

Problem Set 3
Solutions
3.20 MIT
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Problem 1

There are two steps to solving this problem

- (1) What is the pressure difference in terms of the height?
- (2) What is the height of the hill?

Use the following form of the Clapeyron equation (this is valid for equilibrium between an ideal gas and a solid or liquid)

$$d \ln P = -\frac{\Delta H}{R} d\left(\frac{1}{T}\right)$$

Which in this case can be written in terms of the pressure at the top and bottom of the hill, and the respective boiling points

$$\ln\left(\frac{P_{top}}{P_{bottom}}\right) = -\frac{\Delta H}{R} \left[\frac{1}{T_{top}} - \frac{1}{T_{bottom}}\right]$$

Now we write the pressure at the bottom in terms of the pressure at the top

$$P_{bottom} = P_{top} + \rho_{air}gh$$

Substituting this,

$$\ln\left(\frac{P_{top}}{P_{top} + \rho gh}\right) = -\ln\left(\frac{1 + \frac{\rho gh}{P_{top}}}{1}\right)$$

If we expand $\ln(1+x)$ we get,

$$\frac{\rho gh}{P_{top}} = \frac{\Delta H}{R} \left[\frac{1}{T_{top}} - \frac{1}{T_{bottom}}\right]$$

$$h = \frac{\Delta H * P_{top}}{\rho g} \left[\frac{1}{T_{top}} - \frac{1}{T_{bottom}}\right]$$

Assuming that the air is an ideal gas, we can relate the density and pressure to the temperature using the ideal gas law

$$\frac{P}{\rho} = \frac{PV}{M} = \frac{nRT}{M} = \frac{RT}{(MW)}$$

where (MW) is the molecular weight of the air. We now have

$$h = \frac{\Delta H * RT}{g(MW)} \left[\frac{1}{T_{top}} - \frac{1}{T_{bottom}}\right]$$

Plugging in some numbers ($g = 10m/s^2$, $MW = 28.8g/mol$, and we are dealing with air at $25^\circ C$)

$$h = \frac{1000cal/mol * 4.184J/cal * 8.314J/molK * 298K}{10m/s^2 * 0.0288kg/mol} \left[\frac{1}{368K} - \frac{1}{378K}\right]$$

$$h = 2.6km$$

Problem 2

(a) Integrate the Clausius-Clapeyron Equation

$$\frac{d \ln P^*}{d(1/T^*)} = -\frac{\Delta H}{R}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

For this example, $P_1 = 1 \text{ atm}$ (at boiling), $T_1 = 1620\text{K}$, and $T_2 = 1000\text{K}$

$$\ln P_2 = \frac{-156,000}{8.314} \left[\frac{1}{1000} - \frac{1}{1620} \right]$$

$$P_2 = 7.6 \times 10^{-4} \text{ atm}$$

(b) At the melting point of Li, $P_{solid} = P_{liquid}$

$$13.049 - \frac{19,314}{T} = \frac{-156,000}{8.314} \left[\frac{1}{T} - \frac{1}{1620} \right]$$

$$1.47 = \frac{550.5}{T}$$

$$T = 375\text{K}$$

Problem 3

First we can find what the vapor pressure over the liquid would be under these conditions

$$\ln(P^*) = -\frac{30671}{T} + 12.5 = -\frac{30671}{1500} + 12.5 = -7.95$$

$$P^* = 3.54 \times 10^{-4} \text{ atm} = 35.8 \text{ Pa}$$

If all of the silver was in the vapor phase (1 gram)

$$P = \frac{nRT}{V} = \left(\frac{1}{107.87} \right) (8.314) (1500) = 115.61 \text{ Pa}$$

Hence, there must be both liquid and vapor present

$$P = P^* = 35.8 \text{ Pa}$$

Now we can find the moles in the vapor phase

$$n = \frac{PV}{RT} = \frac{35.8}{8.314 * 1500} = 2.87 \times 10^{-3} \text{ moles}$$

Grams of vapor

$$(2.87 \times 10^{-3} \text{ moles}) (107.87 \text{ g/mol}) = 0.31\text{g}$$

So the fraction in the vapor phase is 0.31

(b) In general the amount of heat necessary would be the sum of the mixing enthalpy and the enthalpy of vaporization

$$\Delta H_{total} = \Delta H_{mix} + \Delta H_{vap}$$

However, since we are told to assume the solution is ideal, the enthalpy of mixing is zero. (This is related to the assumption that the mixing species do not interact)

Thus

$$Q = \Delta H_{total} = \Delta H_{vap}$$

Since we were not given the enthalpy of vaporization or the boiling point in the data, we must find these quantities. To find the boiling point, use the given equation for the vapor pressure and find the temperature where the pressure is equal to 1 atm.

$$\ln(1) = -\frac{30671}{T} + 12.5 \rightarrow T_b = 2454\text{K}$$

To find the heat of vaporization, we can use the integrated form of the Clapeyron equation for an ideal gas. We know the temperature and pressure at two points (from the given equation for vapor pressure) and we can then calculate ΔH_{vap} .

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

Choosing $T = 1500$ and 1600 K , the value calculated for ΔH_{vap} is 255 kJ/mole . (If you look this up you get 251 kJ/mole) Now we can get the enthalpy of vaporization at 1500K , which can be done using a loop, since we know enthalpy is a state function

$$\Delta H_{vap}(1500K) = \int_{1500}^{2454} C_p^l dT + \Delta H_{vap}(2454K) + \int_{2454}^{1500} C_p^g dT$$

$$\Delta H_{vap}(1500K) = 33J/molK * (2454 - 1500) + 11,300J/mol + \frac{5}{2}R(1500 - 2454)$$

$$\Delta H_{vap}(1500K) = 267kJ/mol$$

Problem 4

$$P_{total} = P_{N_2} + P_{H_2O} = 1atm$$

At 70°C,

$$P_{H_2O} = 0.3atm \implies P_{N_2} = 0.7atm$$

After the isothermal volume reduction:

P_{H_2O} is still equal to 0.3 atm since P_{H_2O} can not increase since it is the saturation vapor pressure! This will mean that as the volume is being reduced, H₂O will condense, keeping P_{H_2O} at 0.3 atm.

P_{N_2} will double

$$P_{N_2} = n_{N_2} \frac{RT}{V}$$

$$V \rightarrow \frac{V}{2} \implies P_{N_2} \rightarrow 2P_{N_2}$$

So,

$$P_{total} = 1.4 + 0.3 = 1.7 atm$$

Problem 5

(a) The boiling point is where $P^* = P_{atmosphere}$. So $P_{H_2O}^* = 1atm$ at the regular boiling point.

(b) The Clausius-Clapeyron equation allows us to find vapor pressure at some temperature from knowledge of the vapor pressure at another temperature

$$d \ln P^* = -\frac{\Delta H}{R} d\left(\frac{1}{T}\right)$$

We can integrate this between 373K and 288K

$$\ln \frac{P_{373}}{P_{288}} = -\frac{40,000}{8.314} \left[\frac{1}{373} - \frac{1}{288} \right]$$

$$P_{H_2O}^*(288K) = 0.021atm$$

Relative humidity is defined as

$$R.H. = \frac{P_{H_2O}}{P_{H_2O}^*}$$

In this problem the relative humidity is 65% so we can find the P_{H_2O}

$$0.65 = \frac{P_{H_2O}}{0.021} \implies P_{H_2O} = 0.0136atm$$

The dew point is the temperature where $P_{H_2O} = P_{H_2O}^*$. Again we integrate the Clausius-Clapeyron equation, this time solving for T

$$\ln \frac{0.021}{0.0136} = -\frac{40,000}{8.314} \left[\frac{1}{288} - \frac{1}{T} \right]$$

$$T = 281K = 8^\circ C$$

Problem 6

n_{uc} = number of unit cells

$V = n_{uc}V_{uc}$, where V_{uc} is the volume per unit cell

$$\bar{V}_{Li} = \frac{\partial V}{\partial n_{Li}} = \frac{\partial(n_{uc}V_{uc})}{\partial(n_{uc}x)}$$

And since n_{uc} is a constant,

$$\bar{V}_{Li} = \frac{\partial V_{uc}}{\partial x}$$

This is the slope of the curve given. Thus at $x = 1$ the partial molar volume of Li is

$$\bar{V}_{Li} = -1.15 \frac{\text{cm}^3}{\text{atom}}$$

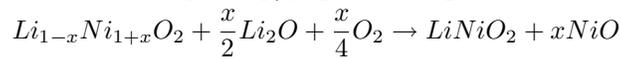
Problem 7

The vapor pressure of pure B at 1000 K is 5×10^{-4} atm. If B is in an ideal solution with another species at 1000 K, its vapor pressure will be:

- Higher than 5×10^{-4}
 Lower than 5×10^{-4}
 Equal to 5×10^{-4}
 Impossible to say

Problem 8

Reaction to go from non-stoichiometric $Li_{1-x}Ni_{1+x}O_2$ to $LiNiO_2$



Principle of LeChatleier indicates that a higher P_{O_2} will push the reaction to the right.

Problem 9

Once again, we start with the Clausius-Clapeyron equation in this form

$$\frac{dP}{dT} = \frac{\Delta H}{\Delta V} \frac{1}{T} \rightarrow dP = \frac{\Delta H}{\Delta V} \frac{dT}{T}$$

Integrating we get

$$P_2 - P_1 = \frac{\Delta H}{\Delta V} \ln \left(\frac{T_2}{T_1} \right)$$

Let P_1 be the pressure at the original interface ($T_1 = -5^\circ C$) and P_2 be the pressure at the new interface ($T_2 = -5.2^\circ C$)

We can also relate the densities to the volume change as follows:

$$\Delta V = \frac{1}{\rho^l} - \frac{1}{\rho^s} = \frac{\rho^s - \rho^l}{\rho^l \rho^s}$$

So,

$$P_2 - P_1 = \frac{\rho^l \rho^s}{\rho^s - \rho^l} \Delta H \ln \left(\frac{T_2}{T_1} \right)$$

Also, we know

$$P_1 = P_2 + \rho^s gh \text{ or } P_2 - P_1 = -\rho^s gh$$

Putting this together we get

$$-\rho^s gh = \frac{\rho^l \rho^s}{\rho^s - \rho^l} \Delta H \ln \left(\frac{T_2}{T_1} \right)$$

Solving for the density of the solid,

$$\rho^s = \rho^l \left[1 - \frac{\Delta H}{gh} \ln \left(\frac{T_2}{T_1} \right) \right]$$

Putting in the values of the know quantities (being very careful with units)

$$\rho^s = 1000g/m^3 \left[1 - \frac{8371J/kg}{9.8m/s^2 * 0.4m} \ln \left(\frac{267.8K}{268K} \right) \right]$$

$$\rho^s = 2.6g/cm^3$$