

8.4: The Clapeyron Equation

Based on the thermodynamic criterion for equilibrium, it is possible to draw some conclusions about the state variables p and T and how they are related along phase boundaries. First, the chemical potentials of the two phases α and β in *equilibrium* with one another must be equal.

$$\mu_{\alpha} = \mu_{\beta} \quad (8.4.1)$$

Also, any infinitesimal changes to the chemical potential of one phase must be offset by an infinitesimal change to the chemical potential of the other phase that is equal in magnitude.

$$\mu_{\alpha} + d\mu_{\alpha} = \mu_{\beta} + d\mu_{\beta} \quad (8.4.2)$$

Taking the difference between these Equations 8.4.1 and 8.4.2 shows that

$$d\mu_{\alpha} = d\mu_{\beta}$$

And since $d\mu$ can be expressed in terms of molar volume and molar entropy

$$d\mu = V dp - S dT$$

It is clear that there will be constraints placed on changes of temperature and pressure while maintaining equilibrium between the phases.

$$V_{\alpha} dP - S_{\alpha} dT = V_{\beta} dP - S_{\beta} dT$$

Gathering pressure terms on one side and temperature terms on the other

$$(V_{\alpha} - V_{\beta}) dP = (S_{\alpha} - S_{\beta}) dT$$

The differences $V_{\alpha} - V_{\beta}$ and $S_{\alpha} - S_{\beta}$ are the changes in molar volume and molar entropy for the phase changes respectively. So the expression can be rewritten

$$\Delta V dp = \Delta S dT$$

or

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \quad (8.4.3)$$

Equation 8.4.3 is the **Clapeyron equation**. This expression makes it easy to see how the phase diagram for water is qualitatively different than that for most substances. Specifically, the negative slope of the solid-liquid boundary on a pressure-temperature phase diagram for water is very unusual, and arises due to the fact that for water, the molar volume of the liquid phase is smaller than that of the solid phase.

Given that for a phase change

$$\Delta S_{phase} = \frac{\Delta H_{phase}}{T}$$

the Clapeyron equation is sometimes written

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \quad (8.4.4)$$

✓ Example 8.4.1: Freezing Water

Calculate the magnitude of the change in freezing point for water ($\Delta H_{fus} = 6.009 \text{ kJ/mol}$) and the density of ice is $\rho_{ice} = 0.9167 \text{ g/cm}^3$ while that for liquid water is $\rho_{liquid} = 0.9999 \text{ g/cm}^3$) for an increase in pressure of 1.00 atm at 273 K .

Solution

The molar volume of ice is given by

$$\left(0.9167 \frac{g}{cm^3}\right) \left(\frac{1 mol}{18.016 g}\right) \left(\frac{1000 cm^3}{1 L}\right) = 50.88 \frac{L}{mol}$$

The molar volume of liquid water at 0 °C is given by

$$\left(0.9999 \frac{g}{cm^3}\right) \left(\frac{1 mol}{18.016 g}\right) \left(\frac{1000 cm^3}{1 L}\right) = 55.50 \frac{L}{mol}$$

So ΔV for the phase change of solid \rightarrow liquid (which corresponds to an endothermic change) is

$$50.88 \frac{L}{mol} - 55.50 \frac{L}{mol} = -4.62 \frac{L}{mol}$$

To find the change in temperature, use the *Clapeyron Equation* (Equation 8.4.4) and separating the variables

$$dp = \frac{\Delta H_{fus}}{\Delta V} \frac{dt}{T}$$

Integration (with the assumption that $\Delta H_{fus}/\Delta V$ does not change much over the temperature range) yields

$$\int_{p_1}^{p_2} dp = \frac{\Delta H_{fus}}{\Delta V} \int_{T_1}^{T_2} \frac{dt}{T}$$

$$p_2 - p_1 = \Delta p = \frac{\Delta H_{fus}}{\Delta V} \ln\left(\frac{T_2}{T_1}\right)$$

or

$$T_2 = T_1 \exp\left(\frac{\Delta V \Delta p}{\Delta H_{fus}}\right)$$

so

$$T_2 = (273 K) \exp\left(\frac{(1 atm) \left(-4.62 \frac{L}{mol}\right)}{6009 \frac{J}{mol}} \underbrace{\left(\frac{8.314 J}{0.08206 atm L}\right)}_{\text{conversion factor}}\right)$$

$$T_2 = 252.5 K$$

$$\Delta T = T_2 - T_1 = 252.5 K - 273 K = -20.5 K$$

So the melting point will decrease by 20.5 K. Note that the phase with the smaller molar volume is favored at the higher pressure (as expected from Le Chatelier's principle)!

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