1.725 Problem Set #2 Solutions

1 - 5, 12, 15, 25, 27

5. Find maximum conc. of sulfide species

start with pH_2S = 1 atm and work through the K values.

for $[H_2S]$:

$$K_H = \frac{pH_2S}{[H_2S]_{aq}} \qquad [H_2S]_{aq} = \frac{pH_2S}{K_H} = 1\,atm \times \frac{mol/L}{10^{0.99}\,atm} = 0.1023\,mol/L$$

for $[HS^-]$:

$$\frac{[H^+][HS^-]}{[H_2S]} = 10^{-7.02} \qquad [HS^-] = \frac{10^{-7.02}[H_2S]}{[H^+]} = \frac{10^{-7.02}(0.1023\,M)}{10^{-6}\,M} = 9.8 \times 10^{-3}\,mol/L$$

for $[S^{2-}]$:

$$\frac{[H^+][S^{2-}]}{[HS^-]} = 10^{-13.9} \qquad [S^{2-}] = \frac{10^{-13.9}(9.8\times10^{-3})}{10^{-6}} = 1.2\times10^{-10}\,mol/L$$

* or we can tell without calculation that $[S^{2-}]$ will be negligible, because only above pH 13.9 will there be more S^{2-} than HS^- (defn. of pKa)

total = $[H_2S] + [HS^-] + [S^{2-}]$ = **0.11 M**

b) reaction. $CH_2Br_2 + HS^- \rightarrow$ products

$$\frac{d[CH_2Br_2]}{dt} = -k[CH_2Br_2][HS^-]$$

assume $[CH_2Br_2] \ll [HS^-]$

then pseudo-first-order kinetics apply, with $k' = k[HS^-]$

So now we need to find $[HS^-]$, which is done in the same way as part a)

$$[H_2S]_{aq} = 0.1\,atm \times \frac{mol/L}{10^{0.99}\,atm} = 0.0102\,mol/L$$

$$[HS^-] = \frac{10^{-7.02}(0.0102)}{10^{-6}} = 9.8\times10^{-4}\,mol/L$$

$k' = k[HS^-]$

$= 5.25 \times 10^{-5}\ M^{-1}s^{-1}\ (9.8 \times 10^{-4}\ M) = 5.1 \times 10^{-8}\ s^{-1}$

$[CH_2Br_2] = [CH_2Br_2]_0\, e^{-k't}$

$0.1 = e^{-k't}$

$-\ln 0.1 = k't$

$t = \frac{-\ln 0.1}{5.1 \times 10^{-8}\ s^{-1}} = 4.49 \times 10^7\ s \times \frac{day}{86{,}400\ s} = \boxed{519\ days}$

12. $^3H \rightarrow {}^3He$

a) $C = C_0 e^{-kt}$

$0.5 = e^{-kt}$

$\ln 2 = kt$ $\qquad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{12 yr} = \boxed{0.058\ yr^{-1}}$

b) $\frac{C}{C_0} = e^{-kt} = e^{-0.058 yr^{-1}(25 yr)} = 0.236$

^3H remaining $= 0.236$

$^3He = 1 - 0.236 = 0.764$

$\frac{^3H}{^3He} = \frac{0.236}{0.764} = \boxed{0.31}$

15. find Cwater, then use Kow and H to figure out partitioning

$C_w = \frac{5.0\ mg}{250\ mL} \times \frac{1000\ mL}{L} \times \frac{g}{1000\ mg} \times \frac{mol}{106.17\ g} = 1.88 \times 10^{-4}\ mol/L$

$K_{OW} = \frac{C_{octanol}}{C_{water}}$ $\qquad C_{oct} = K_{OW} \cdot C_W$

$= 10^{3.12}(1.88 \times 10^{-4}\ mol/L) = 0.248\ mol/L$

convert to mass: $\frac{0.248\ mol}{L} \times 0.2\ L \times \frac{106.17\ g}{mol} = 5.273\ g$ in octanol

$H = \frac{C_{air}}{C_{water}}$ $\qquad C_{air} = H \cdot C_W$ ← value for 20°C; assume same value at 25°C

$= 2.2 \times 10^{-1}(1.88 \times 10^{-4}\ mol/L) = 4.14 \times 10^{-5}\ mol/L$

$\frac{4.14 \times 10^{-5}\ mol}{L} \times 0.05\ L \times \frac{106.17\ g}{mol} = 2 \times 10^{-4}\ g$ in air

total $= 0.005\ g + 5.273\ g + 2 \times 10^{-4}\ g = \boxed{5.278\ g}$

25. a) $H = \frac{C_{air}}{C_{water}} = \frac{\text{pressure}}{\text{solubility}} \times \frac{1}{RT}$

$= \frac{3 \times 10^{-4}\ \text{atm}}{2.6 \times 10^{-4}\ \text{mol/L}} \times \frac{1}{0.08206\ \text{L atm/mol K}\ (293\ \text{K})} = \boxed{0.048}$ (at 20°C)

b) % of napthalene in air

$= \frac{\text{moles in air}}{\text{moles total}} = \frac{C_a \cdot V_a}{C_w \cdot V_w + C_a \cdot V_a}$

C: concentration
V: volume

plug in: $V_a = 19\ L$, $V_w = 1\ L$

$C_a = C_w \cdot H$

$= \frac{C_w (0.048)(19L)}{C_w (1L) + C_w (0.048)(19L)} = 0.477 = \boxed{48\%}$

27. a) species: H^+, OH^-, CH_3COOH, CH_3COO^-, NH_3, NH_4^+

- H_2O doesn't have to be included because its concentration is constant (we're looking for unknowns here)

b) $\frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 10^{-4}$

$\frac{[NH_4^+][OH^-]}{[NH_3]} = 10^{-4.8}$

$[H^+][OH^-] = 10^{-14}$

c) $[CH_3COOH] + [CH_3COO^-] = 0.01$

$[NH_3] + [NH_4^+] = 0.01$

d) electroneutrality: # of ⊕ charges = # of ⊖ charges

$[H^+] + [NH_4^+] = [OH^-] + [CH_3COO^-]$

e) We have 6 equations and 6 unknowns, so we can solve for the concentrations and determine the pH.

random note #1:

The carbonate species are H_2CO_3, HCO_3^-, and CO_3^{2-}. These are always present (because CO_2 from the atmosphere dissolves in the water; $CO_2 + H_2O \rightleftharpoons H_2CO_3$) and serve as a buffer system.