NUMERICAL ANSWERS TO ASSIGNED TUTORIAL PROBLEM SETS FOR CHEM206
FROM KOTZ & TREICHEL'S CHEMISTRY & CHEMICAL REACTIVITY, **6th Ed.**

NOTE: the answers from Ch.18 have <u>not</u> been verified. Please report any errors.

Ch.	Q#	Answer/Comments

18	2a	pH increases ($C_2O_4^{2-}$ is a weak base; what you get when lose 2 H+ from oxalic acid)
	2b	pH decreases (NH_4^+ , a weak acid, is being added to a solution containing strong acid)
	2c	no change (Na^+ is not acid or base; Cl^- is essentially not basic since is conjugate base of strong acid)
18	4	$[CH_3CO_2^-]$ = 0.190 M; use ICE table and K_a expression; solve for x = $[H_3O^+]$ = 1.4x10^{-5} M ⇨ pH = 4.85
18	8a	$[CH_3CHOHCO_2H]$ = 0.0491 M; use ICE table & K_a expression; solve x = $[H_3O^+]$ = 2.9x10^{-4} M ⇨ pH = 3.54
	8b	The buffer solution has a higher pH than the original lactic acid solution (pH = 2.43) because a weak base ($CH_3CHOHCO_2^-$) was added to the lactic acid solution.
18	10	$[H_3O^+]$ = 10^{-pH} = 1.0x10^{-9} M = eqm value; use K_a expression, solve for $[NH_4^+]$ = 0.18 M ⇨ 4.8 g NH_4Cl total
18	14a	pK_a = 7.21; calculate moles of Na_2PO_4 (=0.03999mol; conj.base) and KH_2PO_4 (=0.009994mol; conj.acid) use Henderson-Hasselbalch equation ("H.-H. eqn"): solve for pH of buffer = 7.81
	14b	Given pH, use H.-H. eqn solve for ratio of conj.base to conj.acid = 1.3 / 1 Given # moles of $H_2PO_4^-$ = 0.03999mol, calculate 0.032 mol $H_2PO_4^-$ To prepare: need 4.3g total of KH_2PO_4…but already have 1.360g in buffer ⇨ need to add 2.9g more.
18	16a	H_3PO_4 / NaH_2PO_4 pK_a of H_3PO_4 = 2.12
	16b	NaH_2PO_4 / Na_2HPO_4 pK_a of $H_2PO_4^-$ = 7.21
	16c	Na_2HPO_4 / Na_3PO_4 pK_a of HPO_4^{2-} = 12.44 The best choice here is (b), sodium dihydrogen phosphate-sodium hydrogen phosphate buffer.
18	22	using H.-H. eqn: buffer's initial pH = 9.22 Calculate moles of NH_3 (0.0135mol) and NH_4^+ (0.0146mol) in buffer and NaOH added (0.00200mol) Note total volume after adding base = 0.100L Reaction: OH^- will consume NH_4^+ to yield water and NH_3; now have 0.0126mol NH_4^+, 0.0155mol NH_3 New pH = 9.34; change in pH was 0.12 pH units, increased because added base…
18	24a	$[C_6H_5CO_2H]$ = 0.0192 M initially; use ICE table & K_a to solve for x = $[H_3O^+]$ = 0.0011 M ⇨ pH = 2.96
	24b	Reaction: add known #moles base: calculate how much $C_6H_5CO_2H$ is consumed & $C_6H_5CO_2^-$ formed New initial $[C_6H_5CO_2^-]$ = 0.0163M; and realize system will reequilibrate. Calculate K_b = K_w/K_a = 1.6x10^{-10}; use ICE table & K_b to solve for x = $[OH^-]$ = 1.6x10^{-6} M Then, $[H_3O^+]$ = $K_w/[OH^-]$ = 6.2x10^{-9} M; note $[Na^+]$ = $[C_6H_5CO_2^-]$ = 0.0163 M
	24c	pH = 8.21
18	26a	$[C_6H_5NH_2]$ = 0.180 M based on stoichiometry with HCl…
	26b	total volume = 0.0507 L; so new $[C_6H_5NH_2]$ = 0.0887 M find K_a = K_w/K_b = 2.5x10^{-5}; use ICE table & K_a to solve for x = $[H_3O^+]$ = 0.0015 M
	26c	pH = 2.83

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18   30a   initial pH: use K_a and ICE table to solve for $x = [H_3O^+] = 4.5 \times 10^{-6}$ M $\Rightarrow$ pH = 5.35

         30b   Half-way to the equivalence point: have added ½ the stoichiometric quantity, so [HCN] = [CN-]
                  thus, the pH we would observe would be equal to the pK_a of the weak acid, = 9.40
                          $\rightarrow$ this is the inflection point in the buffer region of the titration curve

         30c   When 95% of the NaOH has been added: have converted 95% of HCN to CN-
                  thus: have 0.0012 mol CN^- and 6×10^{-5} mol HCN present in the same volume of solution
                  so: pH = pK_a + log(CN⁻/HCN) = 10.7 by using moles instead of [ ]'s because V's would cancel out

         30d   volume NaOH added to reach equivalence point = 17 mL

         30e   At equivalence point: CN^- equilibrates with water… $[CN^-]$ starts at 0.030 M (remember new total V)
                  Find $K_b = K_w/K_a = 2.5 \times 10^{-5}$; use ICE table & K_b to solve for $x = [OH^-] = 8.7 \times 10^{-4}$ M
                  pH = 14 – pOH = 10.94

         30f   alizarin yellow R (from Zumdahl's table 15.8) would be suitable since starts turning orange at pH 11

         30g   when have added 105% required NaOH: pH depends primarily on the excess OH- added.
                  Excess = 5% molar excess of OH-...ie calculate 5% of (#moles of HCN) to find extra moles of OH^-
                  = 6×10^{-5} mol OH^- excess. Note we also need to figure out what total volume of NaOH solution added to
                  get to this point. Then, calculate pH of solution with 6×10^{-5} mol/0.042 L OH^- $\Rightarrow$ pH = 14 – pOH = 11.17

18   32

titration	pH at equivalence point	possible indicator
HCO_3^- titrated with HCl	pH < 7 (about 3-4)	bromcresol green
HClO with NaOH	pH > 7 (about 10-11)	thymolphthalein
$(CH_3)_3N$ with HCl	pH < 7 (about 5-6)	methyl red

18   36a   soluble (most nitrate salts are soluble)
         36b   insoluble (most hydroxide salts are insoluble)
         36c   soluble (most chloride salts are soluble)
         36d   insoluble (most sulfide salts are insoluble)

18   38a $PbSO_4(s) \rightleftarrows Pb^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = [Pb^{2+}][SO_4^{2-}]$
         38b $BaF_2(s) \rightleftarrows Ba^{2+}(aq) + 2F^-(aq)$ $K_{sp} = [Ba^{2+}][F^-]^2$
         38c $Ag_3PO_4(s) \rightleftarrows 3Ag^+(aq) + PO_4^{3-}(aq)$ $K_{sp} = [Ag^+]^3[PO_4^{3-}]$

18   42 $[Ca^{2+}] = 0.0140$ M $\Rightarrow$ $K_{sp} = [Ca^{2+}][OH^-]^2 = 5.5 \times 10^{-5}$

18   44   pOH = 1.32; $[OH^-] = 0.048$ M; $[Ca^{2+}] = ½ [OH^-] = 0.024$ M; $\Rightarrow$ $K_{sp} = 5.5 \times 10^{-5}$

18   46 $K_{sp} = [Au^+][Cl^-] = x^2$ $\Rightarrow$ $x = 4.5 \times 10^{-7}$ M = $[Au^+]$

18   50 $K_{sp} = [Pb^{2+}][SO_4^{2-}] = x^2$ $\Rightarrow$ $x = 1.6 \times 10^{-4}$ M = $[Pb^{2+}]$ = concentration of dissolved $PbSO_4$ since 1:1
                thus: use that conc. to find mass of lead sulfate dissolved = 12 mg in 1 L

18   52a   AgSCN -- note: can directly compare K_{sp}s when compounds have same ratios of cations to anions
         52b $SrSO_4$
         52c PbI_2 (caution: solubility must be calculated in order to predict this…because K_{sp}s depend on how many of
                each ion are involved…cannot simply compare K_{sp}s to compare AgI and PbI_2!!)
         52d CaF_2

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18   54 $K_{sp} = 5.4 \times 10^{-13} = [Ag^+][Br^-] = x^2$
               …where solubility of AgBr in pure water $= 7.3 \times 10^{-7}$ mol/L, & note 1Br⁻, 1Ag⁺ per AgBr…
               For a solution of 0.0065M Br-, helpful now to use ICE table along with K_{sp}…
               $K_{sp} = 5.4 \times 10^{-13} = x(0.0065 + x)$ with approximation $= 0.0065x$
               Solve for $x = 8.3 \times 10^{-11}$ mol/L, $= [Ag^+]$ but also = solubility… Note much lower now! Common-ion effect.

18   58a Ag_2CO_3
        58b $PbCO_3$
        58c   AgCN

18   60a $Q = 2.4 \times 10^{-9} < K_{sp}$ therefore $NiCO_3$ will not precipitate
        60b $Q = 2.4 \times 10^{-7} > K_{sp}$ therefore $NiCO_3$ will precipitate

18   64 $[OH^-] = 0.0025$ M; $[Mg^{2+}] = 0.075$ M; $Q = 4.7 \times 10^{-7} > K_{sp}$ therefore $Mg(OH)_2$ will precipitate

18   66   when adding two sequential equilibrium reactions: add the reaction equations, but multiply the K's
               So: net rxn is $AgI(s) + 2\,CN^-(aq) \rightleftarrows Ag(CN)_2^-(aq) + I^-(aq)$
                              $K_{net} = K_{sp}$ (for AgI) $\times K_{formation}$ (for $Ag(CN)^{2-}$) = 480

18   74a   pH > 7. The solution will contain the conjugate base of the weak acid (and counter ion…)
        74b   pH > 7. The solution will contain the NH_3/NH_4^+ pair (a buffer!)
        74c   pH = 7. The solution will contain neutral ions.
        74d   pH = 7. The solution will contain neutral ions.

18   76   For CaF_2 to precipitate, Q must exceed K_{sp} $(5.3 \times 10^{-11}) = [Ca^{2+}][F^-]^2$…
               If $[Ca^{2+}]_{eqm}$ is fixed at 2.0×10^{-3}, then to ppt, $[F^-]_{eqm} = \sqrt{(5.3 \times 10^{-11}/2.0 \times 10^{-3})} = 1.6 \times 10^{-4}$ M
               $\Rightarrow$ any concentration of F^- higher than 1.6×10^{-4} M will make $Q > K_{sp}$ & lead to precipitation

18   78a   use K_b and ICE table $\Rightarrow$ solve for $x = [OH^-] = 5.7 \times 10^{-4}$ M… so pH = 14 - pOH = 10.75
        78b   calculate moles of ethanolamine $= 2.5 \times 10^{-4}$ mol; in total volume 0.0513 L; so [ethanolamine] = 0.049 M
               Find $K_a = K_w/K_b = 3.1 \times 10^{-10}$; use ICE table & K_a to solve for $x = [H_3O^+] = 1.2 \times 10^{-6}$ M $\Rightarrow$ pH = 5.91
        78c   At titration midpoint (half-way to equivalence point), $[HOCH_2CH_2NH_2] = [HOCH_2CH_2NH_3^+]$
               therefore pH = pK_a = 9.51
        78d   methyl red would be a good choice of indicator

18   80 $K_{sp} = [Sr^{2+}][CO_3^{2-}] = 5.6 \times 10^{-10} \ldots = x^2$, where x = solubility of $SrCO_3$. solve $x = 2.4 \times 10^{-5}$ M
               thus, in 1L, have 3.5 mg of $SrCO_3$ dissolved in a saturated solution.

18   82   use H.-H. equation since is a buffer: given pH, can solve for ratio $[HPO_4^{2-}]/[H_2PO_4^-] = 3.5$
               calculate moles H_3O^+ added: 0.0160 mol because added HCl, a strong acid…
               The total H_3O^+ available can be used to produce HPO_4^- (from $H_3O^+ + PO_4^{3-}$) and $H_2PO_4^-$ $(2H_3O^+ + PO_4^{2-})$
               Total $H_3O^+ = 0.160$ mol = (mol HPO_4^{2-} + 2× mol $H_2PO_4^-$) = (3.5× mol $H_2PO_4^-$ + 2× mol $H_2PO_4^-$)
                        So use this expression to solve for moles of $H_2PO_4^-$ (now the only unknown…) = 0.010 mol
               Total mol PO_4^{3-} needed = mol HPO_4^{2-} + mol $H_2PO_4^-$ = 0.0029 mol + 0.010 mol = 0.013 mol PO_4^{3-}
               Convert 0.013 mol Na_3PO_4 into mass: 2.1g

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18 **86a** 0.0123 mol $C_6H_5CO_2H$; 0.0104 mol $NaC_6H_5CO_2$; use H.-H. eqn to solve for buffer's pH: = 4.13

86b to lower pH to 4.00, must additional acid form $C_6H_5CO_2H$. Use H.-H. to find #mol $C_6H_5CO_2H$ needed.
Solve for x = 0.017 mol $C_6H_5CO_2H$; but already have 0.0123 mol, so need (0.017-0.0123 mol) more…
 convert to mass = 0.5g extra $C_6H_5CO_2H$ needed

86c another way to do it would be to add some HCl to the original buffer until reaches pH of 4.00.
to predict how much to add: use H.-H. eqn to find required A-/HA ratio = 0.63

$$\frac{[C_6H_5CO_2^-]}{[C_6H_5CO_2H]} = \frac{mol\ C_6H_5CO_2^-}{mol\ C_6H_6CO_2H} = 0.63 = \frac{0.0104 - x}{0.0123 + x}$$ solve for x, = 0.0016 mol H_3O^+ needed

thus: starting with 2.0M HCl, must add 8.2×10^{-4} L, or 0.82 mL

18 **90** $K_{sp} = 4.9 \times 10^{-17} = [Fe^{2+}][OH^-]^2 = (0.1)[OH^-]^2 \Rightarrow$ [OH⁻] required to ppt $Fe(OH)_2$(s) from soln = 2.2×10^{-8} M
$K_{sp} = 1.4 \times 10^{-15} = [Pb^{2+}][OH^-]^2 = (0.1)[OH^-]^2 \Rightarrow$ [OH⁻] required to ppt $Pb(OH)_2$(s) from soln = 1.2×10^{-7} M
$K_{sp} = 1.3 \times 10^{-33} = [Al^{3+}][OH^-]^2 = (0.1)[OH^-]^2 \Rightarrow$ [OH⁻] required to ppt $Al(OH)_3$(s) from soln = 2.4×10^{-11} M
Thus, $Al(OH)_3$ will precipitate first, followed by $Fe(OH)_2$, then $Pb(OH)_2$

18 **92** add the reactions: $Zn(OH)_2$(s) + 2 CN⁻(aq) $\rightleftarrows$ $Zn(CN)_2$(s) + 2OH⁻(aq)
multiply the eqm constants: $K_{net} = K_{sp}$ (for $Zn(OH)_2$) $\times$ K (for 2nd rxn = $1/K_{sp}$ for $Zn(CN)_2$) = 4×10^{-6}
Thus: overall, the eqm lies to the left. We can tell that the transformation of zinc hydroxide into zinc cyanide will not occur to a large extent because of the unfavourable (small) equilibrium constant.

18 **98** $Ba(OH)_2$ and $BaCO_3$

18 **102a** HB is a stronger acid than HA
102b A⁻ is a stronger base than B⁻.

18 **104a** As the pH increases, the first ionization equilibrium H_2CO_3(aq) + H_2O(l) $\rightleftarrows$ HCO_3^- (aq) + H_3O^+(aq)
shifts to the right and more HCO_3^- is produced. As the pH rises further, the second ionization occurs
HCO_3^- (aq) + H_2O(l) $\rightleftarrows$ CO_3^{2-} (aq) + H_3O^+(aq)   and is shifted to the right with increasing pH, which
decreases the amount of HCO_3^- present in the solution.

104b At pH = 6.0, the solution is 72% H_2CO_3 and 28% HCO_3^-.
At pH = 10.0, the solution is 66% HCO_3^- and 33% CO_3^{2-}.

104c A solution buffered at pH = 11.0 should have a HCO_3^- to CO_3^{2-} ratio of 0.2 to 1.