1. For uranium hexafluoride, the vapor pressure (in Pa) for the solid and liquid are given by

$$\ln p_s = 29.411 - 5893.5/T$$
$$\ln p_l = 22.254 - 3479.9/T$$

Calculate the temperature and pressure of the triple point.

Answer

At the triple point temperature, the equilibrium vapor pressures of the solid and liquid are equal. Therefore, we may equate the two expressions to get the triple point temperature, $\exp(11.935) = 1.5251 \times 10^5$

$$29.411 - 5893.5/T = 22.254 - 3479.9/T, \text{ or}$$
$$\frac{1}{T}(5893.5 - 3479.9) = 29.411 - 22.254,$$
$$T = \frac{(5893.5 - 3479.9)}{(29.411 - 22.254)} = 337.24 \text{ K.}$$

At this temperature,

$$\ln p_l = 29.411 - \frac{5893.5}{337.24} = 11.935.$$
$$p_l(\text{Pa}) = \exp(11.935) = 1.5251 \times 10^5 \text{ Pa}$$
$$= 1.525 \text{ bar.}$$

2. The heats of vaporization and of fusion for water are 2490 J g^{-1} and 333.5 J g^{-1}, respectively, at 0 °C. The vapor pressure of water at 0 °C is 611 Pa. Calculate the sublimation pressure of ice at -15 °C, assuming that the enthalpy changes are independent of temperature.

Answer

Since enthalpy is a state function, the enthalpy of sublimation of water at 0 °C is given by

$$\Delta_{sub}H° = \Delta_{fus}H° + \Delta_{vap}H°$$
$$= (2490 + 333.5) \text{ J g}^{-1} \times 18.02 \text{ g mol}^{-1}$$
$$= 50,879 \text{ J mol}^{-1}$$

Assuming $\Delta_{sub}H°$ to be independent of temperature, and setting $T_1 = 273.15$ K and $T_2 = 258.15$ K (-15 °C), and using

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{sub}H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

we get

$$\ln\left(\frac{p_2}{611}\right) = \frac{\Delta_{sub}H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$= \frac{50879 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{273.15} - \frac{1}{258.15}\right) \text{ K}^{-1}$$
$$= -1.3017$$

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Therefore,

$$p_2 = 611 \text{ Pa} \times e^{-1.3017} = 166.23 \text{ Pa}$$

Answer

3. Water is one of the very few substances (in fact, I don't know of another) for which the slope of the solid-liquid boundary on the phase diagram (see Fig. 5.1), dP/dT, is negative. Make a sketch of this diagram to answer the questions below. (Note that the temperature axis is not at all to scale. The distance between 273.15 and 273.16 K is greatly exaggerated while the distance between 273.16 and 373.15 K is greatly compressed.) Consider a system of liquid water and ice in equilibrium at a temperature of 273.155 K and 0.611 kPa. (a) Mark the position of the system on the phase diagram. (b) What do you expect to see when pressure is increased gradually to 101.325 kPa, holding temperature constant. Draw the variation of the system's position on the phase diagram as a result of this process. (c) Recall Le Chatelier's principle for chemical equilibria. Can you relate this principle to what is happening in this example, even though no reaction is taking place? [Hint: the answer may have something to do with why ice floats on water.] (d) The solid-liquid equilibrium for carbon dioxide has a positive slope. Will solid CO_2 float on liquid CO2? Why, or why not?

Answer
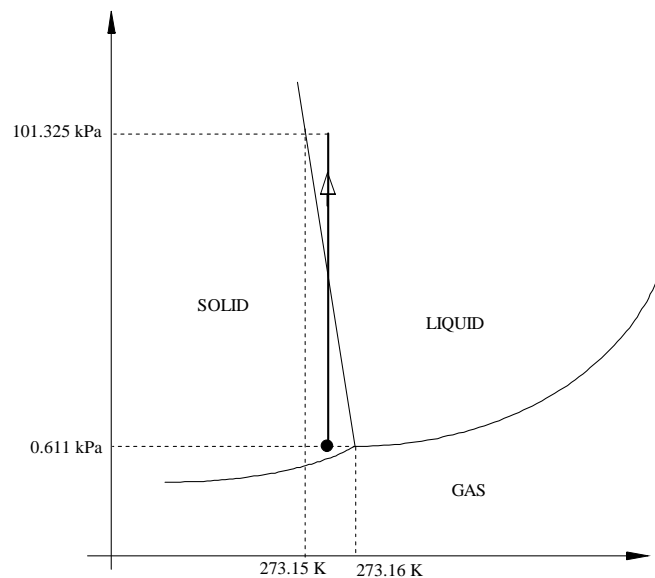
(a) The filled symbol marks the position of the system at 0.611 kPa pressure and 273.155 K temperature.
(b) The system consists of ice initially. As the pressure is increased at constant temperature, some of the ice melts when the pressure reaches the sold-liquid equilibrium value. Further increase in pressure to 101.325 kPa will result in all of the ice melting into liquid.
(c) According to Le Chatelier's principle, when pressure is increased on a system in dynamic equilibrium, the equilibrium shifts in such a way as to decrease the volume of the system. The fact that ice melts when pressure is applied to it at constant temperature indicates that the liquid phase occupies less volume than the solid phase, i.e., water is denser than ice. Therefore, a negative slope for the solid-liquid equilibrium curve in $P-T$ space (dP/dT) is indicative of the fact that the liquid phase is denser than the solid phase.
(d) Since dP/dT is positive for CO2, it is clear that liquid CO_2 is less dense than solid CO2. Therefore, solid CO_2 will not float on liquid CO_2.