_{0A} + xG_{0B}$$

$$G_{mixed} - G_{separated} = Nk_BT\left(\left(1-x\right)\ln(1-x) + x\ln x\right)$$

Also note that $S_{mixed} - S_{separated} = -\left(\frac{\partial\left(G_{mixed} - G_{separated}\right)}{\partial T}\right)_{P,N,x}$

$$= -Nk_B\left(\left(1-x\right)\ln(1-x) + x\ln x\right)$$

Ideal mixing of binary system --

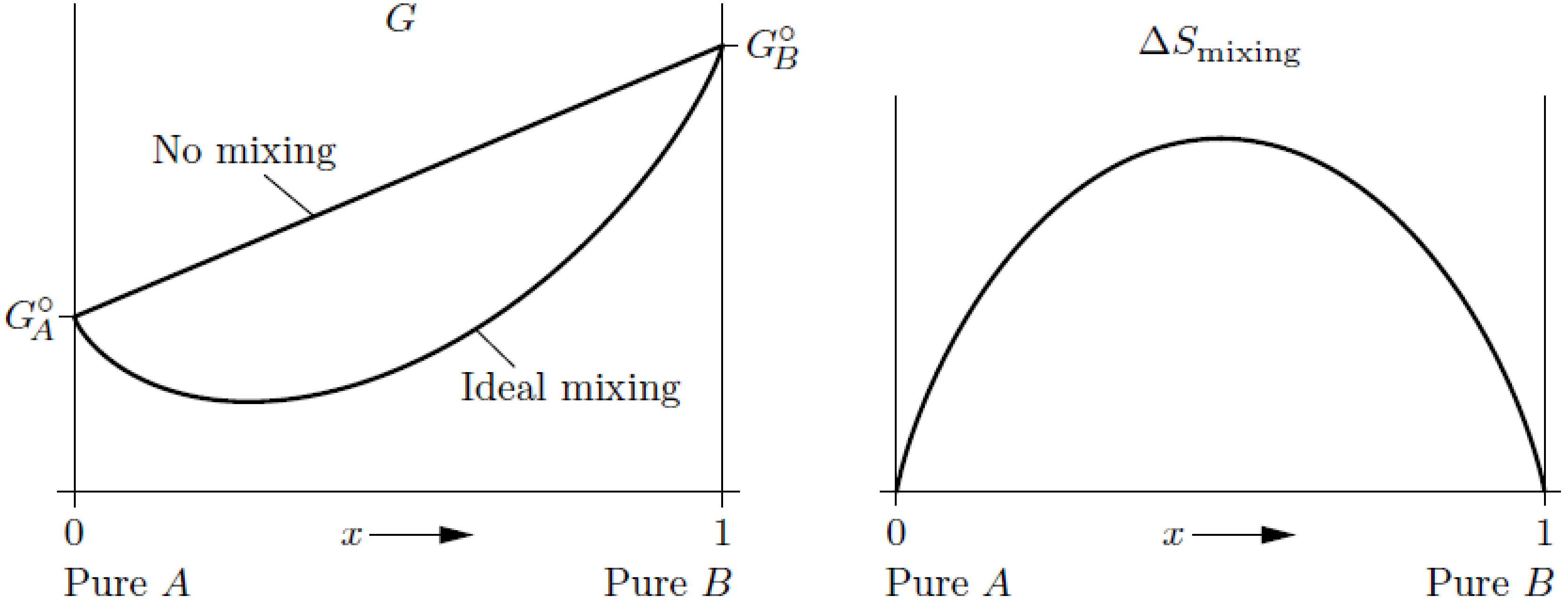
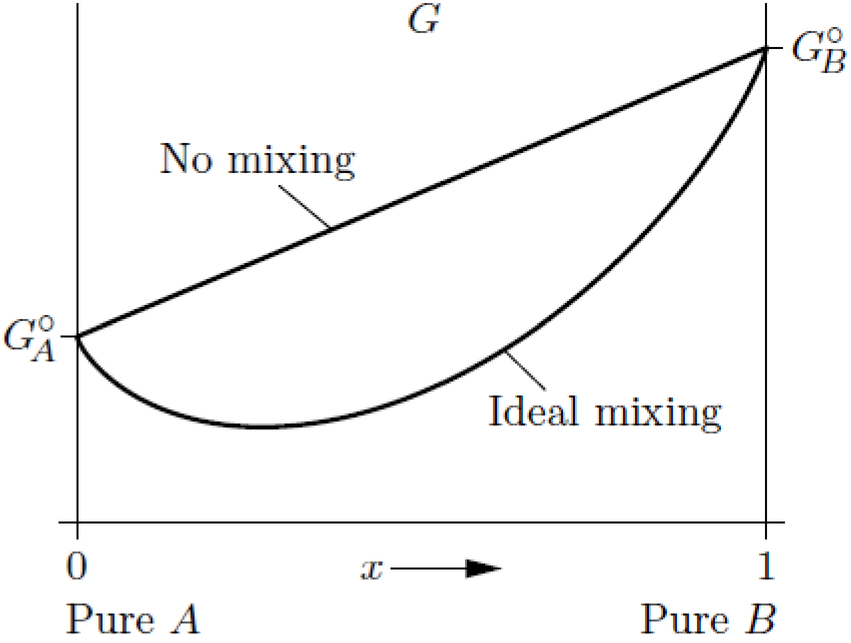


Figure 5.25. Before mixing, the free energy of a collection of A and B molecules is a linear function of $x = N_B/(N_A + N_B)$. After mixing it is a more complicated function; shown here is the case of an "ideal" mixture, whose entropy of mixing is shown at right. Although it isn't obvious on this scale, the graphs of both ΔS_{mixing} and G (after mixing) have vertical slopes at the endpoints. Copyright ©2000, Addison-Wesley.



Given these plots, which configuration is more favorable?

a. A and B separate
b. A and B ideally mixed

Experimentally, it is found that real systems are more complicated

Gibbs free energy diagram of a more complicated mixture

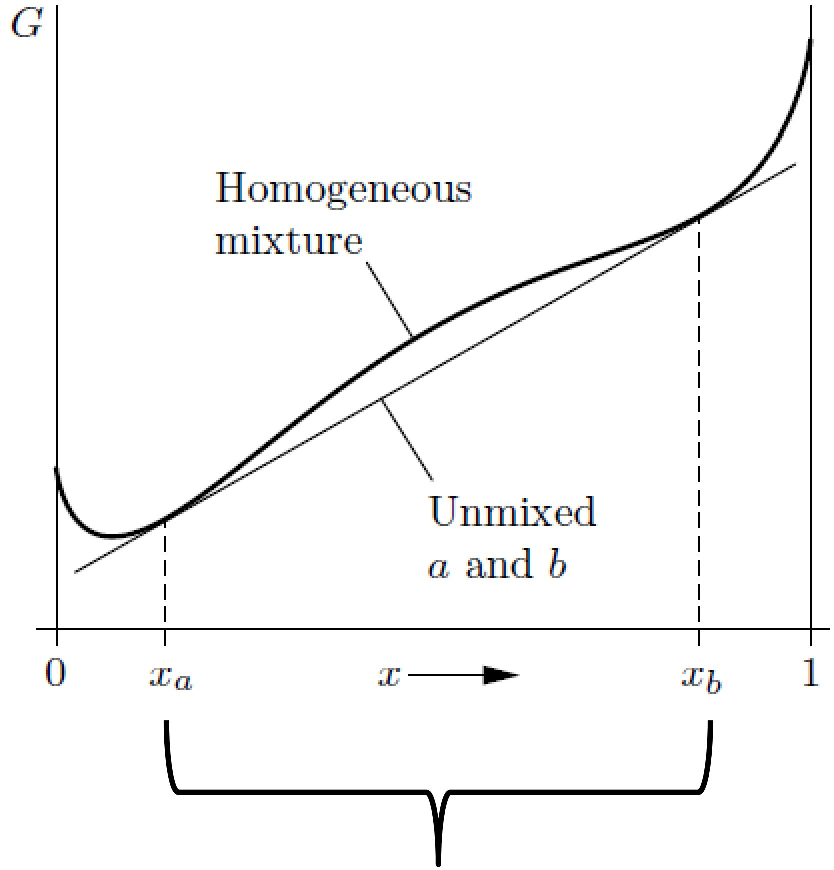


Figure 5.27. To construct the equilibrium free energy curve, draw the lowest possible straight line across the concave-down section, tangent to the curve at both ends. At compositions between the tangent points the mixture will spontaneously separate into phases whose compositions are x_a and x_b, in order to lower its free energy. Copyright ©2000, Addison-Wesley.

At these compositions, separated phases are more stable

Gibbs free energy diagram of a binary mixture based on two crystalline phases α and β

Figure 5.29. Free energy graphs for a mixture of two solids with different crystal structures, α and β. Again, the lowest possible straight connecting line indicates the range of compositions where an unmixed combination of a and b phases is more stable than a homogeneous mixture. Copyright ©2000, Addison-Wesley.

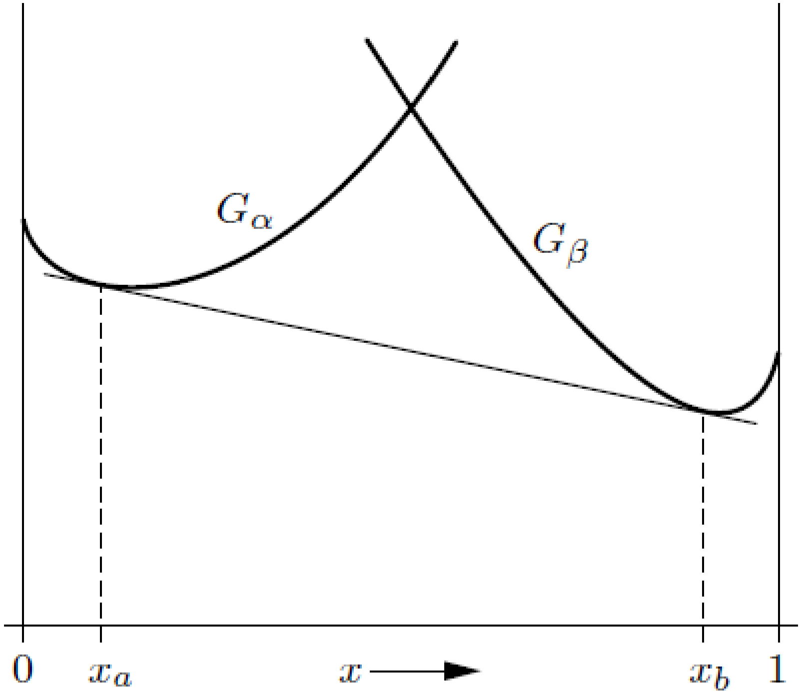


Image of oil and water, example of immicible liquids

Some details from your textbook –

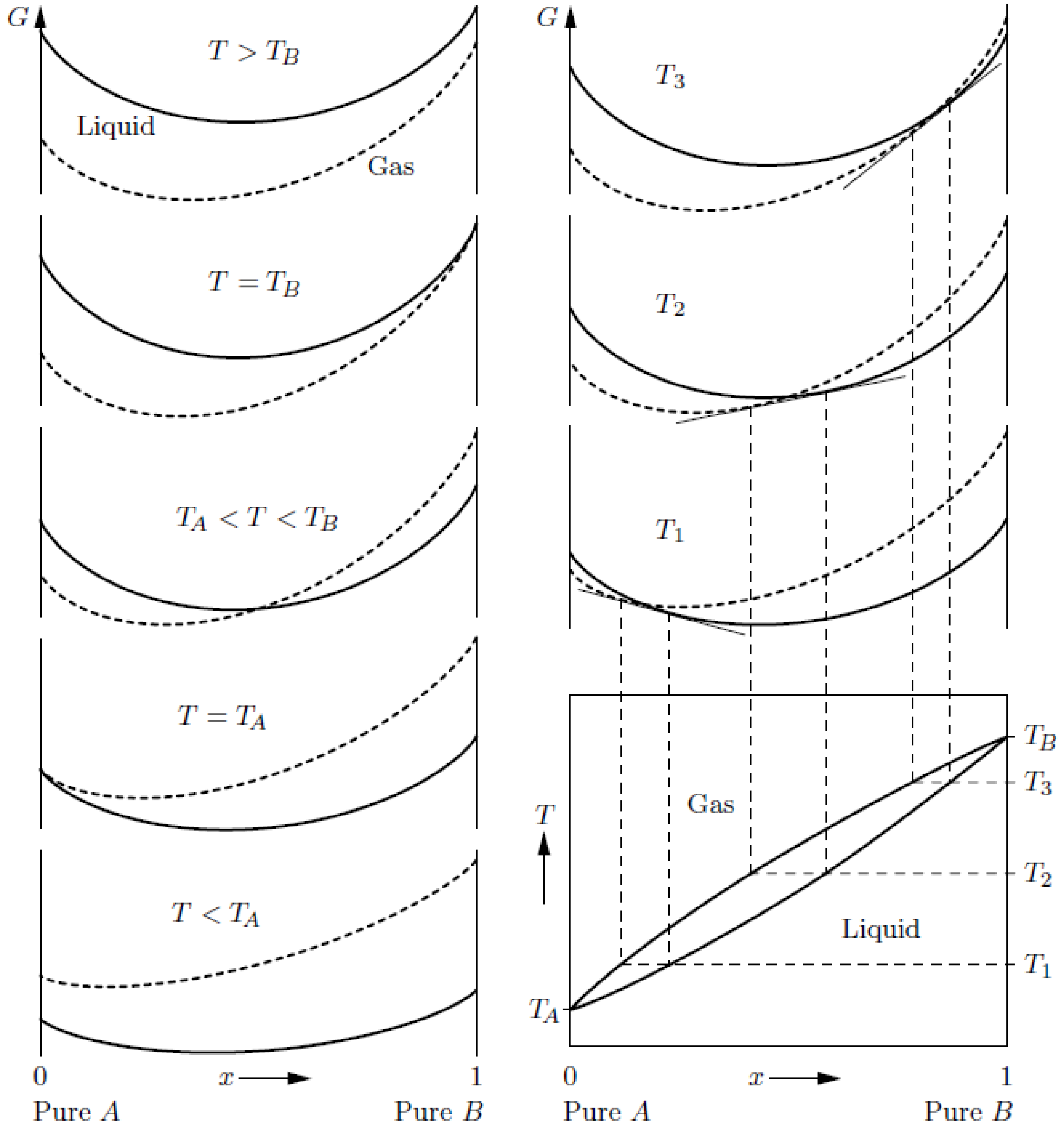


Figure 5.30. The five graphs at left show the liquid and gas free energies of an ideal mixture at temperatures above, below, at, and between the boiling points T_A and T_B. Three graphs at intermediate temperatures are shown at right, along with the construction of the phase diagram. Copyright ©2000, Addison-Wesley.

Example of $(1-x)N_2$ and xO_2 mixture at atmospheric pressure

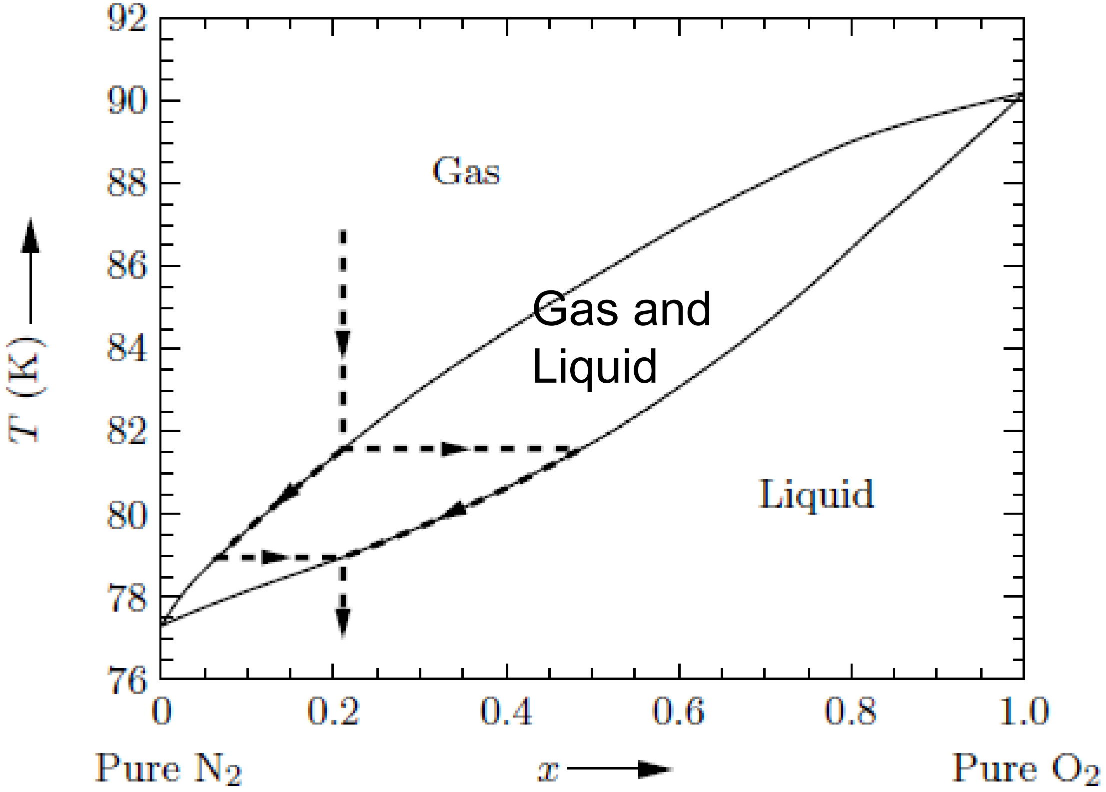


Figure 5.31. Experimental phase diagram for nitrogen and oxygen at atmospheric pressure. Data from *International Critical Tables* (volume 3), with endpoints adjusted to values in Lide (1994). Copyright ©2000, Addison-Wesley.

More complicated systems

This system has an “eutectic” point which is observed to have the lowest solid-liquid melting temperature at a specific composition.

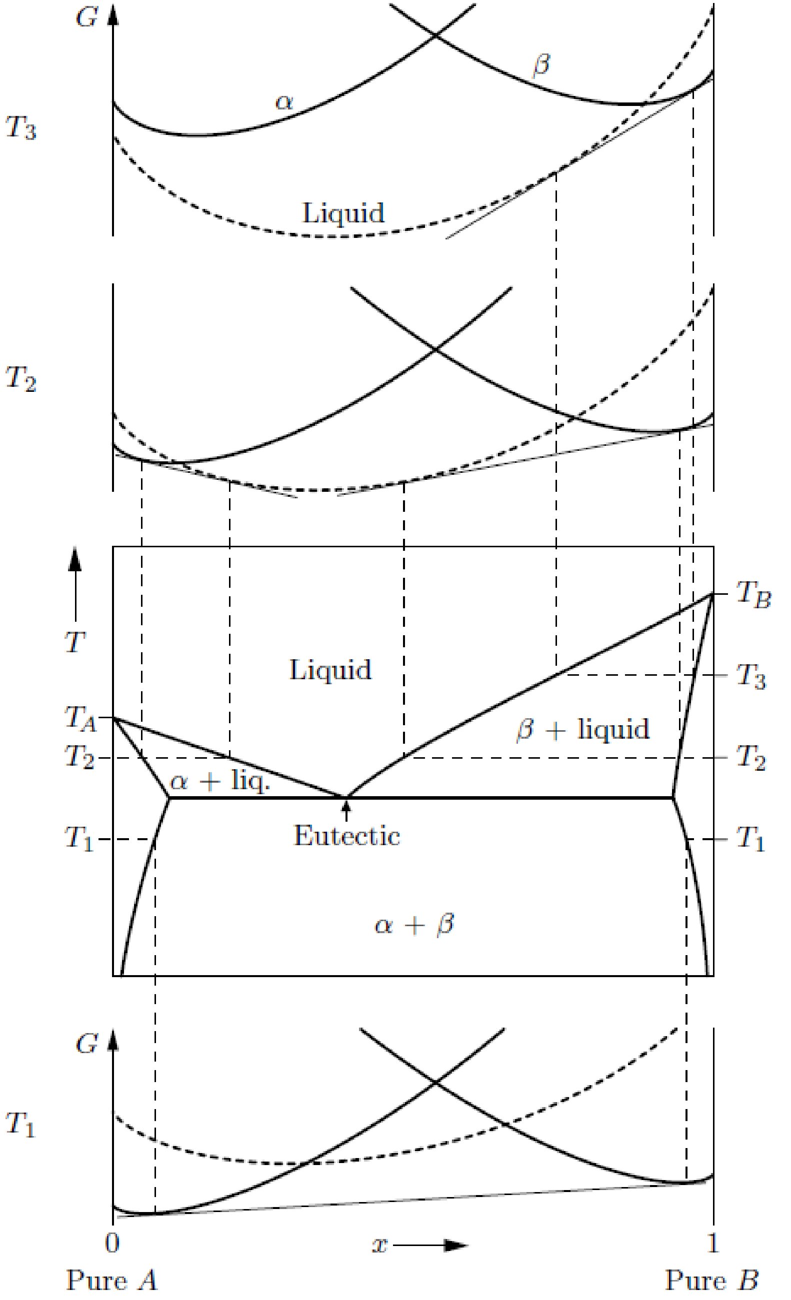


Figure 5.33. Construction of the phase diagram of a eutectic system from free energy graphs. Copyright ©2000, Addison-Wesley.

Phase diagram of tin and lead --

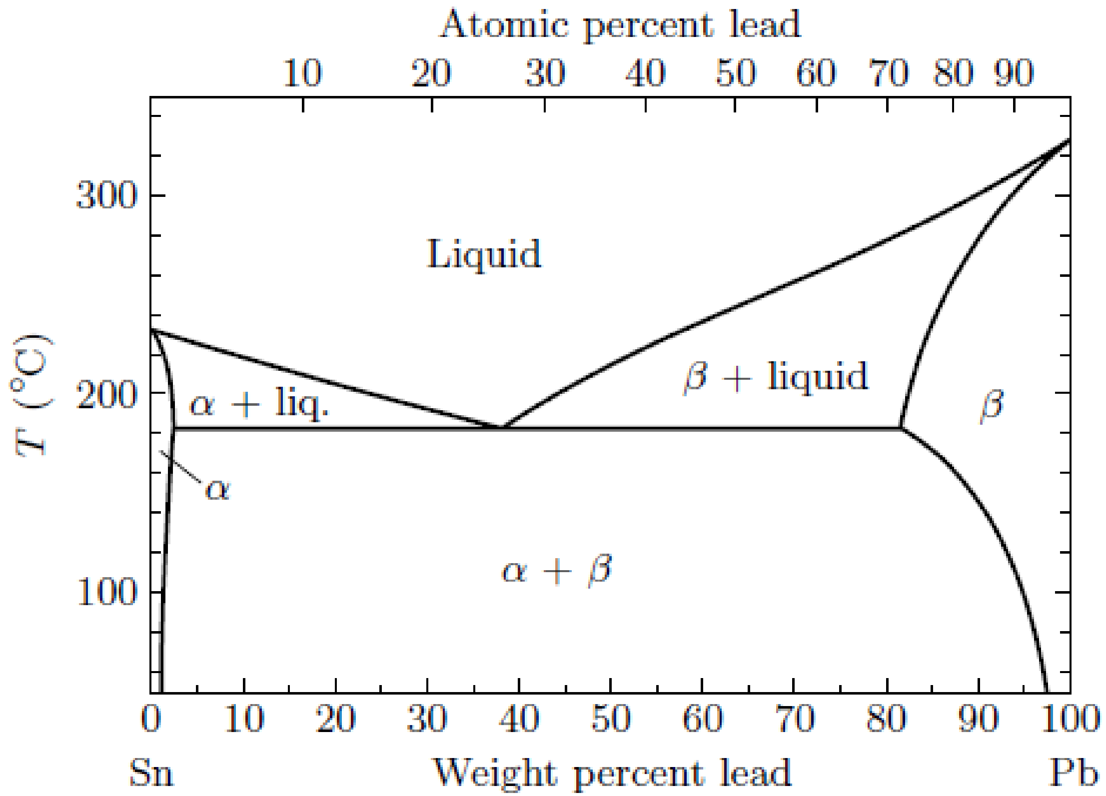


Figure 5.34. Phase diagram for mixtures of tin and lead. From Thaddeus B. Massalski, ed., *Binary Alloy Phase Diagrams*, second edition (ASM International, Materials Park, OH, 1990). Copyright ©2000, Addison-Wesley.

Example from recent Literature from Toyota Research Lab 2015 – looking for solid state electrolytes

DOI: 10.1111/jace.13694

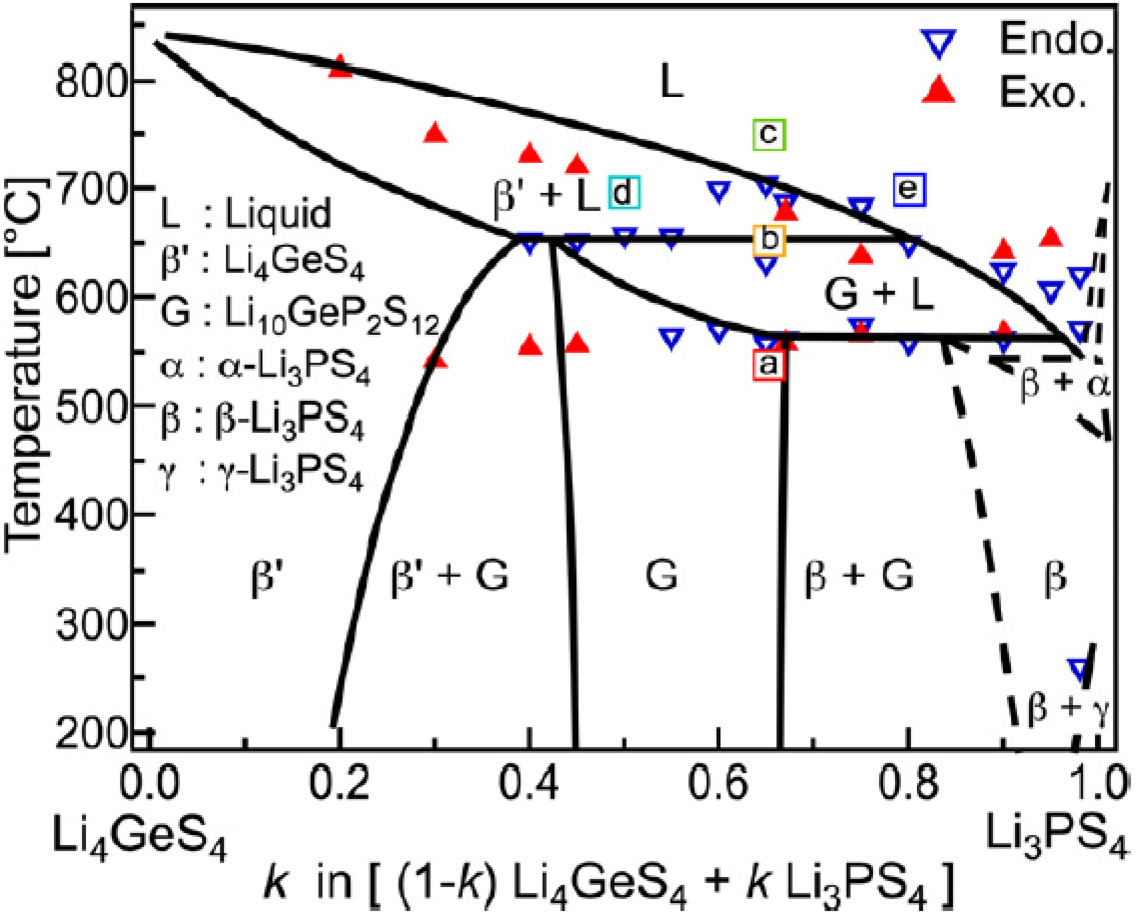


Fig. 1. Phase diagram for the $[(1-k)\ Li_4GeS_4 + k\ Li_3PS_4]$ system. Empty and solid triangles respectively indicate endo- and exothermic reaction temperatures determined from DTA data. Phase boundaries indicated by dotted lines are assumed from experimental results but were not as evident as those shown by solid lines. The symbols in boxes a-e indicate the corresponding SEM image in Fig. 9.

Which of these factors determine the mixing properties of materials?

A. Statistics and probability
B. Forces between particles of the same type
C. Forces between particles of the opposite type
D. Temperature
E. Pressure
F. Other