Homework #7 | Due: November 3
Name ___________________________ | Chemistry 331

1. Calculate the boiling point of water of on the top of Mt. Kilimanjaro (elevation 6000 m).

Solution: Use the barometric pressure formula to obtain the pressure on the top of Kilimanjaro.

$$P = P_0 \exp\left\{-\frac{Mgh}{RT}\right\} = (1\ atm)\exp\left\{\frac{(0.029\ kg/mol)(9.8\ m/s^2)(6000\ m)}{(8.31 J/mol\text{–}K)(298\ K)}\right\}$$

$$= 0.5\ atm$$

Then use the known boiling point of water (373 K) and the vapor pressure of 1 atm substituted into the Clausius-Clapeyron equation.

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

$$\frac{\Delta H_{vap}}{RT_2} = \frac{\Delta H_{vap}}{RT_1} - \ln\left(\frac{P_2}{P_1}\right)$$

$$T_2 = \frac{\Delta H_{vap}}{\Delta H_{vap} - RT_1 \ln\left(\frac{P_2}{P_1}\right)} T_1$$

$$T_2 = \frac{T_1}{1 - \frac{RT_1}{\Delta H_{vap}} \ln\left(\frac{P_2}{P_1}\right)}$$

Written in this way you can see the correction factor in the denominator.

$$\frac{RT_1}{\Delta H_{vap}} \ln\left(\frac{P_2}{P_1}\right) = \frac{(8.31\ J/mol\text{–}K)(373\ K)}{40660\ J / mol} \ln\left(\frac{0.5}{1}\right) = -0.0528$$

$$T_2 = \frac{T_1}{1 - (-0.0528)} = \frac{373\ K}{1.0528} = 354\ K = 81\ ^oC\ !$$

2. A. How many kilograms of water can be evaporated from a 1 m^2 surface in a lake on a hot summer day, if it is assumed that the limiting factor is solar insolation (1000 W/m^2). Assume that the length of the day is 8 hours and that the air and water temperature are both 40 ^{o}C.
B. What volume of air is needed to hold this much water vapor at 40 ^{o}C.
C. When the sun sets, the air temperature drops to 20 ^{o}C. Assuming that the excess water vapor is precipitated as rain, calculate the weight of the rain and the amount of heat released when the water condenses.

Solution: A. For this part we assume that water in be vaporized according to the equilibrium:

$$H_2O\ (l) \rightarrow H_2O\ (g)$$

To convert flux (solar insolation of 1000 W/m^2) into energy we need to compute the seconds in one 8 hour day and an area (which happens to be 1 m^2 so this corresponds exactly to the area in the flux).
# of seconds = (8 hours)(3600 seconds/hour) = 28800 seconds
The total energy per day is E(J) = W x seconds = 1000 x 28000 = 2.88 x 10^7 J
The heat input (q_{solar}) is equal to the heat required to evaporate water ($n\Delta H_{vap}$), where is the number of moles. If the solar insolation were impinging on the lake at 373 K the number of moles evaporated would be:
$n = q_{solar}/\Delta H_{vap} = 2.88 \times 10^7$ J/43360 J/mol = 664.2 moles
mass of water = (664.2 moles)(18 g/mol) = 12 kg.
I used the heat of vaporization at 40 ^{o}C

B. First calculate the saturation vapor pressure at 313 K.

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

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

$$P_2 = (1\ atm)\exp\left\{\frac{40650\ J/mol}{8.31\ J/mol\text{–}K}\left(\frac{1}{373\ K} - \frac{1}{313\ K}\right)\right\}$$

$$= 0.08\ atm$$

The molar volume at 313 K is:

V_m = RT/P = (0.08206 L-atm/mol-K)(313 K)/(0.08 atm) = 321 L/mol.
The 664.2 moles of H_2O will therefore have a volume of 213,200 liter or 213 m^3. Thus, the water will be in column 213 m high above the surface of the lake.

C. At 20 ^{o}C the vapor pressure is:

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

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

$$P_2 = (1\ atm)\exp\left\{\frac{40650\ J/mol}{8.31\ J/mol\text{–}K}\left(\frac{1}{373\ K} - \frac{1}{293\ K}\right)\right\}$$

$$= 0.028\ atm$$

Thus, at 293 K the number of moles above 1 m^2 of lake surface will be reduced by from 0.08 to 0.028 atm. Therefore, only 35% of the water will remain in the air and 65% will condense. The number of moles is
$n_{condense}$ 0.65 (664.2 moles) = 431.7 moles

which corresponds to a mass of $m_{condense}$ = 431.7 moles (18 g/mol) = 7.8 kg.
The heat released by 431.7 grams of water condensing is $q = -n\Delta H_{vap}$.
q = -(431.7 moles)(44.8 kJ/mol) = -1.9×10^7 J.
Note the minus sign because the system (the rain) is releasing heat.

3. One of the important factors responsible for geologic evolution (i.e. erosion) is the pressure developed by freezing of water trapped in enclosed spaces in rock formations. Estimate the maximum pressure that can be developed by water freezing to ice on a cold night (T = -10 °C). The densities of ice and water at –10 °C may be taken as 0.9 g/cm^3 and 1.0 g/cm^3, respectively.

   Solution: Use the Clapeyron equation, which gives the relationship between temperature and pressure along the solid-liquid coexistence curve.

$$P_2 = P_1 - \frac{\Delta H_{fus}}{\Delta V_m} \ln\left(\frac{T_2}{T_1}\right)$$

   Here we use the known temperature and pressure at the freezing point (T_1 = 273 K, P_1 = 1 atm) and the temperature given (T_2 = 263 K) to calculate P_2.
   To do this we need ΔV_m.

$$\Delta V_m = \frac{M}{\rho_{ice}} - \frac{M}{\rho_{water}} = \frac{18\ g/mol}{0.9\ g/cm^3} - \frac{18\ g/mol}{1.0\ g/cm^3} = 2.0\ cm^3/mol$$

   $\Delta V_m = 2 \times 10^{-6}$ m^3/mol

$$P_2 = 1\ atm - \frac{6000\ J/mol}{2 \times 10^{-6} m^3/mol} \ln\left(\frac{263}{273}\right)\left(\frac{1\ atm}{1.01325\ N/m^2}\right)$$

$$= 1105\ atm$$