

Mixtures

- 1) What is the definition of “partial molar property”? Try saying it in words rather than equation.
- 2) Why is the partial molar property not the same as the pure property? What can happen when we mix different species?
- 3) How is excess property defined?
- 4) Do ideal gases always form ideal mixtures when allowed to mix?
- 5) Pick a property, say V . Review the ways we can calculate the partial molar volume. What about straight differentiation? What is the alternative way that only works for binary mixture? What about graphically?
- 6) What is the Gibbs-Duhem equation? In what ways is it useful?
- 7) For ideal solution, what is the molar volume?
- 8) For ideal solution, what is the molar enthalpy?
- 9) For ideal solution, what is the molar entropy?
- 10) For ideal solution, what is the molar Gibbs free energy?
- 11) What is the definition of “infinite dilution property”?

Phase Equilibrium

- 12) How is fugacity defined? What unit does it have?
- 13) How is the fugacity coefficient for a pure component defined?
- 14) For pure vapor, the fugacity coefficient can be calculated using several methods. What are these methods and when are they applicable?
- 15) How is the activity coefficient defined? It describes non-ideality in _____. What information is usually needed to calculate it?
- 16) Fugacity coefficient of a pure gas is related to _____ Gibbs free energy by this equation: _____
- 17) Fugacity coefficient of a gas in a mixture is related to _____ Gibbs free energy by this equation: _____
- 18) Activity coefficient is related to _____ Gibbs free energy by this equation: _____
- 19) How do we calculate the fugacity of the following:
 - a) Pure vapor: i) ideal gas ii) non ideal gas
 - b) Species i in a vapor mixture: i) ideal gas ii) non ideal gas
 - c) Pure liquid
 - d) Species i in a liquid mixture: i) ideal liquid solution ii) non-ideal solution
- 20) What is the Poynting correction factor? When is this term significantly different from 1?
- 21) For a vapor liquid equilibrium, we have the most general expression:

22) Identify each term in the equation above.
- 23) What equation do we have to estimate the saturation pressure of a common chemical species at a given temperature?
- 24) What is Henry’s law constant? This is useful to calculate fugacity of a species in solution when its mole fraction is _____ or when it is very _____
- 25) Draw a P_{xy} diagram for binary system. Pick an arbitrary mole fraction. Show graphically the bubble point and the dew point.
- 26) What is azeotrope? Is azeotrope possible for a system of ideal gas and ideal solution?
- 27) How can we check for azeotrope quickly without having to solve the equilibrium equations.

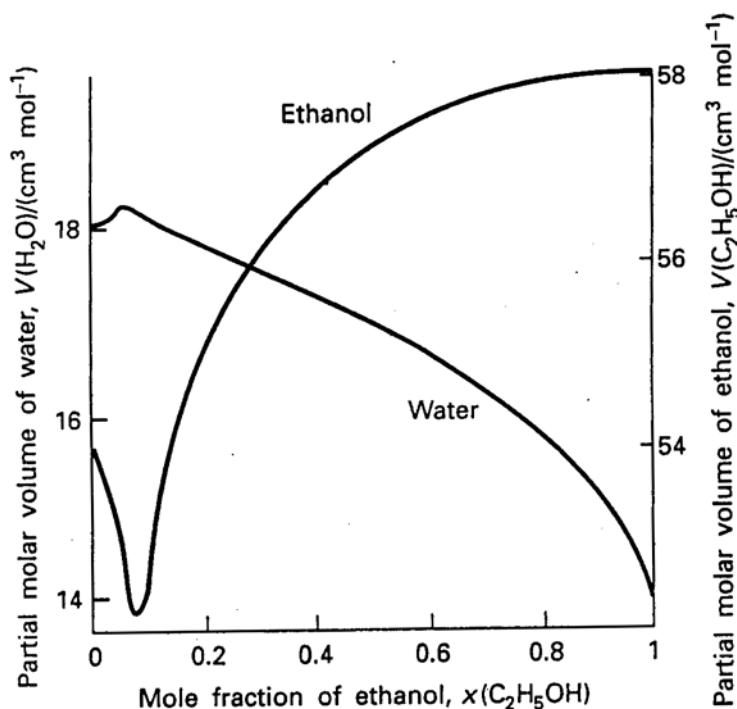
Disclaimer: Not meant to be comprehensive. Not meant to reflect exam’s emphasis either. Consult your notes and textbook before taking prescriptions. Following this guide blindly into the test may cause severe panics, cold sweatings, and unwarranted anger towards your TA.

Quick Problems

- 1) What is wrong with this demand: "I want to set up VLE of a mixture of species A and species B at 100°C and 250 atm, with liquid composition $x_A=0.005$ "?
- 2) For a binary system, we are told that $\gamma_1 = \exp(x_1^2 + Ax_1x_2)$ and $\gamma_2 = \exp(x_2^2 + Ax_2x_1)$
- What is G^E/RT ?
 - Are the expressions for γ_i as given above thermodynamically sound? Why or why not?
- 3) Show that an azeotrope is not possible for a system where the gas is ideal and the liquid solution is ideal.
- 4) (Not too short, not too long)
- For a binary mixture, the following information about entropy (S) and enthalpy (H) are given.
- $$S = x_1 S_1 + x_2 S_2 - R x_1 (Ax_2 + \ln x_1) - R x_2 (Ax_1 + \ln x_2) \quad \text{and} \quad H^E = 0$$
- A = some constant; S_i = entropy of pure component i . Find an expression for γ_1 .

Longer Problems

1) (from Fall 2000 Exam III)

The following V_{xy} chart applies to a binary mixture of ethanol and water.

a) What volumes of pure ethanol and pure water must be mixed in order to produce 100 cm^3 mixture containing 50% ethanol by mass?

b) By how much will the volume of this mixture change if 0.1 cm^3 pure ethanol is added to it?

2)

For a ternary mixture of water(1) and two unknown species (2) and (3), the following information is given:

$$\ln \gamma_1 = x_2 x_3 (1 - 2x_1), \quad \ln \gamma_2 = x_1 x_3 (1 - 2x_2), \quad \ln \gamma_3 = x_1 x_2 (1 - 2x_3).$$
 The mixture forms VLE at 100°C .

- Calculate the fugacity of water in the vapor when the system is at equilibrium at 100°C and 150 atm, with water making up 50 mol% of the liquid solution.
- What is the mole fraction of water in the vapor when the system is at equilibrium at 100°C and 1 atm, with water making up 50 mol% of the liquid solution?

3)

The following information is given for our two favorite species (1) and (2) at 75°C :
$$G^E/RT = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \text{ where } A_{12} = 0.6 \text{ and } A_{21} = 1.5. \quad P_1^{\text{sat}} = 1.2 \text{ atm} \text{ and } P_2^{\text{sat}} = 2.7 \text{ atm.}$$
Henry's law constants: $\mathcal{H}_1 = 2.187 \text{ atm}$ and $\mathcal{H}_2 = 12.10 \text{ atm}$. What is y_2 if $x_1 = 0.99$?

Longer Problems (cont'd)

4)

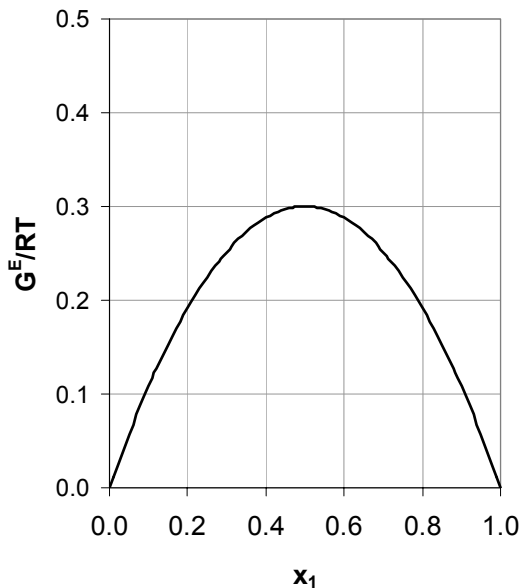
A binary mixture of (1) and (2) was shown to have an azeotrope $x_1 = 0.85$ at $T=25^\circ\text{C}$. The saturation pressures can be approximated as: $P_1^{\text{sat}}/\text{atm} = 0.5 + (0.01)(T/^\circ\text{C})$ and $P_2^{\text{sat}}/\text{atm} = 1 + (0.005)(T/^\circ\text{C})$.

If we assume that G^E/RT can be approximated as Ax_1x_2 ,

- Determine A.
- In a separation process, a mixture of 30 mol% species 1 flows into a flash tank, which is at some T and P. The mixture forms vapor and liquid, which are drawn as two separate streams. The vapor and liquid streams have the same molar flow rate. The liquid composition is 35 mol% species 1. At what temperature and pressure should the tank be kept at?

5)

A binary mixture forms vapor-liquid equilibrium at 100°C . At that temperature, $P_1^{\text{sat}}=1$ atm and $P_2^{\text{sat}}=0.5$ atm. The following chart is given for G^E/RT for temperature and pressure range of interest:



- Calculate the bubble point composition and pressure at 100°C for $x_1 = 0.5$.
- Verify that for $y_1 = 0.63$ the dew point is at $P=0.98$ atm and dew composition $x_1 = 0.40$.

Mixtures

M : U, H, S, G, A, V, $\ln \phi$, $\ln \gamma$

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

$$M = \sum_i x_i \bar{M}_i$$

$$\sum_i x_i d\bar{M}_i = 0 \quad (\text{Gibbs-Duhem, const T\&P})$$

$$\bar{M}_i^\infty = \bar{M}_i \Big|_{x_i \rightarrow 0}$$

For binary only:

$$\begin{aligned} \bar{M}_1 &= M + x_2 \frac{dM}{dx_1} \\ \bar{M}_2 &= M - x_1 \frac{dM}{dx_1} \end{aligned}$$

“graphical method”

Ideal and Real Mixtures

Ideal mixture:

$$\begin{aligned} H^{\text{id}} &= \sum x_i H_i & S^{\text{id}} &= \sum x_i S_i - R \sum x_i \ln x_i \\ V^{\text{id}} &= \sum x_i V_i & G^{\text{id}} &= \sum x_i G_i + RT \sum x_i \ln x_i \end{aligned}$$

Real mixture:

$$\begin{aligned} M &= M^{\text{ig}} + M^{\text{R}} & (\text{gas}) \\ M &= M^{\text{id}} + M^{\text{E}} & (\text{liq}) \end{aligned}$$

Note: A pure liquid is an “ideal” liquid solution, but a pure gas can still be non-ideal.
e.g. $x_i = 1 \Rightarrow \gamma_i = 1$ but $y_i = 1 \not\Rightarrow \phi_i = 1$

Fugacity and Activity

$$\begin{aligned} G_i &= \Gamma_i(T) + RT \ln f_i \quad (\text{pure}) \\ \bar{G}_i &= \Gamma_i(T) + RT \ln \hat{f}_i \quad (\text{mixture}) \end{aligned}$$

$$\phi_i = \frac{f_i^{\text{V}}}{P} \quad \hat{\phi}_i = \frac{\hat{f}_i^{\text{V}}}{y_i P}$$

$$\gamma_i = \frac{\hat{f}_i^{\text{L}}}{x_i f_i^{\text{L}}}$$

VLE

$$\bar{G}_i^{\text{V}} = \bar{G}_i^{\text{L}}$$

→

$$\hat{f}_i^{\text{V}} = \hat{f}_i^{\text{L}}$$

applies to any phase in equilibrium

Vapor

pure	$f_i^{\text{V}} = \phi_i P$	$\ln \phi_i = \frac{G^{\text{R}}}{RT}$
	ϕ_i also from gen. corr.	
mixture	$\hat{f}_i^{\text{V}} = \hat{\phi}_i y_i P$	$\ln \hat{\phi}_i = \frac{\bar{G}_i^{\text{R}}}{RT}$

Liquid

pure	$f_i^{\text{L}} = \phi_i^{\text{sat}} P_i^{\text{sat}}$	$\exp \left[\frac{V_i^{\text{L}}(P - P_i^{\text{sat}})}{RT} \right]$
mixture	$\hat{f}_i^{\text{L}} = \gamma_i x_i f_i^{\text{L}}$	$\ln \gamma_i = \frac{\bar{G}_i^{\text{E}}}{RT}$
mixture $x_i \rightarrow 0$	$\hat{f}_i^{\text{L}} = x_i \mathcal{H}_i$	Henry's law
mixture $x_i \rightarrow 1$	$\hat{f}_i^{\text{L}} = x_i P_i^{\text{sat}}$	Lewis Randall rule

Applications

Txy, Pxy, dew, bubble, azeotrope, flash calculation