

second derivative is discontinuous. See the heat capacity versus temperature plot in Figure 7.17b.

It is very difficult to determine the order of higher-order transformations, and it is common to call all transformations greater than first order, continuous transformations.

7.12 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

The vapor pressure of solid NaF varies with temperature as

$$\ln p \text{ (atm)} = \frac{-34,450}{T} - 2.01 \ln T + 33.74$$

and the vapor pressure of liquid NaF varies with temperature as

$$\ln p \text{ (atm)} = \frac{-31,090}{T} - 2.52 \ln T + 34.66$$

Calculate

1. The normal boiling temperature of NaF
2. The temperature and pressure at the triple point
3. The molar enthalpy of evaporation of NaF at its normal boiling temperature
4. The molar enthalpy of melting of NaF at the triple point
5. The difference between the constant-pressure molar heat capacities of liquid and solid NaF

The phase diagram is shown schematically in Figure 7.18.

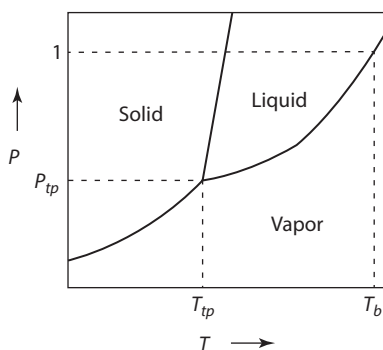


Figure 7.18 Schematic pressure–temperature phase diagram for a one-component system.

Solution to Quantitative Problem 1

1. The normal boiling temperature, T_b , is defined as that temperature at which the saturated vapor pressure of the liquid is 1 atm. Thus, from the equation for the vapor pressure of the liquid, T_b is

$$\ln(1) = 0 = -\frac{31,090}{T_b} - 2.52 \ln T_b + 34.66$$

which has the solution

$$T_b = 2006 \text{ K}$$

2. The saturated vapor pressures for the solid and liquid phases intersect at the triple point. Thus, at the temperature, T_p , of the triple point

$$-\frac{34,450}{T_p} - 2.01 \ln T_p + 33.74 = -\frac{31,090}{T_p} - 2.52 \ln T_p + 34.66$$

which has the solution

$$T_p = 1239 \text{ K}$$

The triple-point pressure is then calculated from the equation for the vapor pressure of the solid as

$$p = \exp\left(-\frac{34,450}{1239} - 2.01 \ln 1239 + 33.74\right) = 2.29 \times 10^{-4} \text{ atm}$$

or from the equation for the vapor pressure for the liquid as

$$p = \exp\left(-\frac{31,090}{1239} - 2.52 \ln 1239 + 34.66\right) = 2.29 \times 10^{-4} \text{ atm}$$

3. For vapor in equilibrium with the liquid:

$$\ln p \text{ (atm)} = -\frac{31,090}{T} - 2.52 \ln T + 34.66$$

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2} = \frac{31,090}{T^2} - \frac{2.52}{T}$$

Thus,

$$\Delta H_{(l \rightarrow v)} = (31,090 - 8.3144) - (2.52 - 8.3144)T = 258,500 - 20.95T$$

and, at the normal boiling temperature of 2006 K,

$$\Delta H_{(l \rightarrow v)} = 258,500 - 20.95 \cdot 2006 = 216,500 \text{ J}$$

4. For vapor in equilibrium with the solid:

$$\ln p \text{ (atm)} = -\frac{34,450}{T} - 2.01 \ln T + 33.74$$

Thus,

$$\begin{aligned}\Delta H_{(s \rightarrow v)} &= (34,450 - 8.3144) - (2.01 - 8.3144)T \\ &= 286,400 - 16.71T \text{ J}\end{aligned}$$

Near the triple point,

$$\Delta H_{(s \rightarrow l)} + \Delta H_{(l \rightarrow v)} = \Delta H_{(s \rightarrow v)}$$

and thus,

$$\begin{aligned}\Delta H_{(s \rightarrow l)} &= 286,400 - 16.71T - 258,500 + 20.95T \\ &= 27,900 + 4.24T\end{aligned}$$

At the triple point,

$$\Delta H_{(s \rightarrow l)} = 27,900 + (4.24 - 12.39) = 33,150 \text{ J}$$

$$5 \quad \Delta H_{(s \rightarrow l)} = 27,900 + 4.24T$$

$$\begin{aligned}\frac{d\Delta H}{dT} &= \Delta c_p = 4.24 \text{ J/K} \\ &= c_p^L - c_p^S > 0\end{aligned}$$

Quantitative Problem 2

Carbon has the following three allotropes: graphite, diamond, and a metallic form called solid III. Graphite is the stable form of 298 K and 1 atm pressure, and increasing the pressure on graphite at temperatures less than 1440 K causes the transformation of graphite to diamond and then the transformation of diamond to solid III. Calculate the pressure which, when applied to one mole graphite at 298 K, causes the transformation of graphite to diamond, given

- $H_{298 \text{ K, (graphite)}} - H_{298 \text{ K, (diamond)}} = -1900 \text{ J}$.
- $S_{298 \text{ K, (graphite)}} = 5.74 \text{ J/K}$.
- $S_{298 \text{ K, (diamond)}} = 2.37 \text{ J/K}$.
- The density of graphite at 298 K is 2.22 g/cm^3 .
- The density of diamond at 298 K is 3.515 g/cm^3 .