Ch18 Aqueous Ionic Equilibrium

Exercises

27) only d) due to common ion NO_2^-

28) $HCHO_2 \rightleftharpoons H^+ + CHO_2^-$

c) $\uparrow CHO_2^-$ pushes $\leftarrow$ $\uparrow pH$

29 + 37) $HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$

a)

$HCHO_2$	H_3O^+	CHO_2^-
0.20	≈ 0	0.15
$-x$	$+x$	$+x$
$0.20-x$	x	$0.15+x$

$K_a = \frac{x(0.15+x)}{0.20-x} = 1.8\times10^{-4}$ assume $x << 0.15 < 0.20$

$\frac{x(0.15)}{0.20} = 1.8\times10^{-4}$ $x = 2.4\times10^{-4} = [H_3O^+]$

$\frac{2.4\times10^{-4}}{0.15}\times100 = 0.16\%$

$pH = 3.62$

$pH = pK_a + \log\frac{[base]}{[acid]} = -\log(1.8\times10^{-4}) + \log\frac{0.15}{0.20} = 3.62$

b) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

NH_3	NH_4^+	OH^-
0.16	0.22	≈ 0
$-x$	$+x$	$+x$
$0.16-x$	$0.22+x$	x

$K_b = 1.76\times10^{-5} = \frac{x(0.22+x)}{0.16-x}$

$x = 1.28\times10^{-5} = [OH^-]$

$pOH = 4.89$ $pH = 9.11$

$pH = pK_a + \log\frac{[base]}{[acid]}$ $K_a = \frac{1.0\times10^{-14}}{1.76\times10^{-5}} = 5.68\times10^{-10}$ $pK_a = 9.25$

$= 9.25 + \log\frac{0.16}{0.22} = 9.11$

31) Benzoic $HC_7H_5O_2$ 0.15M ($\rightarrow K_a = 6.5\times10^{-5}$) % ionized in H_2O vs 0.10M $NaC_7H_5O_2$

$\frac{x^2}{0.15-x} = 6.5\times10^{-5}$

$x = 3.1\times10^{-3} / 0.15 \times 100 = 2.1\%$

$0.15-x$ x $0.10+x$

$\frac{x(0.10+x)}{0.15-x} = 6.5\times10^{-5}$

$x = 9.75\times10^{-5} / 0.15 \times 100 = 0.065\%$

% ionization decreases due to common ion

~~33) a) 0.15M HF $K_a = 3.5\times10^{-4}$~~

~~$\frac{x^2}{0.15-x} = 3.5\times10^{-4}$ $x = 7.2\times10^{-3}$ *4.8% $pH = 2.14$~~

~~c) use HH~~

~~$pH = pK_a + \log\frac{0.15}{0.15}$~~

~~$pH = -\log 3.5\times10^{-4} = 3.46$~~

~~0.15M NaF $K_b = 2.85\times10^{-11}$~~

~~$F^- + H_2O \rightarrow HF + OH^-$~~

F^-	HF	OH^-
0.15	0	0
$0.15-x$	x	x

~~$\frac{x^2}{0.15-x} = 2.85\times10^{-11}$~~

~~$x = 2.1\times10^{-6}$~~

~~$pOH = 5.68$ $pH = 8.32$~~

35) $HC_2H_3O_2$ / $NaC_2H_3O_2$ acid $HCl + NaC_2H_3O_2 \rightarrow HC_2H_3O_2 + NaCl$

$H^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2$ acid reacts w/ CB

base $NaOH + HC_2H_3O_2 \rightarrow H_2O + NaC_2H_3O_2$ base reacts w/ WA

$OH^- + HC_2H_3O_2 \rightarrow H_2O + C_2H_3O_2^-$

39 a) $pH = -\log(2.9\times10^{-8}) + \log\frac{0.155}{0.135} = 7.60$

Ka HClO

c) $\frac{10.0g\ HC_2H_3O_2}{0.1500L} \times \frac{1mol}{60.05g} = 1.11M$

$\frac{10.0g\ NaC_2H_3O_2}{0.1500L} \times \frac{1mol}{82.04g} = 0.812M$

c (cont) $pH = -\log 1.8\times10^{-5} + \log\frac{0.812}{1.11} = 4.61$

41b) $M_{NH_3} = \frac{(0.10M)(125.0mL)}{(375.0mL)} = 0.033M$ $M_{NH_4^+} = \frac{(0.10M)(250.0mL)}{(375.0mL)} = 0.067M$

$pKa = 9.25$

$pH = 9.25 + \log\frac{0.033}{0.067} = 8.94$

45) 150.0mL buffer of 0.15M $HC_7H_5O_2$ + g $NaC_7H_5O_2$? pH = 4.25 $K_a = 6.5\times10^{-5}$

$4.25 = \underbrace{-\log 6.5\times10^{-5}}_{-4.187} + \log\left(\frac{[NaC_7H_5O_2]}{0.15}\right)$ $10^{0.063} = \frac{[NaC_7H_5O_2]}{0.15}$

$[\ ] = 0.173M$

$0.150L \times \frac{0.173mol}{L} \times \frac{144.11g\ NaC_7H_5O_2}{1mol} = 3.7g$

47) Similar to Buffer lab! 250.0mL buffer 0.250M HAc/NaAc

a) $pH = 4.74 + \log\frac{0.250}{0.250}$ $(pH = pKa) = 4.74$

$0.2500L \times 0.250mol/L$
$= 0.0625$ mol HAc/NaAc

b) add 0.0050 mol HCl

	HCl	+ $NaC_2H_3O_2$	$\rightarrow HC_2H_3O_2$	+ NaCl
before	0	0.0625	0.0625	0
add	+0.0050	−0.0050	+0.0050	0.0050
after	all reacted = 0	0.0575 mol	0.0675 mol	

H^+ will react w $C_2H_3O_2^-$
$\longrightarrow$ $C_2H_3O_2^- \downarrow$ while
$HC_2H_3O_2 \uparrow$

L would cancel

$pH = 4.74 + \log\frac{0.0575}{0.0675} = 4.68$

c) add NaOH 0.0050 mol reverse happens $C_2H_3O_2^- \uparrow$ $HC_2H_3O_2 \downarrow$

$pH = 4.74 + \log\frac{0.0675}{0.0575} = 4.81$

53 a) yes $\frac{\text{base}}{\text{acid}} = \frac{0.10}{0.15} = 0.67$ (range betw 0.10 – 10 pg 766)

b) No SA + SB c) Yes NaOH will convert $\frac{20.0}{50.0} \times 100$ 40% of HF to NaF (F^- conj base)
(Not completely neutralized) d) No both are bases

55) a) Blood plasma 0.024 M HCO_3^- 0.0012 M H_2CO_3 (pKa = 6.1)

$pH = 6.1 + \log \frac{0.024}{0.0012} = 7.4$

b) $7.4 = 6.1 + \log \frac{[HCO_3^-]}{[H_2CO_3]}$ $\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{0.9} = \frac{7.9}{1}$ ratio

moles $5.0L \times 0.024 = 0.12$ mol HCO_3^-
$5.0L \times 0.0012 = 0.0060$ mol H_2CO_3

	H^+ +	HCO_3^- →	H_2CO_3
before	0	0.12	0.0060
add	x	−x	+x
after	0	0.12−x	0.0060+x

$\frac{[0.12-x]}{[0.0060+x]} = 7.9$ $0.0474 + 7.9x = 0.12 - x$
$8.9x = 0.0726$
$x = 0.00815$ mol

$0.008\text{mol HCl} \times \frac{36.46\text{g HCl}}{1\text{mol}} = 0.3\text{g HCl}$

c) $7.8 = 6.1 + \log \frac{[HCO_3^-]}{[H_2CO_3]}$ $\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{1.7} = 50.1 = \frac{0.12+x}{0.0060-x}$

reverse for base

$x = 0.0035$ mol NaOH

$0.0035\text{mol} \times \frac{40.00\text{g}}{1\text{mol}} = 0.14$ g NaOH

57) closest pKa is HClO/KClO $-\log(2.9 \times 10^{-8}) = 7.54$

$7.20 = 7.54 + \log \frac{[KClO]}{[HClO]}$ $\frac{[KClO]}{[HClO]} = 10^{-0.34} = \frac{0.457}{1}$

since L will cancel out mol/mol use molar masses

$0.457 \left(\frac{90.55\text{g KClO}}{52.46\text{g HClO}} \right) = \frac{0.79\text{g KClO}}{1\text{ g HClO}}$

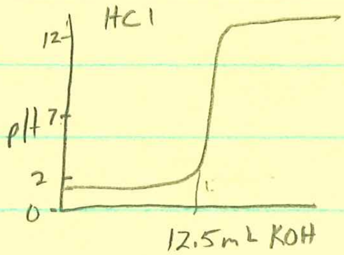
61) i) a → pH ≈ 8 b pH ≈ 7 ii) a is WA b is SA
shows buffer region ↳ flat initial w/ sharper rise @ eq pt

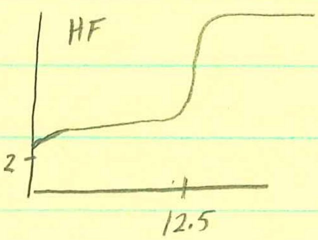
(2) 25.0 mL of 0.100M HCl   0.100M HF   titrate w/ 0.200 M KOH

a) Same volume to reach eq pt for both since init conc + vol of acids are equal
(Both monoprotic)

$25.0\,mL \times \frac{0.100\,mol}{1000\,mL} = 0.00250\,mol\ acid = 0.00250\,mol\ KOH \times \frac{1000\,mL}{0.200\,mol} = 12.5\,mL$
(½ since 2×[ ])

b) HCl ≃ 7 HF will be basic since F^- is produced c) HCl stronger acid ionizes completely

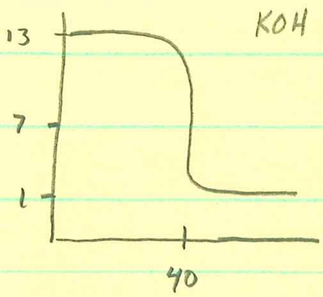
d) 

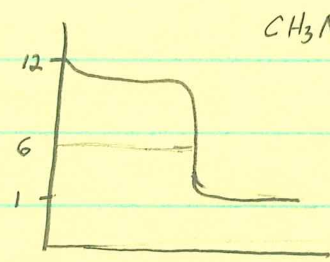


★ Compare to #66

63) a) need 2 vol HI (40.0mL) for both since [ ] ½ b) KOH near 7 CH_3NH_2 will be acidic ($CH_3NH_3^+$ produced)

c) CH_3NH_2 will have lower initial pH since it is a WB vs KOH SB

d) 



★ Compare to # 64

65 a) ~pH 9 Vol ~30mL b) Ø add pH would depend on ICE calc of H^+ e) beyond 30 mL

c) 15mL pH = pKa @ ½ eq pt d) at eq pt 30mL all acid has been converted to conj base

67) 35.0 mL 0.175 M HBr w/ 0.200 KOH a) pH = −log 0.175 = 0.757

b) $35.0\,mL\ HBr \times \frac{0.175\,mol\ HBr}{1000\,mL} \times \frac{1\,mol\ KOH}{1\,mol\ HBr} \times \frac{1000\,mL\ KOH}{0.200\,mol} = 30.6\,mL\ KOH$

c) 10.0 mL added KOH pH = ? $10.0\,mL \times \frac{0.200\,mol}{1000\,mL} = 0.00200\,mol\ KOH$

	KOH +	HBr →	KBr +	H_2O
before	Ø	0.006125	Ø	
add	0.00200	−0.00200		
after	Ø	0.004125	0.00200	

$[HBr] = \frac{0.004125\,mol}{0.0450\,L} = 0.09166\,M$

pH = 1.038

d) pH @ eq should be 7 (No acid or Base)

e) 5.0 mL KOH beyond $5.0\,mL \times \frac{0.200\,mol}{1000\,mL} = 0.0010\,mol\ KOH$ excess

$\frac{0.0010\,mol}{35.0 + 30.6 + 5.0\,mL}$ $\frac{0.0010\,mol}{0.0706\,L} = 0.014\,M\ KOH$ pOH = 1.85   pH = 12.15

#s 72 and 74 similar to examples in text (review in class?)

75) i) Acid "a" is more conc eq pt is near 38mL vs "b" @ 30mL

ii) Acid "b" has larger ka $pH = pKa$ @ ½ eq pH @ ½ eq pt is lower for "b"

76) i) base "b" more conc - higher vol for eq pt

ii) base "b" has larger K_b since pH is higher @ ½ eq pt

77) *Similar to Ka of monoprotic acid Lab calc

eq pt = 25mL $25mL\ NaOH \times \frac{0.112mol\ NaOH}{1000mL} \times \frac{1mol\ HA}{1mol\ NaOH} = \underline{0.0028 mol\ HA}$ $\frac{0.229g}{0.0028mol}$

$= 82g/mol$

81) Methyl red $pKa = 5.0$ in 0.100M HCl it will appear red

acid red
base yellow

pH range ±1 pKa changes from red to yellow between pH= 4.0-6.0

85) a) $BaSO_{4(s)} \rightleftharpoons Ba^{+2}_{(aq)} + SO_{4(aq)}^{-2}$ $Ksp = [Ba^{+2}][SO_4^{-2}]$

b) $PbBr_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Br^-_{(aq)}$ $Ksp = [Pb^{+2}][Br^-]^2$

87) a) AgBr $Ksp = 5.35 \times 10^{-13} = s^2$ $s = 7.31 \times 10^{-7} M$

b) $Mg(OH)_2$ $Ksp = 2.06 \times 10^{-13} = S(2S)^2$ $4s^3 = 2.06 \times 10^{-13}$

☆ $Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2(OH^-)$ $Ksp = [Mg^{+2}][OH^-]^2$ $S = 3.72 \times 10^{-5} M$

S 2S

89) a) Mx $Ksp = s^2 = (3.7 \times 10^{-11})^2 = 1.07 \times 10^{-21}$

b) PbF_2 $S = 5.63 \times 10^{-3} M$ $Ksp = S(2S)^2 = 4(5.63 \times 10^{-3})^3 = 7.14 \times 10^{-7}$

95 a) BaF_2 in H_2O $K_{sp} = s(2s)^2 = 2.45 \times 10^{-5}$ $s = 1.83 \times 10^{-2} M$

b) BaF_2 in 0.15M NaF $BaF_2 \rightleftharpoons Ba^{+2} + 2F^-$ $K_{sp} = [Ba^{+2}][F^-]^2 = 2.45 \times 10^{-5}$

	Ba^{+2}	$2F^-$
	0	0.15
	s	2s
	s	0.15+2s

assume $2s << 0.15$

$(s)(0.15)^2 = 2.45 \times 10^{-5}$

$s = 1.09 \times 10^{-3} M$

$\frac{2(1.09 \times 10^{-3})}{0.15} \times 100 = 1.5\%$

$Ca^{+2} + 2F^- \rightarrow CaF_2$

101) 0.015 M NaF 0.010 M $Ca(NO_3)_2$ K_{sp} $CaF_2 = 1.46 \times 10^{-10}$

$Q = [Ca^{+2}][F^-]^2 = [0.010M][0.015]^2 = 2.3 \times 10^{-6} > 1.46 \times 10^{-10}$

a precip will form (CaF_2)

102) 0.013 M KBr 0.0035 M $Pb(C_2H_3O_2)_2$ K_{sp} $PbBr_2 = 4.67 \times 10^{-6}$

$Q = [Pb^{+2}][Br^-]^2 = [0.0035][0.013]^2 = 6.0 \times 10^{-7} < 4.67 \times 10^{-6}$

No $PbBr_2$ will form