Prof. Anchordoqui

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:

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

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).

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 4180 and 2090 J/kg deg., respectively. The heat fusion of ice is 3.34×10^5 J/kg. Calculate the change in entropy of the universe.

4. The follwoing data apply to the triple point of H_2O: temeprature $\to$ 0.01° C; pressure $\to$ 4.6 mm Hg; specific volume of solid $\to$ 1.12 cm^3/g; specific volume of liquid $\to$ 1.00 cm^3/g; heat of melting $\to$ 80 cal/g; heat of vaporization $\to$ 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.

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

$$0 < \left(\frac{dP}{dT}\right)_{\text{sublimation}} < \left(-\frac{dP}{dT}\right)_{\text{fusion}} < \left(\frac{dP}{dT}\right)_{\text{vaporization}}$$
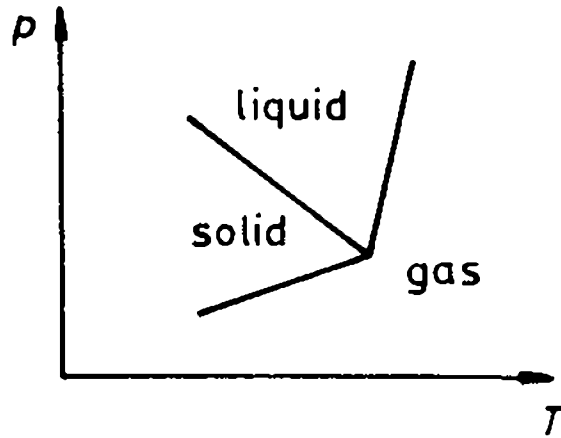
Figure 1: $P - T$ phase diagram of "embalmium."

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.