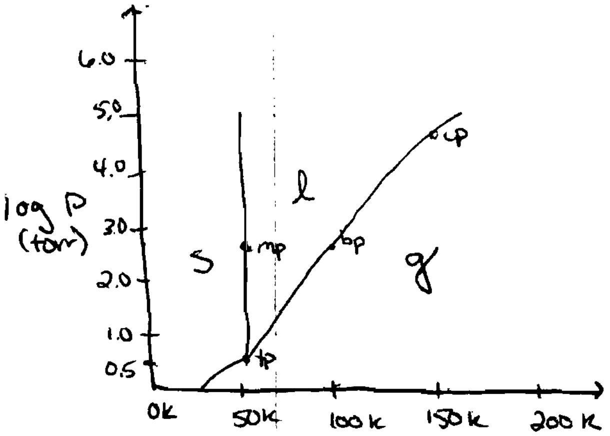
HWK 5 Key

Ch 23

1. Phase diagram for O_2

triple pt : 54.3 K + 1.14 torr ($\log p = 0.569$)
critical pt : 154.6 K + 37828 torr ($\log p = 4.58$)
normal mp : 54.75 K + 760 torr ($\log p = 2.88$)
normal bp : 90.25 K + 760 torr ($\log p = 2.88$)



No, oxygen doesn't melt w/ applied pressure. The solid-liquid coexistence curve has a positive slope (like benzene not water).

16. See Excel /Mathcad

22. $\frac{dP}{dT} = \frac{\Delta H_{vap}}{T \Delta \bar{V}_{vap}}$

need ① dP/dT
② T @ bp
③ $\Delta \bar{V}_{vap}$

② normal bp = 1atm or 760 torr)

$$\ln(760) = -\frac{7060.7}{T} + 17.85 \qquad T = 630.42\ K$$

① $$\boxed{\frac{dP}{dT} = P\frac{d\ln P}{dT}} = P\,\frac{d}{dT}\left(-\frac{7060.7}{T} + 17.85\right)$$
$$= P\left(\frac{7060.7}{T^2}\right) = 760\text{ torr}\left(\frac{7060.7\text{ K}}{630.42\text{ K}^2}\right) = 13.50\ \frac{\text{torr}}{\text{K}} \text{ or } 0.0178\ \frac{\text{atm}}{\text{K}}$$

③ $\bar{V}^l = \frac{1}{\rho^l}$ if ρ is $\frac{\text{mol}}{\text{L}}$ $\quad \rho^l = 12700\ \frac{g}{L} \cdot \frac{1\text{ mol Hg}}{200.59\text{ g Hg}} = 63.31\ \frac{\text{mol}}{\text{L}}$

$\bar{V}^l = 0.0158$ L/mol

$\bar{V}^g = \frac{1}{\rho^g}$ $\quad \rho^g = 3.82\ g/L \times \frac{1\text{ mol}}{200.59\text{ g}} = 0.0190\ \frac{\text{mol}}{\text{L}}$ $\quad \bar{V}^g = 52.51$ L/mol

$\Delta \bar{V}_{vap} = 52.49$ L/mol

$$\Delta H_{vap} = \left(\frac{dP}{dT}\right)(T)(\Delta \bar{V}_{vap})$$

$$= \left(0.0178\ \frac{\text{atm}}{\text{K}}\right)(630.42\text{ K})\left(52.49\ \frac{\text{L}}{\text{mol}}\right)$$

$$= 589.0\ \frac{\text{L}\cdot\text{atm}}{\text{mol}} \times \frac{101.3\text{ J}}{1\ \text{L}\cdot\text{atm}}$$

$$= 59667.\ \text{J/mol} = 59.67\ \text{kJ/mol}$$

27.

$$\ln\frac{P_2}{P_1} = -\frac{\Delta_{vap}\bar{H}}{R}\left(\overset{\frac{1}{T_2}-\frac{1}{T_1}}{\cancel{\frac{T_2-T_1}{T_1T_2}}}\right)$$ nbp of water =

$$\ln\frac{P_2}{1\text{ atm}} = -\frac{40650\ \frac{\text{J}}{\text{mol}}}{8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}}\left(\frac{1}{383\text{ K}} - \frac{1}{373\text{ K}}\right)$$

$$P_2 = e^{0.342} = 1.41\text{ atm} \quad \text{or} \quad 1070\text{ torr}$$

30.

$$\ln(P/\text{atm}) = -\frac{8090.0\text{ K}}{T} - 2.013\ln\left(\frac{T}{\text{K}}\right) + 32.908$$

normal sub T ⇒ 1atm

$$\ln 1 = -\frac{8090.0}{T} - 2.013\ln T + 32.908 = 0$$

Solve in mathcad (attached) $T = 386^{81}\text{ K}$

$$\frac{d\ln P}{dT} = \frac{\Delta_{sub}\bar{H}}{RT^2}$$

$$\frac{\partial \ln P}{dT} = \frac{8090.0\text{ K}}{T^2} - \frac{2.013}{T} = \frac{\Delta_{sub}\bar{H}}{RT^2}$$

$$\Delta_{sub}\bar{H} = 8090.0R - 2.013RT$$

$T = 298$ K
$R = 8.314$ J/mol·K

$$= \overset{62.28}{\cancel{60.8}}\ \text{kJ/mol}$$

Pg 3

#2 ch23

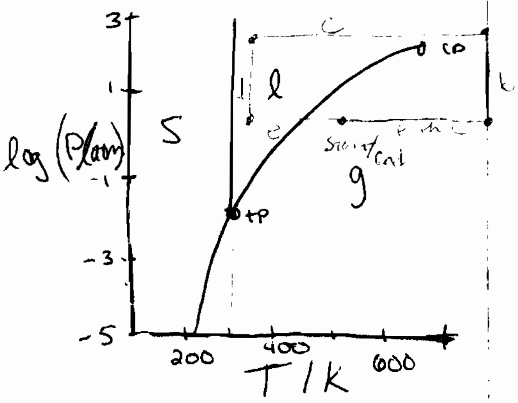


Fig 23.5(b)

1 atm ⇒ log (1) = 0
500 atm ⇒ log(500) = 2.699

a) at start - gas phase
at end - gas phase

b) now in supercritical phase

c) from supercritical phase to liquid phase

no vap. occur

d) stay in liquid phase but now at lower P

e) end at beginning, do see vaporization occur @ ~400 K

ch 24

McQuarrie + Simon - 29

$P_1 = 120 x_1 e^{0.20x_2^2 + 0.10x_2^3}$

$P_2 = 140 x_2 e^{0.35x_1^2 - 0.10x_1^3}$

Find P_1^*, P_2^*, $k_{H,1}$ + $k_{H,2}$ ...

Eq 24.25 … $P_1 \rightarrow x_1 P_1^*$ as $x_1 \rightarrow 1$ $(x_2 \rightarrow 0)$

so $P_1 \rightarrow 120x_1$ as $x_1 \rightarrow 1$ (b/c $e^0 = 1$)
so $P_1^* = 120$ torr

and $P_2 \rightarrow 140x_2$ as $x_2 \rightarrow 1$ (b/c $e^0 = 1$)
so $P_2^* = 140$ torr

Eq 24.26… $P_1 \rightarrow k_{H,1} x_1$ as $x_1 \rightarrow 0$

$P_1 = 120 x_1 e^{0.20(1)^2 + (0.10)^3}$ as $x_1 \rightarrow 0$

$= 120 \cdot e^{0.30} x_1 = 162 x_1$ as $x_1 \rightarrow 0$ ∴ $k_{H,1} = 162$ torr

$P_2 = 140 x_2 e^{0.35 - 0.10}$ as $x_2 \rightarrow 0$ ∴ $P_2 \rightarrow 180x_2$ as $x \rightarrow 0$ $k_{H,2} = 180$ torr

50. see Excel graph

$P_1 \rightarrow k_{H,1} x_1$ as $x_1 \rightarrow 0$

$k_{H,\text{ethanol}}$ is slope of ~~ethanol~~ ethanol plot as $x_{\text{ethanol}} \rightarrow 0$

$$\text{slope} = \frac{\text{rise}}{\text{run}} \approx \frac{17.65}{0.1} \approx 176.5 \text{ torr}$$

$k_{H,\text{water}}$ is slope of water plot as $x_{\text{ethanol}} \rightarrow 1$

$$\text{slope} = \frac{\text{rise}}{\text{run}} \approx \frac{9.89}{0.20} \approx 49.5 \text{ torr}$$

51. see Excel graph

$\gamma_i = P_i / x_i P_i^*$

For ethanol $P_i^* = 59.2$

water $P_i^* = 23.78$

$$\gamma_{\text{ethanol}} = \frac{P_{\text{ethanol}}}{x_{\text{ethanol}} \cdot 59.2}$$

$$\gamma_{\text{water}} = \frac{P_{\text{water}}}{(1 - x_{\text{ethanol}}) \cdot 23.78}$$

~~Absolute~~ A pure liquid has an activity of 1. With this data, as the $x_{\text{ethanol}} \rightarrow 1$, ~~etha~~ the activity coefficient for ethanol, $\gamma \rightarrow 1$. Also when $x_{\text{ethanol}} \rightarrow 0$, the activity coefficient for water, $\gamma \rightarrow 1$. At low concentrations of ethanol γ_{ethanol} is high (+ same for low conc. of water (γ_{water} is high)).

#2 Chapter 24

According to Henry's Law... $P \propto$ concentration let $P = k_{H,c} C$

Henry's law constant in molarity

$P = k_{H,c} C \Rightarrow k_{H,c} = 0.80 \text{ atm} / 5.6 \times 10^{-4} \text{ M} = 1428.6 \text{ M}^{-1}\text{atm}$

$37°C = 310 \text{ K}$

@ 4 atm... $C = P/k_{H,c} = \frac{4 \text{ atm}}{1428.6 \text{ M}^{-1}/\text{atm}} = 0.0028 \text{ M}$ w/ 5 L... 0.014 mol

@ 0.8 atm $c = 5.6 \times 10^{-4} \text{ M}$ w/ 5 L .... 0.0028 mol

mol N_2 expelled = 0.014 − 0.0028 = 0.0112 mol

assume ideal gas $V = \frac{nRT}{P} = \frac{(0.0112)(0.08206)(310 \text{ K})}{0.8 \text{ a}} = \boxed{0.36 \text{ L}}$

Chapter 25

$MW = 92.093 \frac{g}{mo}$

1. 40% glycerol by mass $\rho = 1.101$ g/mL @ 20°C
Calculate molality + molarity of glycerol @ 20°C

g glycerol per mL : $(0.400)(1.101 \text{ g/mL}) = 0.4404$ g/mL

molarity = $\frac{mol}{L}$

$$\frac{0.4404 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{92.093 \text{ g}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 4.78 \text{ M}$$

molality

g H_2O /mL solution = $(0.600)(1.101 \text{ g/mL}) = 0.6606$ g/mL

0.4404 g/mL glycerol / 0.6606 g/mL water = 0.6666 g glycerol / g water

$$\frac{0.6666 \text{ g glycerol}}{1 \text{ g water}} \cdot \frac{1000 \text{ g water}}{1 \text{ kg water}} \cdot \frac{1 \text{ mol glycerol}}{92.093 \text{ g}} = 7.24 \text{ m} \ (\text{mol/kg})$$

2. g H_2SO_4 per mL solution = $(0.98)(1.84 \text{ g/mL})$
$= 1.80$ g H_2SO_4 /mL

molarity

$$\frac{1.80 \text{ g } H_2SO_4}{1 \text{ mL}} \cdot \frac{1000 \text{ mL}}{1 \text{ L}} \cdot \frac{1 \text{ mol}}{98.08 \text{ g}} = 18.4 \text{ M} \ (\text{mol/L})$$

29. 0.80 g protein in 100 mL solution. osmotic pressure = 2.06 torr @ 25°C
what is molecular mass?

$$C = \frac{\Pi}{RT} = \frac{2.06 \text{ torr}/760 \text{ torr/atm}}{\left(0.08206 \frac{\text{L atm}}{\text{K} \cdot \text{mol}}\right)(298 \text{ K})} = 1.11 \times 10^{-4} \text{ mol/L}$$

$$1.11 \times 10^{-4} \frac{\text{mol}}{\text{L}} \cdot 0.100 \text{ L} = 1.11 \times 10^{-5} \text{ mol}$$

$0.80 \text{ g} \times \frac{1}{MW} = 1.11 \times 10^{-5}$ $MW = 0.80/1.11 \times 10^{-5} = 72175$ g/mol

41. $\Delta T_{fus} = \nu K_f m$ $K_f(H_2O) = 1.86 \frac{K\,kg}{mol}$ pg 1022

$\Delta T_{fus} = -2.83\,°C = 2.83\,K$

40.7 g $HgCl_2$ in 100 g water

$$40.7\,g \times \frac{1\,mol\ HgCl_2}{271.49\,g} = 0.150\ mol\ HgCl_2$$

$$m = \frac{0.150\ mol\ HgCl_2}{100\ g\ H_2O} \times \frac{1000\,g}{1\,kg} = 1.50\ mol/kg = 1.50\ m$$

$$\nu = \frac{\Delta T_f}{K_f m} = \frac{2.83\ K}{1.86\frac{K\,kg}{mol} \cdot 1.50\frac{mol}{kg}} = 1.02$$

Since $\nu \approx 1$, $HgCl_2$ doesn't dissociate (under these conditions) and can't conduct electricity.

44. $I_c = \frac{1}{2}\sum_{j=1}^{s} z_j^2 c_j$

$I_c(NaCl) = \frac{1}{2}(1^2 \cdot c + (-1)^2 \cdot c) = c$

$I_c(K_2SO_4) = \frac{1}{2}(1^2 \cdot c + (-2)^2 \cdot c + 1^2 \cdot c) = 3c$

$I_c(NaCl) = 0.315\ mol/L = c$

$I_c(K_2SO_4) = 0.315\ mol/L = 3c$

$c = 0.105\ mol/L$

48. Debye-Hückel @ 25°C (aq): $\ln \gamma_\pm = -1.173\,|z_+ z_-|\,(I_c)^{1/2}$ Eq 25.5

$$I_c(NaCl) = \frac{1}{2}(1^2 \cdot 0.010 + (-1)^2(0.010)) = 0.010\ M$$

$$\ln \gamma_\pm = -1.173\,|1 \cdot -1|\,(0.010)^{1/2} = -0.1173$$

$\gamma_\pm = 0.889$

↑ Exp = −0.103

62. P vs m is not really a straight line but P vs m^2 is a straight line. This makes sense since HCl will dissociate. See Excel sheet for support.

ch 24 ?
#2 .
5-18
??

~~$P = K M$~~ ~~$k'' = \frac{P}{M}$~~ ~~$k'' = \frac{0.80 \text{ atm}}{5.6 \times 10^{-4} M}$~~

~~$k'' = 1428.6 \text{ M}^{-1} \text{ atm}$~~

~~$P = k M$~~

~~$4.0 = 1428.6 M$~~

~~$M = 0.0028 \text{ M } N_2 \times 5 \text{ L} = 0.014 \text{ mol } N_2$~~ ← need to subtract the N_2 remaining in lungs

$\boxed{0.44 \text{ L}}$?

⇐ assuming ideal gas

Ch 25 #2

298 K $P^*_{H_2O} = 23.76$ mm Hg

$P_{seawater} = 22.98$ mm Hg

$\Delta P = 0.78$ mm Hg

$\Delta P = \nu x_2 P^*_1$

$\nu x_2 = 0.033$ $\nu = 2$

$x_2 = 0.016$

#3

$\Delta T_f = K_f m_2$

$\Delta T_f = 1.6\ ^\circ\text{C} = 1.6 \text{ K}$

$K_f = 5.12 \text{ K kg/mol}$ (benzene)

$\frac{1.6}{5.12} = m = 0.3125 \frac{\text{mol}}{\text{kg}}$

$0.3125 \frac{\text{mol}}{\text{kg}} \times 0.008 \text{ kg} = 0.0025$ mol compound

$\frac{0.0025 \text{ mol}}{0.5 \text{ g}} = 0.005 \text{ mol/g} \rightarrow 200 \text{ g/mol}$

cocaine = 303.4 g/mol $\boxed{\text{NOT cocaine}}$

assumptions: pure powder, no dissociation of compound, dilute sol'ns

Ch 25.
#4

K_f (benzene) = 5.12 $\frac{K \cdot kg}{mol}$
$\Delta T_f = 2.0\,°C = 2.0\,K$

$\Delta T_f = k_f\, m$
$m = 2.0/5.12 = 0.3906\ \frac{mol}{kg} \cdot 0.080\ kg$

$= 0.0313\ mol/3.8g$

$3.8g/0.0313\ mol = 121.6\ g/mol$

acetic acid = 60.05 g/mol

might be a dimer of acetic acid ~ MW = 120.1 g/mol