MSE-204 Thermodynamics for Materials Science

L10 Summary

Thermodynamic Laws | Auxiliary Functions | Pure Substances & Multicomponent Systems

Thermodynamics of Gases | Single Component Phase Diagrams | Ideal and Regular Solutions

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THERMODYNAMIC LAWS

Zeroth Law:

First Law:

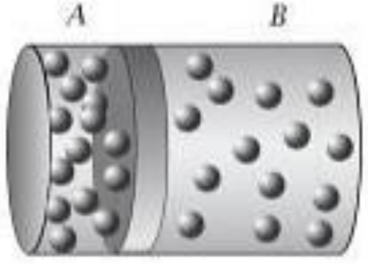
Second Law:

Third Law:

EXAMPLE | HOW DOES A VOLUME CHANGE MAXIMIZE ENTROPY?

Consider a cylinder partitioned in subsystems A and B by a movable, diathermal piston containing an ideal gas.

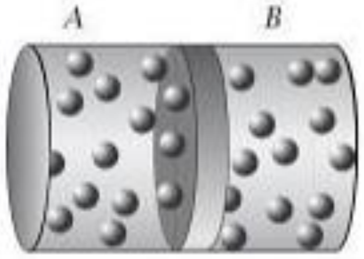
The system is isolated and there is no heat exchange between the subsystems.



Let's find the characteristic variables of the entropy of each subsystem.

Subsystem A has entropy $S_A(U_A, V_A)$ and subsystem B has entropy $S_B(U_B, V_B)$.

Now, allow subsystems A and B to exchange volume, and allow the system to reach equilibrium.



Calculate the change of entropy of the system.

EXAMPLE | WORK IN A REVERSIBLE PROCESS

a. One mole of an ideal gas at 298 K is expanded ***reversibly and isothermally*** from 1.0 L to 10 L. Determine the amount of work in Joule.

EXAMPLE | WORK IN AN IRREVERSIBLE PROCESS

b. One mole of an ideal gas at 298 K is expanded ***irreversibly*** from 1.0 L to 10 L against a ***constant external pressure*** of 1 atm.
Determine the amount of work in Joule.

EXAMPLE | TEA COOLING IN ROOM TEMPERATURE

Sylvie is making a cup of tea. The tea contains 500 grams of water initially at a temperature of 100ºC. While waiting for the tea to cool down, she falls asleep. When she wakes up, the tea is at the room temperature of 20ºC. The temperature of the room has hardly changed. How much has the change of entropy of the universe increased?
Data: the specific heat capacity of water is 4186 J/kg K

AUXILIARY FUNCTIONS

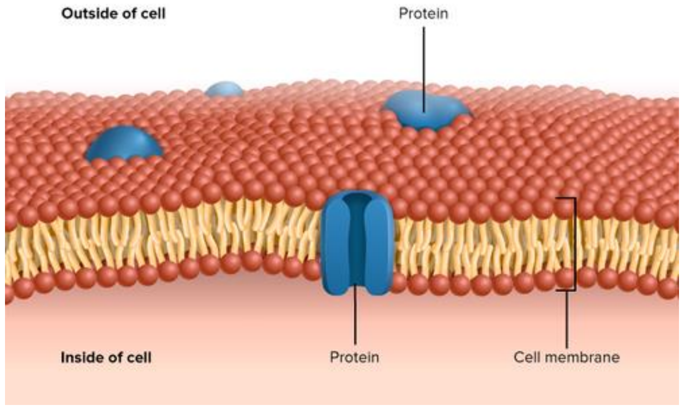
Fundamental Equation of State of a Thermodynamic System with only volume work:

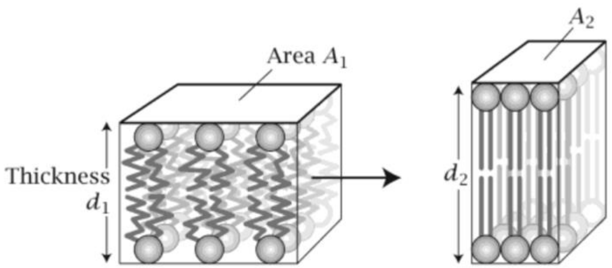
$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

EXAMPLE | SURFACE WORK

Cell membranes are composed of two opposing monolayers of lipid molecules. Lipid bilayers and monolayers have the ability to change their surface area per lipid molecule, *A*, even when temperature, pressure, and the number of molecules are fixed. A lipid bilayer adjust its surface area to have an equilibrium area per molecule *A*=*A**, that minimizes the energy function.

a. Write an expression for the variation of the internal energy.
b. Write an expression for the variation of the Gibbs free energy.
b. Find a Maxwell relation to express $\left(\frac{\partial S}{\partial A}\right)_{T,p,n_i}$ in terms of T.





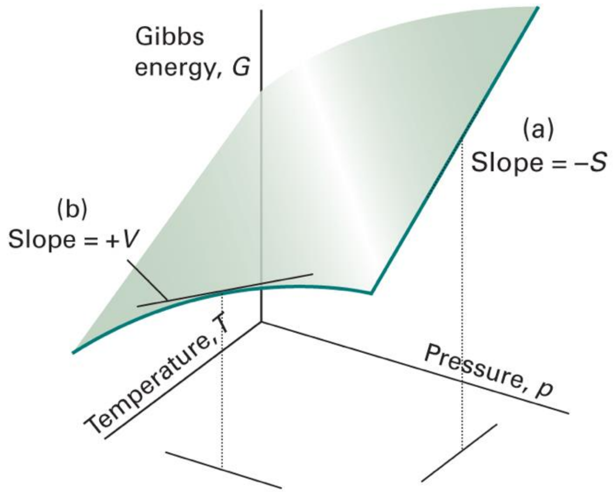
EXAMPLE | FINDING A FUNDAMENTAL EQUATION

While the Gibbs free energy is the fundamental function of the characteristic variables (T, p, n), growing biological cells often regulate not the numbers of molecules but the chemical potential. That is, they control concentrations. What is the fundamental equation for state function Z of characteristic variables (T, p, μ)?

PURE SUBSTANCES & MULTICOMPONENT SYSTEMS

Thermodynamics of Gases and Condensed Phases

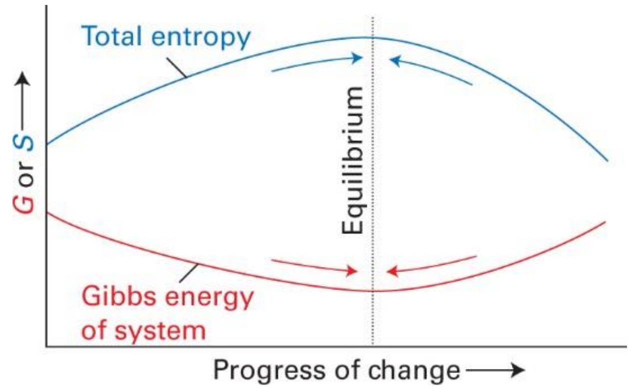
$$dU = TdS - pdV + \sum_i \mu_i dn_i\,, \qquad dS = \frac{\delta q}{T}\,,$$



$$\Delta G = \Delta H - T\Delta S, \qquad dG = -SdT + Vdp + \sum_i \mu_i dn_i\,, \qquad \mu = g, \qquad \mu_i = \bar{G}_i$$

Pure Ideal Gas:

Mixtures of ideal gases:

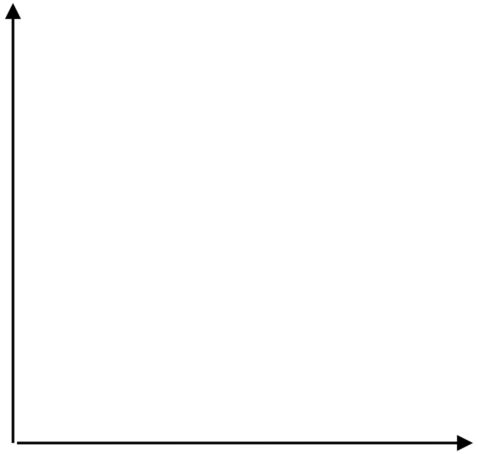


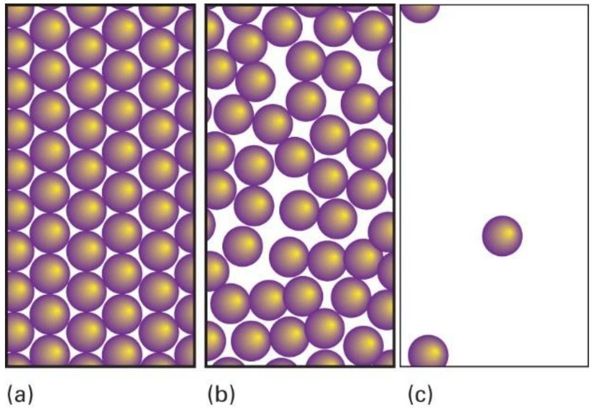
Real gases:

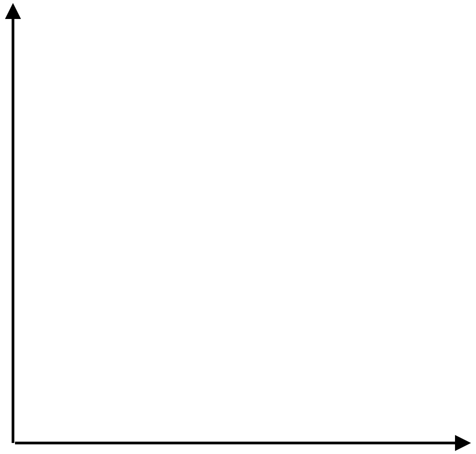
Mixtures/solutions of condensed phases:

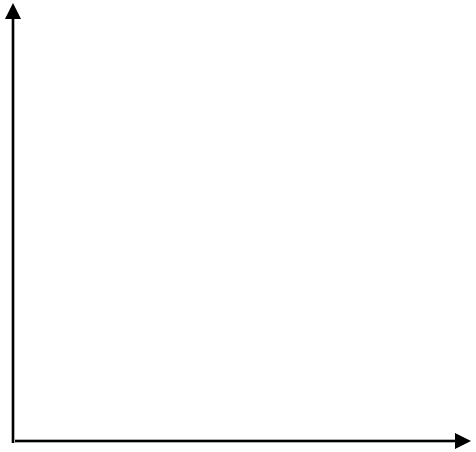
For many phases:

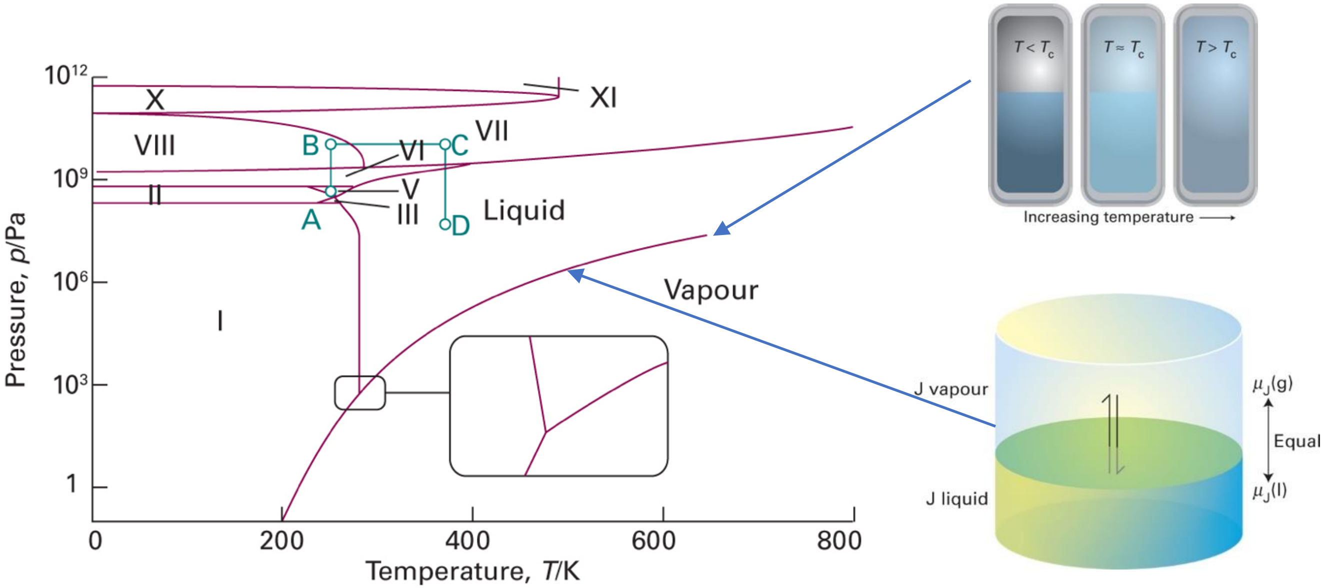
Single Component Phase Diagrams

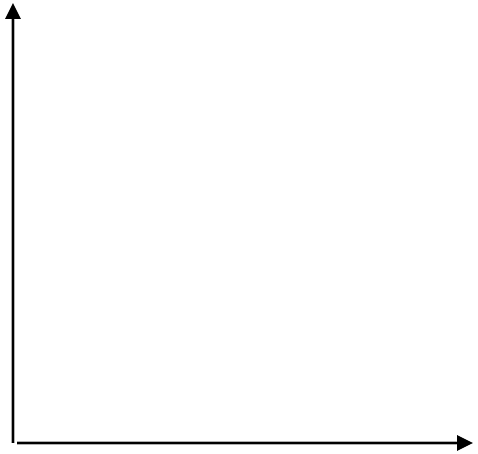






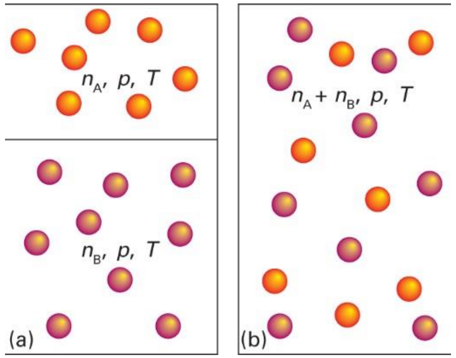


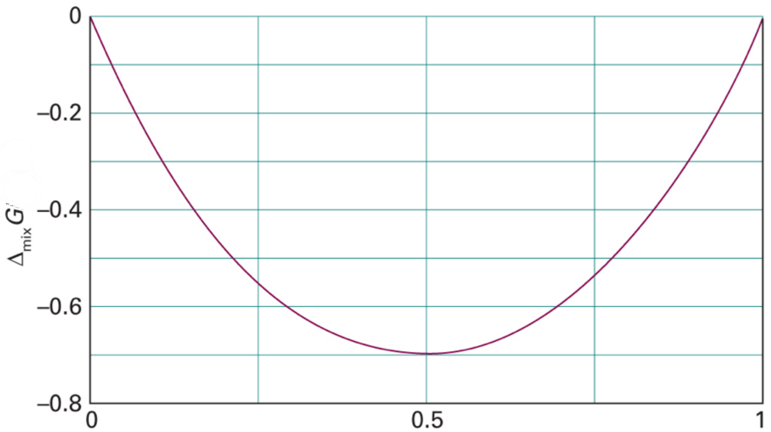


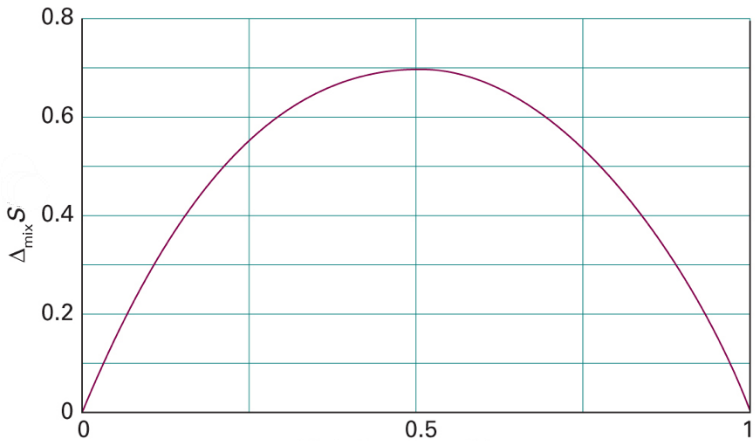


Ideal Solutions of Gaseous and Condensed Phases

Assumptions:

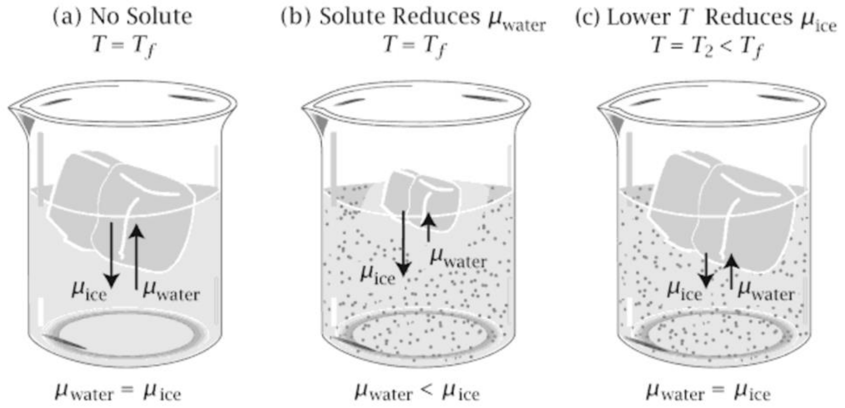






IDEAL SOLUTIONS | TRANSFER OF MOLECULES BETWEEN PHASES

Depression of freezing point with addition of salt



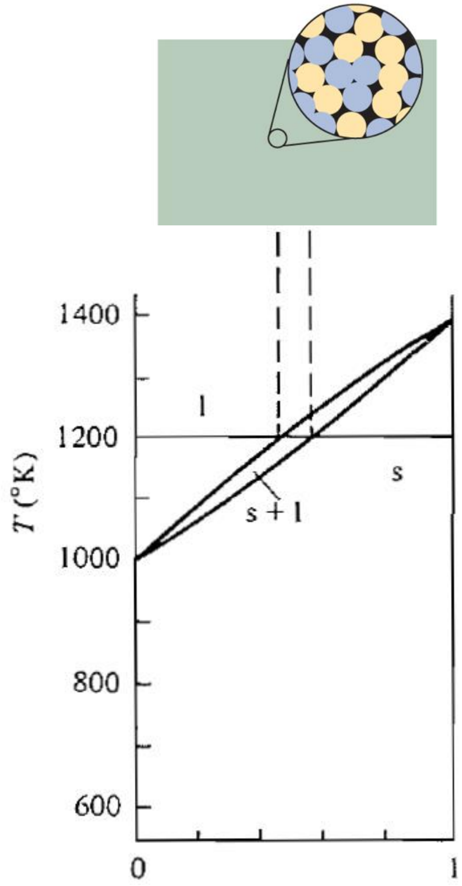
$$\mu_{water\ in\ solution} = \mu^*_{pure\ water} + RT \ln x_{water\ in\ solution}$$

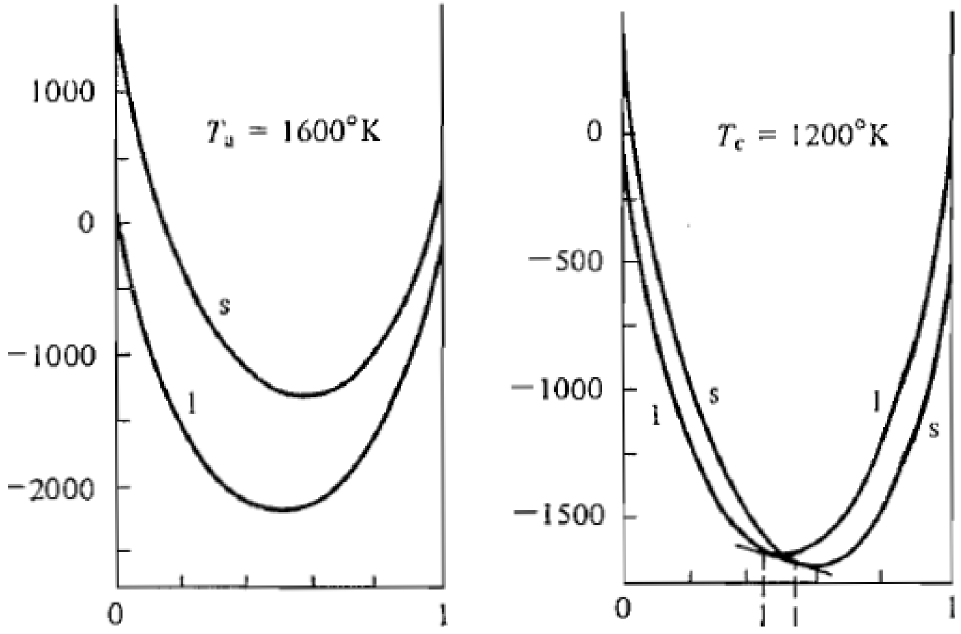
The mechanism of anesthetic drugs. Anesthetic drug action is thought to involve the solubility of an anesthetic in the hydrocarbon region of the lipid bilayer of biological membranes. It is said that anesthesia occurs whenever the concentration of a drug is greater that 0.03 mol/kg per membrane, no matter what the anesthetic.

Lipid bilayers "melt" from a solid-like state to a liquid-like state.

Do you expect introduction of the anesthetic to increase, decrease, or not change the melting temperature?

Ideal Solutions



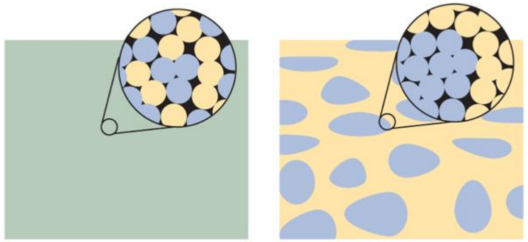


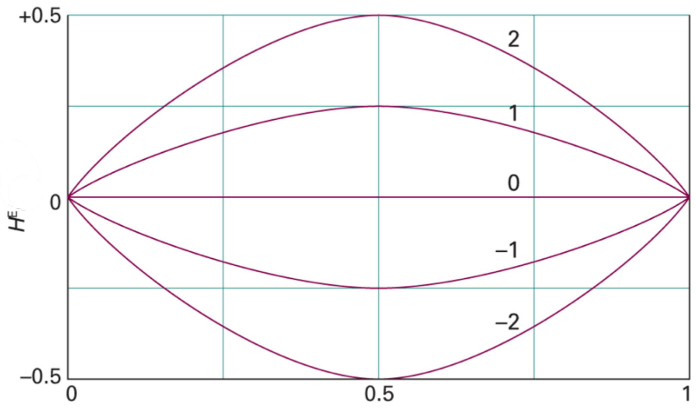
$T_{f,A} = 1000\ °\text{K},$ $\Delta H^{\circ}_{f,A} = 2300\ \text{cal/mol}$

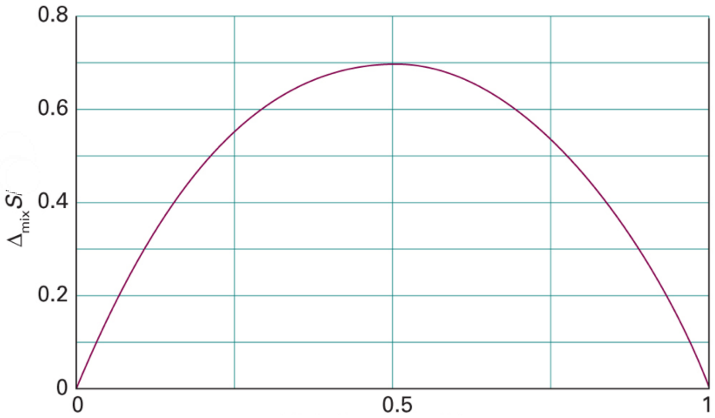
$T_{f,B} = 1400\ °\text{K},$ $\Delta H^{\circ}_{f,B} = 3230\ \text{cal/mol}$

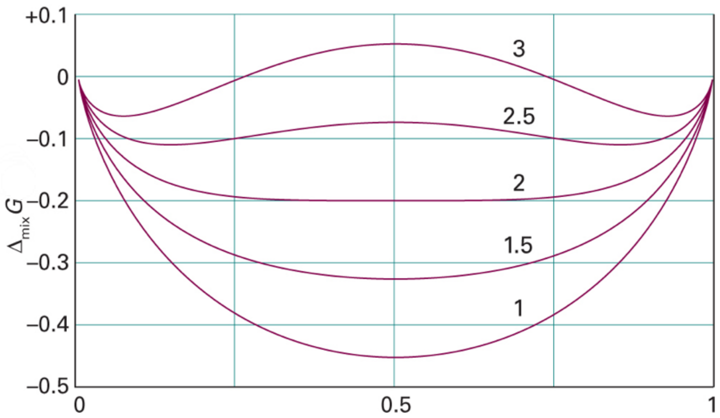
Regular Solutions For Binary Systems

Assumptions:

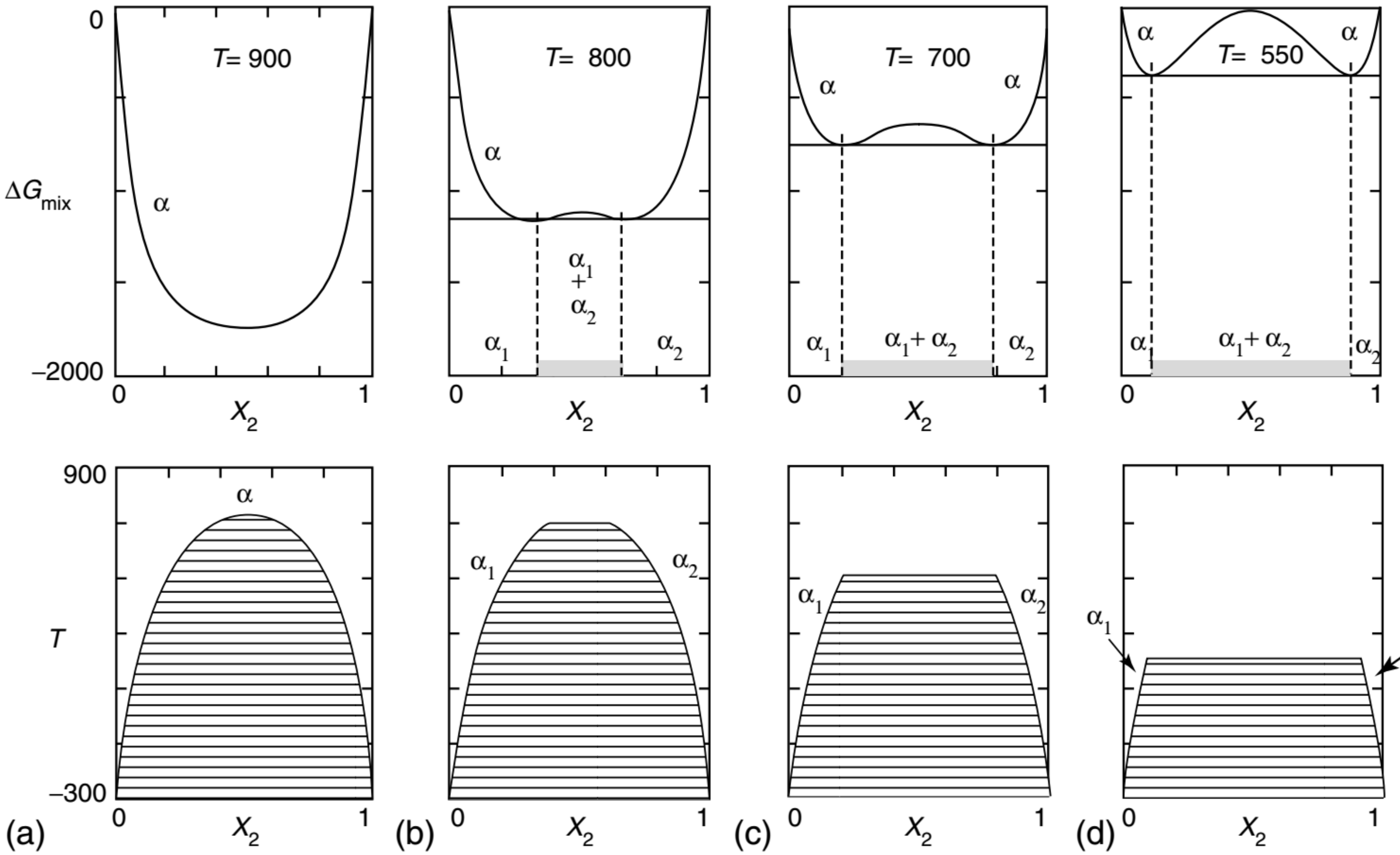


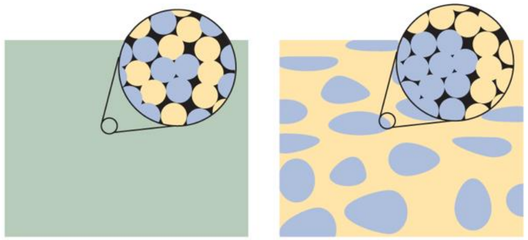


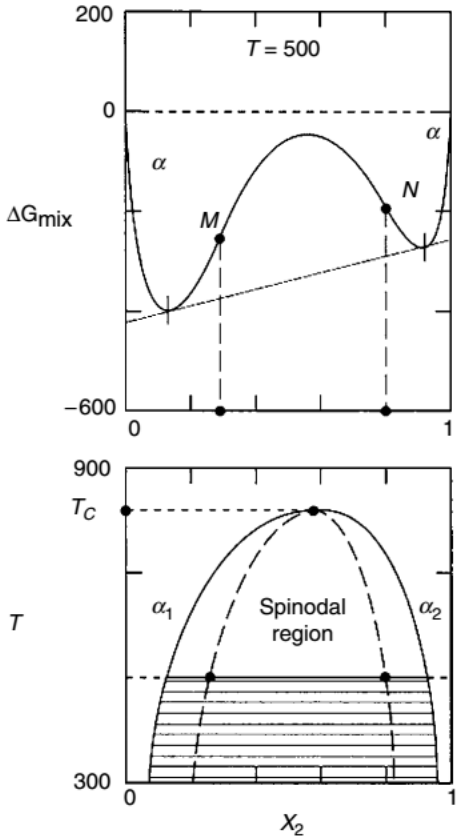




Regular Solution Phase Diagrams & Miscibility Gap



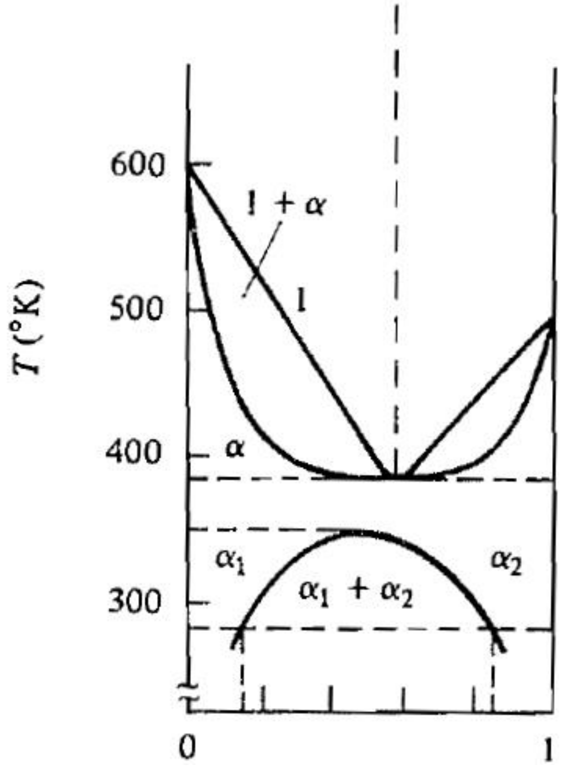




System with the Solid Solution Behaving Regularly

$T_{f,A} = 600\ °\text{K}, \qquad \Delta H^{\circ}_{f,A} = 1300\ \text{cal/mol}$

$T_{f,B} = 500\ °\text{K}, \qquad \Delta H^{\circ}_{f,B} = 1100\ \text{cal/mol}$



$\Omega_{solid} = 0$
$\Omega_{liquid} = 0$

$\Omega_{solid} = 1400\ \text{cal/mol}$
$\Omega_{liquid} = 0$

$\Omega_{solid} \gg 1400\ \text{cal/mol}$
$\Omega_{liquid} = 0$

Phase Diagrams with Intermediate Compounds