

Physics 112

Summary of lecture on Thursday, March 1, 2012

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Since the strike today made it difficult for students who do not live on campus to get to class, I am giving here a summary of the material covered in the lecture. Fortunately, this is covered pretty well in the book, Kittel and Kroemer (2nd. ed.) Ch. 10, and Kittel (1st. ed.) Ch. 20.

We started by pointing out that the conditions for two phases to coexist in equilibrium are

1. Equal pressures, so that the mechanical forces on the interface between the two phases balance.
2. Equal temperatures, so there is no flow of energy from one phase to the other.
3. Equal chemical potentials, so there is no flow of particles from one phase to the other.

In other words

$$\mu_1(P, T) = \mu_2(P, T). \quad (1)$$

We then discussed the slope of the coexistence curve and derived the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{L}{k_B T} \frac{1}{\Delta v}, \quad (2)$$

where Δs and Δv are the change in entropy per particle, and volume per particle, respectively, and L is the latent heat per particle at the transition. If one multiplies the numerator and denominator of the RHS of Eq. (2) by Avogadro's number, N_A , the number of molecules in a mole, then the Clausius-Clapeyron equation has the same form,

$$\frac{dP}{dT} = \frac{\Delta S_{\text{mole}}}{\Delta V_{\text{mole}}} = \frac{L_{\text{mole}}}{RT} \frac{1}{\Delta V_{\text{mole}}}, \quad (3)$$

where S_{mole} is the entropy *per mole*, ΔV_{mole} is the volume per mole, L_{mole} is the latent heat per mole, and $R = N_A k_B$ is called the gas constant. (Remember a mole is the molecular weight in grams, so a mole of water has a mass of 18 gm.)

We pointed out that the Clausius Clapeyron equation implies that the negative slope of the ice-water coexistence curve (in a P - T diagram) is due to the fact that water expands on freezing, i.e. $\Delta v \equiv v_l - v_s < 0$.

We went on to show, by making some simplifying assumptions that an approximate expression for the coexistence line of a vapor (with solid or liquid) is

$$P(T) = P_0 \exp\left(-\frac{L_0}{RT}\right), \quad (4)$$

where P_0 is a constant, and L_0 is the latent heat per mole, which was assumed independent of T in the derivation. For water, this works amazingly well over 8 orders of magnitude of pressure. The data is plotted in Fig. 10.3 of KK (Fig. 3 in Ch. 20 of K). I include, on the separate page, a copy of Fig. 10.3 with annotations which, I hope, will make it easier to understand. The vertical axis is P , on a log-scale, and the horizontal axis is $10^3/T$, so Eq. (4) would appear as a straight line. In the figure, the solid line is the actual data, and the dashed line is a straight line fit to the middle region. As you see the fit works very well over a very broad range of pressure.

Finally we started to discuss the van der Waals equation of state

$$\left(P + a \left(\frac{N}{V}\right)^2\right) (V - Nb) = Nk_B T, \quad (5)$$

where a and b are parameters which vary from material to material. We explained how these parameters represent, in a phenomenological way, the attraction between molecules at large distance (a), and the very strong repulsion at short distance (b).

Figure 10.3 Vapor pressure of water and of ice plotted versus $1/T$. The vertical scale is logarithmic. The dashed line is a straight line.

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 i.e. corresponds to

$$P(T) = P_0 e^{-L_0/RT}$$

