

PHY3750
DEVOIR 5

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Problem 1. (12.1) Gibbs Rule: $f = k - \pi + 2$

a) What is the maximum number of phases (π) that can exist simultaneously in equilibrium in a system composed of two different substances that don't react chemically?

Two substances means $k = 2$. Since they are in equilibrium and there are no chemical reactions, Gibbs' rule applies. Since we can't have negative degrees of freedom, we can impose the restriction $f \geq 0$:

$$\begin{aligned} 0 &\leq f = 2 - \pi + 2 \\ 0 &\leq 4 - \pi \\ \pi &\leq 4 \end{aligned}$$

This means that if we have two substances that don't react chemically, they will only be in equilibrium if there are 4 or less phases. Interestingly, Halliwell and Nyburg published a paper in the sixties arguing that negative degrees of freedom made sense:

<http://www.nature.com/nature/journal/v201/n4924/abs/2011118a0.html>

b) In the same system at normal temperature and pressure (300k and 1atm), how many phases can exist simultaneously at equilibrium state?

There could still be up to 4 phases depending on the phase diagram of the two substances.

Problem 2. (12.2)

a) Determine the range of concentrations for which the liquids are miscible at these conditions.

Drawing a tangent, the liquids are immiscible when $x \in (x^a, x^b)$ which is about the range (0.15, 0.7). The liquids are miscible when $x < 0.15$ and $x > 0.7$.

b) If a mixture has 3 moles of liquid A and 2 moles of liquid B, what is the Gibbs energy of the mixture in equilibrium?

The molar fraction of liquid B is

$$x = \frac{2}{3+2} = 0.4$$

On the graph, this is an unstable point and lies between x^a and x^b , so the mixture will separate into two phases of composition x_a and x_b whose energies are about, respectively

$$G_a = 40\text{kJ/mol} \quad G_b = 9\text{kJ/mol}$$

The total energy is the average of the mixture in equilibrium is

$$G = \frac{40+9}{2} = 24.5\text{kJ/mol}$$

which we could have just gotten directly from the tangent line at $x = 0.4$.

c) How many phases exist in equilibrium for a mixture of this composition? What is the composition and number of moles for each phase?

There are two phases a and b with compositions of liquid B $x_B^a = 0.15$, and $x_B^b = 0.7$ when the mixture reaches equilibrium. The starting mixture has a composition of $x_B = 0.4$ with $n_A = 3\text{mol}$ and $n_B = 2\text{mol}$. Assuming the number of moles of B and the total number of moles, don't change we know

$$n_B = n_B^a + n_B^b \quad n = n^a + n^b$$

Since $n_B = nx_B$, $n_B^a = n^a x_B^a$, and $n_B^b = n^b x_B^b$, we have

$$nx_B = n^a x_B^a + n^b x_B^b$$

Eliminating n^b with $n^b = n - n^a$ we get

$$\begin{aligned} nx_B &= n^a x_B^a + (n - n^a)x_B^b \\ &= n^a x_B^a + nx_B^b - n^a x_B^b \\ &= n^a (x_B^a - x_B^b) + nx_B^b \\ n^a &= \frac{n(x_B - x_B^b)}{x_B^a - x_B^b} = \frac{5(0.4 - 0.7)}{0.15 - 0.7} = 2.72\text{mol} \end{aligned}$$

Thus the number of moles in phase b is $n^b = n - n^a = 5 - 2.72 = 2.28\text{mol}$.

d) Based on the curve compare the molecular forces of cohesion (A-A and B-B) to the molecular forces of adhesion (A-B).

First off, the Gibbs free energy at pure A ($x = 0$) and pure B ($x = 1.0$) represents the cohesion forces A-A and B-B, respectively. We see that B is more stable since it's Gibbs free energy is lower than that of A.

The A-B adhesive forces are at $x = 0.15$ and $x = 0.7$. Both represent a more stable state than A alone. The adhesive forces for the mixture at $x = 0.15$ are about as strong as the cohesive forces for B-B but the adhesive forces for the mixture at $x = 0.7$ are stronger than the cohesive forces for B-B.

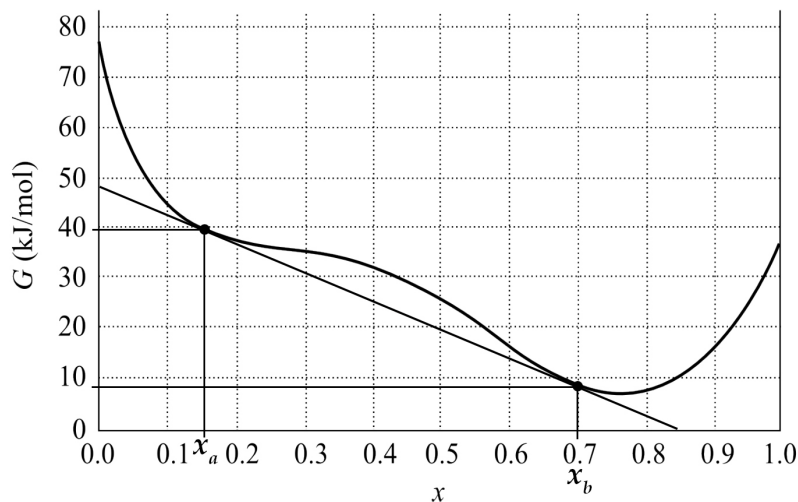


FIGURE 0.1. Gibbs Energy for mixture of liquid A and B

Problem 3. (12.6)

a) A phase diagram of a mixture of ethanol and water.

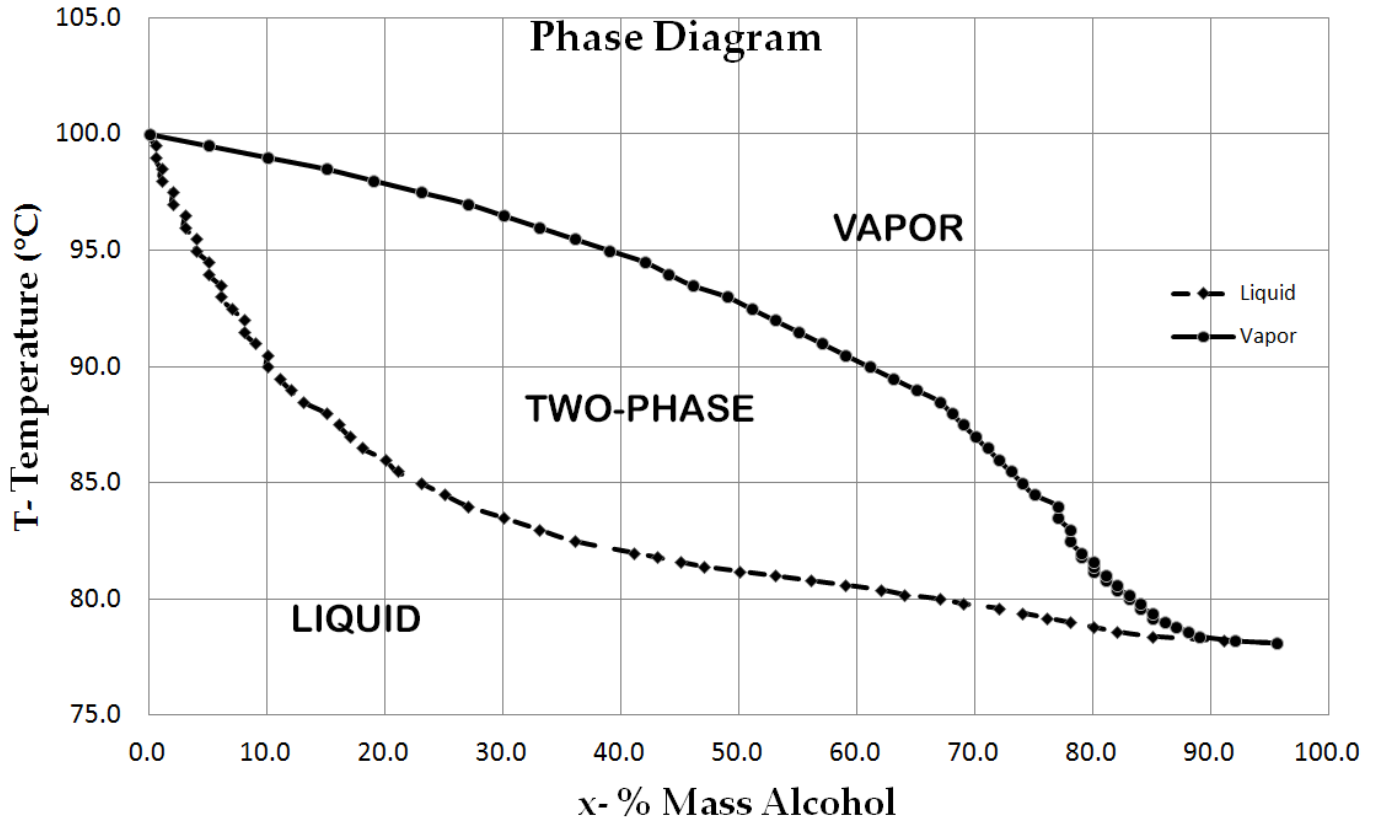


FIGURE 0.2. Phase Diagram

b) Indicate the number of equilibrium phases in each region of the diagram. Apply Gibbs rule to find the degrees of freedom (the dimensionality) for each region and explain the link between the dimensionality and the diagram.

The region below the two curves is 1 phase, liquid. Using Gibbs rule, $f = 2 - 1 + 2 = 3$. This represents the freedom to pick T , x , and P freely within that phase.

The region between the two curves is 2 phases, liquid and vapor. Using Gibbs rule, $f = 2 - 2 + 2 = 2$. This represents the freedom to pick T , and P , but not x , since x is constrained to the line separating the two-phase and the vapor regions and to the line separating the two-phase and the liquid regions.

Problem 4. Using the preceding phase diagram, consider a liquid mixture of ethanol and water with $x = 10\%$.

a) Find the boiling temperature.

Based on the diagram the temperature at which boiling starts is 90°C.

b) At 95°C, calculate the compositions of vapor and liquid.

Draw a horizontal line at 95°C and read off the fractions at the intersections of this horizontal line and the two curves. The percent liquid composition is about $x_L = 5\%$ and the percent vapor composition is about $x_V = 40\%$. The average concentration is $x_0 = 10\%$.

c) At 95°C, calculate the fraction of the initial liquid that evaporated.

The amount of stuff that became vapor n_V is the amount of liquid that evaporated. Using $n = n_L + n_V$, we know

$$\begin{aligned} n_L x_L + n_V x_V &= n x_0 \\ (n - n_V) x_L + n_V x_V &= n x_0 \\ n x_L - n_V x_L + n_V x_V &= n x_0 \\ n x_L + n_V (x_V - x_L) &= n x_0 \\ n_V &= n \frac{x_0 - x_L}{x_V - x_L} \end{aligned}$$

The fraction that became vapor then is

$$\frac{x_0 - x_L}{x_V - x_L} = \frac{0.1 - 0.05}{0.4 - 0.05} = 0.14$$

14% of the initial liquid evaporated.

Problem 5. (12.7)

a) See attached for graphs. Write the combination of the equilibrium phases existing in different ranges of composition at each of the six temperatures.

At $T = 1100\text{K}$, the equilibrium phase is a liquid.

At $T = 1000\text{K}$, the equilibrium phase is a solid for $x < 0.21$, is unmixed with solid and liquid phases for $0.21 < x < 0.52$, and is liquid for $0.52 < x$.

At $T = 900\text{K}$, the equilibrium phase is a solid for $x < 0.32$, is unmixed with solid and liquid phases for $0.32 < x < 0.69$, and is liquid for $0.69 < x$.

At $T = 800\text{K}$, the equilibrium phase is a solid for $x < 0.42$, is unmixed with solid and liquid phases for $0.42 < x < 0.80$, and is liquid for $0.80 < x$.

At $T = 700\text{K}$, the equilibrium phase is a solid for $x < 0.58$, is unmixed with solid and liquid phases for $0.58 < x < 0.91$, and is liquid for $0.91 < x$.

At $T = 600\text{K}$, the equilibrium phase is a solid.

b) DONE

c) OKAY

d) Identify the different regions of the phase diagram and describe the equilibrium phases in each region.

There are three regions. The region below both curves is a region where all the equilibrium phases are solid. The region between the two curves is a region where the mixture will separate into a solid phase and a liquid phase in equilibrium. The region above the curves is always a liquid phase in equilibrium.

e) Consider isobaric fusion of an alloy with composition $x = 0.3$. Determine from the diagram the temperature of the start of fusion, the initial composition of the liquid phase, and the temperature at which fusion stops.

From the diagram, fusion starts at about 900K and ends at about 1100K. The initial composition of the liquid would be 0 since fusion is just starting from the completely solid phase?

Problem 6. (13.2)

The equilibrium constant of the reaction $\text{SO}_3 \rightleftharpoons \text{SO}_2 + \frac{1}{2}\text{O}_2$ is equal to $171.9\text{Pa}^{1/2}$ at $T = 1000\text{K}$. The system contains 2 moles of SO_3 and 1 mole of SO_2 in equilibrium, and the pressure in the reactor is 0.4MPa .

a) Determine the stoichiometric coefficients and write the mass action law for this reaction.

The coefficients are $v_{\text{SO}_3} = -1$, $v_{\text{SO}_2} = 1$, $v_{\text{O}_2} = \frac{1}{2}$. The mass action law is

$$\begin{aligned} x_{\text{SO}_3}^{-1} x_{\text{SO}_2}^1 x_{\text{O}_2}^{1/2} &= P^{-(-1+1+\frac{1}{2})} k(T) \\ \frac{x_{\text{SO}_2} \sqrt{x_{\text{O}_2}}}{x_{\text{SO}_3}} &= \frac{1}{\sqrt{P}} k(T) = \frac{1}{\sqrt{0.4 \times 10^6}} 171.9 = 0.27 \end{aligned}$$

b) Calculate the quantity of oxygen in the system at these conditions.

$$\begin{aligned} n_{\text{SO}_3} &= 2 \implies x_{\text{SO}_3} = \frac{n_{\text{SO}_3}}{n_{\text{tot}}} = \frac{2}{3+n} \\ n_{\text{SO}_2} &= 1 \implies x_{\text{SO}_2} = \frac{1}{3+n} \\ n_{\text{O}_2} &= n \implies x_{\text{O}_2} = \frac{n}{3+n} \end{aligned}$$

Using the mass action law

$$\begin{aligned} 0.27 &= \frac{\frac{1}{3+n} \sqrt{\frac{n}{3+n}}}{2} (3+n) = \frac{1}{2} \sqrt{\frac{n}{3+n}} \\ (0.54)^2 &= \frac{n}{3+n} \\ n &= \frac{3(0.54)^2}{1 - (0.54)^2} = 1.23\text{mol} \end{aligned}$$

There is 1.23mol of oxygen in the system.

Problem 7. (13.4)