Solutions 6

1. The volume of the laboratory is

$V = 5.0\times5.0\times3.0 = 75.0\ \text{m}^3$

a) water: p = 24 Torr

$n = pV/RT$ = (24 Torr) × (75.0×10^3 L) / {(62.364 L Torr K^{-1} mol^{-1}) × (298.15 K)} = 96.855 mol

$m = nM$ = (96.855 mol) × (18.02 g mol^{-1}) = 1745.3 g = 1.7453 kg

b) benzene: p = 98 Torr

$n = pV/RT$ = (98 Torr) × (75.0×10^3 L) / {(62.364 L Torr K^{-1} mol^{-1}) × (298.15 K)} = 395.49 mol

$m = nM$ = (395.49 mol) × (78.11 g mol^{-1}) = 30890.8 g = 30.89 kg

c) mercury: $p = 1.7\times10^{-3}$ Torr

$n = pV/RT$ = (1.7×10^{-3}) × (75.0×10^3 L) / {(62.364 L Torr K^{-1} mol^{-1}) × (298.15 K)} = 0.00686 mol

$m = nM$ = (0.00686 mol) × (200.59 g mol^{-1}) = 1.376 g

2. a) p_1 = 10 Torr, T_1 = 358.95 K and p_2 = 40 Torr, T_2 = 392.45 K

Use the Clausius-Clapeyron equation to calculate $\Delta_{vap}H$:

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

$\Delta_{vap}H$ = (8.3145 J K^{-1} mol^{-1}) × ln(40/10) / {1/(358.95 K) – 1/(392.45 K)} = 48.469 kJ mol^{-1}

b) p_3 = 760 Torr T_3 - ?

$$\ln\frac{p_3}{p_1} = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right) \qquad T_3 = 1\Big/\left(1/T_1 - \frac{R\ln(p_3/p_1)}{\Delta_{vap}H}\right)$$

T_3 = 1/{1/(358.95 K) - (8.3145 J K^{-1} mol^{-1}) × ln(760/10) / (48.469×10^3 J mol^{-1})} = 489.47 K = 216.32°C

c) $\Delta_{vap}S = \Delta_{vap}H/T_b$ = (48.469×10^3 J mol^{-1})/(489.47 K) = 99.0 J K^{-1} mol^{-1}

3. $\Delta_{fus}H$ = 2.292 kJ mol^{-1}, T^* = 234.3 K, $\Delta_{fus}V$ = +0.517 cm^3 mol^{-1}, p^* = 101.325 kPa.

The additional pressure on the bottom of mercury column:

$\Delta p = p - p^* = \rho gh$ = (13.6×10^3 kg m^3) × (9.81 m s^{-2}) × (10 m) = 1334160 Pa

$$p = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V}\ln\frac{T}{T^*} \qquad \ln\frac{T}{T^*} = \frac{(p - p^*)\Delta_{fus}V}{\Delta_{fus}H}$$

$\ln(T/T^*) = (1334160\text{ Pa}) \times (0.517\times10^{-6}\text{ m}^3\text{ mol}^{-1}) / (2.292\times10^3\text{ J mol}^{-1}) = 3.0\times10^{-4}$

$T = (234.3\text{ K}) \times \exp(3.0\times10^{-4}) = 234.37\text{ K}$

4. We assume that a liter of seawater contains roughly 1000 g of water. Then

$n_{\text{water}} = 1000\text{ g} / 18.02\text{ g mol}^{-1} = 55.5\text{ mol}$

$n_{\text{solutes}} = 2\times0.50\text{ mol} = 1.00\text{ mol}$

$x_{\text{water}} = n_{\text{water}} / (n_{\text{water}} + n_{\text{solutes}}) = 55.5/56.5 = 0.982$

$p_{\text{water}} = x_{\text{water}}\times p_{\text{water}}^* = 0.982\times2.338\text{ kPa} = 2.296\text{ kPa}$

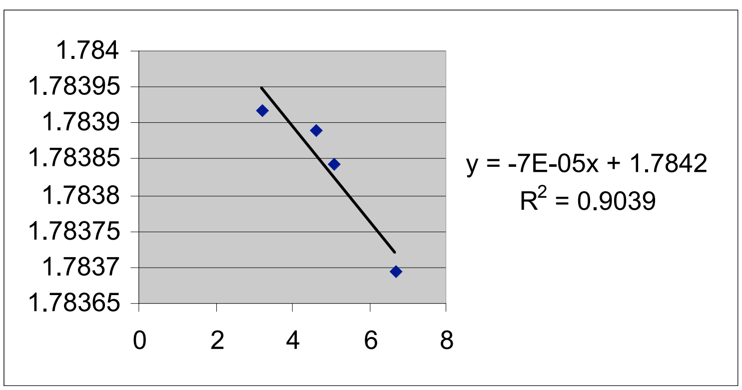
5. Check whether p_B/x_B is equal (at least, approximately) to a constant (K_B)

x	0.005	0.012	0.019
p/x	6.4×10^3	6.408×10^3	6.410×10^3

Hence, $K_B \cong 6.4\times10^3$ kPa

6. We plot h/c against c:

c	3.221	4.618	5.112	6.722
h	5.746	8.238	9.119	11.99
h/c	1.783918	1.783889	1.783842	1.783695



The intercept is $1.7842\times10^{-2}\text{ m}^4\text{ kg}^{-1}$

Intercept = $RT/\rho gM$ $\qquad$ $M = RT/(\rho g\times\text{Intercept})$

$M = (8.31451\text{ J K}^{-1}\text{ mol}^{-1} \times 293.15\text{ K}) / (1000\text{ kg m}^{-3} \times 9.807\text{ m s}^{-2} \times 1.7842\times10^{-2}\text{ m}^4\text{ kg}^{-1}) = 13.93\text{ kg mol}^{-1} = 13.93$ kDa

7. Ebullioscopic constant:

$$\Delta T = Kx_B \qquad K = \frac{RT^{*2}}{\Delta_{vap}H}$$

$$\Delta T = K_b b$$

$$x_B = \frac{n_B}{n_B + n_{CCl_4}} \approx \frac{n_B}{n_{CCl_4}} = \frac{n_B}{m_{CCl_4}} \frac{m_{CCl_4}}{n_{CCl_4}} = bM_{CCl_4}$$

Therefore, $$K_b = KM_{CCl_4} = \frac{RT^{*2}M_{CCl_4}}{\Delta_{vap}H}$$

K_b = (8.3145 J K^{-1} mol^{-1})×(349.9 K)^2×(153.81×10^{-3} kg mol^{-1})/(30.0×10^3 J mol^{-1}) = 5.22 K kg mol^{-1}

Cryoscopic constant: $$K_f = \frac{RT^{*2}M_{CCl_4}}{\Delta_{fus}H}$$

K_f = (8.3145 J K^{-1} mol^{-1})×(250.3 K)^2×(153.81×10^{-3} kg mol^{-1})/(2.47×10^3 J mol^{-1}) = 32.4 K kg mol^{-1}

8. According to Raoult's law,
$p_A = x_A p_A^*$ Therefore, we can calculate mole fraction of benzene:
$x_A = p_A / p_A^*$ = 386 Torr / 400 Torr = 0.965

$$x_A = \frac{n_A}{n_A + n_B} = \frac{m_A/M_A}{m_A/M_A + m_B/M_B} = \frac{m_A}{m_A + M_A m_B/M_B}$$

$$M_B = \frac{x_A M_A}{(1 - x_A)m_A} m_B$$

M_B = 0.965 × (78.11 g mol^{-1}) × (19 g) / {(1 – 0.965) × (500 g)} = 82 g mol^{-1}

9. $y(N_2)$ = 0.78 p = 760 Torr
According to Dalton's law, the partial pressure of N_2 is calculated as
$p(N_2)$ = 0.78×760 Torr = 592.8 Torr
Henry's law: $p(N_2) = K(N_2)x(N_2)$ $x(N_2) = p(N_2)/K(N_2)$
$x(N_2)$ = 592.8 Torr / 6.51×10^7 Torr = 9.1×10^{-6}
$b(N_2) = x(N_2)/M(H_2O)$ – see problem 4 for the relation between mole fraction and molality.
$b(N_2)$ = 9.1×10^{-6} / (18.02×10^{-3} kg mol^{-1}) = 5.05×10^{-4} mol kg^{-1} = 0.51 mmol kg^{-1}
$y(O_2)$ = 0.21 p = 760 Torr
$p(O_2)$ = 0.21×760 Torr = 159.6 Torr
$p(O_2) = K(O_2)x(O_2)$ $x(O_2) = p(O_2)/K(O_2)$
$x(O_2)$ = 159.6 Torr / 3.30×10^7 Torr = 4.8×10^{-6}
$b(O_2) = x(O_2)/M(H_2O)$.
$b(O_2)$ = 4.8×10^{-6} / (18.02×10^{-3} kg mol^{-1}) = 2.68×10^{-4} mol kg^{-1} = 0.27 mmol kg^{-1}

10. K_f(water) = 1.86 K kg mol^{-1}

In 250 cm^3 of water approximately 250 g: m(water) = 250 g

M(sucrose) = $M(C_{12}H_{22}O_{11})$ = 342.3 g mol^{-1}

n(sucrose) = m(sucrose)/M(sucrose) = 7.5 g / 342.3 g mol^{-1} = 0.0219 mol

b = n(sucrose) / m(water) = 0.0219 mol / 0.25 kg = 0.0876 mol kg^{-1}

$\Delta T = K_f b$ = (1.86 K kg mol^{-1}) × (0.0876 mol kg^{-1}) = 0.16 K

The freezing temperature decreases by 0.16 K or 0.16°C.