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| Problems set # 6 | Physics 303 | October 14, 2014 |

1. *(i)* By equating the Gibbs free energy or the chemical potential on the two sides of the liquid-vapor coexistence curve derive the Clausius-Clapeyron relation:

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\Delta v},$$

where $s = S/n$ and $v = V/n$ are the molar entropy and molar volume respectively. Here, v_2 is the volume of vapor, v_1 is the volume of liquid, and $\ell \equiv T\Delta s = T(s_2 - s_1)$ is the molar latent heat of vaporization. *(ii)* Assuming the vapor follows the ideal gas law and has a density which is much less than that of the liquid, show that when the heat of vaporization is independent of T:

$$P = P(T_0) \; e^{\ell/RT_0} \; e^{-\ell/RT}.$$

<u>Solution:</u> *(i)* Define $g = G/n = N\mu$, the Gibbs free energy per mole. Then $dg = -sdT + vdP$, where $s = S/n$ and $v = V/n$ are the molar entropy and molar volume, respectively. Along a coexistence curve between phase #1 and phase #2, you must have $g_1 = g_2$, since the phases are free to exchange energy and particle number, *i.e.* they are in thermal and chemical equilibrium. This means $dg_1 = -s_1 dT + v_1 dP = -s_2 dT + v_2 dP = dg_2$. Therefore, along the coexistence curve, you must have $\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\Delta v}$, where $\ell \equiv T\Delta s = T(s_2 - s_1)$ is the molar latent heat of transition.[1] A heat ℓ must be supplied in order to change from phase #1 to phase #2, even without changing P or T. *(ii)* Along the liquid-gas coexistence curve, typically $v_{\text{gas}} \gg v_{\text{liquid}}$. Assuming the vapor is ideal, you may write $\Delta v \approx v_{\text{gas}} \approx RT/P$. Thus, $\left(\frac{dP}{dT}\right)_{\text{liq}-\text{gas}} = \frac{\ell}{T\Delta v} \approx \frac{P\ell}{RT^2}$. If ℓ remains constant throughout a section of the liquid-gas coexistence curve, you may integrate the above equation to get $\frac{dP}{P} = \frac{\ell}{R}\frac{dT}{T^2} \Rightarrow P = P(T_0) \; e^{\ell/RT_0} \; e^{-\ell/RT}$.

2. *(i)* Deduce from the 1st and 2nd laws of thermodynamics that, if a substance such as H_2O expands by 0.091 cm^3/g when it freezes, its frezing temperature must decrease with increasing pressure. *(ii)* In an ice-skating rink, skating becomes unpleasent (i.e., falling frequently) if the temperature is too cold so that the ice becomes too hard. Estimate the lowest temperature of the ice on a skating rink for which the ice skating for a person of normal weight would be possible and enjoyable (the latent heat of ice is 80 cal/g).

<u>Solution:</u> Denote the liquid and solid phases by 1 and 2, respectively. *(i)* The condition for coexistence of the two phases is $\mu_2 = \mu_1$, so that $d\mu_2 = d\mu_1$, giving $v_1 dP_1 - s_1 dT_1 = v_2 dP_2 - s_2 dT_2$. As $P_2 = P_1 = P$ and $T_2 = T_1 = T$ on the coexistence line, we have $\left(\frac{dP}{dT}\right)_{\text{phase line}} = \frac{s_2 - s_1}{v_2 - v_1}$. For regions whose temperatures are higher than those of phase transformation we have $\mu_1 < \mu_2$, and for the regions whose temperatures are lower than those of phse transformation we have $\mu_1 > \mu_2$. This means that $\left(\frac{\partial\mu_1}{\partial T}\right)_P < \left(\frac{\partial\mu_2}{\partial T}\right)_P$, *i.e*, for any temperature $s_1 > s_2$. For substances such as water,

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[1]Notation: ℓ is the latent heat per mole and $\bar{\ell}$ is the latent heat per gram: $\bar{\ell} = \ell/M$, where M is the molar mass.

$v_2 > v_1$, so $\left(\frac{dP}{dT}\right)_{\text{phase line}} < 0$. *(ii)* The lowest temperature permitted for enjoyable skating is the temperature at which the pressure on the coexistence line is equal to the pressure exerted by the skater on ice. The triple point of water is at $T_0 = 273.16$ K, $P_0 = 1$ atm. The ice skates have blades of width about 5 mm and length about 10 cm. A skater of normal weight, $m \approx 50$ kg, on one foot imparts an additional pressure of $\bar{P} = \frac{mg}{A} \approx \frac{50 \text{ kg} \times 9.8 \text{ m/s}^2}{5 \times 10^{-3} \text{ m} \times 10^{-1} \text{ m}} = 9.8 \times 10^5$ Pa ~ 10 atm, so that $(\bar{P} - P_0)/(T_{\min} - T_0) = \ell/(T_{\min}\Delta v)$. With $\ell = 80$ cal/g, $\Delta v = 0.091$ cm^3/g, we have $T_{\min} = \frac{T_0}{1-(\bar{P}-P_0)\Delta v/\ell} = (1 - 2.5 \times 10^{-3})T_0 = -0.06°$C.

3. 10 kg of water at 20°C are converted to ice at -10°C by being put in contact with a reservoir at $-10°$ C. This process takes place at constant pressure. The heat capacities at constant pressure of water and ice are $4,180$ and $2,090$ J/(kg °C), respectively. The heat fusion of ice is 3.34×10^5 J/kg. Calculate the change in entropy of the universe.

Solution: The conversion of water at 20°C to ice at 10°C consists of the following processes. Water at $20° \xrightarrow{a}$ water at 0°C $\xrightarrow{b}$ ice at 0°C $\xrightarrow{c}$ ice at -10°C, where a and c are processes giving out heat with decreaseof entropy and b is a process of condensation of water giving off the latent heat with a decrease of entropy also. As the process takes place at constant pressure, the changes of entropy are $\Delta S_1 = \int_{293}^{273} \frac{mC_P}{T} dT = mC_P \ln\left(\frac{273}{293}\right) = -2,955$ J/K, $\Delta S_2 = -\frac{|Q|}{T_0} = -\frac{10 \times 3.34 \times 10^5}{273} = -1.2234 \times 10^4$ J/K, $\Delta S_3 = \int_{273}^{263} \frac{mC_P}{T} dT = mC_P \ln\left(\frac{263}{273}\right) = -757$ J/K. In these processes, the increase of entropy of the reservoir due to the absorbed heat is given by $\Delta S_{\text{env}} = \frac{10 \times (4,180 \times 20 + 3.34 \times 10^5 + 2,090 \times 10)}{263}$ J/K $= 16,673$ J/K. Thus, the total change of entropy of the whole system is $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_{\text{env}} = 727$ J/K.

4. The follwoing data apply to the triple point of H_2O: temeprature $\rightarrow 0.01°$ C; pressure $\rightarrow 4.6$ mm Hg; specific volume of solid $\rightarrow 1.12$ cm^3/g; specific volume of liquid $\rightarrow 1.00$ cm^3/g; heat of melting $\rightarrow 80$ cal/g; heat of vaporization $\rightarrow 600$ cal/g. *(i)* Sketch a $P - T$ diagram for H_2O which need not be to scale but which should be qualitatively correct. Label the various phases and critical points. *(ii)* The pressure inside a container enclosing H_2O (which is mantained at $T = -1.0°$ C) is slowly reduced from an initial value of 10^5 mm Hg. Describe what happens and calculate the pressure at which the phases changes occur. Assume the vapor behaves like an ideal gas. *(iii)* Calculate the change in specific latent heat with temperature $d\ell/dT$ at a point (P, T) along a phase equilibrium line. Express your results in terms of ℓ, the specific heat c_P, coeficcient of expanson β, and specific volume v of each phase at the original temperature T and pressure P. *(iv)* If the specific latent heat at 1 atm pressure on the vaporization curve is 540 cal/g, estimate the change in latent heat 10° higher than the curve. Assume the vapor can be treated as an ideal gas with rotational degrees of freedom.

Solution: *(i)* The $P - T$ diagram of H_2O is shown in Fig. 1. *(ii)* The Clausius-Clapeyron relation gives $\left(\frac{dP}{dT}\right)_{\text{ice}-\text{water}} = \frac{\ell}{T(v_{\text{water}}-v_{\text{ice}})} = -2.4$ cal/cm^3 K and $\left(\frac{dP}{dT}\right)_{\text{water}-\text{vapor}} > 0$. When the pressure, which is slowly reduced, reaches the solid-liquid phase line, heat is release by the water while the pressure remains unchanged until all the water is changed into ice. Then at the vapor-solid line, the ice absorbs heat until it is completely changed into vapor. Afterwards the pressure

begins to decrease while the vapor phase is mantained. The pressure at which the water is converted to ice is given by $P_{\text{water}-\text{ice}} = P_0 + \frac{\ell}{v_{\text{water}}-v_{\text{ice}}} \frac{T-T_0}{T_0} = 6.3 \times 10^3$ cm Hg, where $T = 272.15$ K, $T_0 = 273.16$ K, and $P_0 = 4.6$ mm Hg. As $v_{\text{vapor}} = \frac{RT}{P} \gg v_{\text{ice}}$, you may write $\frac{dP}{dT} \approx \frac{\ell}{Tv_{\text{vapor}}} = \frac{\ell P}{T^2 R}$. The pressure at which ice is converted to vapor is $P_{\text{ice}-\text{vapor}} \approx P_0 \exp\left[\frac{\ell}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] = 4.4$ mm Hg.

(iii) From $\ell = T(s_1 - s_2)$ it follows that $\frac{d\ell}{dT} = \frac{\ell}{T} + T\left(\frac{ds_1}{dT} - \frac{ds_2}{dT}\right)$. As $ds_1 = \frac{c_{P_1}}{T}dT - \beta_1 v_1 dP$, where $\beta_1 = \frac{1}{v_1}\left(\frac{\partial v_1}{\partial T}\right)_P$, you have $\frac{d\ell}{dT} = \frac{\ell}{T} + (c_{P_1} - c_{P_2}) - (\beta_1 v_1 - \beta_2 v_2)T\frac{dP}{dT}$. Using $\frac{dP}{dT} = \frac{\ell}{T(v_1-v_2)}$, you finally obtain $\frac{d\ell}{dT} = \frac{\ell}{T} + (c_{P_1} - c_{P_2}) - (\beta_1 v_1 - \beta_2 v_2)\frac{\ell}{v_1-v_2}$. *(iv)* Let 1 and 2 stand for water and vapor respectively. From $v_2 \gg v_1$ you know $\frac{d\ell}{dT} \approx \frac{\ell}{T} + (c_{P_1} - c_{P_2}) - \beta_2 \ell$, where $\beta_2 = T^{-1}$, so $\Delta \ell = (c_{P_1} - c_{P_2})\Delta T$. Substituting $c_{P_1} = 1$ cal/g°C, $c_{P_2} = \frac{2}{9}R$ cal/g°C, $\Delta T = 10$°C, you obtain $\Delta \ell = 6$ cal/g.

5. Some researchers at the Modford Institute of Taxidermy claim to have measured the following pressure-temperature phase diagram of a new substance, which they call "embalmium." Their results show that along the phases lines near the triple point

$$0 < \left(\frac{dP}{dT}\right)_{\text{sublimation}} < \left(-\frac{dP}{dT}\right)_{\text{fusion}} < \left(\frac{dP}{dT}\right)_{\text{vaporization}}$$

as indicated in Fig. 1. If these results are correct, "embalmium" has one rather unusual property and one property which violates the law of thermodynamics. Which are the two properties.

Solution: The property $\left(\frac{dP}{dT}\right)_{\text{fusion}} < 0$ is unsual as only a few substances like water behaves in this way. Use the Clausius-Clayperon equation to write $\left(\frac{dP}{dT}\right)_{\text{vaporization}} = (s_{\text{gas}} - s_{\text{liquid}})/v_{\text{gas}}$ and $\left(\frac{dP}{dT}\right)_{\text{sublimation}} = (s_{\text{gas}} - s_{\text{solid}})/v_{\text{gas}}$. Now, $\left(\frac{dP}{dT}\right)_{\text{vaporization}} > \left(\frac{dP}{dT}\right)_{\text{sublimation}}$ means $s_{\text{solid}} > s_{\text{liquid}}$, *i.e.*, the mole entropy of the solid phase is greater than that of the liquid phase, which violates the second law of thermodynamics, since a substance absorbs heat to transform from solid to liquid and the process should be entropy increasing.
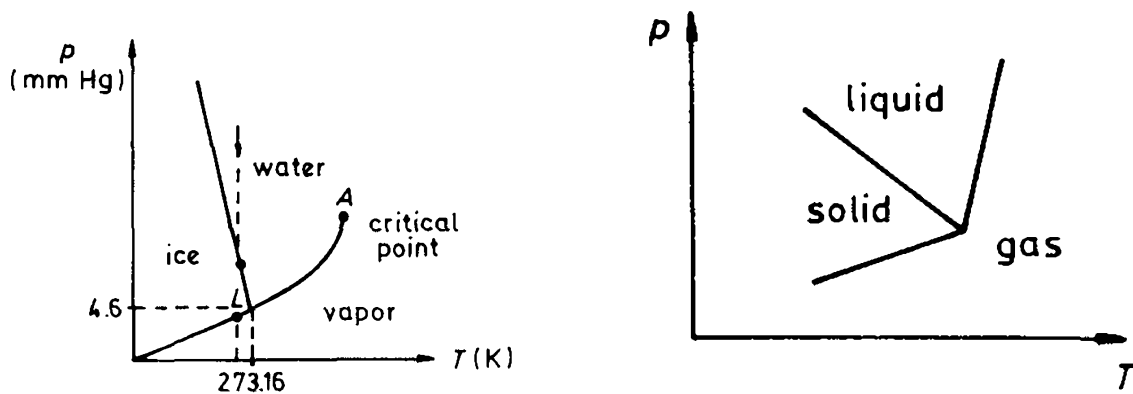

Figure 1: $P - T$ phase diagram of H_2O (left) and "embalmium" (right).