4/4/2013 Lecture 16: Phase changes in Binary Mixtures

I. Ideal liquids (A, B) \( U(x) = U_0 \)
   \[ \rightarrow \text{No phase separation} \quad \text{if} \quad V \quad \text{is different} \]

\( x = 0 \): Pure A: boils at \( T_A \)  
\( x = 1 \): Pure B: boils at \( T_B \)  

\[ F(x) = U_0 - TS(x) \]

a) \( T > T_B \) \( \Rightarrow \) all gas, no liquid

\[ F \quad \text{liquid} \quad \text{g} \quad \text{gas} \]

\[ F_{\text{gas}} > F_{\text{liq}} \]

\( 0 \quad 1 \quad x \quad \Rightarrow \text{here we have homogeneous gas mixture (all x)} \)

6) \( T = T_B \) \( x = 1 \) \( \text{Fl}_{\text{liq}} = F_{\text{gas}} \) (B liquefies)

\( x = 0 \) \( \text{Fl}_{\text{g}} \quad \text{F}_{\text{gas}} \) (A still gas)
1. Coexistence of A-rich (x < X) and B-rich liquid (x > X)

2. T → T_A: Less gas, more liquid

\[ 0 \leq x \leq 1 \]

Let's plot the full T-x phase diagram:

- \( T_A < T < T_B \)
- \( x \approx x \) for gas > liquid → liquid
- \( x < x \) for gas < liquid → gas

Implications:

- Existence of A-rich (x < X) and B-rich liquid (x > X)
- T → T_A: Less gas, more liquid
Observations on T vs X phase diagram:

1. \( T_{\text{bub}}(x) < T < T_{\text{dew}}(x) \) \( \Rightarrow \) persistence of \( \text{Liq} + \text{Gas} \) (like in mol.

gas)

2. \( T > T_{\text{dew}} \) \( \Rightarrow \) homogeneous gas A + gas B

\( T < T_{\text{bub}} \) \( \Rightarrow \) \( \text{Liq A} + \text{Liq B} \)

Example: Liquidation of air

\( \text{air} = 21\% \text{ O}_2 + 79\% \text{ N}_2 \) \( (x=0.21) \)

\[ T \geq 81.6 \text{ K} \]

\[ 77.4 \text{ K} \quad \text{com} \]

Pure \( \text{N}_2 \) \( \Rightarrow \) G-L 77.4 K

Pure \( \text{O}_2 \) \( \Rightarrow \) G-L 90.2 K

\[ x = 0.21 \quad 0.28 \quad x = 1 \quad \Rightarrow \text{all oxygen} \]

\[ x = 0.85 \]

3. Cool dry air to dewpoint \( x=0.21 \Rightarrow T_{\text{dew}}=81.6 \text{ K} \)

2. Air decomposes at \( T=81.6 \text{ K} \)

\( \text{O}_2\)-rich \( \Rightarrow \)

\( T_{\text{bublle}} = 81.6 \text{ K} \) \( \Rightarrow x = 0.48 \)

\( \text{N}_2\)-rich Gas \( T_{\text{dew}} > 81.6 \text{ K} \)
(3) Cool again to $T = 80 \text{K}$ ($x = 0.35$)

i) more liquid since now $0.35 < x < 0.48$ (the two N$_2$-richs are liquid)

ii) Source of N$_2$: N$_2$-rich gas (Bog gas remains, but it is N$_2$-rich)

(4) Continue cooling until $T = T_{\text{LH}_{2}O}$ ($x = 0.21$) = 79 K

i) Liquid H$_2$O produces

ii) discard remaining gas ($79 \text{K} > 77.8 \text{K}$)

Example 2: Distillation - a way to separate liquids + gases into pure constituents

Example: Water + ethanol

$T_{D \text{H}_2O} = 100 \text{C}$

$T_{B \text{ethanol}} = 78 \text{C}$

Diagram:

- Liquid
- Gas
- Azeotrope
- Pure $H_2O$
- Pure ethanol
1. Heat mixture ($x < x_i$) to T to bubble ($X$)

2. Phase separation:
   - Ethanol rich gas $x > x_i$
   - Water rich lig $x < x_i$ (discard)

3. Cool ethanol rich gas $\rightarrow$ ethanol rich lig and repeat (1, 2)

4. Each step produces gas with greater ethanol concentration.

5. $x > 0.95$: Composition with lowest dew point, highest bubble point

   $x > 0.95$: must use chemical means to remove last 5% of water (methanol, freeze, etc.)
Problem 5.62

Consider a completely miscible two component system. The overall concentration of phase B is x. The temperature is fixed to the interval where gas and liquid coexist. What is the proportion of gas phase to liquid phase?

\[ \Rightarrow \text{At some } T \text{ within the interval } T_{b1} < T < T_{b2}, \text{ the concentration of phase B in gas is } x_{gao}, \text{ in liquid is } x_{lig}. \]

If the total number of molecules in the gas phase is \( N_{gao} \) and in liquid is \( N_{lig} \), then:

\[ x_{gao} N_{gao} + x_{lig} N_{lig} = x \left( N_{gao} + N_{lig} \right) \]

\[ \frac{x_{gao}}{x_{gao} + x_{lig}} = x \frac{N_{gao}}{N_{gao} + N_{lig}} \]

\[ x_{gao} = \frac{x - x_{lig}}{N_{lig}} \cdot \frac{N_{gao}}{x_{gao}} = x \]

The ratio of the total number of molecules in gas to total number of molecules in liquid is in the ratio of the lengths of the \( ++ \) and \( -- \) segments below:

\[ x_{gao} \]

\[ N_{gao} \]

\[ x_{lig} \]

\[ N_{lig} \]