Chapter 4 – New Exercises and Solutions

E4.1(c) The vapour pressure of a substance at 50.0°C is 43.0 kPa and its enthalpy of vaporization is 42.2 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 96.0 kPa.

E4.1(c) Assume vapour is a perfect gas and $\Delta_{\text{vap}}H$ is independent of temperature

$$\ln \frac{p^*}{p} = +\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

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

$$= \frac{1}{323.2\,\text{K}} + \frac{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}{42.2\times10^3\,\text{J mol}^{-1}}\times\ln\left(\frac{43.0}{96.0}\right)$$

$$= 2.936\times10^{-3}\,\text{K}^{-1}$$

$$T = \frac{1}{2.93\bar{6}\times10^{-3}\,\text{K}^{-1}} = 341\,\text{K} = \boxed{68^\circ\text{C}}$$

E4.2(c) The molar volume of a certain solid is 122.0 cm^3 mol^{-1} at 1.00 atm and 483.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 142.6 cm^3 mol^{-1}. At 1.29 MPa the melting temperature changes to 485.34 K. Calculate the enthalpy and entropy of fusion of the solid.

E4.2(c)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_{\text{m}}}{\Delta V_{\text{m}}}$$

$$\Delta_{\text{fus}}S = \Delta V_{\text{m}}\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right) \approx \Delta V_{\text{m}}\frac{\Delta p}{\Delta T}$$

assuming $\Delta_{\text{fus}}S$ and ΔV_{m} independent of temperature.

$$\Delta_{\text{fus}}S = \left(142.6\,\text{cm}^3\,\text{mol}^{-1} - 122.0\,\text{cm}^3\,\text{mol}^{-1}\right)\times\frac{\left(1.26\times10^6\,\text{Pa}\right)-\left(1.01\times10^5\,\text{Pa}\right)}{485.34\,\text{K} - 483.15\,\text{K}}$$

$$= \left(20.6\,\text{cm}^3\,\text{mol}^{-1}\right)\times\left(\frac{1\,\text{m}^3}{10^6\,\text{cm}^3}\right)\times\left(5.29\times10^5\,\text{Pa K}^{-1}\right)$$

$$= 10.90\,\text{Pa m}^3\,\text{K}^{-1}\,\text{mol}^{-1} = \boxed{10.9\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

$$\Delta_{\text{fus}}H = T_{\text{f}}\Delta S = \left(483.15\,\text{K}\right)\times\left(10.9\bar{0}\,\text{J K}^{-1}\,\text{mol}^{-1}\right)$$

$$= \boxed{5.27\,\text{kJ mol}^{-1}}$$

E4.3(c) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression ln(*p*/Torr) = 20.465 – 3339.8/(*T*/K). Calculate the enthalpy of vaporization of the liquid.

E4.3(c) The expression for $\ln p$ is the indefinite integral of eqn 4.11

$$\int d\ln p = \int \frac{\Delta_{vap}H}{RT^2}dT; \quad \ln p = \text{constant} - \frac{\Delta_{vap}H}{RT}$$

Therefore, $\Delta_{vap}H = (3339.8\,\text{K}) \times R = (3339.8\,\text{K}) \times (8.314\,\text{J}\,K^{-1}\,\text{mol}^{-1}) = \boxed{+29.77\,\text{kJ}\,\text{mol}^{-1}}$

E4.4(c) The vapour pressure of hexane between -10°C and +90°C fits the expression log(p/Torr) = 7.724 – 1655/(T/K). Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of hexane.

E4.4(c) (a) The indefinitely integrated form of eqn 4.11 is used as in Exercise 4.3(a).

$$\ln p = \text{constant} - \frac{\Delta_{vap}H}{RT}, \quad \text{or} \quad \log p = \text{constant} - \frac{\Delta_{vap}H}{2.303\,RT}$$

Therefore,

$$\Delta_{vap}H = (2.303) \times (1655\,\text{K}) \times R = (2.303) \times (1655\,\text{K}) \times (8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})$$

$$= \boxed{+31.69\,\text{kJ}\,\text{mol}^{-1}}$$

(b) The boiling point corresponds to $p = 1.000\,\text{atm} = 760\,\text{Torr}$.

$$\log 760 = 7.724 - \frac{1655\,\text{K}}{T_b}$$

$$T_b = \boxed{341.7\,\text{K}}$$

E4.5(c) When water freezes at 0.00°C its density changes from 1.000 g cm^{-3} to 0.917 g cm^{-3}. Its enthalpy of fusion is 6.01 kJ mol^{-1}. Estimate the freezing point of water at 1000 atm.

E4.5(c)

$$\Delta T \approx \frac{\Delta_{fus}V}{\Delta_{fus}S} \times \Delta p \text{ [4.6, and Exercise 4.2(a)]}$$

$$\approx \frac{T_f \Delta_{fus}V}{\Delta_{fus}H} \times \Delta p = \frac{T_{f\Delta pM}}{\Delta_{fus}H} \times \Delta\left(\frac{1}{\rho}\right) \quad [V_m = M/\rho]$$

$$\approx \left(\frac{(273.2\text{ K}) \times (999) \times (1.013 \times 10^5\text{ Pa}) \times (18.02 \times 10^{-3}\text{ kg mol}^{-1})}{6.01 \times 10^3\text{ J mol}^{-1}}\right)$$

$$\times \left(\frac{1}{1000\text{ kg m}^{-3}} - \frac{1}{917\text{ kg m}^{-3}}\right) \approx -10.14\text{ K}$$

Therefore, at $1000\,\text{atm}$, $T_f \approx (273.2 - 10.1)\text{ K} = \boxed{263.1\text{ K}}$ [-10.1 °C]

E4.6(c) In the Sahara Desert the incident sunlight at ground level has a power density of 1.44 kW m^{-2} in July at noon. What is the maximum rate of loss of water from a pond in an oasis of area 12 m^2. Assume that all the radiant energy is absorbed.

E4.6(c) $\frac{dm}{dt} = \frac{dn}{dt} \times M_{H_2O}$ where $n = \frac{q}{\Delta_{vap}H}$

$$\frac{dn}{dt} = \frac{dq/dt}{\Delta_{vap}H} = \frac{(1.44\times10^3\ \text{W m}^{-2})\times(10^4\ \text{m}^2)}{44.0\times10^3\ \text{J mol}^{-1}}$$

$$= 327\ \text{J s}^{-1}\ \text{J}^{-1}\ \text{mol}$$

$$= 327\ \text{mol s}^{-1}$$

$$\frac{dm}{dt} = (327\ \text{mol s}^{-1})\times(18.02\ \text{g mol}^{-1})$$

$$= \boxed{5.90\ \text{kg s}^{-1}}$$

E4.8(c) The normal boiling point of heptane is 98.4°C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 37°C and 84°C.

E4.8(c) **(a)** According to Trouton's rule (Section 3.3(b), eqn 3.16)

$$\Delta_{vap}H = (85\ \text{J K}^{-1}\ \text{mol}^{-1})\times T_b = (85\ \text{J K}^{-1}\ \text{mol}^{-1})\times(371.6\ \text{K}) = \boxed{31.\bar{6}\ \text{kJ mol}^{-1}}$$

(b) Use the Clausius–Clapeyron equation [Exercise 4.8(a)]

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

At $T_2 = 371.6\ \text{K}$, $p_2 = 1.000$ atm; thus at 37°C

$$\ln p_1 = -\left(\frac{31.\bar{6}\times10^3\ \text{J mol}^{-1}}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1}}\right)\times\left(\frac{1}{310.2\ \text{K}}-\frac{1}{371.6\ \text{K}}\right) = -2.02\overline{45}$$

$$p_1 = \boxed{0.13\bar{2}\ \text{atm}} = 10\bar{0}\ \text{Torr}$$

At 60°C,

$$\ln p_1 = -\left(\frac{31.\bar{6}\times10^3\ \text{J mol}^{-1}}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1}}\right)\times\left(\frac{1}{357.2\ \text{K}}-\frac{1}{371.6\ \text{K}}\right) = -0.41\overline{23}$$

$$p_1 = \boxed{0.66\bar{2}\ \text{atm}} = 50\bar{3}\ \text{Torr}$$

E4.9(c) Calculate the melting point of ice under a pressure of 500 bar. Assume that the density of ice under these conditions is approximately 0.925 g cm^{-3} and that of liquid water is 1.024 g cm^{-3}.

E4.9(c) $\Delta T = T_f(500\ \text{bar}) - T_f(1\ \text{bar}) \approx \frac{T_f \Delta p M}{\Delta_{fus}H}\Delta\left(\frac{1}{\rho}\right)$[Exercise 4.5(a)]

$\Delta_{fus}H = 6.01\ \text{kJ mol}^{-1}$[Table 2.3]

$$\Delta T = \left(\frac{(273.15\,\text{K})\times(499\times10^{5}\ \text{Pa})\times(18.02\times10^{-3}\ \text{kg mol}^{-1})}{6.01\times10^{3}\ \text{J mol}^{-1}}\right)$$

$$\times\left(\frac{1}{1.024\times10^{3}\ \text{kg m}^{-3}}-\frac{1}{9.25\times10^{2}\ \text{kg m}^{3}}\right) = -4.27\ \text{K}$$

T_f (50 bar) = (273.15 K) - (4.27 K) = $\boxed{268.88\ \text{K}}$

E4.10(c) What fraction of the enthalpy of vaporization of benzene is spent on expanding its vapour?

E4.10(c) $\Delta_{\text{vap}}H = \Delta_{\text{vap}}U + \Delta_{\text{vap}}(pV)$

$$\Delta_{\text{vap}}H = 82.93\,\text{kJ mol}^{-1}$$

$$\Delta_{\text{vap}}(pV) = p\Delta_{\text{vap}}V = p(V_{\text{gas}} - V_{\text{liq}}) = pV_{\text{gas}} = RT\,[\text{per mole, perfect gas}]$$

$$\Delta_{\text{vap}}(pV) = (8.314\,\text{J K}^{-1}\,\text{mol}^{-1})\times(353.2\,\text{K}) = 293\bar{6}\,\text{J mol}^{-1}$$

$$\text{Fraction} = \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}}H} = \frac{2.93\bar{6}\,\text{kJ mol}^{-1}}{82.93\,\text{kJ mol}^{-1}}$$

$$= \boxed{3.54\times10^{-2}} = 3.54\,\text{per cent}$$