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: Thermal Equilibrium

First Law: Energy Conservation $dU = \delta q + \delta w$

Second Law: Entropy is maximum $dS = \left.\frac{\delta q}{T}\right|_{\text{quasistatic processes}}$

$\Delta S_{glob} > 0$ → spontaneity of processes

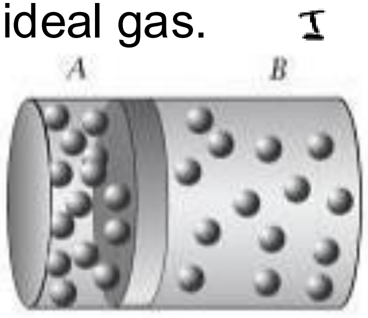
Third Law: Temperature has an absolute value $\underline{0\ K}$, there is the absolute

↳ ΔS_{0K} is the same for all materials

if we have perfect crystalline materials $\Delta S_{0K} = 0$

↳ standard state of entropy

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. $T_A = T_B$

$$dU_i = T_i dS_i - p_i dV_i \rightarrow dS_i = \frac{dU_i}{T_i} + \frac{p_i dV_i}{T_i}$$

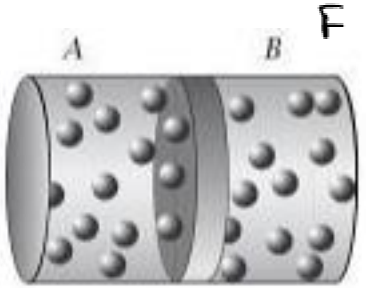
Let's find the characteristic variables of the entropy of each subsystem.

$$S = S(U,V)$$

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

$$S_{tot} = S_A + S_B \qquad V_A + V_B = \text{constant} \qquad U_A + U_B = \text{const.}$$

$$dV_A = -dV_B \qquad dU_A = -dU_B$$



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

Calculate the change of entropy of the system.

$$\Delta S_{tot} = dS_A + dS_B = \overbrace{\cancel{\frac{dU_A}{T_A}} + \frac{p_A dV_A}{T_A} + \cancel{\frac{dU_B}{T_B}}}^{0} + \frac{p_B dV_B}{T_B}$$

$$\Delta S_{tot} = \frac{(p_A - p_B)\, dV_A}{T_B} = 0 \text{ because we have reached equilibrium}$$

$$\Rightarrow \boxed{p_A = p_B}$$

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.

$$w = -\int_{V_1}^{V_2} P_{ext} \cdot dV \qquad P_{ext} = P_{ideal\ gas} = nRT/V$$

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V}\, dV = -nRT \ln\left(\frac{V_2}{V_1}\right) = -5704 \text{ Joule}$$

EXAMPLE | WORK IN AN IRREVERSIBLE PROCESS

1 L·atm = 101.3 Joule

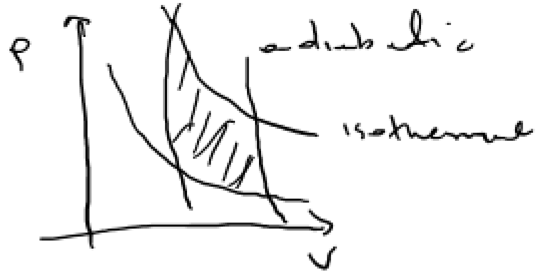
b. One mole of an ideal gas at 298 K is expanded ***irreversibly*** from 1.0 L to 10 L against a ***constant external pressure*** of 1 atm.
Determine the amount of work in Joule.

$$w = -\int_{V_1}^{V_2} p_{ext}\, dV = -p_{ext}(V_2 - V_1) = -9\ \text{L·atm}$$

$$w_{irr} = -911.7\ \text{Joule}$$

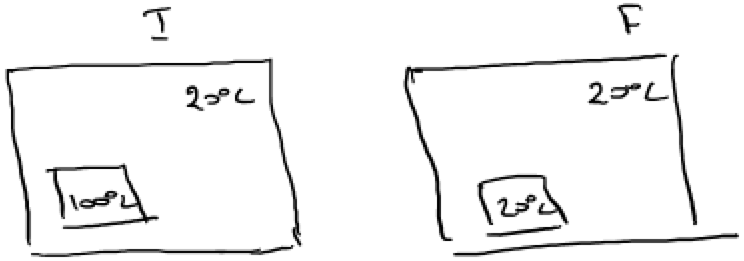
⇒ ~~Work~~ Work done in irreversible processes is lower in magnitude compared to the work done in reversible processes

⇒ Reversible processes yield the maximum amount of work.



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



$$\Delta S_{univ} = \Delta S_{tea} + \Delta S_{room}$$

$$q_{tea} = -q_{room}$$

$$\Delta S_{room} = \frac{q_{room}}{T_{room}} = -\frac{q_{tea}}{T_{roo}}$$

$$\Delta S_{tea} = \int_{T_I}^{T_F} \frac{mc}{T_{tea}} dT = mc \ln \frac{T_F}{T_I} = -505 \text{ J/K}$$

$$\Delta S_{room} = -\int_{T_I}^{T_F} \frac{mc}{T_{room}} dT = -\frac{mc}{T_{room}} (T_F - T_I) = 571 \text{ J/K}$$

$$\Rightarrow \Delta S_{universe} = +66 \text{ J/K} \Rightarrow \text{spontaneous process}$$

Therm. work : Force × extend of the force applied

AUXILIARY FUNCTIONS

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

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

$H \equiv U + pV$ $\qquad dH = TdS + Vdp + \sum_i \mu_i dn_i$

$A \equiv U - TS$ $\qquad dA = -SdT - pdV + \sum_i \mu_i dn_i$

$G \equiv H - TS$ $\qquad dG = -SdT + Vdp + \sum_i \mu_i dn_i$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

$\Rightarrow$ Equilibrium at a minimum of free energies $dA \leq 0$, $dG \leq 0$

$-SdT + Vdp - \sum_i n_i d\mu_i = 0$ Gibbs-Duhem Eq.

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.

$\gamma \, dA$

↳ surface energy

a. Write an expression for the variation of the internal energy.

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

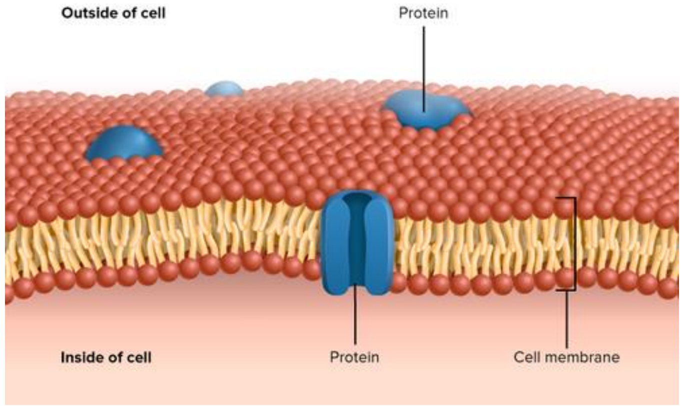
b. Write an expression for the variation of the Gibbs free energy.

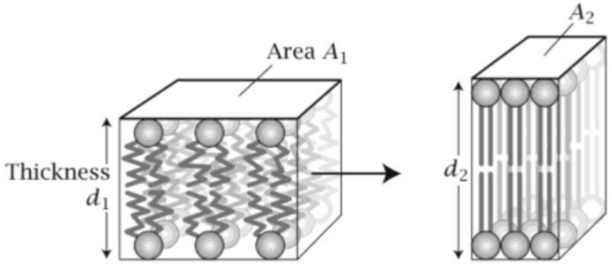
$$dG = -SdT + Vdp + \sum_i \mu_i dn_i + \gamma dA$$

b. Find a Maxwell relation to express $\boxed{\left(\frac{\partial S}{\partial A}\right)_{T,p,n_i}}$ in terms of T.

$$\left(\frac{\partial}{\partial A}\left(\frac{\partial G}{\partial T}\right)_{A,p,n_i}\right)_{T,p,n_i} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial A}\right)_{T,p,n_i}\right)_{A,p,n_i}$$

$$\Rightarrow -\left(\frac{\partial S}{\partial A}\right)_{T,p,n_i} = \left(\frac{\partial \gamma}{\partial T}\right)_{A,p,n_i}$$





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)?

$$dU = TdS - pdV + \mu dn$$

$$Z = H - (TS + \mu n)$$

$$\boxed{dZ = -SdT + Vdp + \underline{nd\mu}}$$

PURE SUBSTANCES & MULTICOMPONENT SYSTEMS

⇓
molar quantities

⇓
molar quantities of each component

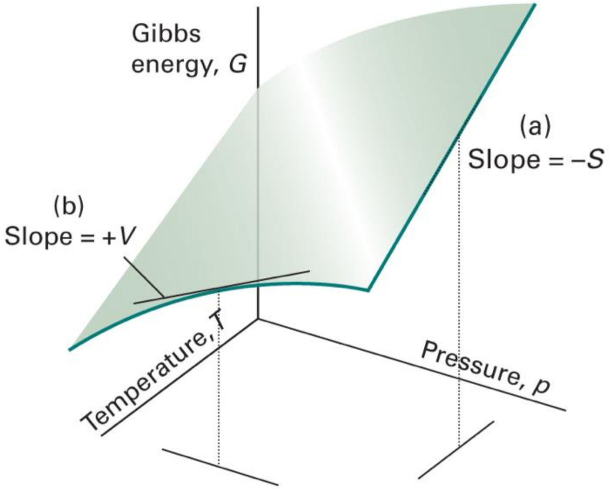
⇒ multicomponent systems after mixing ⇒ partial molar quantities

$$\Rightarrow \quad \bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad \text{by definition}$$

THERMODYNAMICS OF GASES AND CONDENSED PHASES

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

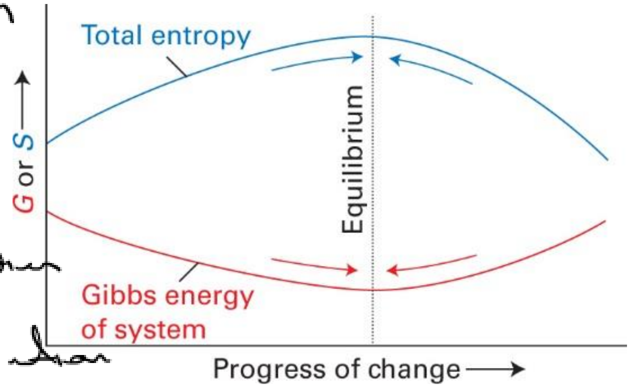
$$\Delta G = \Delta H - T\Delta S, \qquad dG = -SdT + Vdp + \sum_i \mu_i dn_i\,, \qquad \mu = g, \qquad \mu_i = \bar{G}_i$$



Pure Ideal Gas: $pv = RT \Rightarrow \mu = \mu^\circ + RT \ln p$

Mixtures of ideal gases: $\mu_i = \mu_i^\circ + RT \ln p_i \qquad p_i = x_i \cdot p$ where $p = 1$ atm/bar

Real gases: $p \to f$ | definitions of other state functions of the system



Mixtures/solutions of condensed phases:

$\mu_i = \mu_i^\circ + RT \ln a_i \qquad a_i = \gamma_i x_i \qquad \gamma_i = 1$ ideal solution

$0 < \gamma_i < 1$ regular solution

For many phases: $\mu_i^\theta = \mu_i^{\circ,\theta} + RT \ln a_i^\theta$ where $\theta = \alpha, \beta, \gamma, \ldots, \varphi$

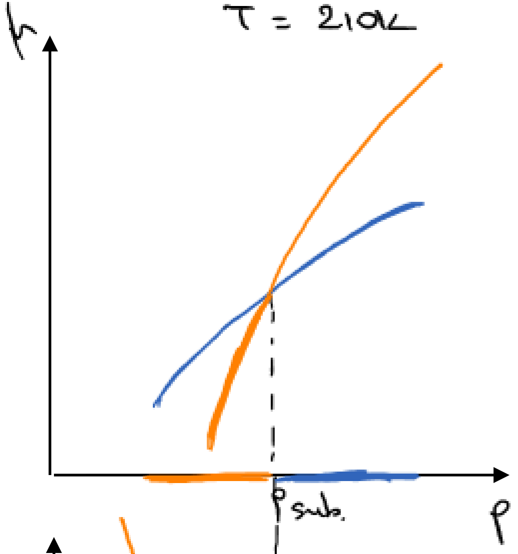
SINGLE COMPONENT PHASE DIAGRAMS

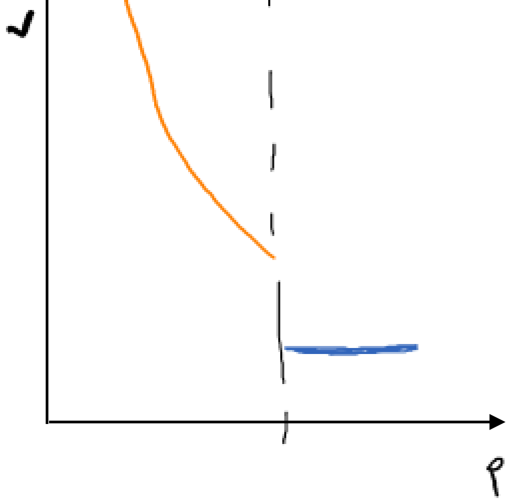
$$\left(\frac{\partial h}{\partial p}\right)_T = v$$

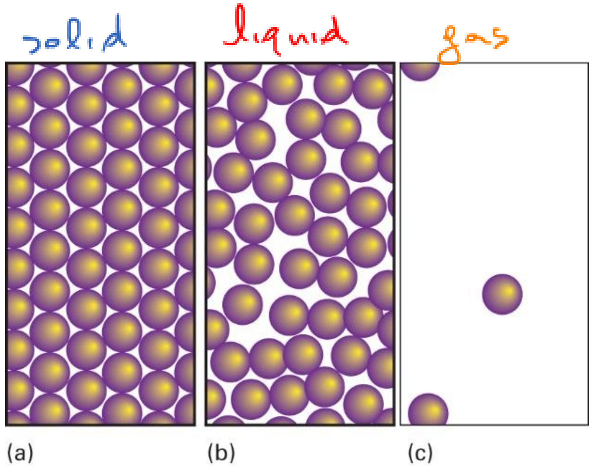
$T = 210K$

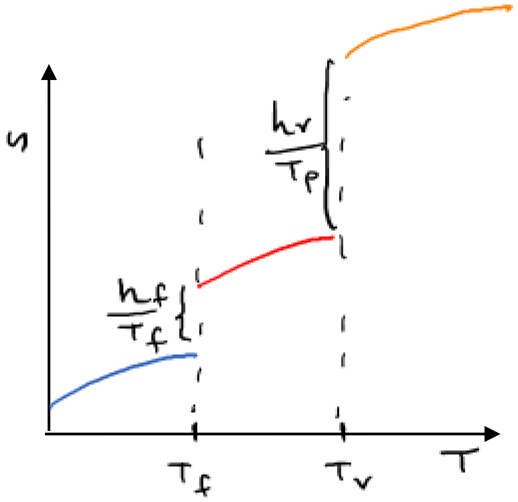
$$\left(\frac{\partial h}{\partial T}\right)_p = -s$$

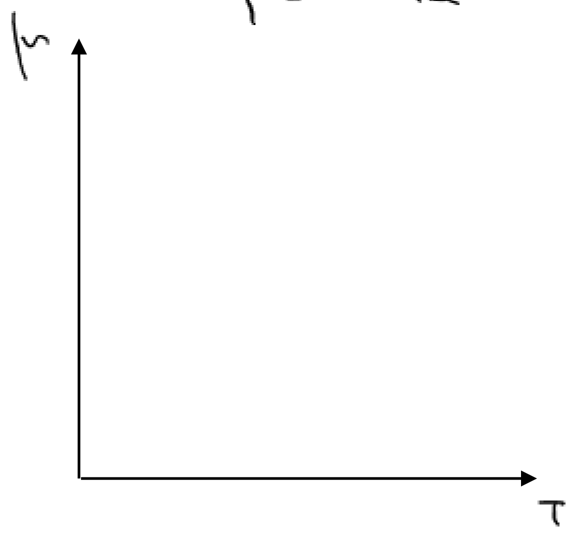
$p = 10^6 Pa$

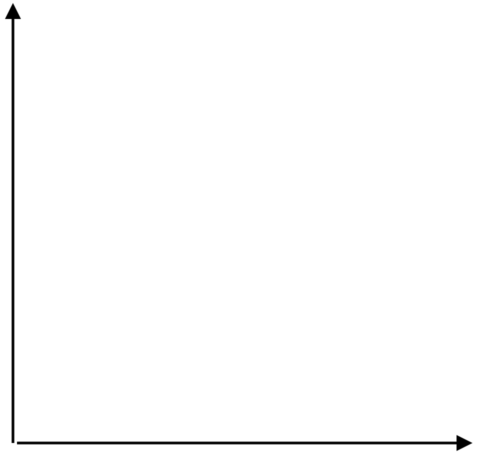


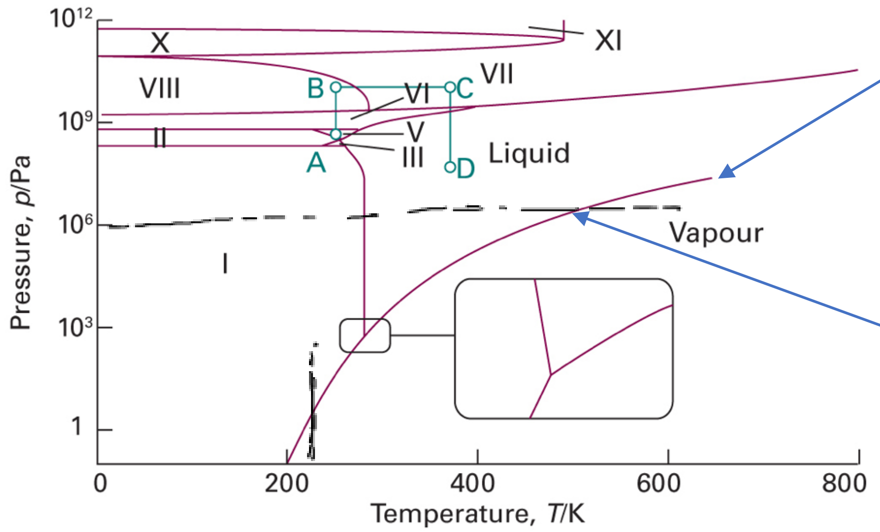


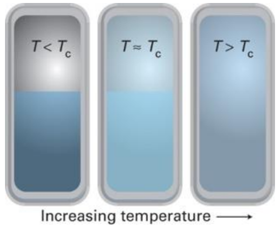


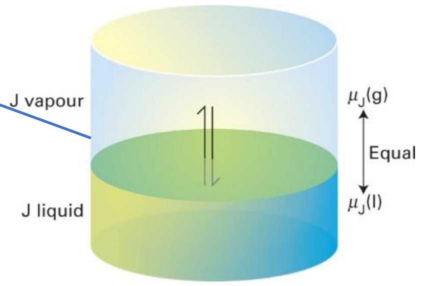












$$\frac{dp}{dT} = \frac{ds}{dv} = \frac{dh}{T\,dv}$$

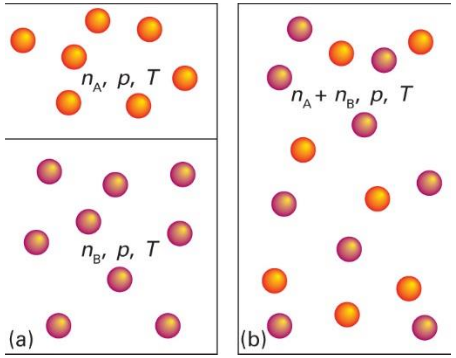
IDEAL SOLUTIONS OF GASEOUS AND CONDENSED PHASES

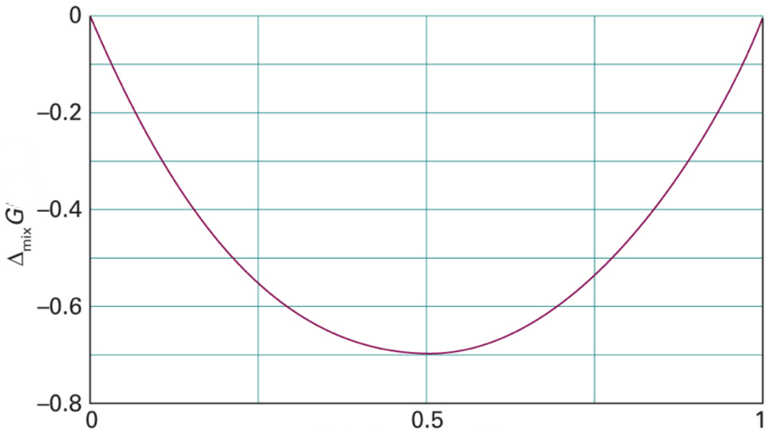
Assumptions:

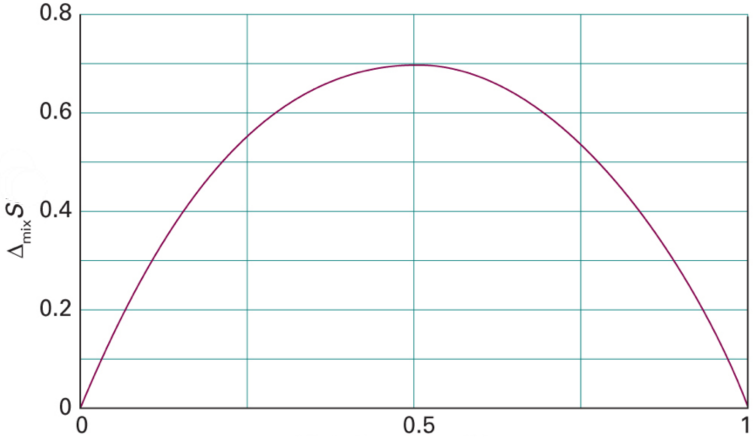
$\Delta_{mix}\bar{H} = 0$, $\Delta_{mix}\bar{V} = 0$

$\Delta_{mix}\bar{S} = -R\sum_i x_i \ln x_i$

$\Delta_{mix}\bar{G} = RT\sum_i x_i \ln x_i \Rightarrow$ spontaneous process

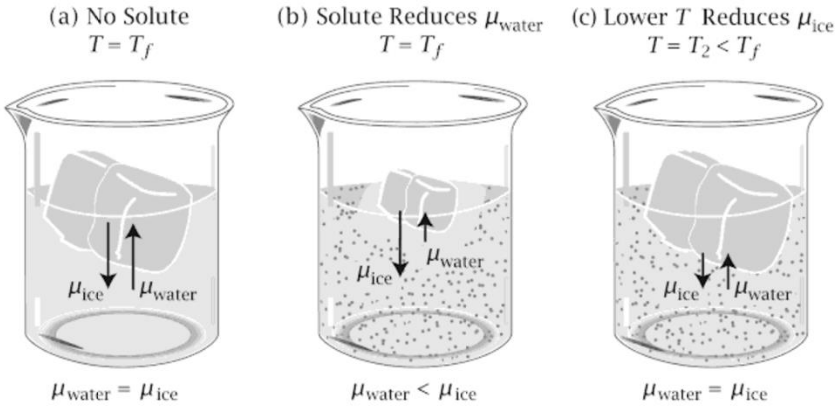






IDEAL SOLUTIONS | TRANSFER OF MOLECULES BETWEEN PHASES

Depression of freezing point with addition of salt



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

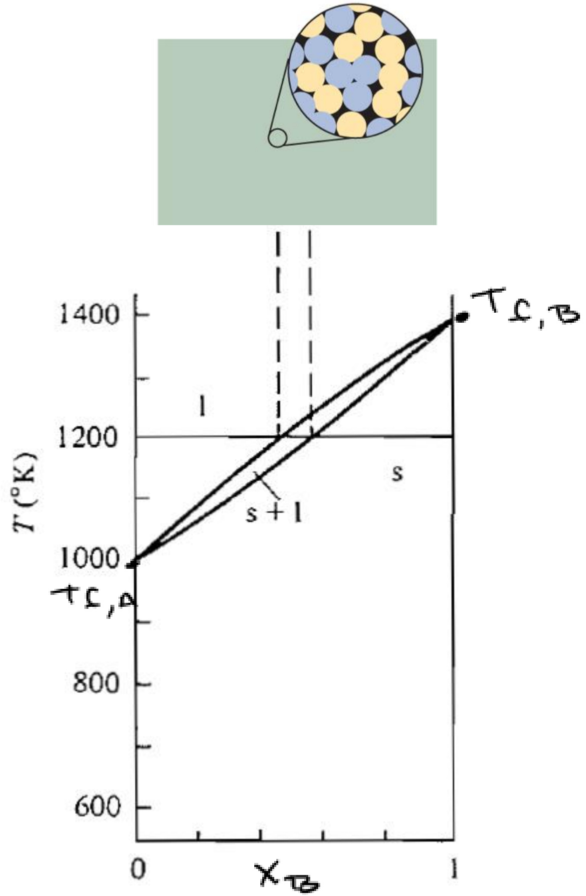
The mechanism of anesthetic drugs. Anesthetic drug action is thought to involve the solubility of an anesthetic in the hydrocarbon region of the lipid bilayer of biological membranes. It is said that anesthesia occurs whenever the concentration of a drug is greater that 0.03 mol/kg per membrane, no matter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

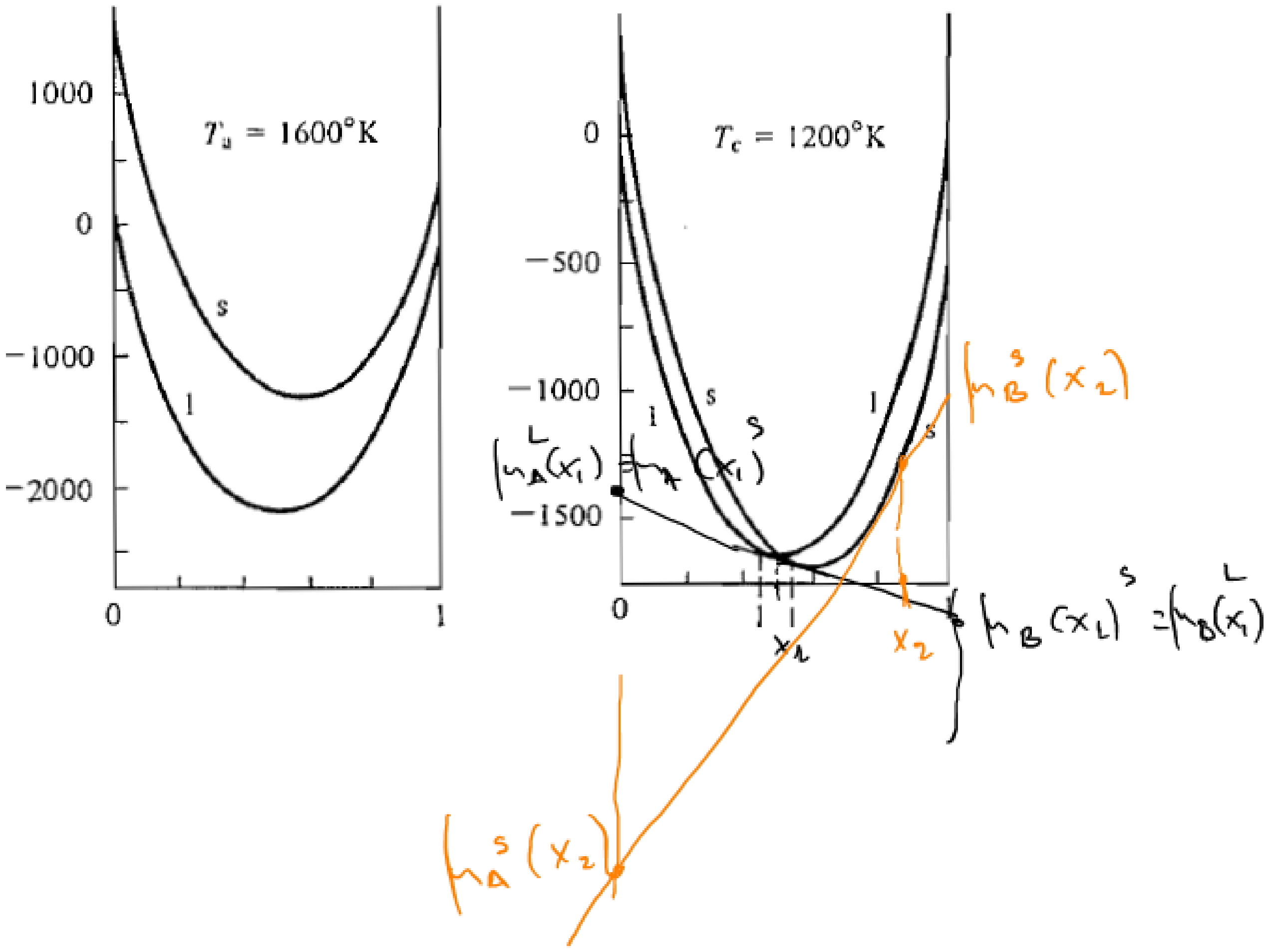
Lipid bilayers “melt” from a solid-like state to a liquid-like state.

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

IDEAL SOLUTIONS

for the solid
& the liquid

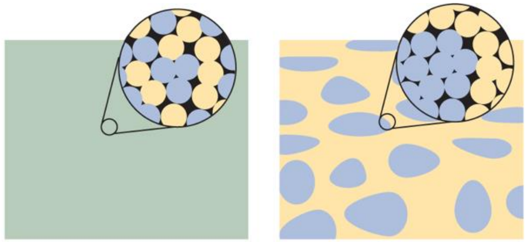




$$T_{f,A} = 1000\ °\text{K}, \qquad \Delta H^{\circ}_{f,A} = 2300\ \text{cal/mol}$$

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

REGULAR SOLUTIONS FOR BINARY SYSTEMS

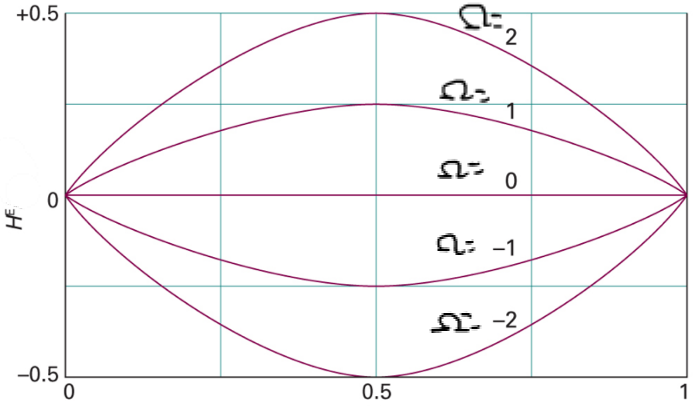


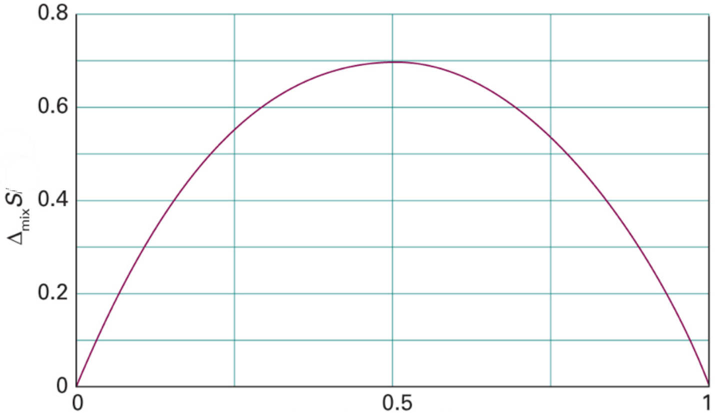
Assumptions:

$$\Delta_{mix}\bar{H} = \Omega x_a x_B$$

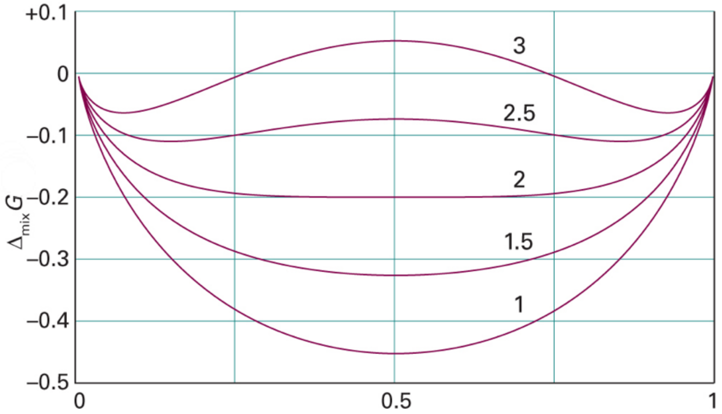
$$\Delta_{mix} G = \Omega x_a x_B + RT\,(x_a \ln x_a + x_B \ln x_B)$$

$$\Delta_{mix}\bar{S} = -R\,(x_a \ln x_a + x_B \ln x_B)$$

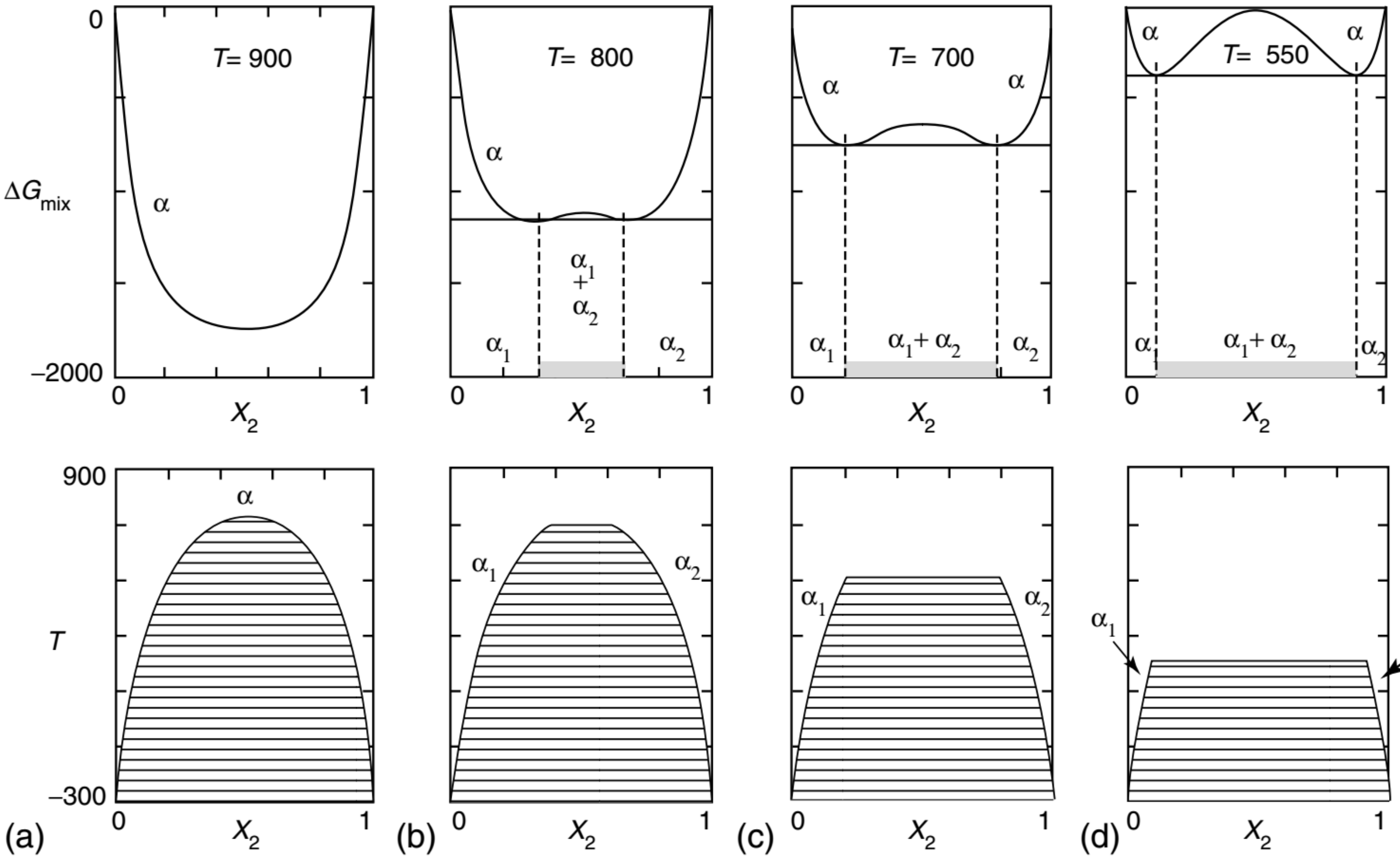


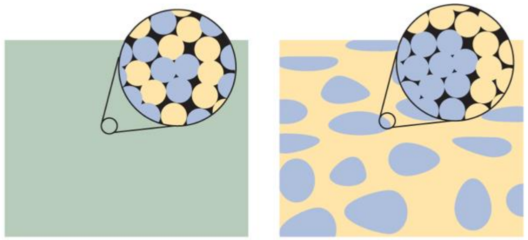


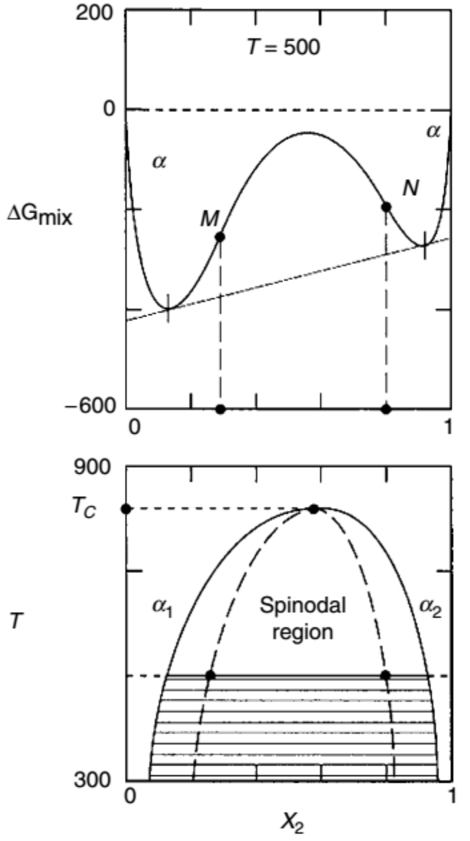
when Ω is positive



REGULAR SOLUTION PHASE DIAGRAMS & MISCIBILITY GAP



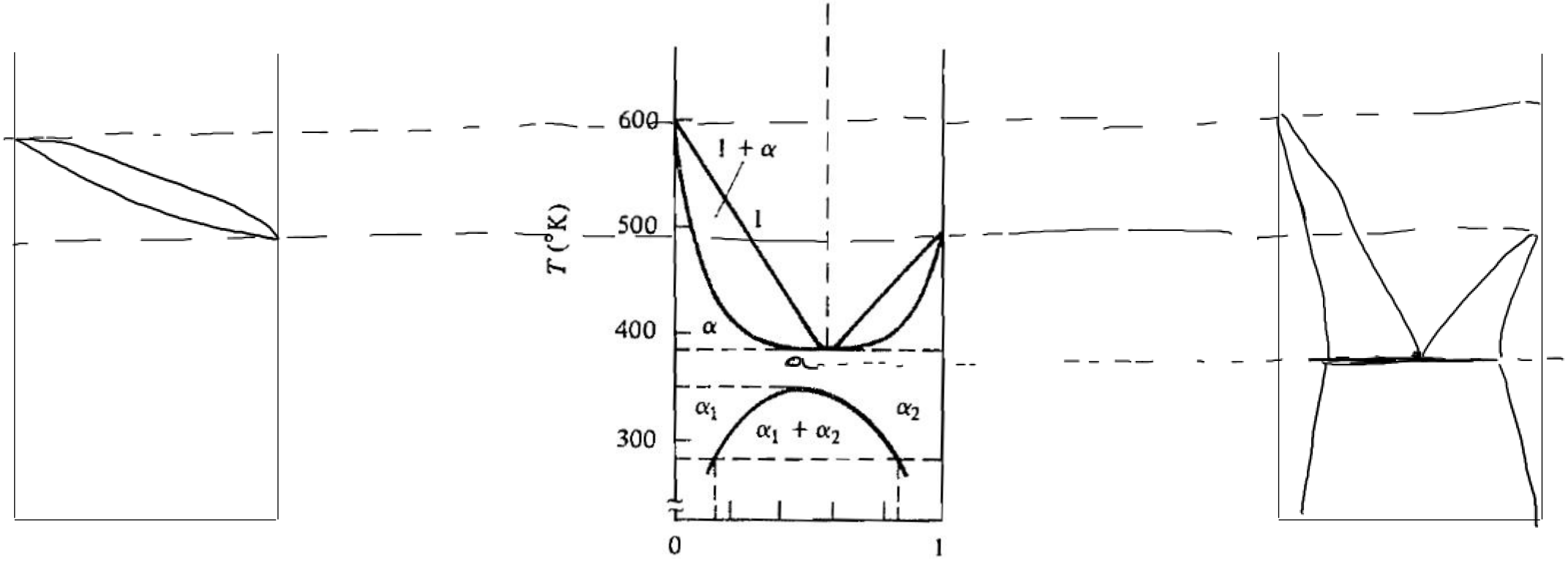




SYSTEM WITH THE SOLID SOLUTION BEHAVING REGULARLY

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

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



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

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

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