Analytical Chemistry
Solutions to Workshop Problems due Week 2

1. Calculate the p-function of ~~(a) the ion-product constant of water at 25C and~~ (b) the concentrations of the four major ions in a solution that is both 2.00×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl.

~~(a) For the ion product of water, pKw is given by~~
~~pKw = - log (1.00 x 10^{-14}) = 14.000~~

☒ The concentration of H^+ is equal to the concentration of HCl.
$$pH = - \log [H^+] = - \log (5.4 \times 10^{-4}) = -(-3.2676) = 3.27$$
$$pOH = 14.000 - pH = 14.00 - 3.27 = 10.73$$
$$pNa = - \log (2.00 \times 10^{-3}) = 2.699$$

The total Cl^- concentration is given by the sum of the concentrations of the two solutes:
$$[Cl^-] = 2.00 \times 10^{-3} M + 5.4 \times 10^{-1} M = 2.54 \times 10^{-3} M$$
$$pCl = - (\log 2.54 \times 10^{-3}) = 2.595$$

Be sure you understand what happens to significant figures when you go between logs and scientific notation.

2. Magnetite is a mineral having the formula Fe_3O_4 or $FeO \cdot Fe_2O_3$. A 1.1324-g sample of a magnetite ore was dissolved in concentrated HCl to give a solution that contained a mixture of Fe^{2+} and Fe^{3+}. Nitric acid was added and the solution was boiled for a few minutes, which converted all of the iron to Fe^{3+}. The Fe^{3+} was then precipitated as $Fe_2O_3 \cdot xH_2O$ by addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the percent Fe (55.847 g/mol) and (b) the percent Fe_3O_4 (231.54 g/mol) in the original ore sample.

(a) mass Fe = 0.5394 g Fe_2O_3 x $\dfrac{1 \text{ mol } Fe_2O_3}{159.69 \text{ g } Fe_2O_3}$ x $\dfrac{2 \text{ mol Fe}}{1 \text{ mol } Fe_2O_3}$ x $\dfrac{55.847 \text{ g Fe}}{1 \text{ mol Fe}}$

= 0.37728 g Fe

percent Fe = $\dfrac{0.37728 \text{ g}}{1.1324 \text{ g}}$ x 100% = 33.317 = 33.32%

(b) In this calculation, we assume that iron is not lost and therefore 3 mol of Fe_2O_3 were formed from 2 mol of Fe_3O_4, or
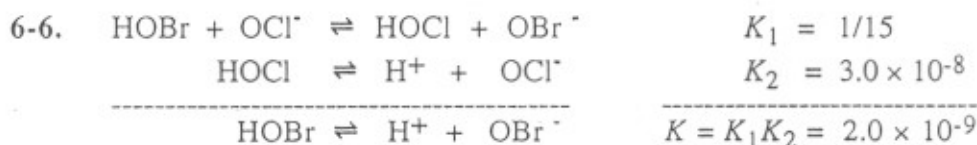
$$3 \ Fe_2O_3 \ ==> 2 \ Fe_3O_4 + \tfrac{1}{2} \ O_2$$

Then,
mass Fe_3O_4 = 0.5394 g Fe_2O_3 x $\dfrac{1 \text{ mol } Fe_2O_3}{159.69 \text{ g } Fe_2O_3}$ x $\dfrac{2 \text{ mol } Fe_3O_4}{3 \text{ mol } Fe_2O_3}$ x $\dfrac{231.54 \text{ g } Fe_3O_4}{1 \text{ mol } Fe_3O_4}$

= 0.521396 g

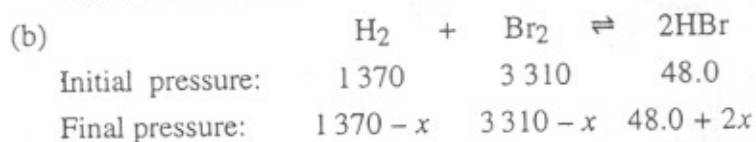percent Fe_3O_4 = $\dfrac{0.521396 \text{ g } Fe_3O_4 \times 100\%}{1.324 \text{ g}}$ = 46.043 = 46.04%

6-5. $K = \dfrac{P_E^3}{P_A^2 [B]} = \dfrac{\left(\dfrac{3.6 \times 10^4 \text{ Torr}}{760 \text{ Torr/atm}} \times 1.013 \dfrac{\text{bar}}{\text{atm}}\right)^3}{\left(\dfrac{2.8 \times 10^3 \text{ Pa}}{10^5 \text{ Pa/bar}}\right)^2 (1.2 \times 10^{-2} \text{ M})} = 1.2 \times 10^{10}$

6-6.

$HOBr + OCl^- \rightleftharpoons HOCl + OBr^-$	$K_1 = 1/15$
$HOCl \rightleftharpoons H^+ + OCl^-$	$K_2 = 3.0 \times 10^{-8}$
$HOBr \rightleftharpoons H^+ + OBr^-$	$K = K_1 K_2 = 2.0 \times 10^{-9}$

6-8. $K = e^{-(59.0 \times 10^3 \text{ J/mol})/(8.314\,472 \text{ J/(K·mol)})(298.15 \text{ K})} = 5 \times 10^{-11}$

6-12. (a) $Q = \left(\dfrac{48.0 \text{ Pa}}{10^5 \text{ Pa/bar}}\right)^2 / \left(\dfrac{1\,370 \text{ Pa}}{10^5 \text{ Pa/bar}}\right)\left(\dfrac{3\,310 \text{ Pa}}{10^5 \text{ Pa/bar}}\right)$

$= 5.08 \times 10^{-4} < K$ The reaction will go to the right.

Note that it was not necessary to convert Pa to atm, since the units cancel.

(b)

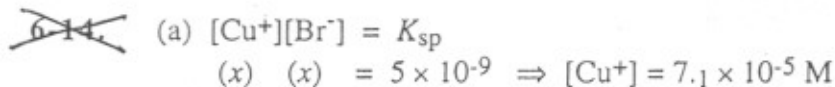|	H_2	$+$	Br_2	$\rightleftharpoons$	$2HBr$
Initial pressure:	1 370		3 310		48.0
Final pressure:	1 370 − x		3 310 − x		48.0 + 2x

Note that 2x Pa of HBr are formed when x Pa of H_2 are consumed.

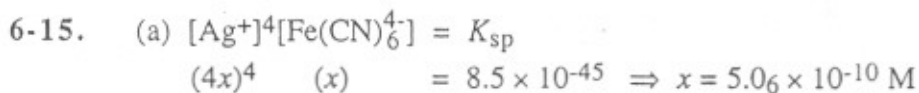$\dfrac{(48.0 + 2x)^2}{(1\,370 - x)(3\,310 - x)} = 7.2 \times 10^{-4} \implies x = 4.50 \text{ Pa}$

$P_{H_2} = 1\,366 \text{ Pa}, \quad P_{Br_2} = 3\,306 \text{ Pa}, \quad P_{HBr} = 57.0 \text{ Pa}$

(c) Neither, since Q is unchanged.

(d) HBr will be formed, since $\Delta H°$ is positive.

6-14. (a) $[Cu^+][Br^-] = K_{sp}$

$(x) \quad (x) \quad = 5 \times 10^{-9} \implies [Cu^+] = 7._1 \times 10^{-5} \text{ M}$
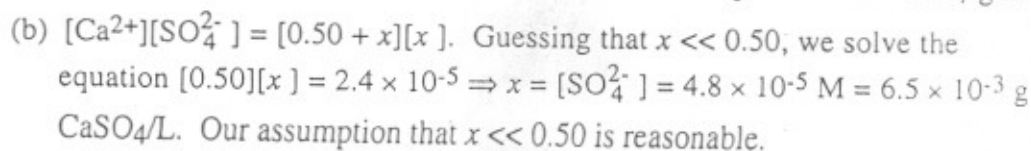
(b) $(143.45 \text{ g/mol})(7.1 \times 10^{-5} \text{ mol/L})(0.100 \text{ L}/100 \text{ mL}) = 1._0 \times 10^{-3} \text{ g}/100 \text{ mL}$

6-15. (a) $[Ag^+]^4[Fe(CN)_6^{4-}] = K_{sp}$

$(4x)^4 \quad (x) \quad = 8.5 \times 10^{-45} \implies x = 5.0_6 \times 10^{-10} \text{ M}$

(b) $(643.42 \text{ g/mol})(5.0_6 \times 10^{-10} \text{ mol/L})(0.100 \text{ L}) = 3.3 \times 10^{-8} \text{ g}/100 \text{ mL}$

(c) $[Ag^+] = 4x = 2.02 \times 10^{-9} \text{ M} = 2.18 \times 10^{-7} \text{ g/L} = 2.18 \times 10^{-7} \text{ mg/mL}$

$= 0.218 \text{ ng/mL} = 0.22 \text{ ppb}$

6-19. (a) $CaSO_4(s) \overset{K_{sp}}{\rightleftharpoons} Ca^{2+} + SO_4^{2-}$ $x^2 = 2.4 \times 10^{-5}$

FM 136.14   x   x $\implies x = 4.9_0 \times 10^{-3} \text{ M} = 0.66_7 \text{ g/L}$

(b) $[Ca^{2+}][SO_4^{2-}] = [0.50 + x][x]$. Guessing that $x \ll 0.50$, we solve the equation $[0.50][x] = 2.4 \times 10^{-5} \implies x = [SO_4^{2-}] = 4.8 \times 10^{-5} \text{ M} = 6.5 \times 10^{-3} \text{ g}$ $CaSO_4/L$. Our assumption that $x \ll 0.50$ is reasonable.

6-25.

Salt	K_{sp}	[Ag$^+$] (M, in equilibrium with 0.1 M anion)	
AgCl	1.8×10^{-10}	$K_{sp}/0.10$	$= 1.8 \times 10^{-9}$
AgBr	5.0×10^{-13}	$K_{sp}/0.10$	$= 5.0 \times 10^{-12}$
AgI	8.3×10^{-17}	$K_{sp}/0.10$	$= 8.3 \times 10^{-16}$
Ag$_2$CrO$_4$	1.2×10^{-12}	$\sqrt{K_{sp}/0.10}$	$= 3.5 \times 10^{-6}$

Order of precipitation : I$^-$ before Br$^-$ before Cl$^-$ before CrO$_4^{2-}$