17

Phase equilibrium and solutions

Answers to worked examples

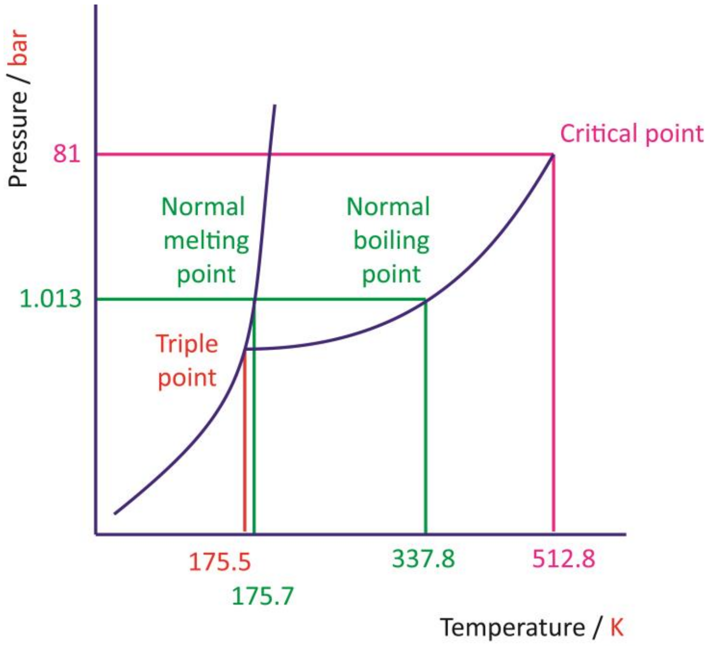
WE 17.1 Using a phase diagram (on p. 772 in *Chemistry*³)

The normal melting and boiling points for methanol (CH_3OH) are 175.7 K and 337.8 K, respectively. The critical temperature and pressure are 512.8 K and 81 bar. The triple point occurs at 175.5 K. Sketch (not to scale) the single-component phase diagram for methanol.

Strategy

Consider Figure 17.4, which shows a typical phase diagram for a one-component system. Remember that the normal melting and boiling points correspond to a pressure of 1 atm = 1.013 bar.

Solution



WE 17.2 Effect of pressure on melting point (on p. 778 in *Chemistry*^{3})

Calculate the pressure at which the melting temperature of sodium is 373 K.

Strategy

Apply the Clapeyron equation, Equation 17.4, using the data in the Worked Example to determine the change in the volume on melting and the enthalpy of fusion.

Solution

The Clapeyron equation, Equation 17.4, has the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}}H}{T\Delta_{\mathrm{fus}}V}$$

From Worked Example 17.2,

$$\Delta_{\mathrm{fus}}V = V_{\mathrm{m}}(\mathrm{liquid}) - V_{\mathrm{m}}(\mathrm{solid}) = +0.60 \times 10^{-6}\mathrm{m^3 mol^{-1}}$$

and

$$\Delta_{\mathrm{fus}}H = +3.00\ \mathrm{kJ\ mol^{-1}} = +3.00 \times 10^{3}\mathrm{J\ mol^{-1}}$$

so that, at a temperature of 373 K, the gradient of the pressure–temperature line on the phase diagram is

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{(+3.00 \times 10^{3}\mathrm{J\ mol^{-1}})}{(373\ \mathrm{K}) \times (+0.60 \times 10^{-6}\mathrm{m^3 mol^{-1}})}$$
$$= 13.5 \times 10^{6}\ \mathrm{J\ m^{-3}K^{-1}} = 13.5 \times 10^{6}\ \mathrm{Pa\ K^{-1}}$$

Assuming that the solid–liquid equilibrium forms a straight line on the pressure–temperature phase diagram, then

$$\frac{\Delta p}{\Delta T} = 13.5 \times 10^{6}\ \mathrm{Pa\ K^{-1}}$$

The normal melting temperature for sodium, which is the temperature at which sodium melts for a pressure of 1 atm = 1.013 × 10^5 Pa, is 97.8°C = 371 K. Thus,

$$\Delta T = 373\ \mathrm{K} - 371\ \mathrm{K} = +2\ \mathrm{K}$$

so that

$$\Delta p = (13.5 \times 10^{6}\ \mathrm{Pa\ K^{-1}}) \times \Delta T = (13.5 \times 10^{6}\ \mathrm{Pa\ K^{-1}}) \times (2\ \mathrm{K})$$
$$= +26.8 \times 10^{6}\mathrm{Pa}$$

The pressure for which sodium melts at a temperature of 373 K is therefore 26.8 Pa higher than the normal melting temperature, which corresponds to a pressure of 1.013×10^5 Pa.

Thus,

$$p = (1.013 \times 10^5\,\mathrm{Pa}) + (26.8\ \times 10^6\,\mathrm{Pa}) = 26.9\ \times 10^6\,\mathrm{Pa}$$

which is equivalent to a pressure of

$$p = \frac{26.9\ \times 10^6\,\mathrm{Pa}}{1.013 \times 10^5\,\mathrm{Pa\ atm^{-1}}} = 266\ \mathrm{atm}$$

WE 17.3 Using the Clausius–Clapeyron equation (on p. 781 in *Chemistry*^{3})

Find the vapour pressure of benzene at 325 K.

Strategy

Apply the integrated form of the Clausius–Clapeyron equation, Equation 17.7, for the calculation of the vapour pressure, using the value for the enthalpy of vaporization from the Worked Example.

Solution

The integrated form of the Clausius–Clapeyron equation, Equation 17.7,

$$\ln\frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

becomes Equation 17.8, if the normal boiling temperature is known

$$\ln\frac{1.01325 \times 10^5\,\mathrm{Pa}}{p} = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_\mathrm{b}}\right)$$

Rearranging this equation gives an expression for the vapour pressure at a particular temperature

$$\begin{aligned}\ln\{p/(1.01325 \times 10^5\,\mathrm{Pa})\} &= -\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_\mathrm{b}}\right)\\ &= -\frac{30.8 \times 10^3\,\mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}mol^{-1}}}\left(\frac{1}{325\ \mathrm{K}} - \frac{1}{353\ \mathrm{K}}\right)\\ &= -0.904\end{aligned}$$

Thus,

$$p = \mathrm{e}^{-0.904} \times (1.01325 \times 10^5\,\mathrm{Pa}) = 41.0 \times 10^3\,\mathrm{Pa} = 41.0\ \mathrm{kPa}$$

WE 17.4 Using Raoult's law (on p. 795 in *Chemistry*^{3})

What is the percentage composition of a solution of benzene and methylbenzene with a total vapour pressure of 9.50 kPa?

Strategy

Use Raoult's law to write an expression for the total vapour pressure in terms of the mole fraction of benzene. Use the data for the vapour pressures of the two components given in the Worked Example to solve for the unknown mole fraction of benzene. Hence calculate the percentage composition of benzene and methylbenzene.

Solution

The partial pressure of the benzene and methylbenzene are, from Raoult's law, Equation 17.23,

$$p_\mathrm{b} = x_\mathrm{b} p_\mathrm{b}^\mathrm{o}$$
$$p_\mathrm{m} = x_\mathrm{m} p_\mathrm{m}^\mathrm{o}$$

so that the total vapour pressure is

$$p_\mathrm{total} = p_\mathrm{b} + p_\mathrm{m} = x_\mathrm{b} p_\mathrm{b}^\mathrm{o} + x_\mathrm{m} p_\mathrm{m}^\mathrm{o}$$

There are only two components, so that

$$x_\mathrm{b} + x_\mathrm{m} = 1$$

and therefore

$$x_\mathrm{m} = 1 - x_\mathrm{b}$$

Hence,

$$p_\mathrm{total} = x_\mathrm{b} p_\mathrm{b}^\mathrm{o} + (1 - x_\mathrm{b}) p_\mathrm{m}^\mathrm{o} = x_\mathrm{b}(p_\mathrm{b}^\mathrm{o} - p_\mathrm{m}^\mathrm{o}) + p_\mathrm{m}^\mathrm{o}$$

Rearranging,

$$x_\mathrm{b} = \frac{p_\mathrm{total} - p_\mathrm{m}^\mathrm{o}}{p_\mathrm{b}^\mathrm{o} - p_\mathrm{m}^\mathrm{o}} = \frac{9.50\ \mathrm{kPa} - 3.85\ \mathrm{kPa}}{12.85\ \mathrm{kPa} - 3.85\ \mathrm{kPa}} = 0.628$$

and therefore

$$x_m = 1 - x_b = 0.372$$

which corresponds to a percentage composition of 62.8% benzene and 37.2% methylbenzene.

WE 17.5 Deviations from Raoult's law (on p. 797 in *Chemistry*^{3})

In a mixture of ethanol and trichloromethane, the mole fraction of ethanol is 0.6. The vapour pressure of ethanol above the mixture is 0.087 bar and that of trichloromethane is 0.256 bar. Calculate the activity coefficient of each component.

(At the same temperature, the saturated vapour pressures of the pure components are: ethanol 0.137 bar and trichloromethane 0.393 bar.)

Strategy

Rearrange Equation 17.25, which defines the vapour pressure of a real component in terms of the mole fraction in the liquid, the vapour pressure when pure and the activity coefficient.

Solution

From Equation 17.25,

$$p_E(\text{real}) = \gamma_E x_E p_E$$

then

$$\gamma_E = p_E(\text{real})/x_E p_E = 0.087\ \text{bar}/(0.6 \times 0.137\ \text{bar}) = 1.06$$

There are only two components, so that

$$x_E + x_T = 1$$

and therefore

$$x_T = 1 - x_E = 1 - 0.6 = 0.4$$

Hence

$$\gamma_T = \frac{p_T(\text{real})}{x_T p_T} = \frac{0.256\ \text{bar}}{(0.4 \times 0.393\ \text{bar})} = 1.63$$

WE 17.6 Henry's law and gas solubilities (on p. 799 in *Chemistry*^{3})

Depending on the weather, the pressure of the atmosphere can vary from 960 mbar to 1067 mbar. What is the range of oxygen concentration in water due to this variation at 298 K?

Strategy

Use Henry's law, Equation 17.27, taking the value for the Henry's law constant and the mole fraction of oxygen in the air from the Worked Example.

Solution

Oxygen, O_2, comprises 21 mol% of air, so that the partial pressure of oxygen in air must vary from

$$0.21 \times (960\ \mathrm{mbar}) = 201.6\ \mathrm{mbar} = 201.6 \times 10^{-3}\ \mathrm{bar}$$

to

$$0.21 \times (1067\ \mathrm{mbar}) = 224.7\ \mathrm{mbar} = 224.7 \times 10^{-3}\ \mathrm{bar}$$

Thus, rearranging Henry's law, Equation 17.27, the mole fraction of oxygen in water must be

$$x_{\mathrm{O_2}} = p_{\mathrm{O_2}}/K_{\mathrm{O_2}} = (201.6 \times 10^{-3}\mathrm{bar})/(4.3 \times 10^{4}\ \mathrm{bar}) = 4.69 \times 10^{-6}$$

and

$$x_{\mathrm{O_2}} = p_{\mathrm{O_2}}/K_{\mathrm{O_2}} = (224.7 \times 10^{-3}\mathrm{bar})/(4.3 \times 10^{4}\ \mathrm{bar}) = 5.21 \times 10^{-6}$$

which is equivalent to a composition range of 4.69 ppm to 5.21 ppm.

The concentrations of dissolved gases in water are very small, so that for a sample, the amount of substance

$$n_{\mathrm{total}} = n_{\mathrm{H_2O}} + n_{\mathrm{N_2}} + n_{\mathrm{O_2}} \approx\ n_{\mathrm{H_2O}}$$

A volume of 1 dm^3 of water contains 55.6 mol, so that

$$n_{\mathrm{total}} \approx 55.6\ \mathrm{mol}$$

The concentration of oxygen in water is

$$[\mathrm{O_2}] = n_{\mathrm{O_2}}/V = x_{\mathrm{O_2}} n_{\mathrm{total}}/V$$

and so ranges from

$$4.69 \times 10^{-6} \times (55.6\ \mathrm{mol})/(1\ \mathrm{dm}^3) = 2.61 \times 10^{-4}\mathrm{mol\ dm}^{-3}$$

to

$$5.21 \times 10^{-6} \times (55.6\ \mathrm{mol})/(1\ \mathrm{dm}^3) = 2.90 \times 10^{-4}\mathrm{mol\ dm}^{-3}$$

The molar mass of oxygen is

$$M_{\mathrm{O}_2} = (2 \times 16.00)\mathrm{g\ mol}^{-1} = 32.00\ \mathrm{g\ mol}^{-1}$$

so that these concentrations correspond, using Equation 1.6, to mass concentrations of

$$\begin{aligned}\overbrace{(2.61 \times 10^{-4}\mathrm{mol\ dm}^{-3})}^{\text{molarity}} \times \overbrace{(32.00\ \mathrm{g\ mol}^{-1})}^{\text{molar mass,}M} &= \overbrace{8.35 \times 10^{-3}\mathrm{g\ dm}^{-3}}^{\text{mass concentration}}\\ &= 8.35\ \mathrm{mg\ dm}^{-3}\end{aligned}$$

and

$$\begin{aligned}(2.90 \times 10^{-4}\mathrm{mol\ dm}^{-3}) \times (32.00\ \mathrm{g\ mol}^{-1}) &= 9.27 \times 10^{-3}\mathrm{g\ dm}^{-3}\\ &= 9.27\ \mathrm{mg\ dm}^{-3}\end{aligned}$$

WE 17.7 Using osmosis to find relative molecular mass, M_r (on p. 803 in *Chemistry*^{3})

Lysozyme is a protein with M_r = 16 500. What is the osmotic pressure generated at 298 K by a solution of 1.00 g of lysozyme in 50.00 cm^3 of water?

Strategy

Calculate the molar concentration and use Equation 17.28 to determine the osmotic pressure.

Solution

A mass of 1.00 g of lysozyme corresponds to an amount

$$n_\mathrm{L} = m_\mathrm{L}/M_\mathrm{L} = (1.00\ \mathrm{g})/(16500\ \mathrm{g\ mol}^{-1}) = 6.06 \times 10^{-5}\mathrm{mol}$$

and therefore a concentration of

$$\begin{aligned}c = n_\mathrm{L}/V &= (6.06 \times 10^{-5}\mathrm{mol})/(50.00\ \mathrm{cm}^3)\\ &= 1.21 \times 10^{-6}\mathrm{mol\ cm}^{-3} = 1.21\ \mathrm{mol\ m}^{-3}\end{aligned}$$

Using Equation 17.28, the osmotic pressure is

$$\begin{aligned}\pi &= cRT\\ &= (1.21\ \mathrm{mol\ m^{-3}}) \times (8.3145\ \mathrm{J\ K^{-1} mol^{-1}}) \times (298\ \mathrm{K})\\ &= 3000\ \mathrm{J\ m^{-3}} = 3000\ \mathrm{Pa} = 3.00\ \mathrm{kPa}\end{aligned}$$

Answers to boxes

Box 17.1 Liquid crystals (on p. 773 in *Chemistry*^{3})

Suggest some reasons why cyanobiphenyls form mesophases.

Strategy

Consider the structure of the molecules and the effect of the alkyl chains and polar head groups on the rigidity and polarity of the molecules.

Solution

The cyanobiphenyls are relatively flat molecules. The rigid biphenyl groups tend to line up to give an ordered crystalline material—but the alkyl chains introduce enough flexibility to stop well-ordered crystals forming at anything but low temperatures. The polar –CN group means that the molecules can be influenced by an electric field.

Box 17.4 Perfluorocarbons and blood substitutes (on p. 800 in *Chemistry*^{3})

(a) Suggest explanations for the different shapes of the plots in Figure 2. (*Hint*: Look at Box 28.7 (p.1292) on the way O_2 binds to haemoglobin).
(b) What is the partial pressure of oxygen in air? Estimate the percentage of perfluorocarbon emulsion that would be needed to carry the same amount of oxygen as blood at this partial pressure of oxygen.

Strategy

(a) Consider the mechanism for absorption of oxygen in the various fluids, noting from Box 28.7 that a special cooperative mechanism occurs in blood.
(b) Use the plot showing how the concentration of oxygen in blood and perfluorocarbon emulsion varies with pressure.

Solution

(a) The plot showing how the concentration of oxygen varies with pressure shows that a special mechanism operates in blood; absorption of a small amount of oxygen allows more oxygen to be absorbed. This cooperative effect is due to chemical binding of oxygen causing changes in haemoglobin structure. Blood becomes saturated with oxygen at relatively low gas pressures. Plasma and perfluorocarbon show a linear relation of solubility to pressure; there is no special cooperative effect and the oxygen simply dissolves in the fluid.

(b) The partial pressure of O_2 is 0.21 atm which is equivalent to 21 kPa. From Figure 2, at this pressure, blood carries about 20 vol% O_2, whilst a 10% perfluorocarbon emulsion carries about 4 vol% oxygen. Since the amount of O_2 dissolved is proportional to amount of perfluorocarbon present, about 5 times more perfluorocarbon would be needed, or an approximately 50% emulsion.

Box 17.5 Reverse osmosis and water purification (on p. 804 in *Chemistry*^{3})

1 dm^3 of sea water contains about 35 g of dissolved substances. Assuming that this is all sodium chloride, estimate the minimum pressure needed for reverse osmosis to take place at 25 °C.

Strategy

Calculate the concentration of sodium chloride in sea water and apply Equation 17.28.

Solution

The molar mass of sodium chloride is

$$M = (23.99 + 35.45)\ \text{g mol}^{-1} = 59.44\ \text{g mol}^{-1}$$

Thus, 35 g of dissolved substances, would correspond, from Equation 1.2, to an amount

$$n = m/M = (35\ \text{g})/(59.44\ \text{g mol}^{-1}) = 0.59\ \text{mol}$$

This amount of sodium chloride would result in

$$2 \times (0.59\ \text{mol}) = 1.2\ \text{mol}$$

of ions, because every NaCl unit results in a Na^+ and a Cl^- ion. This is the amount dissolved in 1 dm^3, so that the concentration of ions in solution must be 1.2 mol dm^{-3}. From Equation 17.28, the osmotic pressure that would be generated by a solution with this concentration is

$$\begin{aligned}\pi = cRT &= (1.2 \times 10^3\ \text{mol m}^{-3}) \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K}) \\ &= 2.9 \times 10^6\ \text{Pa} = 2.9\ \text{MPa} = 29\ \text{bar}\end{aligned}$$

A minimum pressure of 29 bar would be needed to prevent osmosis taking place and the pressure used would need to be somewhat higher to force water through the membrane against this osmotic pressure. In fact, sea water contains around 27 g dm^{-3} of NaCl, the remainder being other salts. The above calculation relies on Equation 17.28, which assumes ideal behaviour. Aqueous solutions of salt at high concentrations will not act ideally so that the pressure calculated here is only an estimate. However, it does show that high pressures are needed for reverse osmosis to operate efficiently.

Answers to end of chapter questions

1. Figure 1 shows a generalised phase diagram.

(a) What phase(s) is/are present at W, X, Y and Z?

(b) What is the significance of points X, Y, T and C?

(c) What phase change would occur if you started at point U and

(i) increased the temperature with the pressure constant?

(ii) increased the pressure with the temperature constant?

Strategy

Compare the phase diagram with the typical single-component diagrams shown in Figure 17.4.

Solution

(a) W, solid; X, solid and liquid; Y, liquid and vapour; Z, vapour.

(b) X, normal melting point; Y, normal boiling point; T, triple point; C, critical point.

(c) (i) The liquid would boil at the temperature and pressure indicated by the liquid–vapour equilibrium curve between the triple point, T, and critical point C.

(ii) The liquid would eventually solidify, or freeze, at the pressure and temperature indicated by the solid–liquid equilibrium line that passes from the triple point, T, through X.

2. For the phase diagram shown:

(a) Which area of the phase diagram (A, B or C) represents the liquid phase?

(b) Which phases exist at SATP?

(c) If a sample of this substance is cooled from 250 K to 50 K, what phases will occur?

(d) What name is given to the change from phase A to phase C?

(e) What sign do the values of enthalpy change and entropy change have for the change from phase B to phase A?

(f) Estimate the conditions of the triple point of this substance.

(g) What are the melting and boiling points of this substance at 25 bar?

(h) What phase(s) can exist at 300 K and 40 bar?

(i) At a pressure of 25 bar, does the liquid or the solid have the higher density at the melting point?

(j) What is the lowest temperature at which the liquid phase can exist?

(k) Place the enthalpy changes for the following phase changes in increasing order of energy: A → B, A → C, B → C.

(l) What changes would happen when the pressure over a quantity of the substance is changed from 35 bar to 5 bar at a constant temperature of 135 K?

Strategy

Compare the phase diagram given with those shown in Figure 17.1.

Solution

(a) The liquid phase exists at high pressure and high temperature, and is therefore represented by area B.

(b) Standard ambient temperature and pressure (SATP) corresponds to 1 atm = 1.0325 bar and 25 °C = 298 K. This point falls within area C, which corresponds to the gas or vapour phase.

(c) The phases that occur depend upon the pressure of the sample. At 35 bar, the substance exists as a liquid (area B) at 250 K, but becomes a solid (area A) at 150 K. However, at 5 bar, the substance exists as a vapour (area C) at 250 K, and sublimes to become a solid (area A) at 100 K.

(d) The transformation of a vapour (area C) to a solid (area A) is called sublimation.

(e) The change of Phase B (liquid) to phase A (solid) is freezing. Energy is released so that the enthalpy change is negative. The liquid is more disordered so that there is a loss of entropy on freezing and the entropy change is negative.

(f) The triple point occurs at approximately 12.5 bar and 120 K.

(g) At 25 bar, the melting point is approx. 130 K and the boiling point approx. 225 K.

(h) At 300 K and 40 bar, the substance will exist as a supercritical fluid.

(i) At a pressure of 25 bar, the solid have the higher density since the solid-liquid equilibrium line has a positive slope.

(j) The lowest temperature at which the liquid phase can exist corresponds to the triple point so approx. 120 K.

(k) The enthalpy change for vaporization is larger than that for melting. ΔH for sublimation is the sum of the other two changes. Therefore: $A \rightarrow C > B \rightarrow C > A \rightarrow B$

(l) At 35 bar and 135 K the substance is in the solid phase. As the pressure is lowered, it will melt when the pressure reaches ~ 30 bar. On further lowering the pressure, vaporization will occur at ~ 14 bar. No further phase changes occur until 5 bar is reached.

3. Use the phase diagrams in Figures 17.5 to 17.8 (pp. 765–768) to answer the following questions.

(a) CO_2 fire extinguishers contain liquid CO_2 in equilibrium with gas. At 298 K, estimate the pressure of CO_2 (g) above the liquid.

(b) Which form of sulfur will crystallize from liquid sulfur at normal atmospheric pressure?

(c) Which has the lower density: Ice I or Ice II?

(d) What will happen when water is:

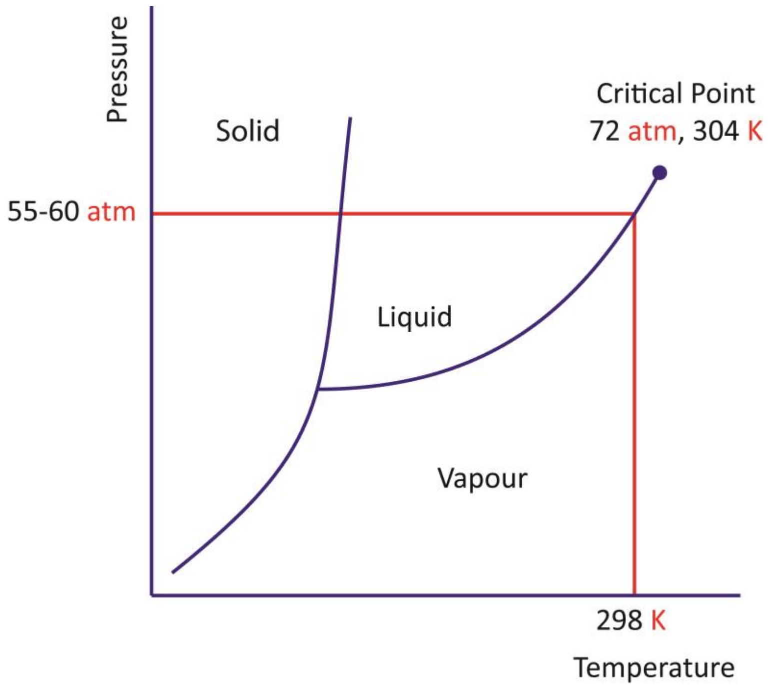
(i) heated from 250 K to 300 K at a pressure of 0.005 bar, then(ii) compressed to 10 bar with the temperature held at 300 K, then (iii) cooled to 250 K with the pressure held at 10 bar?

Strategy

Consider the phase diagrams for carbon dioxide, Figure 17.6, sulfur, Figure 17.7 and water, Figures 17.5 and 17.8, noting the stable phase that corresponds to the particular conditions noted.

Solution

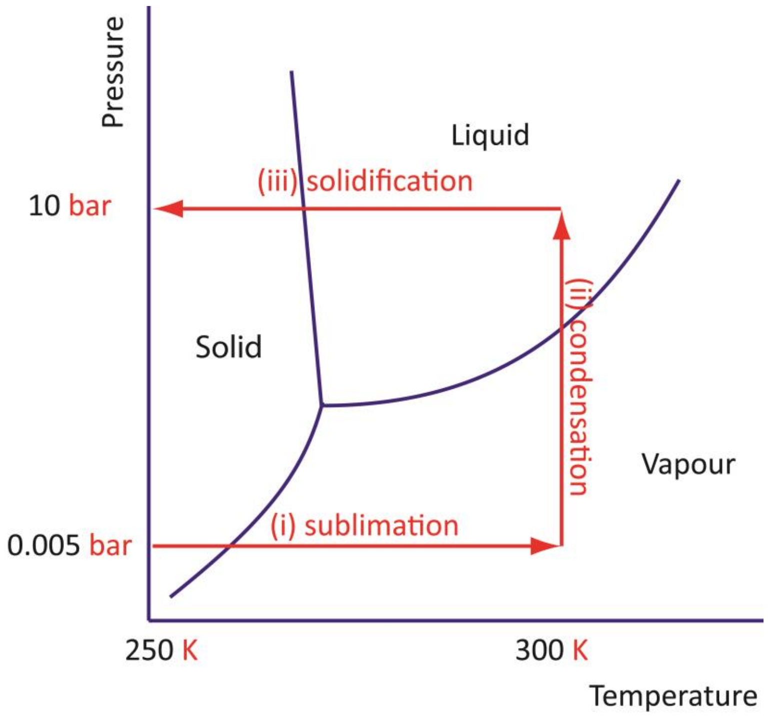
(a) Reading from Figure 17.6, which is the pressure–temperature phase diagram for carbon dioxide, it can be seen that 298 K is somewhat below the critical temperature, at which the pressure is 72 atm. The pressure at 298 K is, in fact, around 55–60 atm.



(b) From the phase diagram in Figure 17.7(b), at 1 atm the liquid freezes to the monoclinic form of solid sulfur.

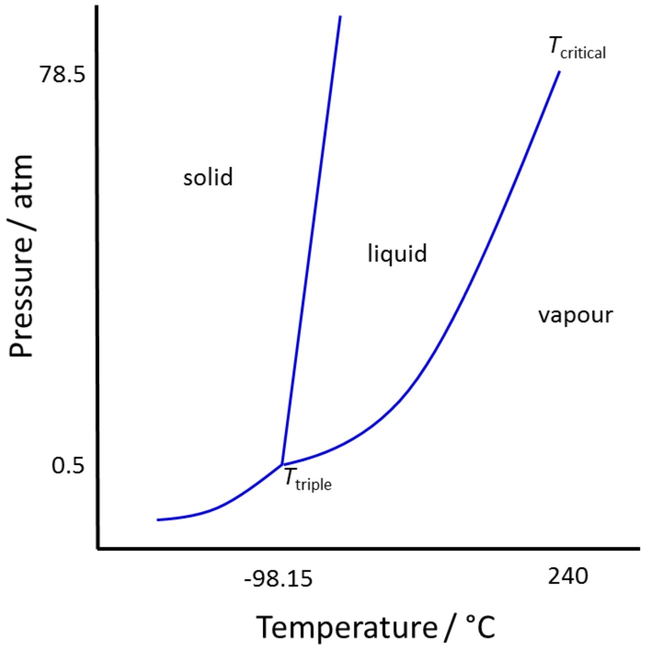
(c) From Figure 17.8, it can be seen that, for a given temperature, Ice I exists at low pressures and Ice II at high pressures. This implies that Ice II has the lower density.

(d) From Figure 17.5, it can be seen that when the temperature is raised from 250 K to 300 K at 0.005 bar, the solid ice will sublime to water vapour. Raising the pressure will cause the vapour to condense to liquid. Reducing the temperature at this elevated pressure will result in solidification.



4. The conditions at the triple point of methanol are −98.15 °C and 0.5 atm while those at its critical point are 240 °C and 78.5 atm.

Use this information to <u>sketch</u> (not to scale) and fully label a phase diagram for methanol.



5. Mercury has a melting point of 234.3 K. At this temperature, the density of Hg (l) is 13.690 g cm^{-3} and that of Hg (s) is 14.193 g cm^{-3}. The enthalpy change of fusion is 9.75 J g^{-1}. Find the pressure needed to change the melting temperature by 1 K.

Strategy

Use the Clapeyron equation, Equation 17.4. There is no need to calculate the molar volume change and molar enthalpy change using the molar mass. Instead, calculate the volume change per unit mass from the density and use the enthalpy change per unit mass as given.

Solution

The Clapeyron equation, Equation 17.4, has the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{fus}}H}{T\Delta_{\text{fus}}V}$$

The change in volume on melting of 1 g is

$$\Delta_{\text{fus}}V = V(\text{liquid}) - V(\text{solid})$$

where, because the volume may be expressed in terms of the mass and the density as

$$V = 1/\rho$$

then

$$\begin{aligned}\Delta_{\text{fus}}V &= 1/\rho_{\text{m}}(\text{liquid}) - 1/\rho_{\text{m}}(\text{solid})\\ &= \{1/(13.690\ \text{g cm}^{-3}) - 1/(14.193\ \text{g cm}^{-3})\}\\ &= +2.589 \times 10^{-3}\ \text{cm}^3\ \text{g}^{-1}\\ &= +2.589 \times 10^{-9}\ \text{m}^3\ \text{g}^{-1}\end{aligned}$$

Then, because the enthalpy change for 1 g is

$$\Delta_{\text{fus}}H = +9.75\ \text{J g}^{-1}$$

at a temperature of 234.3 K, the gradient of the solid–liquid pressure–temperature line on the phase diagram is

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}T} &= \frac{(+9.75\ \text{J g}^{-1})}{(234.3\ \text{K}) \times (2.589 \times 10^{-9}\ \text{m}^3\ \text{mol}^{-1})}\\ &= 16.1 \times 10^6\ \text{J m}^{-3}\text{K}^{-1} = 16.1 \times 10^6\ \text{Pa K}^{-1}\end{aligned}$$

Assuming that the solid–liquid equilibrium forms a straight line on the pressure–temperature phase diagram, then

$$\frac{\Delta p}{\Delta T} = 16.1 \times 10^6 \text{ Pa K}^{-1}$$

so that a temperature change of $\Delta T = +1$ K requires a change in pressure of

$$\Delta p = (16.1 \times 10^6 \text{ Pa K}^{-1}) \times \Delta T = (16.1 \times 10^6 \text{ Pa K}^{-1}) \times (1 \text{ K}) = 16.1 \text{ MPa}$$

6. Sulfur melts at a temperature of 115.2°C under a pressure of 1 atm. In one process for its mining, sulfur is melted and pumped from underground deposits as a liquid under a pressure of 6 bar. Use the Clapeyron equation to estimate the lowest temperature at which sulfur is a liquid at this pressure. (The enthalpy change of fusion at 115.2°C is 53.67 J g^{-1} and the densities of solid and liquid sulfur are 2.15 g cm^{-3} and 1.811 g cm^{-3}, respectively.)

Strategy

Use the Clapeyron equation, Equation 17.4. There is no need to calculate the molar volume change and molar enthalpy change using the molar mass. Instead, calculate the volume change per unit mass from the density and use the enthalpy change per unit mass as given. Remember to convert the temperature from units of °C to K, and pressures from bar and atm to Pa.

Solution

The Clapeyron equation, Equation 17.4, has the form

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V}$$

The change in volume on melting of 1 g is

$$\Delta_{\text{fus}} V = V(\text{liquid}) - V(\text{solid}) =$$

where, because the volume may be expressed in terms of the mass and the density as

$$V = 1/\rho$$

then

$$\begin{aligned}\Delta_{\text{fus}}V &= 1/\rho_{\text{m}}(\text{liquid}) - m/\rho_{\text{m}}(\text{solid})\\ &= \{1/(1.811\ \text{g cm}^{-3}) - 1/(2.15\text{g cm}^{-3})\}\\ &= +87.1 \times 10^{-3}\ \text{cm}^3\ \text{g}^{-1}\\ &= +87.1 \times 10^{-9}\ \text{m}^3\ \text{g}^{-1}\end{aligned}$$

Then, because the enthalpy change for 1 g is

$$\Delta_{\text{fus}}H = +53.67\ \text{J g}^{-1}$$

then, at a temperature of

$$(115.2\ + 273.15)\ \text{K}\ = 388\ \text{K}$$

the gradient of the pressure–temperature line on the phase diagram is

$$\begin{aligned}\frac{\text{d}p}{\text{d}T} &= \frac{(+53.67\ \text{J g}^{-1})}{(388\ \text{K}) \times (87.1 \times 10^{-9}\ \text{m}^3\ \text{mol}^{-1})}\\ &= 1.59 \times 10^6\ \text{J m}^{-3}\text{K}^{-1} = 1.59 \times 10^6\ \text{Pa K}^{-1}\end{aligned}$$

Assuming that the solid–liquid equilibrium forms a straight line on the pressure–temperature phase diagram, then

$$\frac{\Delta p}{\Delta T} = 1.59 \times 10^6\ \text{Pa K}^{-1}$$

A pressure of 1 atm is equivalent to 1.01325×10^5 Pa, whilst 1 bar is 10^5 Pa, so that the difference in pressure is

$$\Delta p = (6 \times 10^5\text{Pa}) - (1.01 \times 10^5\text{Pa}) = 5 \times 10^5\text{Pa}$$

This, therefore, corresponds to a temperature change of

$$\begin{aligned}\Delta T &= \Delta p/(1.59 \times 10^6\ \text{Pa K}^{-1}) = (5 \times 10^5\text{Pa})/(1.59 \times 10^6\ \text{Pa K}^{-1})\\ &= 0.3\ \text{K} \equiv 0.3\text{°C}\end{aligned}$$

Thus, the lowest temperature at which sulfur will remain liquid at this pressure is

$$115.2\text{°C} + 0.3\text{°C} = 115.5\text{°C}$$

7. Explain the observation that if a liquid evaporates from an open container, the temperature remains about constant but if it evaporates from an insulated flask, the temperature falls.

Strategy

Vaporization is an endothermic process. Consider from where the heat may be supplied in the two containers.

Solution

Vaporization is an endothermic process and so requires an input of energy. In an open container the energy can come from the surroundings so the temperature does not change very much. In an insulated container, the energy has to come from the liquid so that it cools down.

8. The vapour pressure of tetrachloromethane (CCl_4) at 0°C is 44.0 mbar and at 50°C is 422.0 mbar. Use these data to estimate the enthalpy change of vaporization of CCl_4 and to estimate its standard boiling point.

Strategy

Use the integrated form of the Clausius–Clapeyron Equation, Equation 17.7 and substitute in the data for the vapour pressures at two temperatures. Rearrange to determine the enthalpy of vaporization. Use the same equation to determine the standard boiling point, which is the temperature at which the vapour pressure is exactly 1 bar = 10^3 mbar.

Solution

Substituting the data into the Clausius–Clapeyron equation, Equation17.7,

$$\ln\frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and remembering to convert the temperatures from units of °C to K,

$$\ln\frac{44.0\ \text{mbar}}{422.0\ \text{mbar}} = \frac{\Delta H}{R}\left(\frac{1}{(273+50)\text{K}} - \frac{1}{(273+0)\text{K}}\right)$$

$$-2.261 = -6.820 \times 10^{-5}(\text{J mol}^{-1})^{-1} \times \Delta H$$

so that

$$\Delta H = 33.2 \times 10^3 \text{J mol}^{-1} = 33.2\ \text{kJ mol}^{-1}$$

It is now possible to determine the temperature at which the vapour pressure is 10^3 mbar, by substituting the enthalpy change and one pressure–temperature pair into the Clausius–Clapeyron equation, Equation17.7. Thus, if

$$\ln \frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

then

$$\ln\{p/(10^3\,\mathrm{mbar})\} = \frac{\Delta H}{R}\left(\frac{1}{T_\mathrm{b}} - \frac{1}{T}\right)$$

and choosing

$$p = 44.0\ \mathrm{mbar}$$

and

$$T = 273\ \mathrm{K}$$

then

$$\ln(44.0\ \mathrm{mbar}/10^3\,\mathrm{mbar}) = \frac{33.2 \times 10^3\,\mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1} mol^{-1}}}\left(\frac{1}{T_\mathrm{b}} - \frac{1}{273\ \mathrm{K}}\right)$$

Solving gives

$$T_\mathrm{b} = 347\ \mathrm{K}$$

9. Mount Everest is the highest mountain on Earth with a height of 8850 m. At this altitude, the atmospheric pressure is about one-third that at sea-level. Find the melting and boiling temperatures of water at this pressure.

(The densities of ice and water at 0°C are 0.92 and 1.00 g cm^{-3}, respectively, and the enthalpy change of fusion of ice is +6.01 kJ mol^{-1}. The enthalpy change of vaporization of H_2O (l) at the normal boiling point is +40.7 kJ mol^{-1}.)

<u>Strategy</u>

For the melting temperature, calculate the molar volume change on melting and substitute into the Clapeyron equation, Equation 17.4. Use the Clausius–Clapeyron equation, Equation 17.7, for the boiling temperature.

<u>Solution</u>

The Clapeyron equation, Equation 17.4, has the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trans}}H}{T\Delta_{\mathrm{trans}}V}$$

The change in molar volume on melting is

$$\Delta_{\mathrm{fus}}V = V(\mathrm{liquid}) - V(\mathrm{solid})$$

where, because the molar volume may be expressed in terms of the molar mass and the density as

$$V_{\mathrm{m}} = M/\rho$$

then, because the molar mass of water is

$$M = [16.00 + (2 \times 1.01)]\ \mathrm{g\ mol^{-1}} = 18.02\ \mathrm{g\ mol^{-1}}$$

then

$$\begin{aligned}\Delta_{\mathrm{fus}}V_{\mathrm{m}} &= M/\rho_{\mathrm{m}}(\mathrm{liquid}) - M/\rho_{\mathrm{m}}(\mathrm{solid})\\ &= M/\big(1/\rho_{\mathrm{m}}(\mathrm{liquid}) - 1/\rho_{\mathrm{m}}(\mathrm{solid})\big)\\ &= 18.02\ \mathrm{g\ mol^{-1}}\{1/(1.00\ \mathrm{g\ cm^{-3}}) - 1/(0.92\ \mathrm{g\ cm^{-3}})\}\\ &= -1.57\ \mathrm{cm^3\ mol^{-1}}\\ &= -1.57 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}\end{aligned}$$

Using the Clapeyron equation to find how melting temperature varies with pressure at 273 K

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}}H}{T\Delta_{\mathrm{fus}}V} = \frac{(6.01 \times 10^3\mathrm{J\ mol^{-1}})}{(273\ \mathrm{K}) \times (-1.57 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})} = -14.0 \times 10^6\ \mathrm{Pa\ K^{-1}}$$

Hence, the change in melting temperature for a change in pressure is given by

$$\Delta T = -\Delta p/14.0 \times 10^6\ \mathrm{Pa\ K^{-1}}$$

Thus, if the pressure at the top of Mount Everest is a third of that at sea level,

$$\Delta p = 0.333\ \mathrm{atm} - 1.000\ \mathrm{atm} = -0.666\ \mathrm{atm}$$

which is equivalent to

$$\Delta p = (0.666\ \mathrm{atm}) \times (1.01325 \times 10^5\mathrm{Pa\ atm^{-1}}) = -67.5 \times 10^3\mathrm{Pa}$$

The melting temperature therefore changes by

$$\Delta T = (-67.5 \times 10^3\mathrm{Pa})/(-14.0 \times 10^6\ \mathrm{Pa\ K^{-1}}) = +0.005\ \mathrm{K}$$

The melting temperature of ice therefore increases by 5 mK from sea level to the top of Mount Everest.

Using the Clausius–Clapeyron equation, Equation 17.7

$$\ln\frac{p_2}{p_1}=\frac{\Delta H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

to determine the effect of the change in pressure on the boiling temperature, then, if the ratio of the pressures at sea level and at the top of Mount Everest is

$$\frac{p_2}{p_1}=\frac{0.333\ \text{atm}}{1.000\ \text{atm}}=0.333$$

and the boiling temperature at sea level is 373 K, then substituting gives

$$\ln 0.333=\frac{40.7\times 10^3\,\text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{373\ \text{K}}-\frac{1}{T_\text{b}}\right)$$

and solving for the unknown boiling temperature at the top of Mount Everest gives

$$T_\text{b}=344\ \text{K}$$

The change in pressure therefore has a much greater effect on the boiling temperature than the melting temperature.

10. Determine the melting point of ice under a pressure of 500 bar. The density of ice at 0 °C is 0.9158 g cm^{-3} and that of water is 0.9987 g cm^{-3}. The enthalpy of fusion of ice is 6.008 kJ mol^{-1}. (Section 17.2)

Strategy

Follow the method used in Worked Example 17.2. Using the Clapeyron equation, Equation 17.4, calculate the rate, $\Delta T/\Delta p$ at which the melting temperature changes with pressure. Express the change in volume upon melting in terms of the difference in the mass density of ice and water, and the molar mass.

Solution

The pressure–temperature phase diagram for water is shown in Figure 17.5. It can be seen that the solid–liquid transition line is straight, implying that the gradient is constant. We may therefore write the Clapeyron equation, Equation

17.4, in terms of measurable rather than infinitesimally small changes in pressure and temperature

$$\frac{\Delta p}{\Delta T} = \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}}H}{T\Delta_{\mathrm{fus}}V}$$

The change in molar volume on melting is

$$\Delta_{\mathrm{fus}}V = V(\mathrm{liquid}) - V(\mathrm{solid})$$

where, because the molar volume may be expressed in terms of the molar mass and the density as

$$V_{\mathrm{m}} = M/\rho$$

then

$$\begin{aligned}\Delta_{\mathrm{fus}}V_{\mathrm{m}} &= \overbrace{M/\rho_{\mathrm{m}}(\mathrm{liquid})}^{V(\mathrm{liquid})} - \overbrace{M/\rho_{\mathrm{m}}(\mathrm{solid})}^{V(\mathrm{solid})} \\ &= M/\big(1/\rho_{\mathrm{m}}(\mathrm{liquid}) - 1/\rho_{\mathrm{m}}(\mathrm{solid})\big)\end{aligned}$$

$$\begin{aligned}&= (18.02\ \mathrm{g\ mol^{-1}}) \times \{1/(0.9987\ \mathrm{g\ cm^{-3}}) - 1/(0.9158\ \mathrm{g\ cm^{-3}})\} \\ &= -1.633\ \mathrm{cm^3\ mol^{-1}} = -1.633 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}\end{aligned}$$

Hence, substituting and rearranging, the gradient of the solid–liquid transition line at 273 K is

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}}H}{T} \times \overbrace{\frac{1}{M}\left\{\frac{\rho_{\text{m}}(\text{solid}) \times \rho_{\text{m}}(\text{liquid})}{\rho_{\text{m}}(\text{solid}) - \rho_{\text{m}}(\text{liquid})}\right\}}^{1/\Delta_{\text{fus}}V}$$

$$= \frac{(6.008\ \text{kJ mol}^{-1})}{(273.15\ \text{K}) \times (-1.633 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})}$$

$$= -13.47 \times 10^6\ \text{J m}^{-3}\text{K}^{-1} = -13.47 \times 10^6\ \text{Pa K}^{-1}$$

The pressure–temperature phase diagram for water is shown in Figure 17.5. It can be seen that the solid–liquid transition line is straight, implying that the gradient is constant. We may therefore calculate the change in melting temperature ΔT caused by a change in pressure Δp

$$\Delta T = \frac{dT}{dp} \times \Delta p = \{1/(dT/dp)\} \times \Delta p$$

at the normal melting temperature and assume that it remains constant throughout the range of interest.

Hence, for a change in pressure

$$\Delta p = 500\ \text{bar} - 1\ \text{bar} = 499\ \text{bar} = 499\ \text{bar} \times (10^5\text{Pa bar}^{-1}) = 499 \times 10^5\ \text{Pa}$$

the melting temperature changes by

$$\Delta T = \{1/(-13.47 \times 10^6\ \text{Pa K}^{-1})\} \times (499 \times 10^5\ \text{Pa}) = -3.71\ \text{K}$$

The melting point of ice under a pressure of 500 bar is therefore

$$T = T_b + \Delta T = 273.15\ \text{K} + (-3.71\ \text{K}) = 269.44\ \text{K}$$

Thus the melting temperature of ice decreases with increasing pressure.

11. The vapour pressure exerted by carbon disulphide (CS_2) was measured at different temperatures.

Temperature / °C	**0**	**10**	**20**	**30**	**40**
Pressure / bar	0.168	0.262	0.394	0.576	0.820

Determine the enthalpy and entropy changes of vaporization of CS_2. (Section 17.2)

Strategy

Apply the integrated form of the Clausius–Clapeyron equation, Equation 17.7 to determine the enthalpy of vaporisation. Then use Equation 17.3b to calculate the equivalent entropy of vaporisation.

Solution

The Clausius–Clapeyron expresses how the vapour pressure of a liquid or solid varies with temperature. We may rearrange Equation 17.7

$$\ln\frac{p_2}{p_1} = -\frac{\Delta H}{R}\left\{\frac{1}{T_2} - \frac{1}{T_1}\right\}$$

so that it has the form of a straight-line graph, *y* = *mx* + *c*,

$$\overbrace{\ln p_2}^{y} = \overbrace{-\frac{\Delta H}{R}}^{m}\overbrace{\frac{1}{T_2}}^{x} + \overbrace{\frac{\Delta H}{RT_1}}^{c}$$

which we may rewrite as

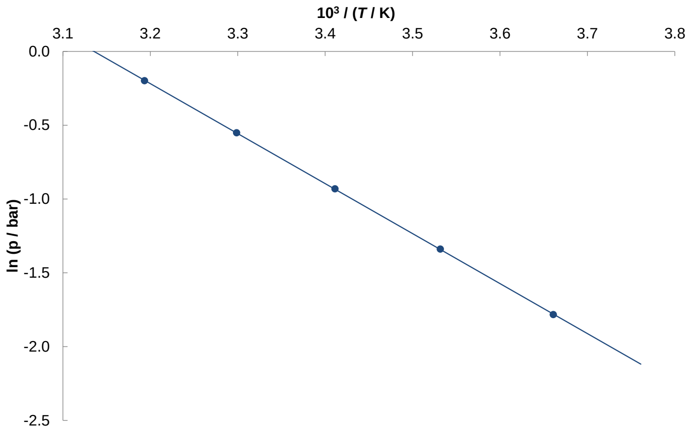
$$\ln p = -\frac{\Delta_{\text{vap}}H}{R}\frac{1}{T} + c$$

Thus, a graph of the logarithm of vapour pressure against the reciprocal of temperature should be a straight line with a gradient of $\left(-\Delta_{\text{vap}}H/R\right)$. The following figure shows such a graph for the data given. Note that in plotting the points, it is necessary to convert the temperatures into kelvin. The gradient of the graph is $m = -3.389 \times 10^3$ K, so that

$$\begin{aligned}\Delta_{\text{vap}}H &= -m \times R \\ &= -(-3.389 \times 10^3\,\text{K}) \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \\ &= +28.18 \times 10^3\ \text{J mol}^{-1} = +28.18\ \text{kJ mol}^{-1}\end{aligned}$$

Taking the value for the normal boiling temperature of carbon disulphide from Table 17.1, the entropy of vaporization is therefore, from equation 17.3b,

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_\text{b}} = \frac{28.18 \times 10^3\ \text{J mol}^{-1}}{(46.3 + 273.15)\ \text{K}} = +88.2\ \text{J K}^{-1}\text{mol}^{-1}$$



12. The vapour pressures of sulphur dioxide in the solid and liquid states are given by:

Solid: $\ln (p / \text{Pa}) = 29.28 - \left(\dfrac{4308}{T / K}\right)$

Liquid: $\ln (p / \text{Pa}) = 24.055 - \left(\dfrac{3284}{T / K}\right)$

Calculate (i) the temperature and pressure of the triple point of sulphur dioxide and (ii) the enthalpy and entropy changes of fusion at the triple point.

Strategy

At the triple point, the vapour pressures of the solid and the liquid must be equal so that the two given equations can be equated. You have the equations for the vapour pressures in similar form to the Clausius Clapeyron equation. By comparison with the equation, the terms in the Clausius Clapeyron equation can be found.

Solution

(i) At the triple point, the vapour pressures of solid and liquid must be equal so :

$$29.28 - \left(\frac{4308}{T_{triple} / \text{K}}\right) = 24.055 - \left(\frac{3284}{T_{triple} / K}\right)$$

Rearranging, $5.230 = \left(\dfrac{1024}{T_{triple} / K}\right)$

From which, $T_{triple} = 195.8$ K

Using the data from the solid SO_2 and substituting for T_{triple}

$$\ln (p \,/\, \mathrm{Pa}) = 29.28 - \left(\frac{4308}{195.8\ \mathrm{K}}\right) \quad \text{so that} \quad p = 1480\ \mathrm{Pa}.$$

(ii) From the Clausius-Clapeyron equation,

$$\ln (p) = \text{constant} - \left(\frac{\Delta H}{RT}\right)$$

so the term in the brackets is equivalent to $(-\Delta_{vap}H \,/\, R)$ for the liquid and $(-\Delta_{sub}H \,/\, R)$ for the solid. Hence,

$(-\Delta_{sub}H \,/\, R) = -4308\ \mathrm{K}^{-1} \times R = 35820\ \mathrm{J\ mol^{-1}} = 35.82\ \mathrm{kJ\ mol^{-1}}$

$(-\Delta_{vap}H \,/\, R) = -284\ \mathrm{K}^{-1} \times R = 27300\ \mathrm{J\ mol^{-1}} = 27.30\ \mathrm{kJ\ mol^{-1}}$

From Hess' law,

$\Delta_{fus}H = (\Delta_{sub}H - \Delta_{vap}H)$

$= 35.82\ \mathrm{kJ\ mol^{-1}} - 27.30\ \mathrm{kJ\ mol^{-1}}$

$= 8.52\ \mathrm{kJ\ mol^{-1}}$

To find the entropy change,

$$\Delta_{fus}S = \Delta_{fus}S = \frac{\Delta_{fus}H}{T_m} = \frac{8520}{195.8} = 43.5\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

13. The vapour pressure of a liquid is 2.026 kPa at 20.0 °C and 44.209 kPa at 80 °C.

(i) Find the enthalpy change of vapourization of the liquid.

(ii) Estimate the normal boiling point of the liquid

(iii) Trouton's rule states that $\Delta_{vap}S$ for liquids $\approx 88\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Comment on the liquid under investigation here.

Strategy

Since you have two vapour pressures at two temperatures you can use the Clausius Clapeyron equation and solve the equations simultaneously to find the enthalpy change. You can use one of the pieces of data with the fact that the normal boiling point is where the vapour pressure becomes 1 atm to find the boiling point. The enthalpy change and boiling point allow you to calculate the entropy change for comparison with Trouton's rule.

Solution

(i) From the Clausius Clapeyron equation at two temperatures:

$$\ln\left(\frac{2.026\,\text{kPa}}{44.209\,\text{kPa}}\right)=\frac{\Delta_{vap}H\,/\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}mol^{-1}}\left(\frac{1}{353.15\,\text{K}}-\frac{1}{293.15\,/\,\text{K}}\right)$$

$\Delta_{\text{vap}}H$ = 42860 J mol^{-1} = 42.9 kJ mol^{-1}.

(ii) The normal boiling point is where the vapour pressure becomes 1 atm = 101.3 kPa.

$$\ln\left(\frac{101.3\,\text{kPa}}{44.209\,\text{kPa}}\right)=\frac{42900\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{353.15\,\text{K}}-\frac{1}{T_B\,/\,\text{K}}\right)$$

T_B = 374.3 K

(iii) $\Delta_{\text{vap}}S = \Delta_{\text{vap}}H\,/\,T_\text{B}$ = 42900 J mol^{-1} / 374.3 K = 114.6 J K^{-1} mol^{-1}

There is a larger change in entropy on vaporization of this liquid. It has relatively strong interactions between the molecules in the liquid e.g. hydrogen bonding.

14. At 1 bar, two solid forms of tin (grey tin and white tin) are in equilibrium at 291 K. The densities of the two forms are 5750 kg m^{-3} and 7280 kg m^{-3} respectively. The entropy change for the transition is 8.8 J K^{-1} mol^{-1}. At what temperature will the two forms be in equilibrium at a pressure of 200 bar?

Strategy

The equilibrium between two solid phases is described by the Clapeyon equation. Since you have the two densities then the volume change for the phase transition can be calculated and hence the effect of pressure on the transition temperature.

Solution

(i) Using the Clapeyron equation in the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

Shows that we need the change in volume for the transition.

$\Delta_{\mathrm{fus}}V = V_{\mathrm{m}}$ (white) - V_{m} (grey)

$$V_{\mathrm{m}}\,(\text{white}) = \frac{118.71\times10^{-3}\ \text{kg mol}^{-1}}{7280\ \text{kg m}^{-3}} = 1.631\times10^{-5}\ \text{m}^3\ \text{mol}^{-1} \quad ;$$

$$V_{\mathrm{m}}\,(\text{grey}) = \frac{118.71\times10^{-3}\ \text{kg mol}^{-1}}{5750\ \text{kg m}^{-3}} = 2.065\times10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$

$\Delta_{\mathrm{fus}}V = (2.065 - 1.631) \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1} = 0.434 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$

Substituting into the Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{8.8\ \text{J mol}^{-1}\text{K}^{-1}}{(0.434\times10^{-5}\text{m}^3\ \text{mol}^{-1})} = 2.03\times10^{6}\ \text{Pa K}^{-1}$$

Hence, a pressure change of 2.03×10^6 Pa is needed to change the melting temperature by 1 K^{-1}

Thus, for a pressure change of 200 bar, (1 bar = 1×10^{-5} Pa) the change in temperature is

$\mathrm{d}T = 200 \times 10^5\ \text{Pa} \ / \ 2.03 \times 10^6\ \text{Pa K}^{-1} = 9.9\ \text{K}$

Hence,

temperature = 291 K – 9.9 K = 281.1 K.

15. Calculate the energy of attraction between a Mg^{2+} ion and a Cl^{-} ion separated by 0.2 nm in a vacuum.

Strategy

Use Equation 17.11, which shows how the electrostatic potential energy between two charges varies with separation.

Solution

The energy of attraction can be calculated from Equation 17.11,

$$E_{\mathrm{PE}} = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

where, because the charges are separated by a vacuum, with $\epsilon = \epsilon_0$. Mg^{2+} ions have a charge of +2 and so carry a charge of

$$q_{\mathrm{Mg^{2+}}} = 2e = 2 \times (1.602 \times 10^{-19}\mathrm{C}) = 3.204 \times 10^{-19}\mathrm{C}$$

and Cl^{-} ions have a charge of –1 and so carry a charge of

$$q_{\mathrm{Cl^-}} = -e = -1.602 \times 10^{-19}\mathrm{C}$$

so that

$$E_{\mathrm{PE}} = \frac{(3.204 \times 10^{-19}\mathrm{C}) \times (-1.602 \times 10^{-19}\mathrm{C})}{(4\pi \times 8.854 \times 10^{-12}\ \mathrm{C^2 J^{-1} m^{-1}}) \times (0.2 \times 10^{-9}\mathrm{m})} = -2.3 \times 10^{-18}\mathrm{J}$$

which is equivalent to a molar energy of

$$(-2.3 \times 10^{-18}\mathrm{J}) \times (6.022 \times 10^{23}\mathrm{mol^{-1}}) = 1400\ \mathrm{kJ\ mol^{-1}}$$

16. Compare the energy of interaction between two singly charged ions separated by a distance of 0.1 nm in (a) vacuum, (b) water (relative permittivity = 78), (c) a hydrocarbon oil (relative permittivity = 2). (Section 17.3)

Strategy

You can use equation 17.11 to find the energy of interaction in a vacuum. The relative permittivity measures how much this energy is reduced by the medium in which the ions are found.

Solution

(a) The energy of attraction can be found using the charge on a single charged ion and the permittivity of a vacuum ($\varepsilon_0 = 8.85 \times 10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}$) from

$$U = \frac{q_1 q_2}{4\pi\varepsilon o}$$

$$U = \frac{(+1.602\times10^{-19}\,\text{C})(-1.602\times10^{-19}\,\text{C})}{4\times(3.142)\times(8.85\times10^{-12}\,\text{J}^{-1}\text{C}^2\text{m}^{-1})\times(1\times10^{-9}\,\text{m})} = -2.3 \times 10^{-19}\ \text{J}$$

The negative value shows that *U* is an energy of attraction.

(b) When the ions are not in a vacuum, the **permittivity** of the medium is expressed as

$$\varepsilon = \varepsilon_0\ \varepsilon_r$$

where ε_r is the **relative permittivity**. The energy is therefore reduced by a factor equal to ε_r . For water $\varepsilon_r = 78$ so that the interaction is 78 times less.

$$U = -2.3 \times 10^{-19}\ \text{J} / 78 = 3.0 \times 10^{-21}\ \text{J}$$

(c) By the same argument as (b), if $\varepsilon_r = 2$ so that the interaction is halved.

$$U = -2.3 \times 10^{-19}\ \text{J} / 2 = 1.2 \times 10^{-19}\ \text{J}$$

17. Show that for a molecule following the Lennard-Jones potential, the equilibrium separation, r_o, is given by $r_o = 2^{\frac{1}{6}}\ \sigma$.

Strategy

You can use equation 17.19 to express the energy of interaction for the Lennard-Jones potential. At the equilibrium separation, the energy reaches a minimum so that differentiating the expression with respect to distance allows r_o to be found in terms of σ.

Solution

The Lennard-Jones potential gives the energy, U, as

$$U = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

At the equilibrium separation, $r = r_o$ and $\frac{dU}{dr} = 0$.

Writing the potential differently, $U = 4\varepsilon\{(\sigma^{12} r_o{}^{-12}) - (\sigma^6 r_o{}^{-6})\}$

Differentiating,

$$dU/dr = 0 = 4\varepsilon\, dU/d\{(\sigma^{12} r_o{}^{-12}) - (\sigma^6 r_o{}^{-6})\}$$

$$= 4\varepsilon\{(-12\,\sigma^{12} r_o{}^{-13}) - (-6\,\sigma^6 r_o{}^{-7})\}$$

Since $4\varepsilon \neq 0$ then

$$0 = \{(-12\,\sigma^{12} r_o{}^{-13}) - (-6\,\sigma^6 r_o{}^{-7})\}$$

Dividing by $6\,\sigma^6 r^{-7}$

$$0 = \{(-2\,\sigma^6 r_o{}^{-6}) + (1)\}$$

$$1 = 2\,\sigma^6 r_o{}^{-6}$$

Multiply both sides by $r_o{}^6$

$$r_o{}^6 = 2\,\sigma^6$$

Taking the sixth-roots

$$r_o = 2^{1/6}\,\sigma$$

18. For each of the following pairs, which compound would you expect to have the higher enthalpy change of vaporization? Give the reason for your answer in each case.

(a) ethanol and methoxymethane

(b) propane and methoxymethane

(c) butane and propanone

(d) *E*-1,2-dichloroethene and *Z*-1,2-dichloroethene

Strategy

Consider the types of intermolecular interaction. Stronger interactions such as those arising from hydrogen bonding or between polar molecules will lead to higher values of enthalpy of vaporization.

Solution

(a) Ethanol can form hydrogen bonds whereas methoxymethane cannot. Hence ethanol would have the higher enthalpy change of vaporization.

(b) The two compounds are similar in size and so similar dispersion interactions would be expected. Methoxymethane is polar and has a dipole moment whereas propane is non polar. Methoxymethane would have the higher enthalpy change of vaporization.

(c) Butane is non-polar and has only dispersion interactions. Propanone has a similar size and so similar dispersion interactions might be expected. However, the carbonyl bond is polar and so propanone also has polar interactions. Propanone would thus have the higher enthalpy change of vaporization.

(d) *E*-1,2-dichloroethene is polar and so has dipole interactions. *Z*-1,2-dichloroethene has no overall dipole since the two individual dipoles cancel out. Hence *E*-1,2-dichloroethene would have the higher enthalpy change of vaporization.

19. Arrange the following in order of increasing boiling point, giving detailed reasons for your answer.

He, H_2O, Ar, N_2, HCl, NaCl

Strategy

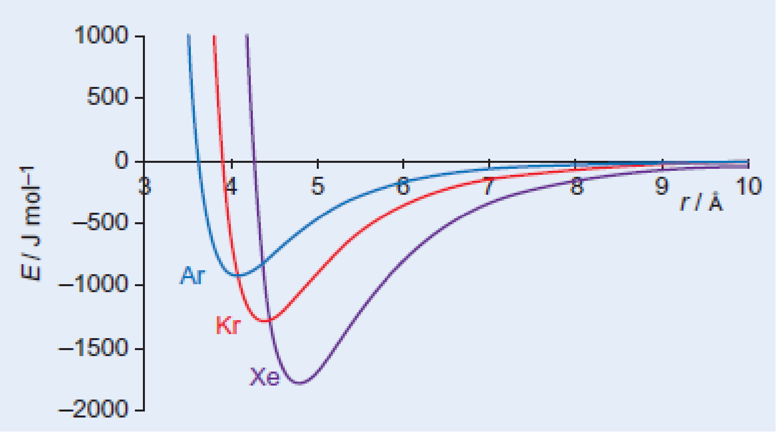
The boiling point depends on the strength of intermolecular interactions so you need to consider what interactions occur in each atom/molecule and their relative strengths

Solution

He, Ar, N_2, HCl, H_2O, NaCl

He and Ar are both inert gases but Ar is bigger and hence more polaizable so has stronger van der Waals interactions. N_2 is non polar; HCl has a dipole contribution to the van der Waals interactions. Water can hydrogen bond; NaCl is ionic and so has strong ionic interactions.

20. The sketch shows the Lennard-Jones potential for three inert gases. Explain the variation in the three curves.



Strategy

You need to consider which physical properties give rise to the curves and relate these to the three species involved.

Solution

Xe is the biggest of the three atoms and so the minimum in the curve occurs at the highest distance; the repulsive part of the curve also is the highest distance. Xe is also the heaviest atom and has the highest polarizability and so has the strongest intermolecular interactions by van der Waals interactions. Hence, the minimum in the curve occurs at more negative potential energies. Ar is the smallest/lightest and so the values occur at the smallest distances and least negative energies.

21. A diver descends to a depth where the pressure is 5 atm. The diver's body contains around 5 dm^3 of blood. The Henry's law constant for N_2 (g) in water at 310 K is 1.07×10^5 bar.

(a) Calculate the amount of nitrogen gas absorbed from the air in the diver's blood at a pressure of 1 atm and at 5 atm. (Assume that the solubility of nitrogen in the blood is the same as in water at 298 K.)

(b) If all the gas dissolved at 5 atm was suddenly released, what volume would it occupy at 1 atm and 298 K?

Strategy

(a) Use Henry's law, Equation 17.27, remembering to convert the pressures quoted from units of atm to bar for consistency with the units of the Henry's law constant. (b) Determine the amount of gas released and use the ideal gas law, Equation 8.5, to determine the volume.

Solution

(a) Assuming that air is made up of 78% N_2, then the partial pressure of N_2 for a total pressure of p = 1 atm is

$$p_{\mathrm{N_2}} = 0.78 \times p = 0.78 \times (1\ \mathrm{atm}) = 0.78 \times (1.01325\ \mathrm{bar}) = 0.79\ \mathrm{bar}$$

then, rearranging Equation 17.27, the mole fraction of N_2 in the diver's blood is

$$x_{\mathrm{N_2}} = p_{\mathrm{N_2}}/K_{\mathrm{N_2}} = (0.79\ \mathrm{bar})/(1.07 \times 10^5\ \mathrm{bar}) = 7.4 \times 10^{-6} = 7.4\ \mathrm{ppm}$$

In the same way, for a pressure of 5 atm, because the mole fraction scales linearly with the total pressure, then

$$x_{\mathrm{N_2}} = 5 \times 7.4 \times 10^{-6} = 37 \times 10^{-6} = 37\ \mathrm{ppm}$$

(b) It is not unreasonable to assume that blood is made up principally with all other components making only a small contribution to the total number of molecules. Thus,

$$n_{\mathrm{total}} \approx n_{\mathrm{H_2O}}$$

The molar mass of water is

$$M = [16.00 + (2 \times 1.01)]\ \mathrm{g\ mol^{-1}} = 18.02\ \mathrm{g\ mol^{-1}}$$

The density of water is 1.00×10^3 g dm^{-3}, so that a volume of 1 dm^3 contains an amount

$$n_{\mathrm{H_2O}} = \rho/M = (1.00 \times 10^3\ \mathrm{g\ dm^{-3}})/(18.02\ \mathrm{g\ mol^{-1}}) = 55.5\ \mathrm{mol}$$

The amount of N_2 is thus

$$n_{\mathrm{N_2}} = x_{\mathrm{N_2}} n_{\mathrm{total}} \approx x_{\mathrm{N_2}} n_{\mathrm{H_2O}}$$

which at 1 atm equates to

$$n_{\mathrm{N_2}} = 7.4 \times 10^{-6} \times (55.5\ \mathrm{mol}) = 4.1 \times 10^{-4}\ \mathrm{mol}$$

Then, applying the ideal gas law, Equation 8.5,

$$\begin{aligned} V &= n_{\mathrm{N_2}}RT/p \\ &= \frac{(4.1 \times 10^{-4}\ \mathrm{mol}) \times (8.3145\ \mathrm{J\ K^{-1} mol^{-1}}) \times (310\ \mathrm{K})}{5 \times (1.01325 \times 10^5\ \mathrm{Pa})} \\ &= 5.2 \times 10^{-5} \mathrm{m^3} = 52\ \mathrm{cm^3} \end{aligned}$$

22. The vapour pressure of pure $CHCl_3$ at 318 K is 58 kPa. What would be the partial vapour pressure of $CHCl_3$ above a mixture of 1 mol of $CHCl_3$ with 1 mol of ethanol, assuming the mixture behaves as an ideal solution? Comment on the fact that the measured value of the partial vapour pressure of $CHCl_3$ above the mixture is 42 kPa.

Strategy

Deduce the mole fraction of dichloromethane, $CHCl_3$, and use Raoult's law, Equation 17.23, along with the vapour pressures of the pure liquid to determine the total pressure.

Solution

The mixture is equimolar, so that

$$x_{\mathrm{C_2H_5OH}} = x_{\mathrm{CHCl_3}} = 0.5$$

Then, using Equation 17.23,

$$p_{\mathrm{CHCl_3}} = x_{\mathrm{CHCl_3}} p^{\mathrm{o}}_{\mathrm{CHCl_3}} = 0.5 \times (58\ \mathrm{kPa}) = 29\ \mathrm{kPa}$$

The real vapour pressure, 42 kPa, is greater than the ideal value. This system therefore shows positive deviations from Raoult's law. Each component disrupts the polar interactions in the pure components so that interactions between dichloromethane and ethanol in the mixture are weaker than those in the pure components.

23. Ethanol and methanol form nearly ideal solutions. At 20°C, the vapour pressure of pure ethanol is 5930 Pa and of methanol is 11830 Pa. Calculate (a) the vapour pressure of each compound and (b) the total vapour pressure over a solution formed by mixing 50 g of each. (M_r (CH_3OH) = 32.04; M_r (C_2H_5OH) = 46.07)

Strategy

Determine the mole fractions of the two components using the molar masses of the two components. Use Raoult's law, Equation 17.23, to calculate the partial pressures of the individual components and Equation 17.24 to determine the total vapour pressure.

Solution

The molar mass of methanol, CH_3OH, is

$$M_{\mathrm{CH_3OH}} = [12.01 + (4 \times 1.01) + 16.00]\ \mathrm{g\ mol^{-1}} = 32.05\ \mathrm{g\ mol^{-1}}$$

so that the amount of methanol is

$$n_{\mathrm{CH_3OH}} = m_{\mathrm{CH_3OH}}/M_{\mathrm{CH_3OH}} = (50\ \mathrm{g})/(32.05\ \mathrm{g\ mol^{-1}}) = 1.56\ \mathrm{mol}$$

In the same way for ethanol,

$$M_{\mathrm{C_2H_5OH}} = [(2 \times 12.01) + (6 \times 1.01) + 16.00]\ \mathrm{g\ mol^{-1}} = 46.08\ \mathrm{g\ mol^{-1}}$$

so that the amount of ethanol is

$$n_{\mathrm{C_2H_5OH}} = m_{\mathrm{C_2H_5OH}}/M_{\mathrm{C_2H_5OH}} = (50\ \mathrm{g})/(46.08\ \mathrm{g\ mol^{-1}}) = 1.08\ \mathrm{mol}$$

The mole fraction of methanol is thus

$$x_{\mathrm{CH_3OH}} = \frac{n_{\mathrm{CH_3OH}}}{n_{\mathrm{CH_3OH}} + n_{\mathrm{C_2H_5OH}}} = \frac{1.56\ \mathrm{mol}}{1.56\ \mathrm{mol} + 1.08\ \mathrm{mol}} = 0.59$$

and ethanol is

$$x_{\mathrm{C_2H_5OH}} = 1 - x_{\mathrm{CH_3OH}} = 0.41$$

Assuming ideal behaviour, then from Raoult's law, Equation 17.23, the partial pressure of methanol above the mixture must be

$$p_{\mathrm{CH_3OH}} = x_{\mathrm{CH_3OH}} p^{\mathrm{o}}_{\mathrm{CH_3OH}} = 0.59 \times (11830\ \mathrm{Pa}) = 6980\ \mathrm{Pa}$$

and ethanol

$$p_{\mathrm{C_2H_5OH}} = x_{\mathrm{C_2H_5OH}} p^{\mathrm{o}}_{\mathrm{C_2H_5OH}} = 0.41 \times (5930\ \mathrm{Pa}) = 2430\ \mathrm{Pa}$$

(b) The total vapour pressure is the sum of the two components (Dalton's law) assuming ideal gas behaviour, Equation 17.24, so that

$$p_{\mathrm{total}} = p_{\mathrm{CH_3OH}} + p_{\mathrm{C_2H_5OH}} = 6980\ \mathrm{Pa} + 2430\ \mathrm{Pa} = 9410\ \mathrm{Pa}$$

24. In a solution of ethanol ($p°$ = 0.174 bar) and 2-methylhexane ($p°$ = 0.059 bar), the mole fraction of ethanol, x_{ethanol}, is 0.90. The vapour in equilibrium with the solution has a total vapour pressure of 0.248 bar. The mole fraction of ethanol in the vapour is 0.67. Calculate the activity coefficients of each component in the solution.

Strategy

Use Dalton's law to determine the partial pressure of ethanol, and hence 2-methylhexane, in the vapour. Then use Equation 17.25 to determine the activity coefficient for the two components.

Solution

The mole fraction of ethanol in the vapour phase is

$$y_{\mathrm{E}} = 0.67$$

and therefore of 2-methylhexane is

$$y_{\mathrm{M}} = 1 - y_{\mathrm{E}} = 1 - 0.67 = 0.33$$

The partial pressures of the two components are thus

$$p_{\mathrm{E}} = x_{\mathrm{E}} p_{\mathrm{total}} = 0.67 \times (0.248\ \mathrm{bar}) = 0.166\ \mathrm{bar}$$

and

$$p_{\mathrm{M}} = x_{M} p_{\mathrm{total}} = 0.33 \times (0.248\ \mathrm{bar}) = 0.082\ \mathrm{bar}$$

The mole fraction of ethanol in the liquid phase is

$$x_{\mathrm{E}} = 0.90$$

and therefore of 2-methylhexane is

$$x_{\mathrm{M}} = 1 - x_{\mathrm{E}} = 1 - 0.90 = 0.10$$

Then, from the definition of activity coefficients, Equation 17.25,

$$\gamma_E = p_E/x_E p_E^o = (0.166\ \text{bar})/\{0.90 \times (0.174\ \text{bar})\} = 1.06$$
$$\gamma_M = p_E/x_M p_M^o = 0.082\ \text{bar}/\{0.10 \times (0.059\ \text{bar})\} = 13.9$$

25. A protein has a molar mass of 69 000 g mol^{-1}. Assuming ideal behaviour, calculate the osmotic pressure of a solution containing 20 g dm^{-3} of the protein at 298 K.

Strategy

Calculate the molar concentration from Equation 1.6 and use Equation 17.28 to determine the osmotic pressure.

Solution

The concentration of the protein is, from Equation 1.6,

$$c = (20\ \text{g dm}^{-3})/(69000\ \text{g mol}^{-1}) = 29 \times 10^{-3}\text{mol dm}^{-3} = 0.29\ \text{mol m}^{-3}$$

Then, from Equation 17.28,

$$\begin{aligned}\pi &= cRT\\ &= (0.29\ \text{mol m}^{-3}) \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})\\ &= 720\ \text{J m}^{-3} = 720\ \text{Pa}\end{aligned}$$

26. The figure shows a sketch of the vapour-liquid phase diagram for mixtures of butanone and dichloromethane. For a solution with composition, $x_{\text{butanone}} = 0.4$ and $x_{\text{dichloromethane}} = 0.6$:

(a) estimate the boiling temperature of this mixture.

(b) estimate the composition of the vapour that boils from it.

(c) if this vapour was condensed, what would be the boiling temperature of the resulting liquid?

(d) if the boiling and condensing cycles continued, what would be the composition of (i) the distillate and (ii) the residue.

Strategy

(a) Draw a vertical line on the phase diagram at the appropriate composition and determine the point at which it intersects the liquid composition line, which is marked in red. (b) Draw a horizontal tie line and deduce the compositon of the vapour from the blue line. (c) Determine the temperature at which a liquid with this composition would boil from the liquid composition line in red. (d) Repeat the method until the mixture has been separated.

Solution

(a) The boiling temperature can be read from the liquid line, which is shown in red on the graph, as 332 K.

(b) Drawing a horizontal line at this temperature across to the vapour line, which is shown in blue, gives $x_{\text{dichloromethane}} \approx 0.82$.

(c) The boiling temperature of a liquid with this composition may be determined from the value of the red liquid composition line as 326 K.

(d) If the process is repeated, then the more volatile dicholormethane is collected as the distillate and the less volatile butanone as the residue.

27. A solution of iodoethane, I, and propanone, P, with a mole fraction of I, $x_I = 0.55$ had a partial vapour pressure of I of 28.44 kPa and a partial vapour pressure of P of 19.21 kPa at 50 °C. At this temperature, the saturated vapour pressures of I is 47.12 kPa and of P is 37.38 kPa. Calculate the activity coefficients of both components in the solution.

Strategy

Rearrange Equation 17.25, which defines the vapour pressure of a real component in terms of the mole fraction in the liquid, the vapour pressure when pure and the activity coefficient.

Solution

From Equation 17.25,

$$p_E(\text{real}) = \gamma_E x_E p_E$$

then

$$\gamma_I = p_I(\text{real})/x_I p_I = 28.44\ \text{kPa}/(0.55 \times 47.12\ \text{kPa}) = 1.10$$

$$\gamma_P = p_P(\text{real})/x_P p_P = 19.21\ \text{kPa}/(0.45 \times 37.38\ \text{kPa}) = 1.14$$

28 When a patient suffers severe dehydration, why will medical treatment involve giving 'saline' solution rather than pure water? (Section 17.4)

Strategy

Consider the effect of injecting pure water into the blood stream on the cells in blood.

Solution

If pure water is injected, it will dilute the plasma so that the concentration gradient across the cell wall is increased. There is a risk that osmosis will drive water into the cell and cause damage. The saline is designed to keep the concentrations more or less equal.

29 Use the Phase Rule to calculate the number of degrees of freedom at the triple point of water. Comment on your answer. (Section 17.4)

Strategy

Use the phase rule, equation 17.20 and consider the number of phases that are present at the triple point.

Solution

From the phase rule

$F = C - P + 2$

For a single component, $C = 1$. At the triple point, solid, liquid and gas are in equilibrium so $P = 3$. Hence,

$F = 1 - 3 + 2 = 0$

There are no degrees of freedom. Hence, pressure and temperature are fixed and there is a unique single set of conditions at the triple point.

30. The vapour pressure over a mixture of 2 mol of hexane and 1 mol of octane is 9.6 kPa at 40 °C. An equimolar solution has a vapour pressure of 8.2 kPa at the same temperature. What are the vapour pressures of the two pure liquids?

Strategy

Hexane and Octane can be assumed to form an ideal solution so the pressures of the two vapours, which can be calculated from Raoult's Law can be added together.

Solution

From Raoult's Law, $p_{A,} = x_A\, p°_A$.

The first solution has a mole fraction of hexane of ⅔ and $x_{octane} = ⅓$. Hence

$9.6\text{ kPa} = ⅔\, p_{hexane} + ⅓\, p_{octane}$ or $28.8\text{ kPa} = 2 \times p_{hexane} + p_{octane}$

Also, for the second solution

$8.2\text{ kPa} = ½\, p_{hexane} + ½\, p_{octane}$ or $16.4\text{ kPa} = p_{hexane} + p_{octane}$

Solving the simultaneous equations

$p_{hexane} = 12.4\text{ kPa}$ and $p_{octane} = 4.0\text{ kPa}$

31. The vapour pressure of pure toluene is 0.0285 bar at 20 °C and that of benzene is 0.0974 bar. One mole of each compound were mixed and formed an ideal solution. Calculate the mole fraction of each compound in the vapour over the solution.

Strategy

Since the compounds form an ideal solution, the pressures can be calculated from Raoult's Law.

Solution

Using Raoult's Law, the vapour pressure of each compound in the vapour can be calculated.

$p_{benzene} = 0.5 \times 0.0974\text{ bar} = 0.0487\text{ bar}$.

$p_{toluene} = 0.5 \times 0.0285\text{ bar} = 0.0143\text{ bar}$.

Assuming the mixture forms an ideal vapour, $y_{\text{benzene}} = \dfrac{p_{\text{benzene}}}{p_{\text{benzene}} + p_{\text{toluene}}}$

$$\frac{p_{\text{benzene}}}{p_{\text{benzene}} + p_{\text{toluene}}} = \frac{0.0487\ \text{bar}}{0.0487\ \text{bar} + 0.0143\ \text{bar}} = 0.77$$

$y_{\text{toluene}} = 1 - 0.77 = 0.23$

32. The transport of water up a tree occurs partially through osmosis; the concentration of sugar in the tree sap is higher than the water around the tree roots. The sap in a certain species of tree can be represented as a 3 % (m/v) solution of sucrose in water. Find the osmotic pressure generated by this solution.

Strategy

You can assume ideal osmotic behaviour and use equation 17.29 to find the pressure having converted the concentration of the solution to molar units.

Solution

A 3 % (m/v) solution has 3 g of sucrose in 100 cm^3 of solution. Hence the concentration is 3 g / 342.3 g mol^{-1} = 8.8×10^{-3} mol(100 cm^3)$^{-1}$ = 8.8×10^{-2} mol dm^{-3}

Assuming ideal behaviour,

$$\pi = c\,R\,T = 8.8 \times 10^{-2}\ \text{mol dm}^{-3} \times (1000\ \text{dm}^3\ \text{m}^{-3}) \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}$$

$$\pi = 2.18 \times 10^5\ \text{Pa} = 2.18\ \text{bar}$$