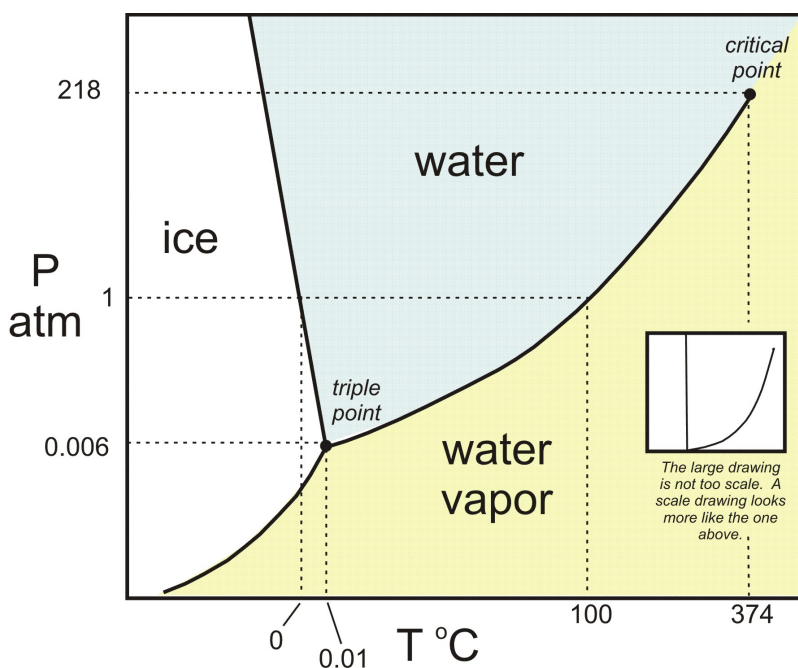


Phys 112 : Lecture 26

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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1 Phase Diagrams



Above is the phase diagram for water. Some features to notice about this diagram include the fact that the solid-liquid phase transition line has a slightly negative slope; due to the fact that ice has a slightly higher volume than water. Another interesting thing is that we have a triple point which is in contact with all three phases. Now, if we want to solve some physics at the phase transition points, we can consider a chemical equilibrium between the two phases, where we require:

$$\tau_1 = \tau_2; \quad P_1 = P_2; \quad \mu_1 = \mu_2$$

where $\mu_1 = \mu_2$ means that the two phases are in chemical equilibrium. Now, recalling that we have $G = N\mu$ where G is the Gibbs free energy, we have that:

$$\mu_1 = \mu_2; \quad \frac{G_1}{N_1} = \frac{G_2}{N_2}; \quad N_2 G_1 = N_1 G_2$$

So taking the differential of both sides, we have:

$$N_2 dG_1 + dN_2 dG_1 = N_1 dG_2 + dN_1 dG_2$$

But we know that

$$dG = \mu dN - \sigma d\tau + V dP$$

so substituting this in and cancelling out, we have:

$$\left(\frac{\sigma_2}{N_2} - \frac{\sigma_1}{N_1} \right) d\tau = \left(\frac{V_2}{N_2} - \frac{V_1}{N_1} \right) dP$$

or in other words:

$$\frac{dP}{d\tau} = \frac{s_2 - s_1}{v_2 - v_1}$$

where we define $s = \sigma/N$ and $v = V/N$. i.e. the change in pressure when you change the temperature depends on the change of entropy of a single particle over the change in volume over a single particle, if that particle were to move from one phase to another. Now, for convenience we define a quantity:

$$dQ = \tau(s_g - s_l) = L$$

where L is the latent heat (per particle), g represents the gas phase, and l represents the liquid phase. So we have that:

$$\frac{dP}{d\tau} = \frac{L}{\tau \Delta V}$$

where $\Delta V = v_g - v_l$. Now, for practical matters, we often have that:

$$v_g \approx (v_g - v_l)$$

which holds for example for water at one atmosphere; i.e. the gas takes up much more volume than the solid. In this case, if we assume that the vapor is an ideal gas, we have that:

$$pV_g = N_g \tau; \quad v_g = \frac{V_g}{N_g} = \frac{\tau}{P}$$

$$\frac{dP}{d\tau} = \frac{L}{\tau^2} P$$

Now, making the further assumption that $L(\tau) \approx L_0$, i.e. the latent heat doesn't change much with temperature (which is true for water in normal conditions), we can integrate the above to find that:

$$P(\tau) = P_0 e^{-L_0/\tau}$$

If we wanted to put it in terms of molar, we have $L_m = L_0 N_A$ where N_A is avogadros number, so we have:

$$P(\tau) = P_0 e^{-L_m/RT}$$

where $R = N_A k_b$. Now, note that we have:

$$dU = \tau d\sigma - p dV + (\mu_g - \mu_l) dN$$

in equilibrium, $\mu_g = \mu_l$ so

$$dU = \tau d\sigma - p dV$$

but $\tau d\sigma = dH$ for isobaric conditions, so we have that:

$$L = \tau \Delta\sigma = \Delta H = H_g - H_l$$

in isobaric conditions.

2 Corrections to Ideal Gas law

We don't yet have a model to describe why different phases occur; to this end we want to add some perturbations to our ideal gas law to allow for interactions between particles. The Van der Waals equation is a correction to the ideal gas law:

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = N\tau$$

where a depends on the long range interaction, and b depends on short range repulsion. To motivate this, we can imagine that each particle occupies a volume of b , so the effective volume of the system is actually $V' = V - Nb$ which describes this term in the Van der Waals equation. Now, we have an additional perturbation due to the attractive force at long range. The energy for each particle due to this new attractive force is:

$$\Delta U_1 \alpha - n$$

where n is the density of the particles, negative for attractive force. Now, the total extra energy is:

$$U = N\Delta U_1 \alpha - Nn = \frac{-N^2}{V}$$

so the change in free energy is:

$$\Delta F = \Delta U = \frac{-aN^2}{V}$$

So our new perturbed free energy is given by:

$$F = -N\tau \left[\ln \left(\frac{n_a(V - Nb)}{N} + 1 \right) \right] - \frac{aN^2}{V}$$

for some constants a, b . Now we have:

$$P = - \left(\frac{\partial F}{\partial V} \right)_{\tau, N}$$

so we recover the Van der Waals equation:

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = N\tau$$