

CHE 312 Midterm1 Review

By James

Key ideas in pure species phase equilibrium

Generally,

$$\Delta G = g^a - g^b \quad \text{Steam tables}$$

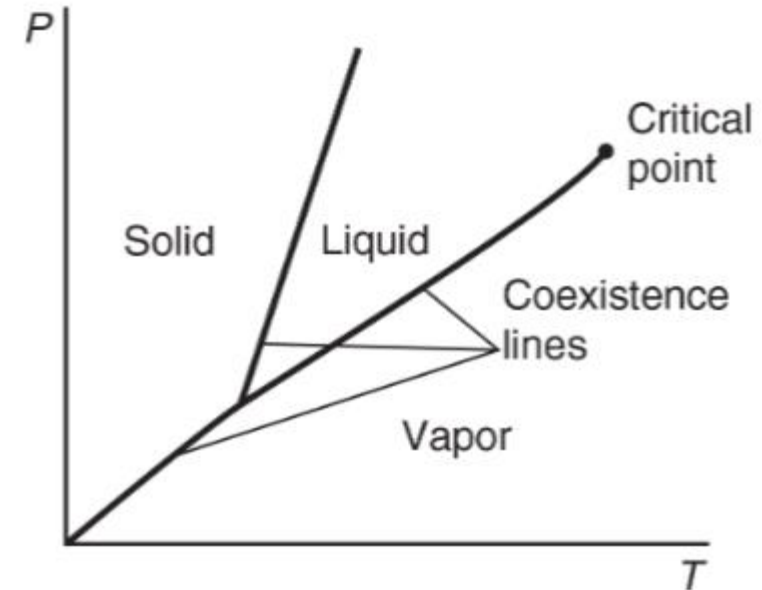
For equilibrium

$$\Delta G = 0 \rightarrow g^a = g^b$$

$$\begin{cases} g^s = g^l & S - L \text{ equilibrium} \\ g^s = g^v & S - V \text{ equilibrium} \\ g^l = g^v & L - V \text{ equilibrium} \end{cases}$$

Equilibrium occurs to balance out energetic states.

$$g_i^{\text{final}} - g_i^{\text{initial}} = \begin{cases} > 0 & \text{initial state is more energetic favorable} \\ = 0 & \text{equilibrium} \\ < 0 & \text{final state is more energetic favorable} \end{cases}$$



$$g = h - Ts$$

A lower gibbs energy means the phase change will occur spontaneously, and is more stable

$\Delta G^{a \rightarrow b}$ is negative, the final phase “b” is more stable

Pure Species Phase Equilibria Equations

Clausius Equation

$$\frac{dP}{dT} = \frac{\Delta h_{\text{fus}}^T}{(v^s - v^l) T}$$

$$\frac{dP}{dT} = \frac{h_i^\alpha - h_i^\beta}{(v_i^\alpha - v_i^\beta) \cdot T}$$

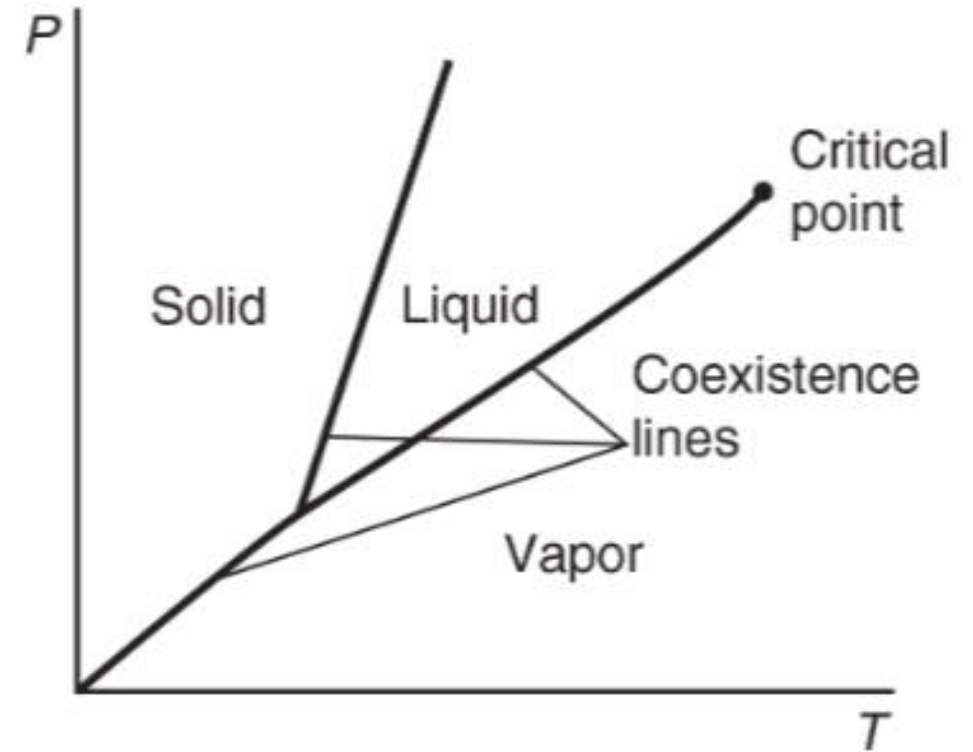
Valid anywhere on the coexistence lines (S-L, L-V, S-V)

*assumes enthalpy not a function of temperature (constant)

If we assume from the Clausius equation:

- 1) L-V equilibrium
- 2) ΔH_{vap} constant
- 2) $v^v \gg v^l$
- 3) Ideal gas (low pressure) $v^v = RT/P$

$$\frac{dP_i^{\text{sat}}}{P_i^{\text{sat}}} = \frac{\Delta h_{\text{vap},i} dT}{RT^2}$$



Clausius-Clapeyron Equation

$$\ln \left(\frac{P_2^{\text{sat}}}{P_1^{\text{sat}}} \right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2[\text{K}]} - \frac{1}{T_1[\text{K}]} \right)$$

$$\Delta h_{\text{sub}} = \Delta h_{\text{fus}} + \Delta h_{\text{vap}}$$

Valid for LVE

To use this, need reference temperature and pressure on the coexistence line (usually triple point)

Antoine Equation

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{C_i + T}$$

Hypothetical Paths

Temperature change: $\Delta H = nC_p\Delta T$

Phase change: $\Delta H = n\Delta h_{\text{fus}}$

Mixing: $\Delta H = n\Delta h_{\text{mix}}$

$\Delta H = n\Delta h_{\text{vap}}$

$\Delta H = -n\Delta h_{\text{unmix}}$

Useful to find final temperature

Temperature change: $\left(\frac{\partial g}{\partial T}\right)_p = -s \rightarrow \Delta G = -s\Delta T$

Phase change: $\Delta G = 0$

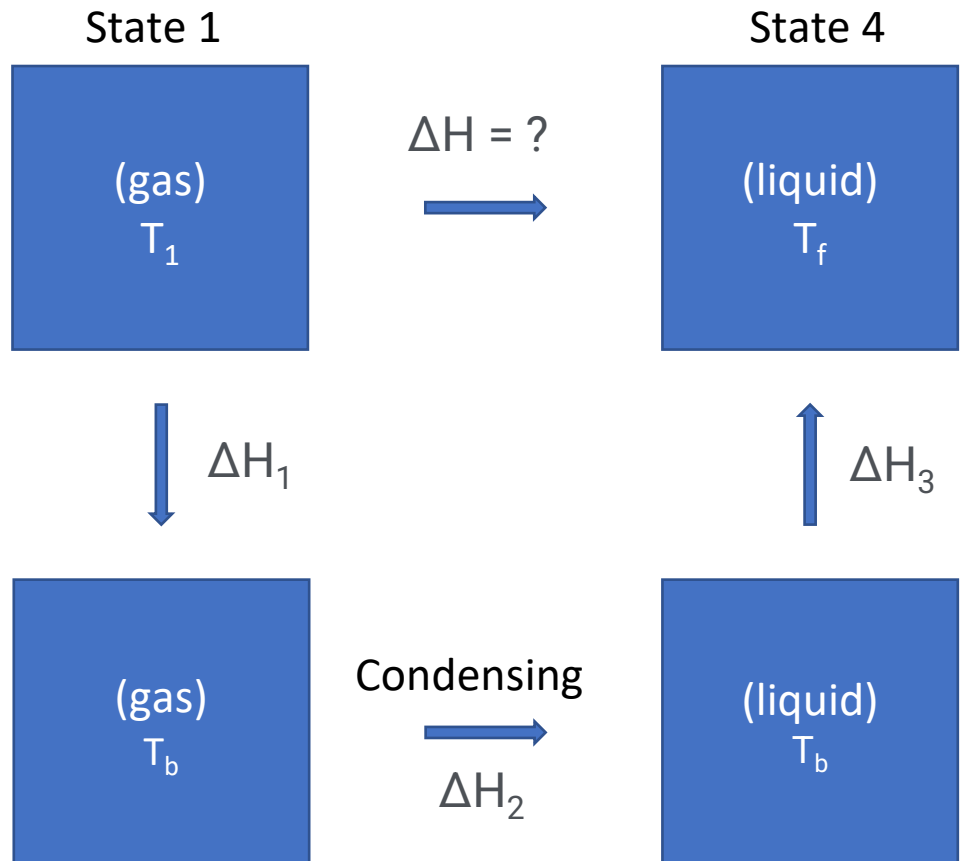
Mixing: $\Delta G = n\Delta g_{\text{mix}}$

Useful to find phase stability

Temperature and Phase Changes

Examples:

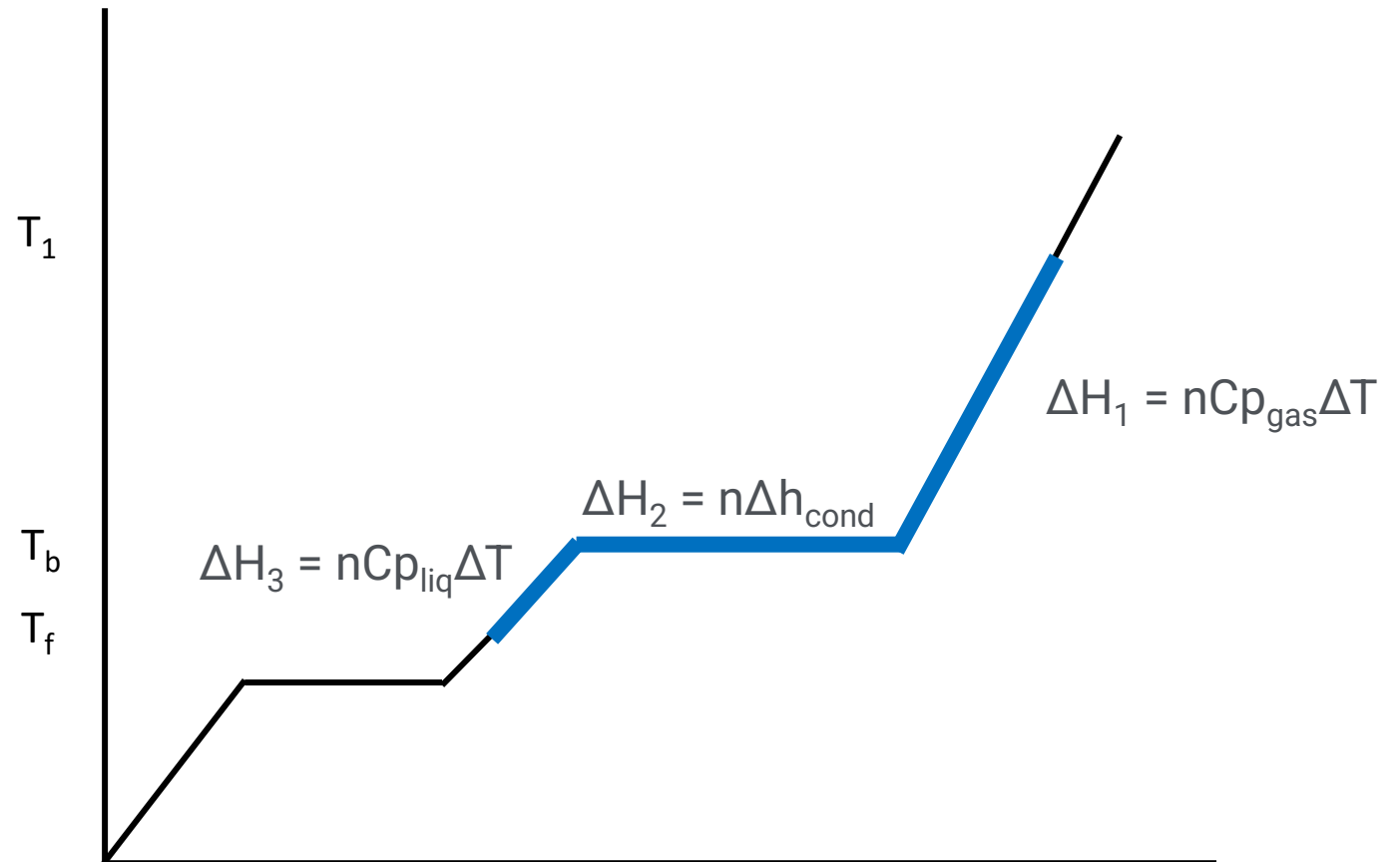
Condensing gas to liquid



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H = nC_{p_{\text{gas}}}\Delta T + n\Delta h_{\text{cond}} + nC_{p_{\text{liq}}}\Delta T$$

$$\Delta H = n(C_{p_{\text{gas}}}(T_b - T_2) + \Delta h_{\text{cond}} + C_{p_{\text{liq}}}(T_f - T_b))$$



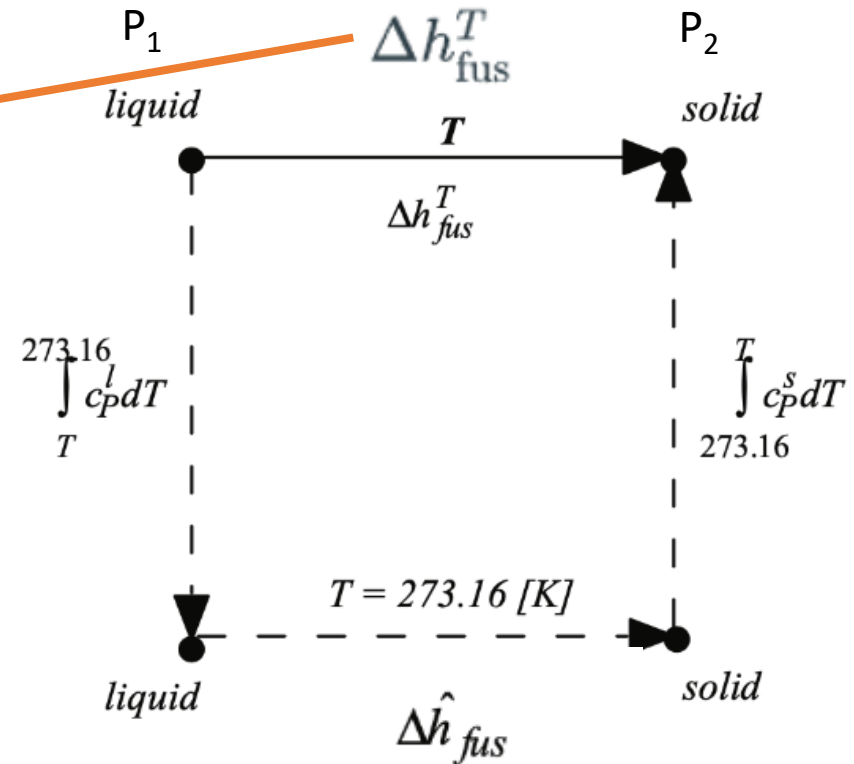
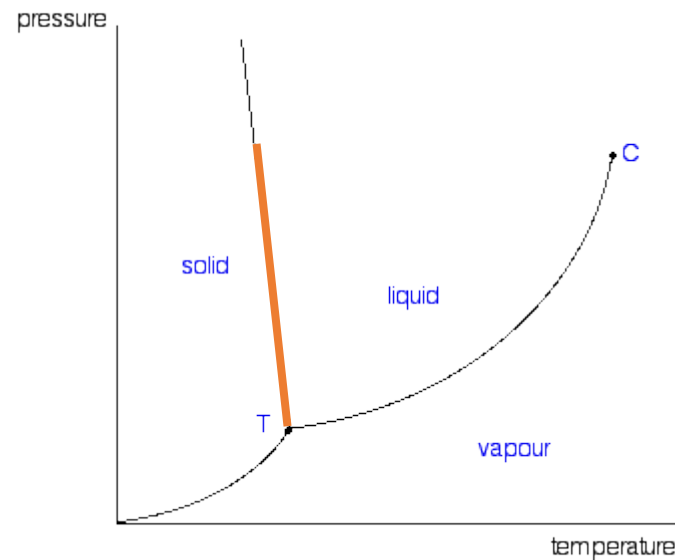
This can be useful for the Clausius Equation

If we are looking at phase changes (hence coexistence line)

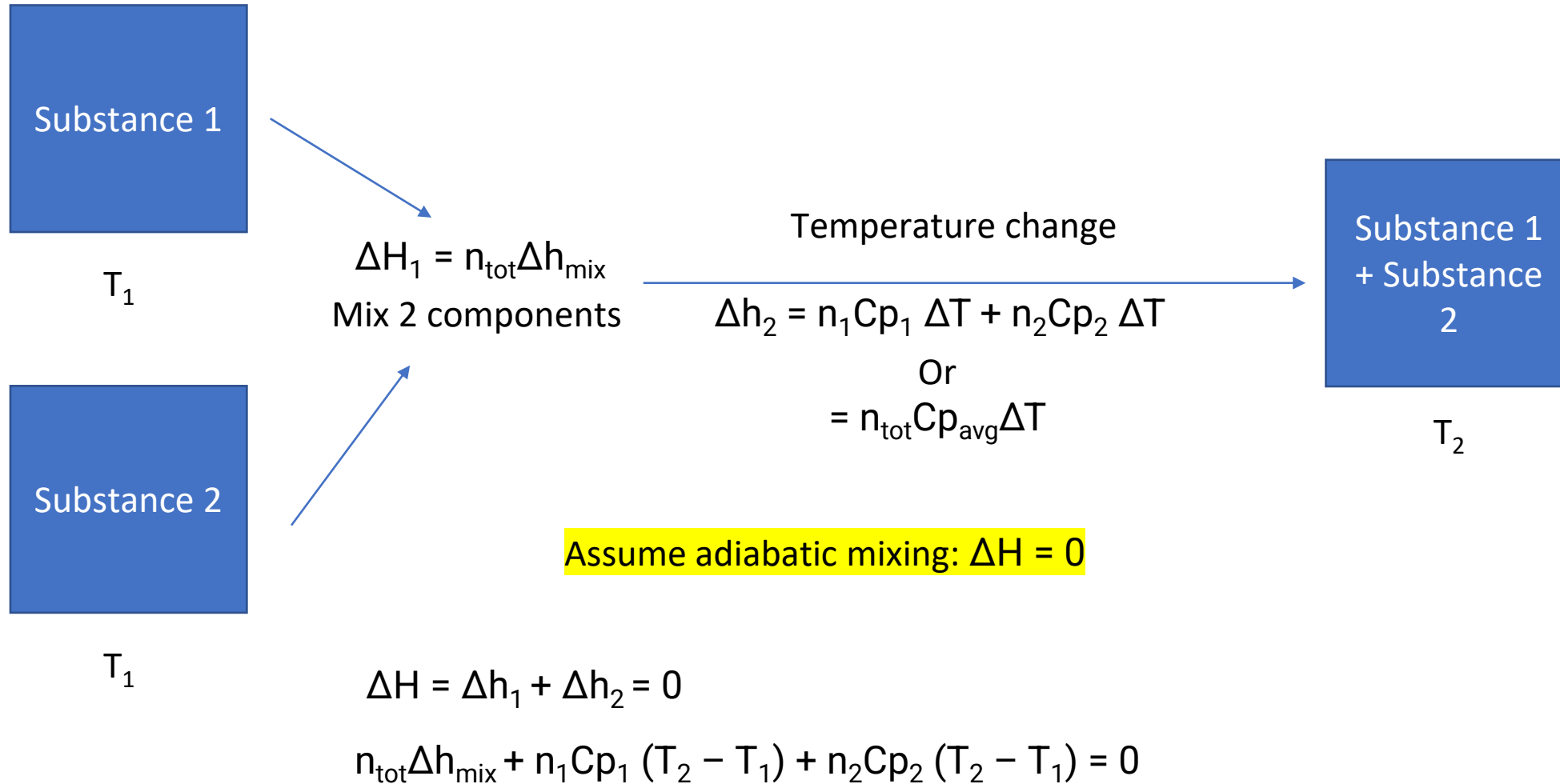
Example:

What pressure is needed to isothermally compress ice initially at -5°C and 1 bar so that it **changes phase**?

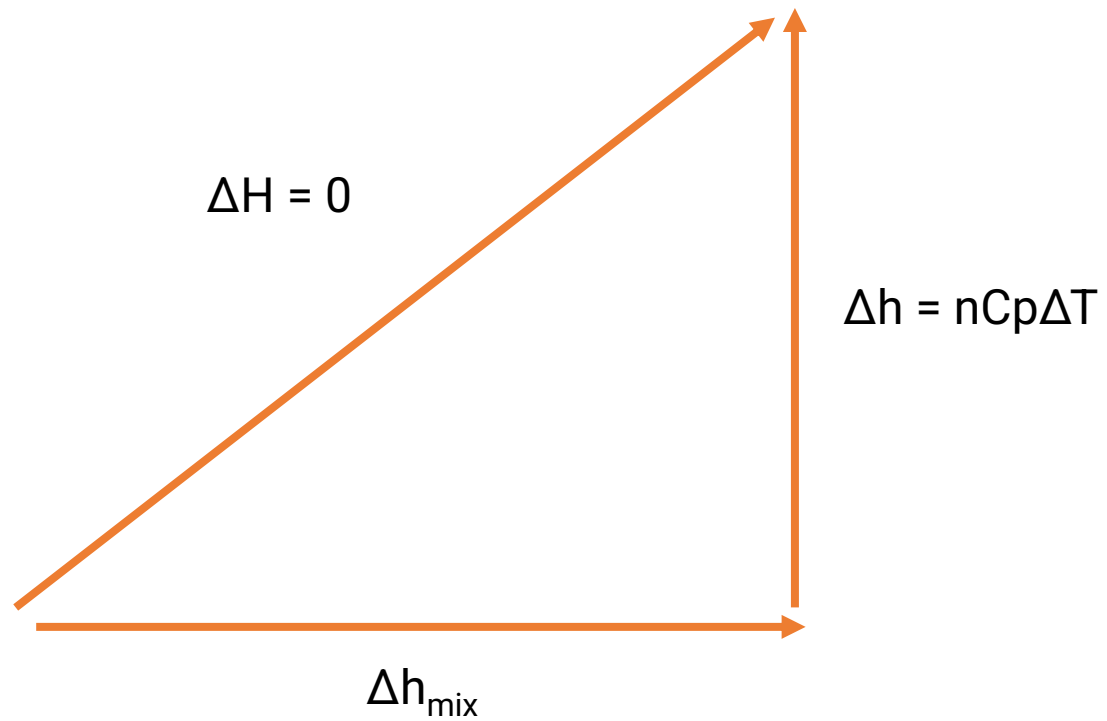
$$\frac{dP}{dT} = \frac{\Delta h_{\text{fus}}^T}{(v^s - v^l) T}$$



Simple Mixing



$$\Delta H = \Delta H_{\text{mix}} + \Delta H_2 = 0$$

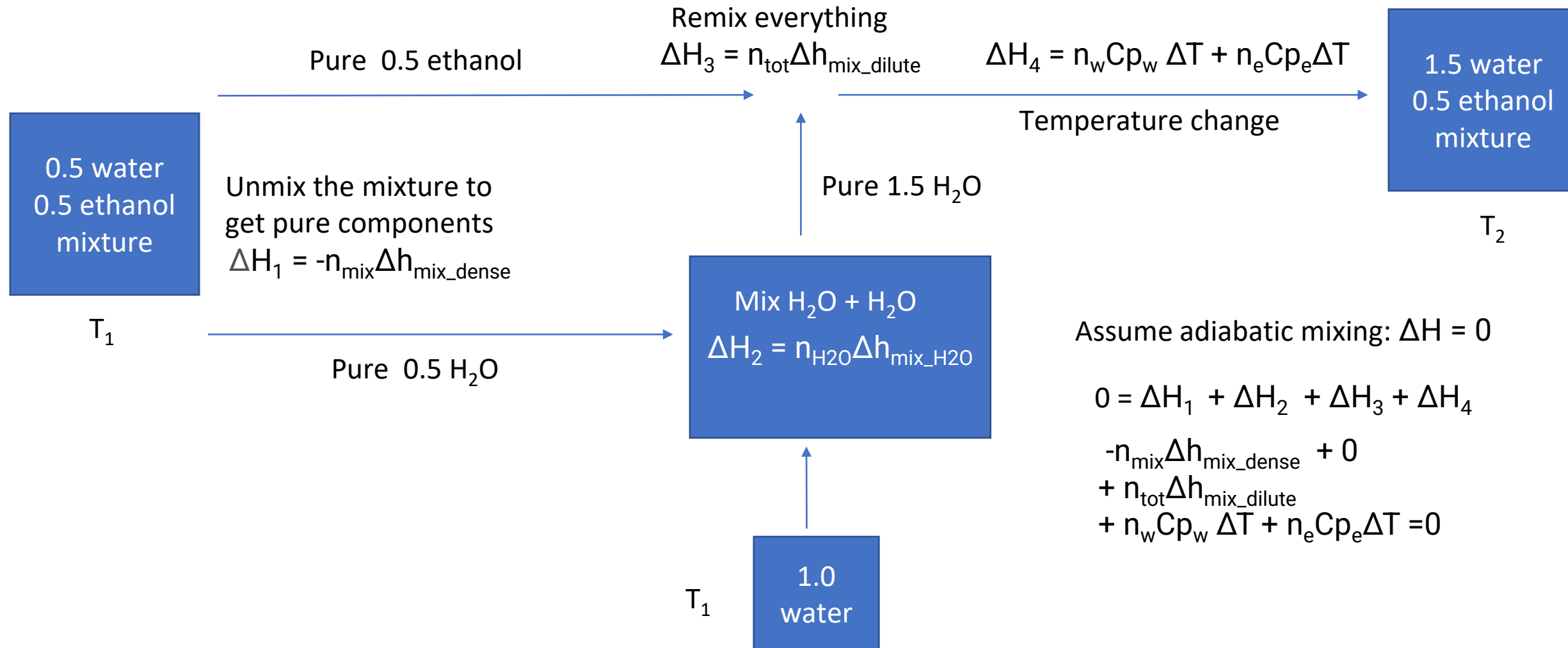


Problem 6.10.4:

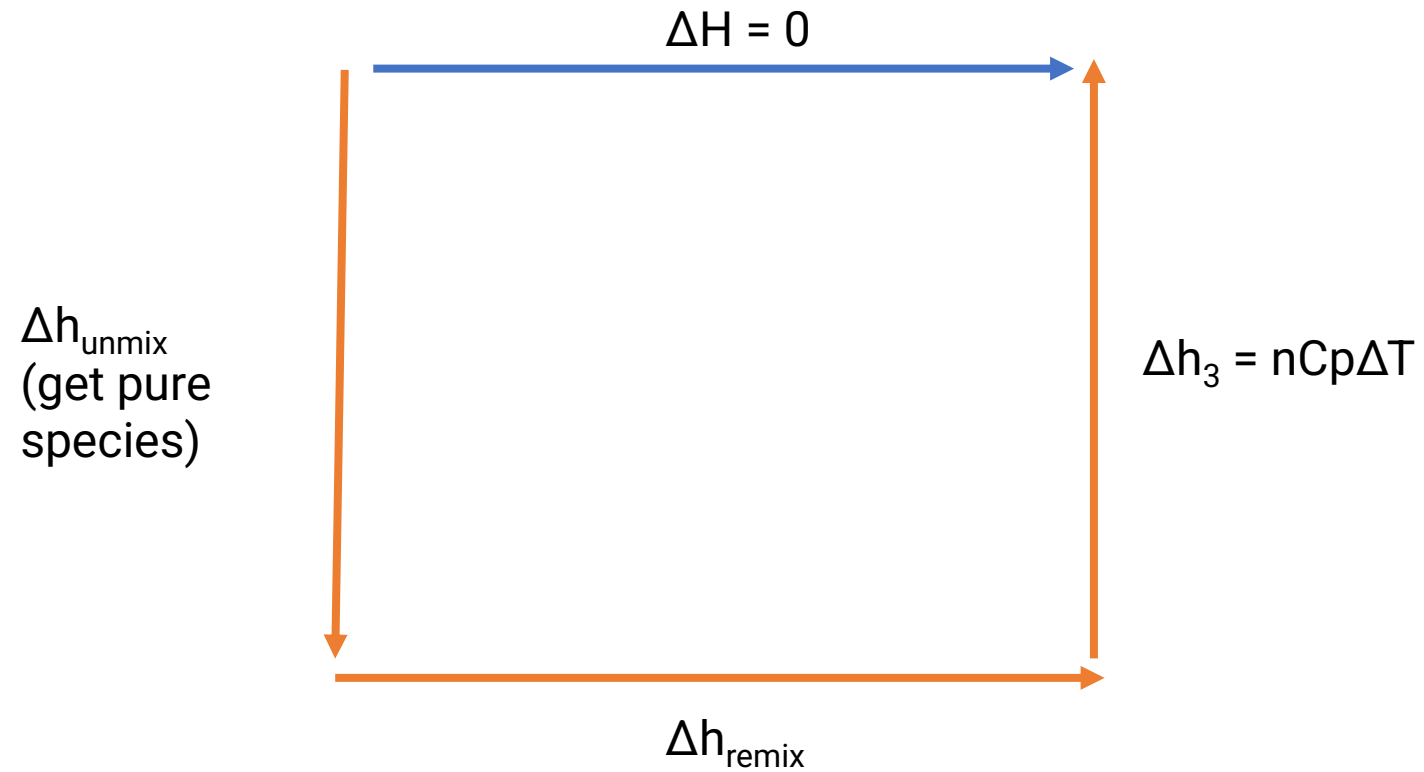
Mixing a 1.0 mole stream of water with a 0.5/0.5 equimolar stream of ethanol/water.

Find final temperature

Mixing Mixtures

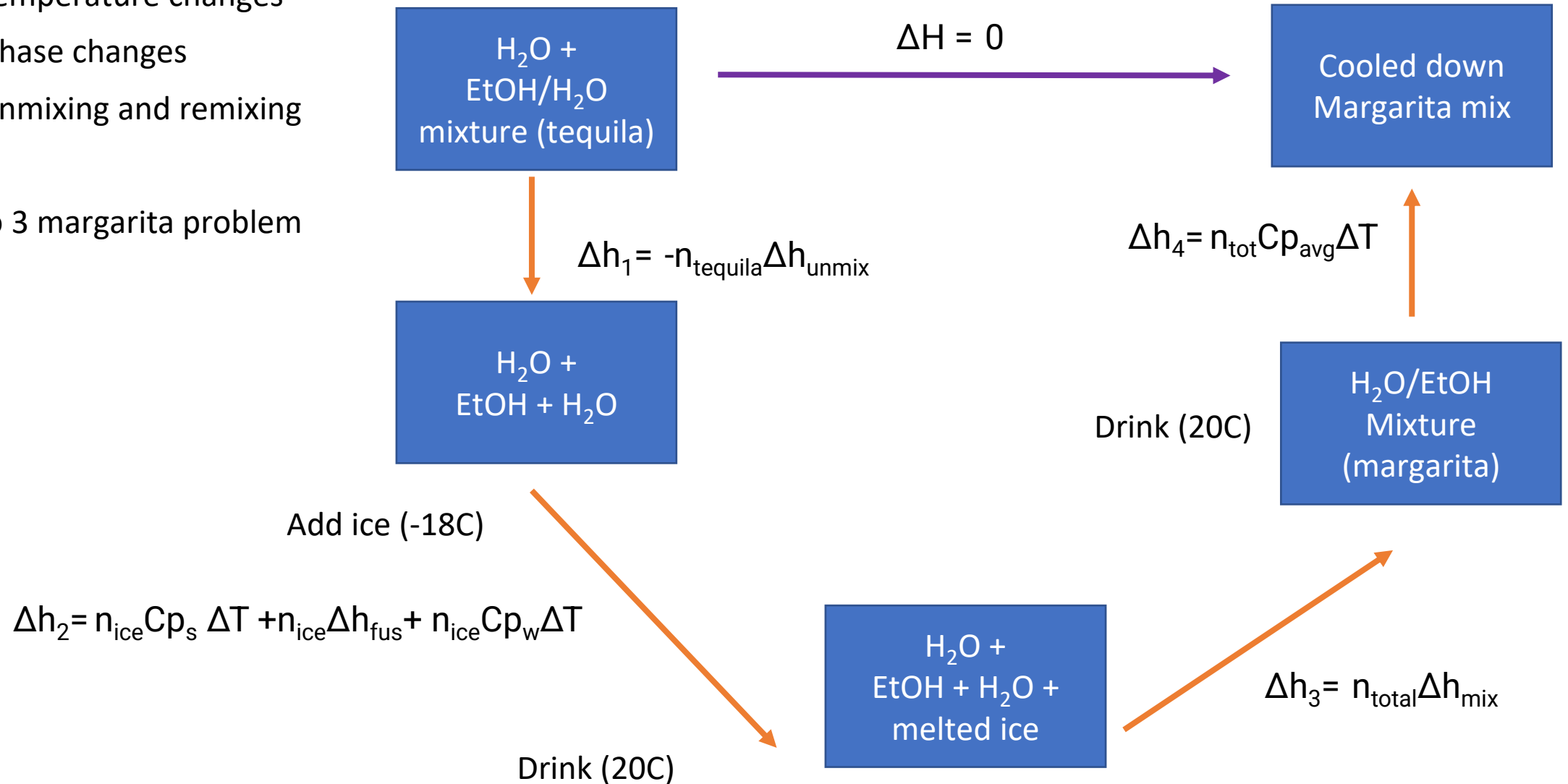


$$\Delta H = \Delta h_{\text{unmix}} + \Delta h_{\text{remix}} + \Delta h_3 = 0$$



Complex mixing problems

- Involves temperature changes
- Involves phase changes
- Involves unmixing and remixing
- See studio 3 margarita problem



Mixing Properties

Table 6.4.2: Types of thermodynamic properties.

| | Extensive | Intensive - molar | Intensive - specific |
|--|--|--|--|
| Pure species property i at the T and P of the mixture | $K_i : V_i, G_i, U_i, H_i, S_i, \dots$ | $k_i : v_i, g_i, u_i, h_i, s_i, \dots$ | $\hat{k}_i : \hat{v}_i, \hat{g}_i, \hat{u}_i, \hat{h}_i, \hat{s}_i$ |
| Total solution property | $K : V, G, U, H, S, \dots$ | $k : v, g, u, h, s, \dots$ | $\hat{k} : \hat{v}, \hat{g}, \hat{u}, \hat{h}, \hat{s}$ |
| Property change of mixing | $\Delta K_{mix} : \Delta V_{mix}, \Delta G_{mix}, \Delta H_{mix}, \Delta S_{mix}, \dots$ | $\Delta k_{mix} : \Delta v_{mix}, \Delta g_{mix}, \Delta h_{mix}, \Delta s_{mix}, \dots$ | $\Delta \hat{k}_{mix} : \Delta \hat{v}_{mix}, \Delta \hat{g}_{mix}, \Delta \hat{h}_{mix}, \Delta \hat{s}_{mix}, \dots$ |
| Partial molar property of species i | — | $\bar{K}_i : \bar{V}_i, \bar{G}_i, \bar{U}_i, \bar{H}_i, \bar{S}_i, \dots$ | — |

K represents any property, (V, G, U, H, I, S etc)
and depends on T, P and n_i

How do I go from extensive to intensive
property?

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K represents any property, (V, G, U, H, I, S etc)
and depends on T, P and n_i

How do I find partial molar property?

$$\bar{K}_i = \left(\frac{\partial K}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

Derivative of extensive property, K,
with respect to n_i under constant
T, P and moles that are not n_i

The partial molar property is the contribution for
molecular interactions of n_i towards a mixture

Mixing Properties Relations

K represents any property(H,V,G,S...) thus their relationships are similar:

$$\begin{cases} K(H, V, G, S, \dots) & \text{Extensive properties} \\ k(h, v, g, s, \dots) & \text{Molar properties} \\ \bar{K}_i = \frac{dK}{dn_i} & \text{Partial molar property} \end{cases}$$

Partial Molar Property:

$$\bar{K}_i = \left(\frac{\partial K}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

$$\bar{S} = \left(\frac{\partial S}{\partial n_i} \right)_{T, P, n_i},$$

$$\bar{H} = \left(\frac{\partial H}{\partial n_i} \right)_{T, P, n_i}$$

...

Property change of mixing (extensive):

$$\Delta K_{\text{mix}} = K - \sum n_i k_i$$

$$\Delta V_{\text{mix}} = V - \sum n_i v_i$$

$$\Delta H_{\text{mix}} = H - \sum n_i h_i$$

$$\overline{\Delta K}_{\text{mix}, i} = \bar{K}_i - k_i$$

...

Property change of mixing (intensive):

$$\Delta k_{\text{mix}} = k - \sum x_i k_i$$

$$\Delta v_{\text{mix}} = v - \sum x_i v_i$$

$$\Delta h_{\text{mix}} = h - \sum x_i h_i$$

...

—

Notation

Mixing water(1)+ ethanol(2)

\bar{V}_i = Volume that 1 mol of species i taken up by mixture. It is the contribution of that mol towards that total volume

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

V = Total volume of mixture = $v n_{tot}$

$$V = \sum n_i \bar{V}_i$$

v = molar volume of mixture = V/n_{total}

$$v = \sum x_i \bar{V}_i$$

V_1 = Volume of pure species 1

v_1 = Molar Volume of pure species 1 = V_1/n_1

\hat{v}_1 = inverse density of species 1

V_2 = Volume of pure species 2 =

v_2 = Molar Volume of pure species 1 = V_2/n_2

\hat{v}_2 = inverse density of species 2

ΔV_{mix} = Change in volume after mixing

Δv_{mix} = Change in molar volume of mixture = $\Delta V_{mix}/n_{total}$ or $\Delta v_{mix} = v - \sum x_i v_i$

| | Extensive | Intensive - molar | Intensive - specific |
|--|------------------|-------------------|------------------------|
| SI units | m^3 | $\frac{m^3}{mol}$ | $\frac{m^3}{kg}$ |
| Volume of pure species i at the T and P of the mixture | V_i | v_i | \hat{v}_i |
| Volume of the mixture itself | V | v | \hat{v} |
| Volume change of mixing | ΔV_{mix} | Δv_{mix} | $\Delta \hat{v}_{mix}$ |
| Partial molar volume of species i | — | \bar{V}_i | — |

A negative ΔV_{mix} reflects that the interactions between species 1/2 are stronger than 1/1 or 2/2 alone, thus they pull the species closer together.

Mixing Property Relations

Example) how do I go from some mixing property to partial molar property?

Given Δk_{mix} for a mixture, find \overline{K}_i

$$\Delta k_{mix} \rightarrow \Delta K_{mix} \rightarrow \overline{\Delta K}_{mix,i} \rightarrow \overline{K}_i$$

$$n_{tot} \Delta k_{mix} = \Delta K_{mix} \quad \left(\frac{\partial \Delta K_{mix}}{\partial n_i} \right)_{T,P,n_i} = \overline{\Delta K}_{mix,i} \quad \overline{\Delta K}_{mix,i} = \overline{K}_i - k_i$$

Ideal Solution/Mixture

No molecular interactions between molecules (similar to ideal gasses), thus $\Delta h_{\text{mix}} = \Delta v_{\text{mix}} = 0$

$$\Delta H = \cancel{\Delta U} + \cancel{\Delta PV}$$

$$\Delta H_{\text{mix}} = 0$$

$$\Delta \bar{G}_{\text{mix},1} = \cancel{\bar{H}_{\text{mix},1}} - T \Delta \bar{S}_{\text{mix},1}$$

$$\Delta \bar{G}_{\text{mix},1} = -T \Delta \bar{S}_{\text{mix},1}$$

$$\Delta \bar{G}_{\text{mix},1} = RT \ln(y_1) \quad \text{Partial molar Gibbs of mixing}$$

$$\Delta g_{\text{mix}} = RT \sum x_i \ln(x_i) \quad \text{Overall molar Gibbs of mixing}$$

$$\Delta s_{\text{mix}} = -R \sum_{i=1}^m y_i \ln y_i$$

Overall molar entropy of mixing

$$\Delta \bar{S}_{\text{mix},1} = -R \ln(y)$$

Partial molar entropy of mixing
(derivation in goulas review)

Entropy of mixing will always be positive as there are more molecular configurations in a mixture compared to a pure species

Notice resemblance between partial molar and molar properties for ideal solution

Example

Molar Gibb's Free Energy (intensive): g

Gibb's Free Energy (extensive): G ; $G = nh$ (moles times GFE)

Partial Molar Gibb's Free free energy: $\Delta\bar{G}_{\text{mix}} = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial n_i} \right)_{T,P,n_i}$

Given Δg_{mix} for a binary mixture, derive expression to find $\Delta\bar{G}_a$

Mixture of species a and b behaves ideally

$$\Delta g_{\text{mix}} = RT \sum x_i \ln(x_i)$$

$$\Delta g_{\text{mix}} = RT[x_a \ln x_a + x_b \ln x_b] \quad \text{multiply by } n_{\text{tot}}$$

$$\Delta G_{\text{mix}} = RT \left[n_a \ln \frac{n_a}{n_a + n_b} + n_b \ln \frac{n_b}{n_a + n_b} \right]$$

$$\Delta\bar{G}_{\text{mix},a} = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial n_a} \right)_{T,P,n_b}$$

$$\Delta\bar{G}_{\text{mix},a} = RT \left[n_a \ln \frac{n_a}{n_a + n_b} + n_a \left(\frac{1}{n_a} - \frac{1}{n_a + n_b} \right) - \frac{n_b}{n_a + n_b} \right]$$

$$\Delta\bar{G}_{\text{mix},a} = RT \ln x_a$$

Partial molar Gibbs for species a, same solution as last slide

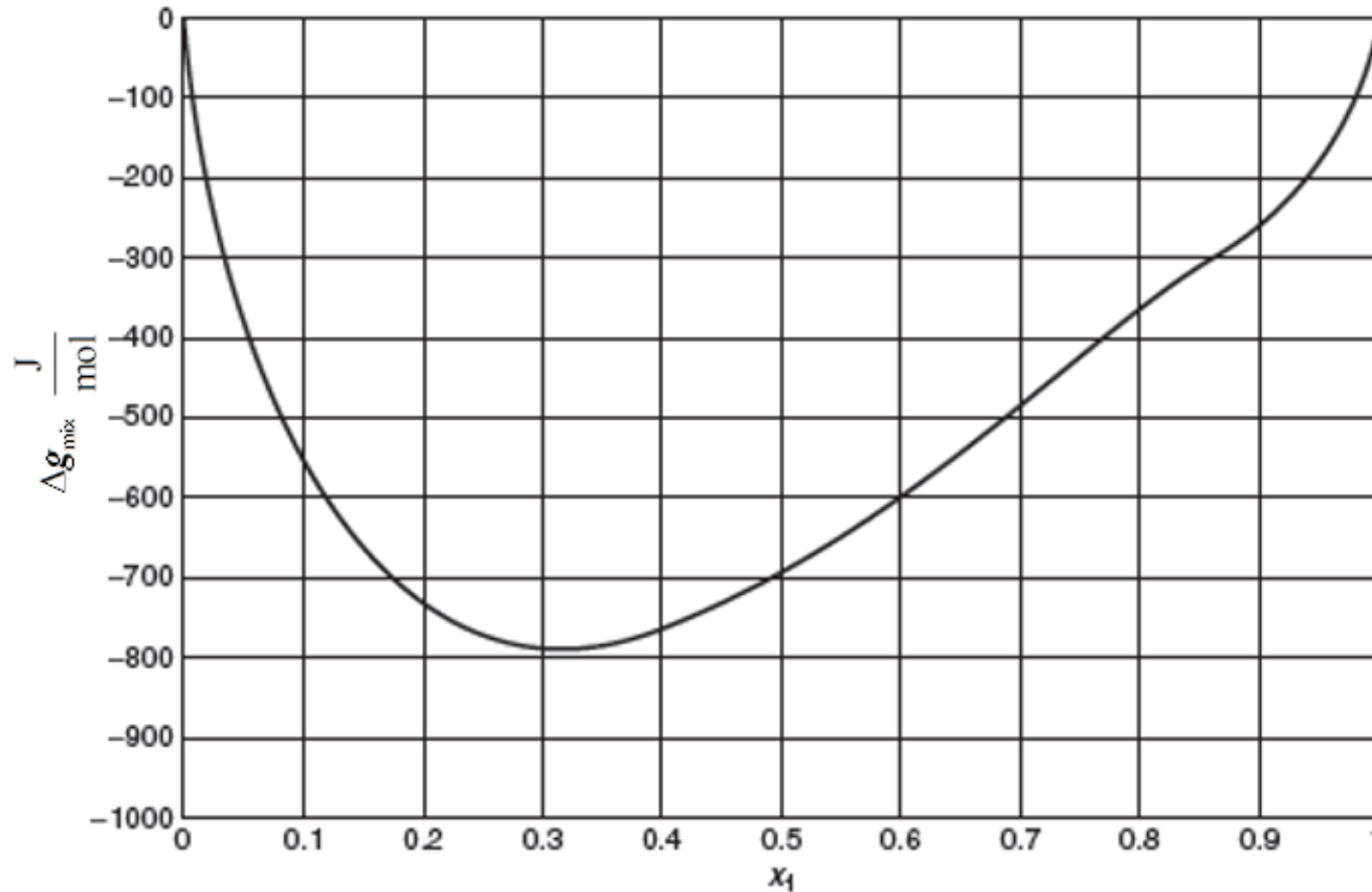
To find \bar{G}_a , recall that

$$\Delta\bar{G}_{\text{mix},a} = \bar{G}_a - g_a$$

$$\bar{G}_a = RT \ln x_a + g_a$$

Concept Review

The Gibbs energy of mixing of a binary liquid mixture of water (1) and 1-propanol (2) vs. mole fraction water (x_1) is shown

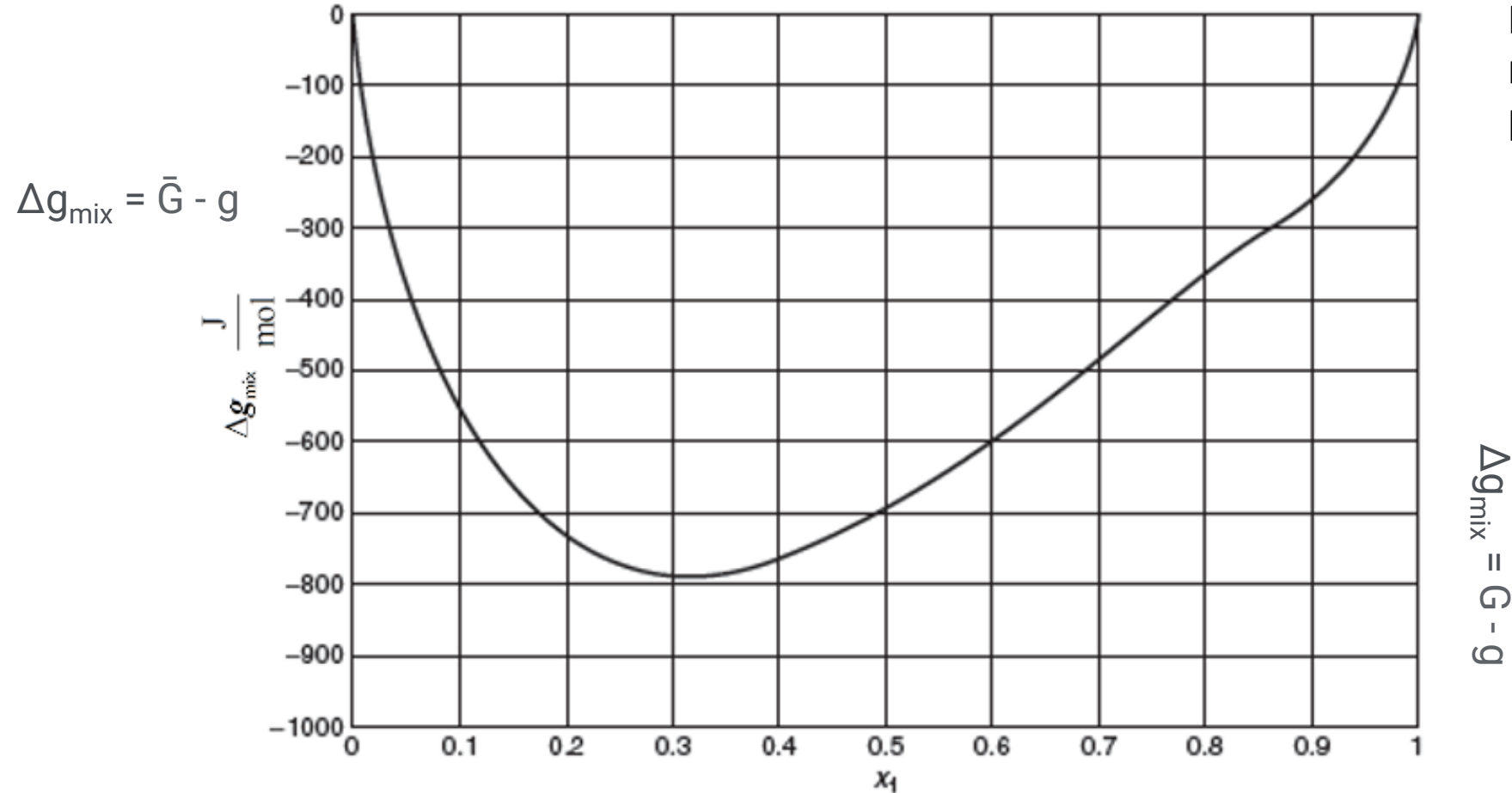


Determine the partial molar Gibbs energy of water in the liquid, \bar{G}_1^l for a mixture of 2 moles water and 3 moles of 1-propanol at 40 C

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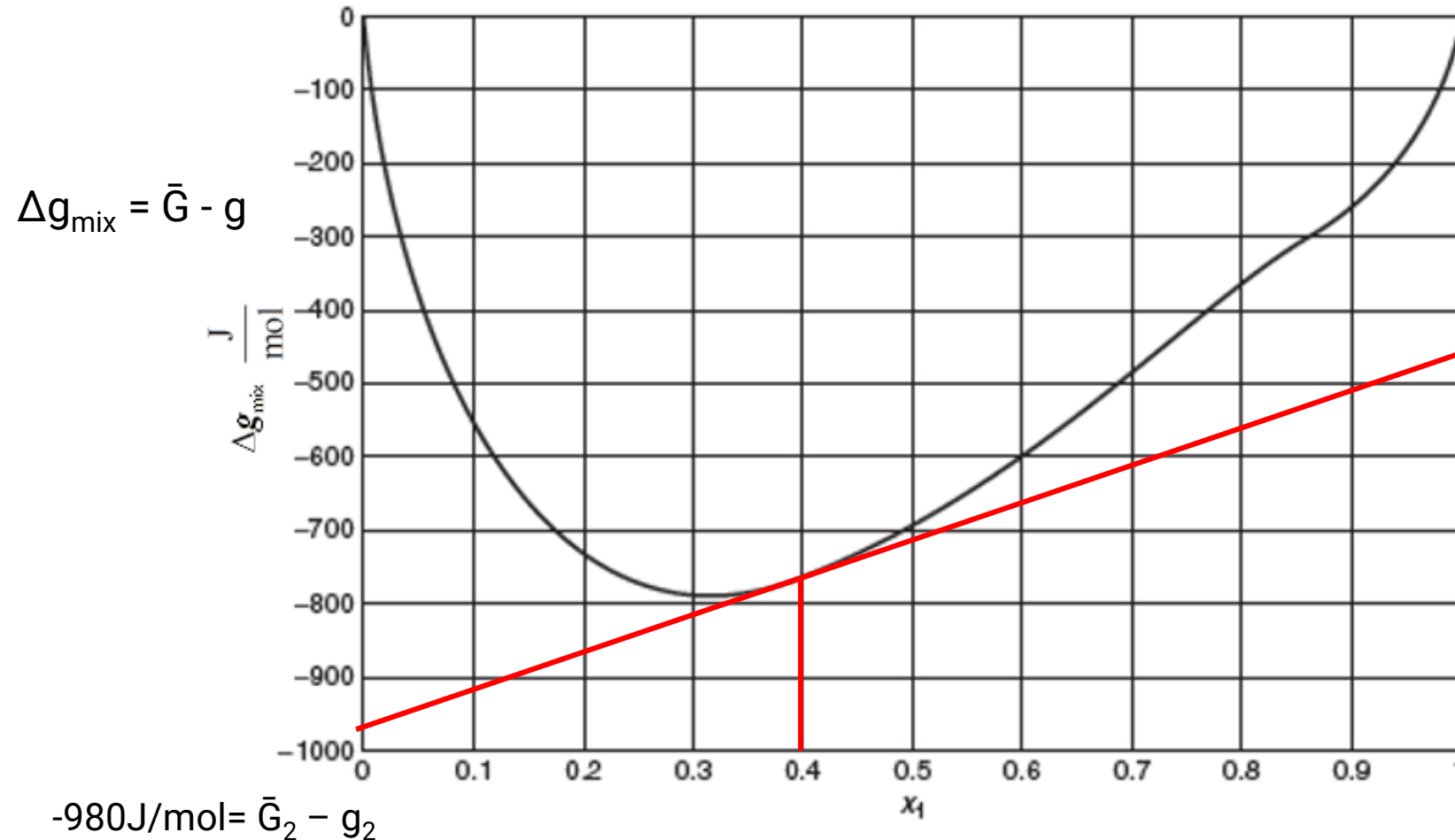


$$X_1 = n_1 / (n_1 + n_2) = 0.4$$

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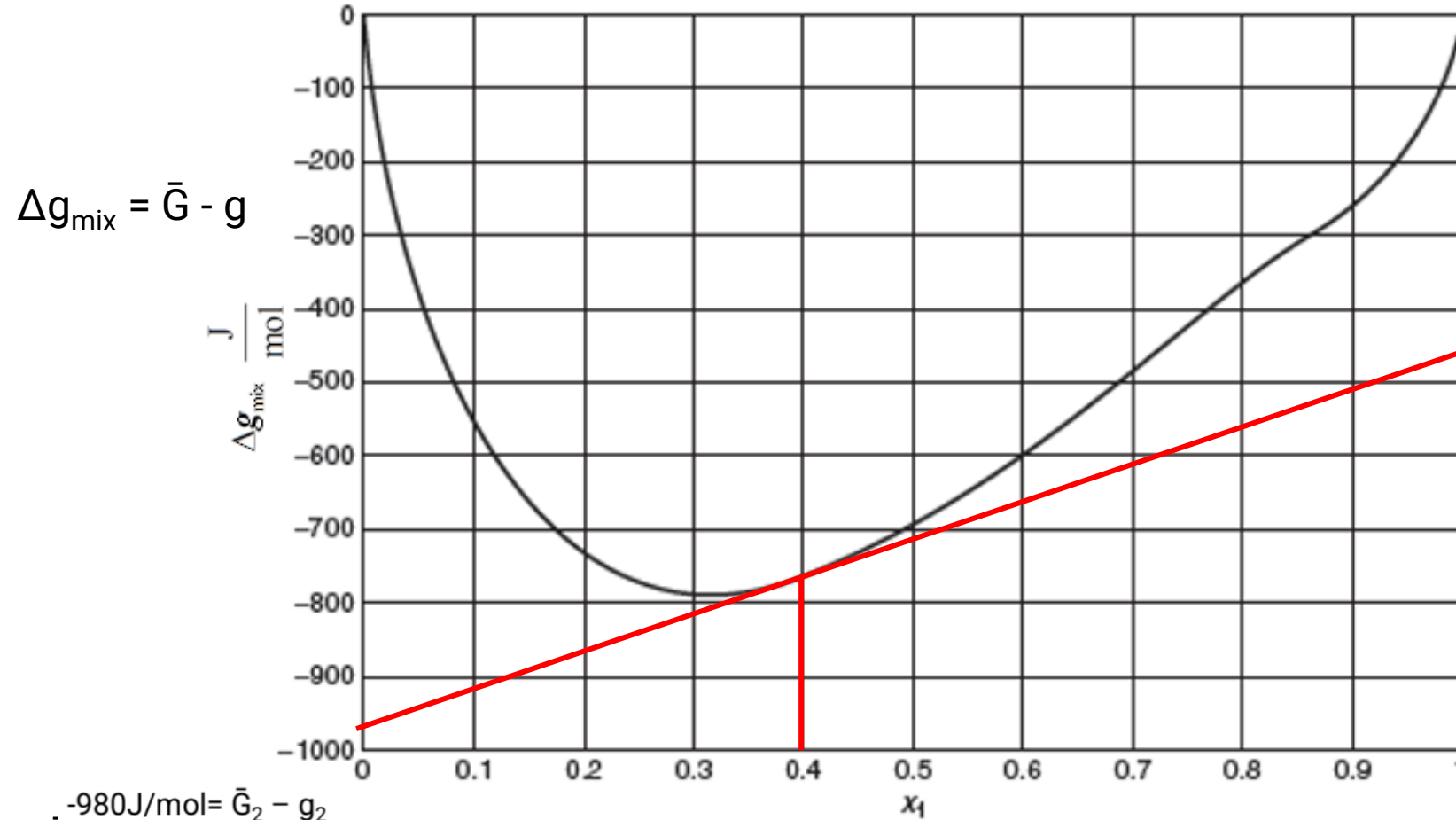
$$-460 \text{ J/mol} = \bar{G}_1 - g_1$$

$$\Delta g_{\text{mix}} = \bar{G} - g$$

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This is also $\Delta \bar{G}_{\text{mix,acetone}}$

This is also $\Delta \bar{G}_{\text{mix,water}}$

$$-460 \text{ J/mol} = \bar{G}_1 - g_1$$

$$\bar{G}_1 = -460 \text{ J/mol} + g_1$$

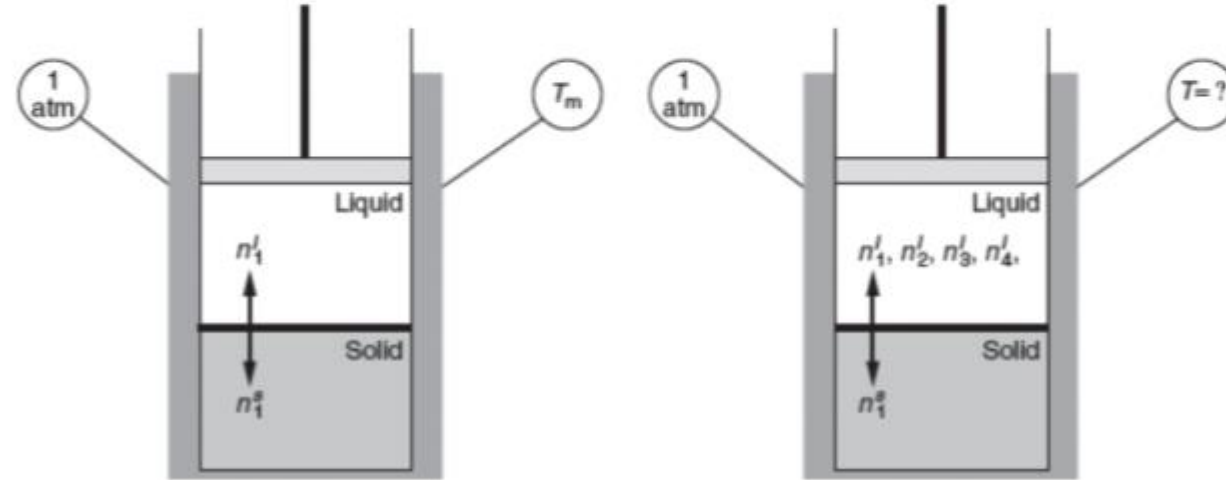
$$\Delta g_{\text{mix}} = \bar{G} - g$$

Steam tables
 $g = h - Ts$

Equilibrium

The following diagram shows the normal melting point of pure solid 1 to be T_m . Consider now that the same pure solid 1 is in a liquid mixture with four species 1, 2, 3, and 4 as shown on the right. How does the temperature at which 1 will be in equilibrium with liquid, T , compare to the case on the left ($T < T_m$, $T = T_m$, $T > T_m$, or you cannot tell without more information)? Explain your answer.

Recall that for a mixture,
 g is $\text{J/mol}_{\text{tot}}$ and
 \bar{G} is J/mol_i

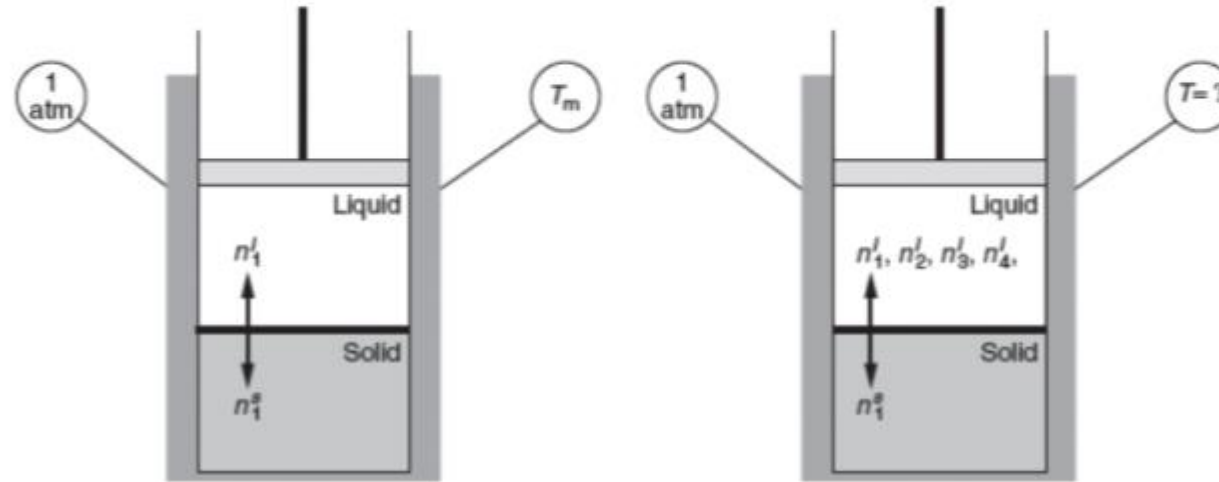


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Recall that for a mixture,
 g is J/mol_{tot} and
 \bar{G} is J/mol_i

A few ways to think about this problem:



$$g_1^s = g_1^l$$

$$G_1^s = G_1^l$$

$$g_1^s = \bar{G}_1^l$$

$$g_1^s > g_1^l$$

Species 1 in the liquid mixture (right) has higher entropy than pure 1 (left). According to $g = h - Ts$, the right will have a **lower** molar Gibbs, g , in the liquid phase than the solid: $g_1^s > g_1^l$. As the liquid is more favorable (more negative), the solid will melt. To return to phase equilibrium the temperature must decrease such that $g_1^s = g_1^l$.

Concept Review

- 1) Explain why $H_1 + H_2$ is not H_{1+2} , similar situation with V. Explain using molecular interactions
- 2) What is meant by infinite dilution and what is the gibb's energy of a species that is infinitely diluted?
- 3) Why does water boil then freeze under a vacuum?
- 4) The Clausius Clapeyron equation is used for VLE but if we assume it is valid for SVE, how can we determine the triple point temperature?
- 5) Ethanol and water mix. Explain the molecular interactions that occur and what results in them
- 6) For an ideal mixture of two gasses under constant T and P, how will Δv_{mix} , Δh_{mix} , Δg_{mix} , and Δs_{mix} be affected? (greater, less than or equal to zero)
- 7)) Practice/memorize/recognize simple derivations for given equations for a property when you find the partial molar property