8.5: Chapter 8 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

8.1

Consider the system described in Sec. 8.1.5 containing a spherical liquid droplet of radius r surrounded by pure vapor. Starting with Eq. 8.1.15, find an expression for the total differential of U. Then impose conditions of isolation and show that the equilibrium conditions are $T^{\mathrm{g}} = T^{\mathrm{l}}$, $\mu^{\mathrm{g}} = \mu^{\mathrm{l}}$, and $p^{\mathrm{l}} = p^{\mathrm{g}} + 2\gamma/r$, where γ is the surface tension.

8.2

This problem concerns diethyl ether at $T = 298.15\,\mathrm{K}$. At this temperature, the standard molar entropy of the gas calculated from spectroscopic data is $S_{\mathrm{m}}^{\circ}(\mathrm{g}) = 342.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The saturation vapor pressure of the liquid at this temperature is $0.6691\,\mathrm{bar}$, and the molar enthalpy of vaporization is $\Delta_{\mathrm{vap}}H = 27.10\,\mathrm{kJ\,mol^{-1}}$. The second virial coefficient of the gas at this temperature has the value $B = -1.227 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$, and its variation with temperature is given by $\mathrm{d}B/\mathrm{d}T = 1.50 \times 10^{-5}\,\mathrm{m^3\,K^{-1}\,mol^{-1}}$.

(a) Use these data to calculate the standard molar entropy of liquid diethyl ether at $298.15\,\mathrm{K}$. A small pressure change has a negligible effect on the molar entropy of a liquid, so that it is a good approximation to equate $S_{\mathrm{m}}^{\circ}(\mathrm{l})$ to $S_{\mathrm{m}}(\mathrm{l})$ at the saturation vapor pressure.

(b) Calculate the standard molar entropy of vaporization and the standard molar enthalpy of vaporization of diethyl ether at $298.15\,\mathrm{K}$. It is a good approximation to equate $H_{\mathrm{m}}^{\circ}(\mathrm{l})$ to $H_{\mathrm{m}}(\mathrm{l})$ at the saturation vapor pressure.

8.3

Explain why the chemical potential surfaces shown in Fig. 8.12 are concave downward; that is, why $(\partial\mu/\partial T)_p$ becomes more negative with increasing T and $(\partial\mu/\partial p)_T$ becomes less positive with increasing p.

8.4

Potassium has a standard boiling point of $773\,^{\circ}\mathrm{C}$ and a molar enthalpy of vaporization $\Delta_{\mathrm{vap}}H = 84.9\,\mathrm{kJ\,mol^{-1}}$. Estimate the saturation vapor pressure of liquid potassium at $400.\,^{\circ}\mathrm{C}$.

8.5

Naphthalene has a melting point of $78.2\,^{\circ}\mathrm{C}$ at $1\,\mathrm{bar}$ and $81.7\,^{\circ}\mathrm{C}$ at $100\,\mathrm{bar}$. The molar volume change on melting is $\Delta_{\mathrm{fus}}V = 0.019\,\mathrm{cm^3\,mol^{-1}}$. Calculate the molar enthalpy of fusion to two significant figures.

8.6

The dependence of the vapor pressure of a liquid on temperature, over a limited temperature range, is often represented by the *Antoine equation*, $\log_{10}(p/\mathrm{Torr}) = A - B/(t + C)$, where t is the Celsius temperature and A, B, and C are constants determined by experiment. A variation of this equation, using a natural logarithm and the thermodynamic temperature, is

$$\ln(p/\mathrm{bar}) = a - \frac{b}{T + c} \tag{8.5.1}$$

The vapor pressure of liquid benzene at temperatures close to $298\,\mathrm{K}$ is adequately represented by the preceding equation with the following values of the constants:

$$a = 9.25092 \qquad b = 2771.233\,\mathrm{K} \qquad c = -53.262\,\mathrm{K} \tag{8.5.2}$$

(a) Find the standard boiling point of benzene.

(b) Use the Clausius–Clapeyron equation to evaluate the molar enthalpy of vaporization of benzene at $298.15\,\mathrm{K}$.

8.7

At a pressure of one atmosphere, water and steam are in equilibrium at $99.97\,^{\circ}\mathrm{C}$ (the normal boiling point of water). At this pressure and temperature, the water density is $0.958\,\mathrm{g\,cm^{-3}}$, the steam density is $5.98 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$, and the molar enthalpy of vaporization is $40.66\,\mathrm{kJ\,mol^{-1}}$.

(a) Use the Clapeyron equation to calculate the slope $\mathrm{d}p/\mathrm{d}T$ of the liquid–gas coexistence curve at this point.

(b) Repeat the calculation using the Clausius–Clapeyron equation.

(c) Use your results to estimate the standard boiling point of water. (Note: The experimental value is $99.61\,^{\circ}\mathrm{C}$.)

8.8

At the standard pressure of 1 bar, liquid and gaseous H_2O coexist in equilibrium at $372.76\,\mathrm{K}$, the standard boiling point of water.

(a) Do you expect the standard molar enthalpy of vaporization to have the same value as the molar enthalpy of vaporization at this temperature? Explain.

(b) The molar enthalpy of vaporization at $372.76\,\mathrm{K}$ has the value $\Delta_{\mathrm{vap}}H = 40.67\,\mathrm{kJ\,mol^{-1}}$. Estimate the value of $\Delta_{\mathrm{vap}}H^\circ$ at this temperature with the help of Table 7.5 and the following data for the second virial coefficient of gaseous H_2O at $372.76\,\mathrm{K}$:

$$B = -4.60 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}} \qquad dB/dT = 3.4 \times 10^{-6}\,\mathrm{m^3\,K^{-1}\,mol^{-1}} \tag{8.5.3}$$

(c) Would you expect the values of $\Delta_{\mathrm{fus}}H$ and $\Delta_{\mathrm{fus}}H^\circ$ to be equal at the standard freezing point of water? Explain.

8.9

The standard boiling point of H_2O is $99.61\,^\circ\mathrm{C}$. The molar enthalpy of vaporization at this temperature is $\Delta_{\mathrm{vap}}H = 40.67\,\mathrm{kJ\,mol^{-1}}$. The molar heat capacity of the liquid at temperatures close to this value is given by

$$C_{p,\mathrm{m}} = a + b(t - c)$$

where t is the Celsius temperature and the constants have the values

$$a = 75.94\,\mathrm{J\,K^{-1}\,mol^{-1}} \qquad b = 0.022\,\mathrm{J\,K^{-2}\,mol^{-1}} \qquad c = 99.61\,^\circ\mathrm{C} \tag{8.5.4}$$

Suppose $100.00\,\mathrm{mol}$ of liquid H_2O is placed in a container maintained at a constant pressure of $1\,\mathrm{bar}$, and is carefully heated to a temperature $5.00\,^\circ\mathrm{C}$ above the standard boiling point, resulting in an unstable phase of superheated water. If the container is enclosed with an adiabatic boundary and the system subsequently changes spontaneously to an equilibrium state, what amount of water will vaporize? (Hint: The temperature will drop to the standard boiling point, and the enthalpy change will be zero.)