Solutions to CHEM 301 Review Exercises

naming

1. a) calcium phosphate
b) chromium (III) oxide
c) chlorine dioxide

2. a) **NaOCl**
b) **HgSO$_4$**

significant figures

3. $[H^+] = 1.25$ x 10^{-6} M has <u>three</u> significant figures, therefore the pH is reported to three places after the decimal point. So pH = 5.903 is reported. (The whole number to the left of the decimal point reports the order of magnitude in powers of ten).

4. $pK_{sp} = - \log K_{sp} = - \log (2$ x $10^{-30}) = 29.7$
(note: there is only one significant figure in this result)

units of concentration

5. a) We must convert mmol of **P** into mass (mg) of **PO$_4$$^{3-}$**. Since each mol of **PO$_4$$^{3-}$** contains one **P**, there must be 3.2 mmol of **PO$_4$$^{3-}$** per liter. So all we need to do is multiply the number of mols of **PO$_4$$^{3-}$** by its molar mass (94.97 g/mol).

$$\frac{3.2 \text{ mmol P}}{L} \text{ x } \frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol P}} \text{ x } \frac{94.97 \text{ g PO}_4^{3-}}{1 \text{ mol PO}_4^{3-}} \text{ x } \frac{1000 \text{ mg}}{1 \text{ g}} = 3.0 \text{ x } 10^2 \text{ ppm PO}_4^{3-} \text{ (in freshwater)}$$

b) Recall, 1 ppb in freshwater is equivalent to the ratio 1 μg/kg which in dilute solution (freshwater d ~ 1.00 g/mL) is equal to 1 μg/L.

$$\frac{1.9 \text{ x } 10^{-6} \text{ molCu}}{L} \text{ x } \frac{63.54 \text{g Cu}}{\text{molCu}} \text{ x } \frac{10^6 \text{ ug}}{1 \text{g}} = 1.2 \text{ x } 10^2 \text{ ppb Cu}$$

6. a) Converting mass (mg) to moles involves dividing by the molar mass of the species involved. In this case we are dealing with molecular oxygen (**O$_2$**), so the molar mass is 32.00 g/mol or 32000 mg/mol.

$$\frac{9.8 \text{ mg O}_2}{L} \text{ x } \frac{1 \text{ molO}_2}{32000 \text{mg O}_2} = 3.1 \text{ x } 10^{-4} \text{ M O}_2$$

b)

$$\frac{150\,\mu g\ As}{1\,kg} \times \frac{1\,mol\,As}{74.92g\ As} \times \frac{1g}{10^6\,\mu g} \times \frac{1.035kg}{1\,L} = 2.1 \times 10^{-6}\ M\ As$$

Where the last term has been introduced to correct for the density of seawater.

7. To carry out a charge balance, one must calculate the equivalents of charge (both positive and negative). Therefore, one must convert the given ion concentrations to molar concentrations and then multiply by the magnitude of the ion charge in each case.
Note: equiv charge = # mol of ion (n_{ion}) x # unit charge/mol (Z)

Σ (+'ve) = 6.08 meq/L
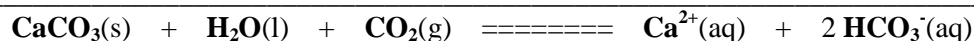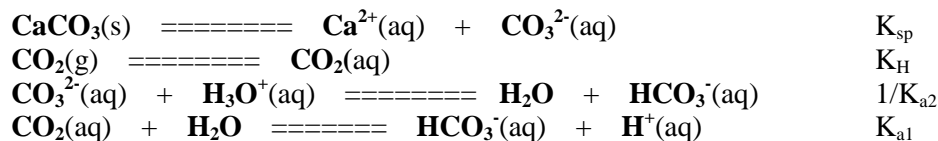 and
Σ (-'ve) = 2.60 meq/L.

Since in solution the charge must balance, the calculated discrepancy means one of two things. Either one (or more) of the analysis is in error or one (or more) ion/s have been neglected. (Since, humic substances (e.g., DOC) carry a negative charge, they are sometimes associated with small anion deficiencies).

8. Equivalents of acid refer to the number of moles of protons (rather than the number of moles of unit charge, as above). Since each mole of sulfuric acid (H_2SO_4) supplies 2 moles of H^+, a 0.1034 M solution is 'equivalent' to 0.2068 moles of H^+/L (N or equivalents/L). Thus, the number of equivalents of acid neutralized in this reaction is:

$$22.62\,mL \times \frac{1\,L}{1000mL} \times \frac{0.2068equiv}{L} \times \frac{1000mequiv}{1\,equiv} = 4.678mequiv\ of\ H^+$$

equilibrium expressions

9. Very often, we will be required to evaluate an equilibrium constant of a 'complex' reaction by combining the known equilibrium expressions of known 'simpler' reactions. In this case, we will rearrange and combine the given expressions such that they sum to equal the reaction of interest.

$CaCO_3(s) \ ======== \ Ca^{2+}(aq) \ + \ CO_3^{2-}(aq)$	K_{sp}
$CO_2(g) \ ======== \ CO_2(aq)$	K_H
$CO_3^{2-}(aq) \ + \ H_3O^+(aq) \ ======= \ H_2O \ + \ HCO_3^-(aq)$	$1/K_{a2}$
$CO_2(aq) \ + \ H_2O \ ====== \ HCO_3^-(aq) \ + \ H^+(aq)$	K_{a1}

$$CaCO_3(s) \ + \ H_2O(l) \ + \ CO_2(g) \ ======== \ Ca^{2+}(aq) \ + \ 2\ HCO_3^-(aq)$$

Thus,

$$K_{eq} = \frac{K_{sp}\ K_H\ K_{a1}}{K_{a2}} = \frac{[Ca^{2+}][HCO_3^-]^2}{P_{CO2}}$$

Since all of the equilibrium constants on the right hand side of this expression are known, we could calculate the value of K_{eq} for the reaction of interest. This value could be used then, for example to calculate the equilibrium concentration of HCO_3^- if $[\mathbf{Ca^{2+}}]$ and the P_{CO2} were measured or known.

10. a) At pH = 8.0, the activity (concentration) of $[\mathbf{H^+}] = 1 \times 10^{-8}$ M.
Since,

$$K_{eq} = \frac{[H_3O^+][OCl^-]}{[HOCl]}$$

can be rearranged

$$\frac{[HOCl]}{[OCl^-]} = \frac{[H_3O^+]}{K_{eq}}$$

Since K_{eq} and $[\mathbf{H_3O^+}]$ are known, this ratio is given by $1 \times 10^{-8}/2.5 \times 10^{-8} = 0.4$
Hence, $[\mathbf{HOCl}]/[\mathbf{OCl^-}] = 0.4$ (in other words, $[\mathbf{HOCl}] = 0.4\ [\mathbf{OCl^-}]$)

The total 'active chlorine' $= [\mathbf{HOCl}] + [\mathbf{OCl^-}]$, so the percent of $\mathbf{HOCl}$ to the total is given by:

$$\frac{[HOCl]}{[HOCl]+[OCl^-]} \times 100 = \frac{0.4[OCl^-]}{0.4[OCl^-]+[OCl^-]} \times 100 = \frac{0.4}{1.4} \times 100 = 29\%$$

b) Substituting the instantaneous concentrations into the equilibrium expression to calculate Q yields,

$$Q = (10^{-7})(10^{-4})/(10^{-3}) = 10^{-8}$$

Since $Q < K_{eq}$, the reaction will proceed to right to increase to concentration of the products relative to that of the reactants. Consequently, the $[\mathbf{HOCl}]$ will decrease as the reaction approaches equilibrium.

acids/bases

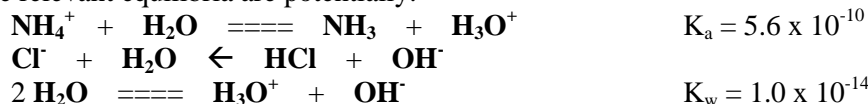**11.** Using the rules for predicting the pH of aqueous solutions.
a) acidic ($\mathbf{Cu^{2+}}$ metal cations other than alkali and alkali earth metals are slightly acidic, $\mathbf{Cl^-}$ is neutral)
b) basic ($\mathbf{Na^+}$ is an alkali metal, therefore neutral and $\mathbf{PO_4^{3-}}$ is the conjugate base of $\mathbf{HPO_4^{2-}}$, which is a weak acid. Therefore the solution is basic)
c) acidic (ammonium ion is acidic, chloride is neutral)
d) basic ($\mathbf{Mg^{2+}}$ is an alkali earth metal, therefore neutral and $\mathbf{S^{2-}}$ is the conjugate base of a weak acid $\mathbf{HS^-}$. Therefore the solution is basic)

12. The relevant equilibria are potentially:
$$NH_4^+ + H_2O \ ==== \ NH_3 + H_3O^+ \qquad\qquad K_a = 5.6 \times 10^{-10}$$
$$Cl^- + H_2O \ \leftarrow \ HCl + OH^-$$
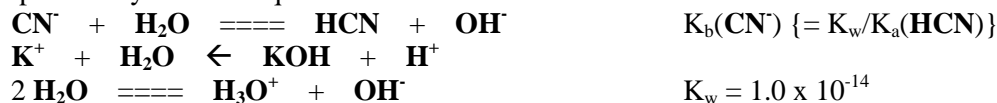$$2\,H_2O \ ==== \ H_3O^+ + OH^- \qquad\qquad K_w = 1.0 \times 10^{-14}$$

Using the first and last of these, we can set up an equilibrium table as follows.
Where $x = 7.31 \times 10^{-6}$, since pH = 5.13, the $[H^+] = 10^{-5.13} = 7.41 \times 10^{-6}$ M

	NH_4^+	+	H_2O	====	NH_3	+	H_3O^+	K_a
I	i				0		10^{-7}	
C	$-x$				x		x	
E	$i - x$				x		$x + 10^{-7}$	
	$i - 7.31 \times 10^{-6}$				7.31×10^{-6}		7.41×10^{-6}	

Using the expression for $K_a(NH_4^+)$
$K_a = [NH_3][H_3O^+]/[NH_4^+] = 5.6 \times 10^{-10}$
So, $(7.41 \times 10^{-6})(7.31 \times 10^{-6})/(i - 7.31 \times 10^{-6}) = 5.6 \times 10^{-10}$
Solving for i yields, $i = 0.0097$ M

(this is the initial concentration of NH_4^+, which corresponds to the number of moles of NH_4Cl dissolved per liter. In grams, this is 0.52 g/L)

13. The potentially relevant equilbria are:

CN^-	+	H_2O	====	HCN	+	OH^-		$K_b(CN^-) \{= K_w/K_a(HCN)\}$
K^+	+	H_2O	$\leftarrow$	KOH	+	H^+		
$2 H_2O$			====	H_3O^+	+	OH^-		$K_w = 1.0 \times 10^{-14}$

Using the first and last of these, we can set up an equilibrium table as follows.
Where $x = 5.75 \times 10^{-4}$ M, since pH = 10.76, the pOH = 3.24 and $[OH^-] = 10^{-3.24} = 5.75 \times 10^{-4}$ M,

	CN^-	+	H_2O	====	HCN	+	OH^-	K_b
I	1.6×10^{-2} M				0		10^{-7}	
C	$-x$				x		x	
	-5.75×10^{-4} M				5.75×10^{-4}		5.75×10^{-4}	
E	$1.6 \times 10^{-2} - 5.75 \times 10^{-4}$				5.75×10^{-4}		$10^{-7} + 5.75 \times 10^{-4}$	
	1.54×10^{-2} M				5.75×10^{-4}		$\tilde{} 5.75 \times 10^{-4}$	

$K_b = [HCN][OH^-]/[CN^-] = (5.75 \times 10^{-4})^2/(1.54 \times 10^{-2}) = 2.1 \times 10^{-5}$
(From reference tables of K_a values $K_a(HCN) = 4.9 \times 10^{-10}$, so $K_b(CN^-) = K_w/K_a = 2.0 \times 10^{-5}$)

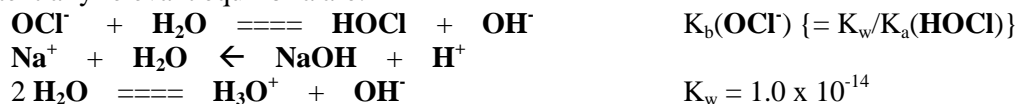**14.** a) Sodium hypochlorite is basic since OCl^- is the conjugate base of a weak acid.
b) $K_b = K_w/K_a(HOCl) = 1.0 \times 10^{-14}/2.8 \times 10^{-8} = 3.6 \times 10^{-7}$
c) First, we must convert the 5% (wt/wt) concentration into one we can use in chemical calculations, molarity (or more precisely activities).
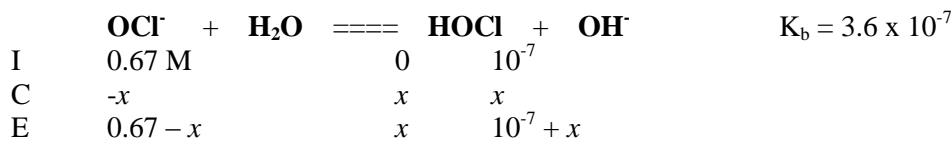For a 5% soln there is 5 g $NaOCl$ per 100 g of solution. Assuming the density of the solution is close to 1000 g/L, we have;

$$\frac{5\,g\,NaOCl}{100\,g\,soln} \times \frac{1\,mol\,NaOCl}{74.45\,g\,NaOCl} \times \frac{1000g}{1\,L} = 0.67\,M$$

The potentially relevant equilibria are:

OCl^-	+	H_2O	====	$HOCl$	+	OH^-		$K_b(OCl^-) \{= K_w/K_a(HOCl)\}$
Na^+	+	H_2O	$\leftarrow$	$NaOH$	+	H^+		
$2 H_2O$			====	H_3O^+	+	OH^-		$K_w = 1.0 \times 10^{-14}$

Using the first and last of these, we can set up an equilibrium table as follows.

$$\begin{array}{lccccc} & \mathbf{OCl^-} & + & \mathbf{H_2O} & ==== & \mathbf{HOCl} & + & \mathbf{OH^-} \end{array} \qquad K_b = 3.6 \text{ x } 10^{-7}$$

	$\mathbf{OCl^-}$ + $\mathbf{H_2O}$	$\mathbf{HOCl}$	$\mathbf{OH^-}$
I	0.67 M	0	10^{-7}
C	$-x$	x	x
E	$0.67 - x$	x	$10^{-7} + x$

$K_b = [\mathbf{HOCl}]\,[\mathbf{OH^-}]/[\mathbf{OCl^-}] = (x)\,(10^{-7} + x)/(0.67\text{-}x) = 3.6 \text{ x } 10^{-7}$
Expand and solve using quadratic formula
OR
If $x \gg 10^{-7}$ and x $\ll$ 0.67,
Then the above expression simplifies to
$x^2/0.67 = 3.6 \text{ x } 10^{-7}$
so, $x = 4.9 \text{ x } 10^{-4}$ and *assumptions check*

Therefore, $[\mathbf{OH^-}] = 4.9 \text{ x } 10^{-4}$ M and pOH = 3.31
Therefore, pH = 14 – pOH = 10.7

solubility

15. a) **AgCl**(s)
b) **CdS**(s)
c) **Cu(OH)2**(s), **BaSO₄**(s)
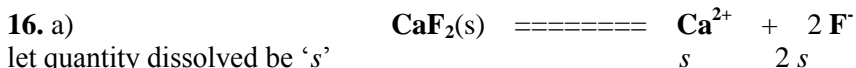
16. a) $\qquad\qquad\qquad$ **CaF₂**(s) $\quad=======\quad$ **Ca²⁺** $\quad+\quad$ 2 **F⁻**
let quantity dissolved be 's' $\qquad\qquad\qquad\qquad\qquad$ s $\qquad$ $2\,s$
$\qquad K_{sp} = [\mathbf{Ca^{2+}}][\mathbf{F^-}]^2 = 5.3 \ 10^{-9}$
$\qquad (s)\,(2s)^2 = 5.3 \text{ x } 10^{-9}$
$\qquad 4s^3 = 5.3 \text{ x } 10^{-9}$
Therefore, $s = 1.1 \text{ x } 10^{-3}$ M (this is the molar solubility)
Since **CaF₂** has a molar mass of 78 g/mol, $8.6 \text{ x } 10^{-2}$ g of **CaF₂** will dissolve per liter of **H₂O**
b) less
c) less

oxidation states

17. a) (+V), (-III), (-III), (0)
b) (-II), (+IV), (+II), (+VI) on sulfur
c) (+VII), (+V), (+III), (+I)
d) (+IV), (+IV), (-III and –I), (-III and +I)

18.
a) reduction
b) oxidation
c) reduction
b) both (disproportionation)
19. $\qquad$ oxidized $\qquad\qquad\qquad$ reduced

a)   **I⁻**   **IO$_4^-$**
b)   **Cl⁻**   **NO$_3^-$**
c)   **Cu**   **NO$_3^-$**
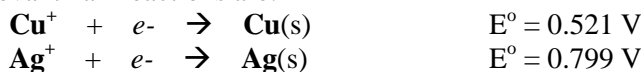
20. a) oxidation
b) reduction
c) oxidation

21. See reference tables of standard half reaction reduction potentials. Half reactions (written as reductions) with a large positive E° value are energetically favorable. Therefore, species on the left-hand side of the half reactions with large positive reduction potentials are the most powerful oxidizing agents.

Increasing order of oxidizing ability is given by   **O$_2$ < ClO$_2$ < Cl$_2$ < O$_3$**

22. The potential reaction is:

     Cu(s)   +   **Ag⁺**   ====   **Cu⁺**   +   **Ag**(s)
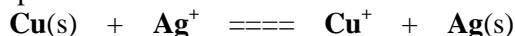
The relevant half reactions are:

     Cu⁺   + e-   →   **Cu**(s)   E° = 0.521 V
     Ag⁺   + e-   →   **Ag**(s)   E° = 0.799 V

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Reversing the first of these, and combining yields the reaction above with E° = 0.278 V
Since E° > 0, ΔG° < 0 and therefore the reaction will proceed as written at standard state conditions.
Since the concentrations of the relevant ions was not given, we could use the Nernst equation
To check the effect of other ion concentrations.

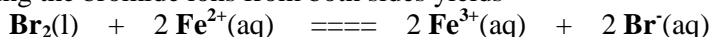   E = 0.278 V – 0.0257/1 ln {[**Cu⁺**]/[**Ag⁺**]} (at room temp)

Where n = 1, and Q = [**Cu⁺**]/[**Ag⁺**]
So even if the [**Cu⁺**]/[**Ag⁺**] = 10⁴, E = 0.041 V and the reaction still proceeds as written.

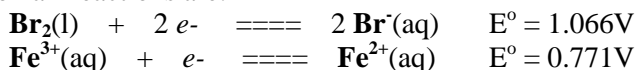**23.** This is a tricky one. First of all, the aqueous iron salts should be written out in their dissociated forms.

     Br$_2$(l)   +   2 **Fe^{2+}**(aq)   +   4 **Br⁻**(aq)   ====   2 **Fe^{3+}**(aq)   +   6 **Br⁻**(aq)
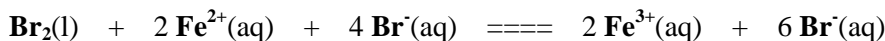
Canceling the bromide ions from both sides yields

     Br$_2$(l)   +   2 **Fe^{2+}**(aq)   ====   2 **Fe^{3+}**(aq)   +   2 **Br⁻**(aq)

The two half reactions are:

     Br$_2$(l)   +   2 e-   ====   2 **Br⁻**(aq)   E° = 1.066V
     Fe^{3+}(aq)   + e-   ====   **Fe^{2+}**(aq)   E° = 0.771V

     ΔG° = -nFE° = -2(96480 C/mol) (0.295 V) = -56.9 kJ/mol

     K = exp -{ΔG°/RT} = e²²·⁹ = 9.5 x 10⁹
     where R = 8.314 J/mol K and T = 298 K