Clouds and Precipitation
Homework 1, due August 28

1. You have a closed container with volume V and temperature T with only pure water vapor in it (no air). You know the value of the Gibbs free energy per unit mol, and let's call it "g_v". Write down what the total Gibbs free energy of the water in the system is. Assume water vapor is an ideal gas.

$g_v \equiv$ intensive Gibbs free energy (per mol)

water vapor is a gas and assuming ideality $n = \frac{PV}{RT}$

$G_v \equiv$ extensive Gibbs free energy

$$G_v = g_v \frac{PV}{RT}$$

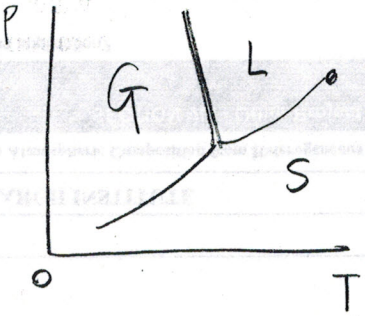
2. In the same system as above, you now add in V_l amount of liquid water, with density ρ and molar Gibbs free energy "g_l". Assuming that the temperature of the system does not change, and that you have no evaporation of liquid water (or condensation of water vapor), what is the total Gibbs free energy of the water in the system?

$$G = G_v + G_L$$

$$G = g_v \frac{PV}{RT} + g_L \frac{\rho V_l}{MW_l}$$, where $MW_l \equiv$ molecular weight of liquid water

3. In problem 2, we assumed that there is no evaporation or condensation of water between phases. As you can imagine, this is very rarely going to happen. What is the requirement that needs to be satisfied though so that #2 does actually happen?

The system should be somewhere along the vapor-liquid coexistence line in the H_2O phase space:



(constant T, P)

The Gibbs free energy must be a minimum

$dG = 0$ and $d^2G > 0$

The chemical potential in the liquid phase = chemical potential in vapor phase $\mu_l = \mu_v$

4. In problem of number 2, you actually realize that what you know is the chemical potential at temperature T, and pressure P_o for both liquid water and water vapor. What would the Gibbs Free Energy (per unit mol) of liquid water and water vapor be temperature T and pressure P? Prove your points using the appropriate equations (hint: start off from what dg is, assuming that the temperature is constant). Isothermal

$dG = Vdp - SdT + \mu_1 dn_1 + \mu_v dn_v$ $\quad dG = Vdp$

$dg = \hat{v}dp$

For water vapor $(\hat{v} = \frac{RT}{P}$ IGL)

$$\int_{g_v}^{g_{v,f}} dg = \int_{P_o}^{P} \frac{RT}{P} dP$$

$$g_{v,f} = g_v + RT\ln\left(\frac{P}{P_o}\right) \qquad \mu_v = \mu_v^* + RT\ln\left(\frac{P}{P_o}\right)$$

For liquid water

$$\int_{g_l}^{g_{l,f}} dg = \int_{P_o}^{P} \frac{MW_L}{\rho} dP$$

$$g_{l,f} = g_l + \frac{MW_L}{\rho}(P - P_o) \qquad \mu_L = \mu_L^* + \frac{MW_L}{\rho}(P - P_o)$$

Poynting correction

5. Combine the answers you got in problems 3 and 4 so that equilibrium between liquid water and the vapor phase is established.

$$\mu_v^* + RT\ln\left(\frac{P}{P_o}\right) = \mu_l^* + \frac{MW_L}{\rho}(P - P_o)$$

$$RT\ln\left(\frac{P}{P_o}\right) \cong \mu_L^* - \mu_v^*$$ assuming a small Poynting correction

Because at equilibrium $\mu_l = \mu_v$

$G = n_l g_l + n_v g_v$

$dG = d(n_l g_l) + d(n_v g_v) = g_l dn_l + g_v dn_v$ $\quad g_{l,v}$ do not change

$$= \frac{\partial G}{\partial n_l} dn_l + \frac{\partial G}{\partial n_v} dn_v = 0$$

$\Rightarrow \mu_l = \mu_v$ since $dn_l = -dn$

6. Based on your answer to problem #5, what should the water vapor pressure in the vessel be, *before liquid water is introduced,* to prevent evaporation of liquid water when V_l of it is introduced in the vessel.

$$P_{sat} \exp\left[\frac{-(\mu_L^* - \mu_v^*)}{RT}\right] = P_o$$

To prevent evaporation of liquid, the water vapor needs to be at saturation vapor pressure for the system temperature

$m_d c_{pd} \sim (1\ kg)(1\times10^3\ J/kgK) \sim O(10^3)$

$m_l c_{pl} \sim (10^{-3}\ kg/kg)(4\times10^3\ J/kgK) \sim O(1)$

$m_v c_{pv} \sim (10^{-3}\ kg/kg)(1\times10^3\ J/kgK) \sim O(1)$

7. The enthalpy of a water cloud is
$dH = \left(m_d c_{pd} + m_v c_{pv} + m_l c_l\right) dT + L_{lv}\, dm_v$
where the subscripts d, v, and l refer to dry air, water vapor and liquid water, respectively. Which terms in the parentheses are usually neglected and why?

The first and last terms are retained $(dH = m_d c_{pd} dT + L_{lv} dm_v$

8. During the isobaric cooling of unsaturated air, the relative humidity U (increases, decreases, remains the same).

$H = e/e_{sat}$ and e constant $\quad T\downarrow \Rightarrow e_{sat}\downarrow$ exponentially (Clausius-Clapeyron)

9. During the isobaric cooling of saturated air, the relative humidity U (increases, decreases, remains the same).

Same explanation as above unless ∃ particle surfaces on which new droplets can form

10. As the dew point depression decreases, U (increases, decreases, remains the same)

$T - T_d$ ✗

11. The frost point temperature is (greater than, less than, equal to) the dew point temperature

12. During the isobaric cooling of saturated air the temperature decrease of the air is proportional to the cooling (true, false) $dH_{sys} \cong m_a c_{p,a} dT + L_{lv} dm_v$
$\Rightarrow dH \propto dT$

13. During reversible condensation (i.e. no water falls out), which of the following is true
a) $dw_l < -dw_s$
b) $dw_l = -dw_s$ by conservation of mass
c) $dw_l > -dw_s$

14. The wet bulb temperature is (greater, less) the (physical) temperature

15. The wet bulb temperature is (greater, less) than the dew point temperature.

16. What is the temperature of a rain drop falling through an unsaturated layer
a) T, the temperature of the air
b) T_w, wet bulb temperature
c) T_d, dew point temperature
d) none of the above

For a pressure of 1000 hPa, determine the following. You may use the attached e_s table.

Given:

17. $w_S = 5\ g\ kg^{-1}$, find T

associated in table

$T = 3.9°C$

$\hookrightarrow w_s = \varepsilon \frac{e_s}{p - e_s} = \frac{M_{H_2O}}{M_{air}} \frac{e_s}{p - e_s} \cong 0.62 \frac{e_s}{p}$

$e_s = \frac{w_s p}{0.62}$

$e_s = \frac{(5\times10^{-3})(1000\ hPa)}{0.62}$

$= 8.06$

$T_D < T$, subsaturated

$T_D = T$, saturated

18. $T = 25°C$, find w_S

$$w_s = \varepsilon \frac{e_s}{p - e_s} = 0.62 \frac{(31.668)}{1000 - 31.668} = \boxed{20.3\ g/kg}$$

19. $T = 30°C$ and $w = 15$ g/kg, find $\mathcal{H}$

$$w = \varepsilon \frac{e}{p-e} = 0.62 \left(\frac{e}{1000-e}\right) = 15 \times 10^{-3}$$

$$e = 0.02419\,(1000 - e)$$

$$e = 23.618\ hPa$$

$$\mathcal{H} = \frac{e}{e_s} = \frac{23.618}{42.427} = \boxed{0.557 \text{ or } 55.7\%}$$

20. $T = 20°C$ and $T_D = 15$, find $\mathcal{H}$

$$\mathcal{H} = \exp\left\{\frac{-L_{lv}}{R}\left(\frac{T - T_D}{T T_D}\right)\right\} = \exp\left\{\frac{-40680\ \frac{J}{mol}}{8.314\ \frac{J}{mol\,K}}\left(\frac{5\ K}{(293\ K)(288K)}\right)\right\}$$

$$= \boxed{0.748 \text{ or } 74.8\%}$$

21. $T = 15°C$ and $\mathcal{H} = 0.8$, find T_D

$$0.8 = \exp\left\{\frac{-40680\ \frac{J}{mol}}{8.314\ \frac{J}{mol\,K}}\left(\frac{288\ K - T_D}{288\ T_D}\right)\right\}$$

$$0.000045605\,(288\,T_D) = 288 - T_D \Rightarrow \boxed{T_D = 11.3°C}$$

22. $w = 20$ g/kg, find T_D

$$w = w_s(T_D) = \varepsilon \frac{e_s(T_D)}{p - e_s(T_D)}$$

$$20 \times 10^{-3} = 0.62 \frac{e_s}{1000 - e_s}$$

$$0.032258\,(1000 - e_s) = e_s$$

$$e_s = 31.25\ hPa$$

$$\boxed{T_D \approx 24.8°C}$$

23. $T_F = -10°C$, find T_D

$$e_{s,i}(T_F) = 2.597\ hPa$$

$$w_{s,i}(T_F) = \varepsilon \frac{e_{s,i}(T_F)}{p - e_{s,i}(T_F)} = w_s(T_D) = \varepsilon \frac{e_s(T_D)}{p - e_s(T_D)}$$

$$\frac{2.597}{1000 - 2.597} = \frac{e_s(T_D)}{1000 - e_s(T_D)}$$

$$e_s(T_D) = 2.59624\ hPa$$

$$0.002603\,(1000 - e_s(T_D)) = e_s(T_D) \Rightarrow \boxed{T_D = -11.23°C}$$