1B

# Answers-Review Problems for Final Part 1

1. a. $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

$\Delta H^\circ = +55.89$ kJ , $\Delta S^\circ = -80.45$ J/K

$\Delta G^\circ = 55890\,J - (310.K)(-80.45\,J/K) = 80829.5\,J$

$K = e^{-\Delta G^\circ/RT} = e^{\left[\frac{-80829.5\,J}{(8.314\,J/mol)(310K)}\right]} = e^{-31.36}$

$K = 2.4 \times 10^{-14}$

b. Neutral: $[H^+]=[OH^-]$

$x^2 = 2.4 \times 10^{-14}$

$x = 1.55 \times 10^{-7}$ M $H^+$

pH = 6.81

$H_2O \rightleftharpoons H^+ + OH^-$

$K_w = [H^+][OH^-] = x^2$

| | | |
|---|---|---|
| lots | 0 | 0 |
| $-x$ | $+x$ | $+x$ |
| | $x$ | $x$ |

also: pOH = 6.81 and pH + pOH = 13.62, not 14.00!

2. $HX + H_2O \rightleftharpoons H_3O^+ + X^-$

| | | | |
|---|---|---|---|
| 0.10 | lots | 0 | 0 |
| $-x$ | | $+x$ | $+x$ |
| $0.10-x$ | | $x$ | $x$ |

$K_a = \frac{x^2}{0.10-x}$

pH = 3.72

$[H_3O^+] = 1.905 \times 10^{-4}$ M $= x$

$K_a = \frac{(1.905\times10^{-4})^2}{(0.10-1.905\times10^{-4})}$

$K_a = 3.6 \times 10^{-7}$ so $K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{3.6\times10^{-7}} = 2.755 \times 10^{-8} = K_b$ of $X^-$

$X^- + H_2O \rightleftharpoons HX + OH^-$

| | | | |
|---|---|---|---|
| 0.10M | lots | 0 | 0 |
| $-x$ | | $+x$ | $+x$ |
| $0.10-x$ | | $x$ | $x$ |

$K_b = \frac{x^2}{0.10-x} = 2.755 \times 10^{-8}$ $K_b$ small neglect $x$

$x = \sqrt{K_b(0.10)} = 5.25 \times 10^{-5}$ M $OH^-$

pOH = 4.28 pH = 9.72

3. a) They have different coefficients, so they must have diff values of $\Delta G^\circ$ -- $\Delta G^\circ$ is per mole of reactants + products as written.

b) different $\Delta G^\circ$, different K value $\Delta G^\circ = -RT \ln K$

K also depends on how you write the rxn.

c) The solubility is always the same under the same conditions. It doesn't "know" how you're writing the reaction! You'll get the same result using either equation.

3. d) $\Delta G = \Delta G^\circ + RT \ln Q$

using first eq $Q = \frac{[Mg^{2+}]}{[H^+]^2} = \frac{0.10}{(0.50)^2} = 0.40$

$\Delta G = -95.3\times10^3 J + (8.314)(298) \ln 0.4$

$\Delta G = -97570\ J$ spontaneous yes some $Mg(OH)_2$ will dissolve.

e) $Q = \frac{2.0}{(0.010)^2} = 20000$ $\Delta G = -95.3\times10^3 J + (8.314)(298) \ln 20000$

$\Delta G = -70763\ J$ yes spont.

f) want $\Delta G$ to be ⊕. Use $\Delta G = 0$ as the "dividing line" spont/nonspont

$\Delta G = 0 = -95300 J + (8.314)(298) \ln Q$ $\ln Q = 38.47$

$Q = \frac{[Mg^{2+}]}{[H^+]^2} = \frac{2}{(H^+)^2} = 5.1\times10^{16}$ $Q = e^{38.47} = 5.1\times10^{16}$

$H^+ = \sqrt{\frac{2.0}{5.1\times10^{16}}} = 6.3\times10^{-9}$

$pH = 8.20$

4. ⓐ $\underset{A}{HPO_4^{2-}} + \underset{B}{CN^-} \rightleftharpoons \underset{A}{HCN} + \underset{B}{PO_4^{3-}}$ Look up $K_a$ values for $HPO_4^{2-}$ and HCN

ⓑ $K_a$ HCN > $K_a$ $HPO_4^{2-}$ Rxn lies toward weaker acid/base lies to left. $K < 1$

ⓒ ① $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$ $K_a = 3.6\times10^{-13}$

② $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$ $K_a = 4.0\times10^{-10}$

reverse Rxn 2, add, cancel

$HPO_4^{2-} + CN^- \rightleftharpoons HCN + PO_4^{3-}$ $K = \frac{3.6\times10^{-13}}{4.0\times10^{-10}} = 9.0\times10^{-4}$

5. $HAc + OH^- \rightarrow H_2O + Ac^-$ at eq. point, equal moles HA + $OH^-$ added.

0.005 0.005 0 0.005 mol

$0.050\ L \times 0.100 \frac{mol}{L} = 0.0050$ mol HA

so 0.0050 mol $OH^-$

$(0.0050\ mol\ OH^-)\left(\frac{L}{.200\ mol}\right) = 0.025\ L$ 25.0 mL KOH used $V_{tot} = 75$ mL

@ end, have $Ac^-$, a weak base. $\frac{0.005\ mol}{0.075\ L} = 0.06667\ M\ Ac^-$

$Ac^- + H_2O \rightleftharpoons HAc + OH^-$ $K_b = \frac{K_w}{K_a HAc} = 5.5556\times10^{-10}$

| | | | |
|---|---|---|---|
| 0.06667 | lots | 0 | 0 |
| −x | | +x | +x |
| 0.06667−x | | x | x |

$K_b = \frac{x^2}{0.06667-x} = 5.5556\times10^{-10}$ neglect x

$x = \sqrt{K_b(0.06667)} = 6.086\times10^{-6}\ M\ OH^-$

$pOH = 5.22$ $pH = 8.78$

6. $N_2O_4 \rightleftharpoons 2\,NO_2$ 12.8% dissociated x = amt dissociated

| | | |
|---|---|---|
| 1.50 atm | 0 | |
| −x | +2x | |
| 1.50−x | 2x | |

so x is 12.8% of 1.50

$\frac{x}{1.50} \times 100 = 12.8$ x = 0.192 atm

1.50 − x = 1.308 atm 2x = 0.384 atm

$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(0.384)^2}{(1.308)} = 0.113$

7. a) Strong acid M $H_3O^+$ = 0.205 M pH = 0.69 red

b) weak base + strong acid 0.3500 L × 0.205 M = 0.07175 mol $HNO_3$

0.2500 L × 0.500 M = 0.125 mol $NaNO_2$

$NO_2^- + H_3O^+ \rightarrow HNO_2 + H_2O$

| | | | |
|---|---|---|---|
| 0.125 | 0.07175 | 0 | lots |
| −0.07175 | −0.07175 | +0.07175 | |
| 0.05325 | 0 | 0.07175 mol | |

buffer

$K_a = (H_3O^+)\left(\frac{mol\ A^-}{mol\ HA}\right)$

$[H_3O^+] = K_a\left(\frac{mol\ HA}{mol\ A^-}\right) = 6.1 \times 10^{-4}$ M $H_3O^+$

pH = 3.22

c) To our buffer, add 0.150 L × .100 M = 0.015 mol NaOH - will react w/ $HNO_2$

$HNO_2 + OH^- \rightarrow H_2O + NO_2^-$

| | | |
|---|---|---|
| 0.07175 | 0.015 | 0.05325 |
| −0.015 | −0.015 | +0.015 |
| 0.05675 | 0 | 0.06825 |

$H^+ = K_a\left(\frac{mol\ HA}{mol\ A^-}\right) = 4.5 \times 10^{-4}\left(\frac{0.05675}{0.06825}\right)$

$H^+ = 3.7 \times 10^{-4}$ pH = 3.42 yellow

d) 5.00 g $Ba(OH)_2$ MM = 171.3 $(5.00\ g)\left(\frac{1\ mol}{171.3\ g}\right) = 0.0292$ mol $Ba(OH)_2$ × 2

= 0.0584 mol $OH^-$

$HNO_2 + OH^- \rightarrow NO_2^- + H_2O$

| | | |
|---|---|---|
| 0.05675 | 0.0584 | 0.06825 |
| −0.05675 | −0.05675 | +0.05675 |
| 0 | 0.00165 | 0.125 mol |
| | 0.0022 M | 0.167 M |

weak base + strong base
common-ion effect
Need [ ] $V_{tot}$ = 750 mL

$NO_2^- + H_2O \rightleftharpoons OH^- + HNO_2$

| | | | |
|---|---|---|---|
| 0.167 M | lots | 0.0022 M | 0 |
| −x | | +x | +x |
| 0.167−x | | 0.0022+x | x |

$K_b = 2.2 \times 10^{-11} = \frac{(x)(0.0022+x)}{(0.167-x)}$

neglect x

$x = 2.2 \times 10^{-11}\left(\frac{0.167}{0.0022}\right) = x = 1.67 \times 10^{-9}$ M

$[OH^-] = 0.0022\,M + x \approx 0.0022\,M$

pOH = 2.66 pH = 11.34 blue

8. 0.25 M $H_3PO_4$

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

| | | | |
|---|---|---|---|
| 0.25 | lots | 0 | 0 |
| −x | | +x | +x |
| 0.25−x | | x | x |

$K_a = 7.5\times10^{-3} = \frac{x^2}{0.25-x}$

Can't neglect x - use successive approx. $\frac{HA}{K_a} = 33$

① neglect x $\quad x = \sqrt{K_a(0.25)}$ $\quad x_1 = 0.0433$ M

②
$x_2 = \sqrt{K_a(0.25-x_1)} = 0.0394$ M
$x_3 = \sqrt{K_a(0.25-x_2)} = 0.0397$ M
$x_4 = \sqrt{K_a(0.25-x_3)} = 0.0386$ M
$x_5 = \sqrt{\phantom{x}} = 0.0384$ M
$x_6 = 0.0397$ close enough.

$[H_3O^+] = 0.040$ M $\quad$ pH = 1.40 $\quad [H_2PO_4^-] = 0.040$ M

$H_3PO_4 = 0.25 - 0.040 = 0.21$ M

2nd ionization:

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$

| | | | |
|---|---|---|---|
| 0.040 | lots | 0.040 | 0 |
| −x | | +x | +x |
| 0.040−x | | 0.040+x | x |

$K_{a2} = \frac{(x)(0.040+x)}{(0.040-x)} = 6.2\times10^{-8}$

neglect x

$K_{a2} = \frac{x(0.040)}{(0.040)}$

$x = 6.2\times10^{-8} = [HPO_4^{2-}]$

3rd ionization

$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$

| | | | |
|---|---|---|---|
| $6.2\times10^{-8}$ | lots | 0.040 | 0 |
| −x | | +x | +x |
| $6.2\times10^{-8}-x$ | | 0.040+x | x |

$K_{a3} = \frac{(x)(0.040+x)}{(6.2\times10^{-8}-x)} = 3.6\times10^{-13}$

neglect x

$x = \frac{K_{a3}(6.2\times10^{-8})}{0.040} = 5.6\times10^{-19}$ M $PO_4^{3-}$

9. $PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$

| | | | |
|---|---|---|---|
| 0.10 M | lots | 0 | 0 |
| −x | | +x | +x |
| 0.10−x | | x | x |

$K_b = \frac{K_w}{K_a \text{ of } HPO_4^{2-}} = 2.778\times10^{-2}$

$K_b = \frac{x^2}{0.10-x}$ $\quad$ can't neglect x!

Successive approx

① neglect x $\quad x_1 = \sqrt{K_b(0.10)} = 0.0527$ M $\quad x_4 = 0.0401$ M

② $x_2 = \sqrt{K_b(0.10-x_1)} = 0.0362$ M $\quad x_5 = 0.0408$ M

$x_3 = \phantom{x} = 0.0421$ M $\quad x_6 = 0.0405$ M close enough.

9. $x = [OH^-] = 0.0405\ M$ $\quad pOH = 1.39$ $\quad pH = 12.61$

10. $AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$ need K

$AgCl \rightleftharpoons Ag^+ + Cl^-$ $\quad K_{sp} = 1.8 \times 10^{-10}$

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $\quad K_f = 1.6 \times 10^7$ add rxns

$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$ $\quad K = K_{sp}K_f = 0.00288$

| | | | |
|---|---|---|---|
| some | 3.00 M | 0 | 0 |
| $-x$ | $-2x$ | $+x$ | $+x$ |
| | $3.00-2x$ | $x$ | $x$ |

$K = \frac{x^2}{(3.00-2x)^2} = 0.00288$

$\sqrt{\ }$ of both sides

$\frac{x}{3.00-2x} = 0.05367$

$x = 0.05367(3-2x)$

$x = 0.161 - 0.10734x$

$+0.10734x \quad +0.10734x$

$1.10734x = 0.161$

$x = \cancel{0.556}\ 0.1454\ M$ AgCl dissolves $\times \left(\frac{143.35\ g}{mol}\right) = \cancel{80.}\ 20.8\ g/L$ in $3\ M\ NH_3$

In $Cl^-$ (assume no complex ion formation!)

$AgCl \rightleftharpoons Ag^+ + Cl^-$

| | | |
|---|---|---|
| some | 0 | 3.00 M |
| $-x$ | $+x$ | $+x$ |
| some $-x$ | $x$ | $3.00+x$ |

$K_{sp} = (x)(3.00+x) = 1.8 \times 10^{-10}$ neglect $x$

$x = \frac{1.8 \times 10^{-10}}{3} = 6.0 \times 10^{-11}\ M$ AgCl dissolves

$\times 143.35\ g/mol = 8.6 \times 10^{-9}\ g/L$

In water $AgCl \rightleftharpoons Ag^+ + Cl^-$

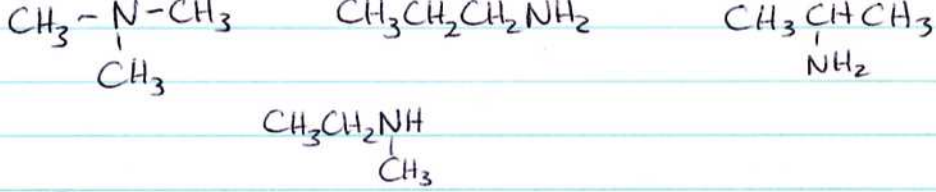
| | | |
|---|---|---|
| some | 0 | 0 |
| $-x$ | $+x$ | $+x$ |
| some $-x$ | $x$ | $x$ |

$K_{sp} = x^2 = 1.8 \times 10^{-10}$

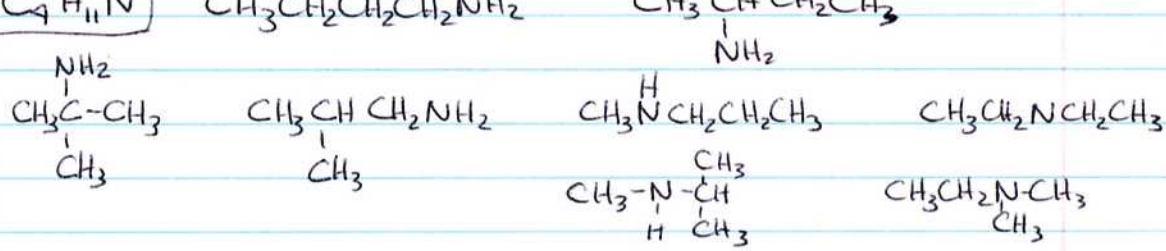
$x = 1.34 \times 10^{-5}\ M$ AgCl dissolves

$\times 143.35\ g/mol = 1.9 \times 10^{-3}\ g/L$ in water

11. $C_3H_9N$



12. $C_4H_{11}N$



13. Expt 1,2 [A] quadruples, rate $\frac{19.5}{1.22} = 16$ up by a factor of 16

Rate = $A^x$ $16 = 4^x$ $x = 2$ 2nd order in A

Expt 2,3 [C] doubles, rate $\frac{156}{19.5} = 8$

$8 = 2^y$ $y = 3$ 3rd order in C

Expt 1,4 B doubles, rate decreases! $\frac{0.61}{1.22} = 0.5$ $1/2$

$0.5 = 2^x$ $x = -1$

$$\text{Rate} = \frac{k[A]^2[C]^3}{[B]}$$

$$k = \frac{\text{Rate}\,[B]}{[A]^2[C]^3} = \frac{(1.22\ M/min)(0.10\ M)}{(0.10\ M)^2(0.20\ M)^3}$$

$k = 1525\ M^{-3}min^{-1}$

$1.5 \times 10^3\ M^{-3}min^{-1}$

b. C must be a catalyst.

c. $$-\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{-\Delta[B]}{\Delta t} = \frac{\Delta[D]}{\Delta t} = +\frac{1}{3}\frac{\Delta E}{\Delta t}$$

$$\frac{\Delta B}{\Delta t} = \frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{1}{2}(-0.50\ M/min) = -0.25\ M/min$$

$$\frac{\Delta D}{\Delta t} = \frac{-1}{2}\frac{\Delta[A]}{\Delta t} = +0.25\ M/min \qquad \frac{\Delta E}{\Delta t} = \frac{-3}{2}\frac{\Delta[A]}{\Delta t} = +0.75\ M/min$$

14. 2nd order in B

a) $$\frac{1}{[B]_t} - \frac{1}{[B]_0} = kt \qquad \frac{1}{0.50\ M} - \frac{1}{2.0\ M} = kt = 2.0\ M^{-1} - 0.50\ M^{-1}$$

$= 1.5\ M^{-1} = kt$

$$k = \frac{1.5\ M^{-1}}{5.0\ min} = 0.30\ M^{-1}min^{-1}$$

b) $$\frac{1}{0.125\ M} - \frac{1}{0.50\ M} = kt = 8.0\ M^{-1} - 2.0\ M^{-1}$$

$kt = 6.0\ M^{-1}$ $$t = \frac{6.0\ M^{-1}}{0.30\ M^{-1}min^{-1}} = 20.\ min$$

15. 1st order in A $$\ln\frac{A_t}{A_0} = -kt$$

a) $$\ln\frac{0.50\ M}{2.0\ M} = -1.386 = -kt$$

$t = 5.0\ min$ $$k = \frac{-1.386}{-t} = 0.277\ min^{-1}$$

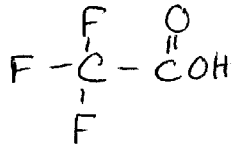
b) $$\ln\frac{0.125}{0.50} = -1.386 = -kt \qquad k = 0.277\ min^{-1}$$

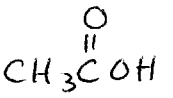
$t = 5.0\ min$

* a) 2.0 M → 0.50 M conc ↘ to 1/4 or 25% of initial. Takes 2 half-lives.

b) 0.50 M → 0.125 M conc ↘ to 25% of initial Takes 2 half-lives!

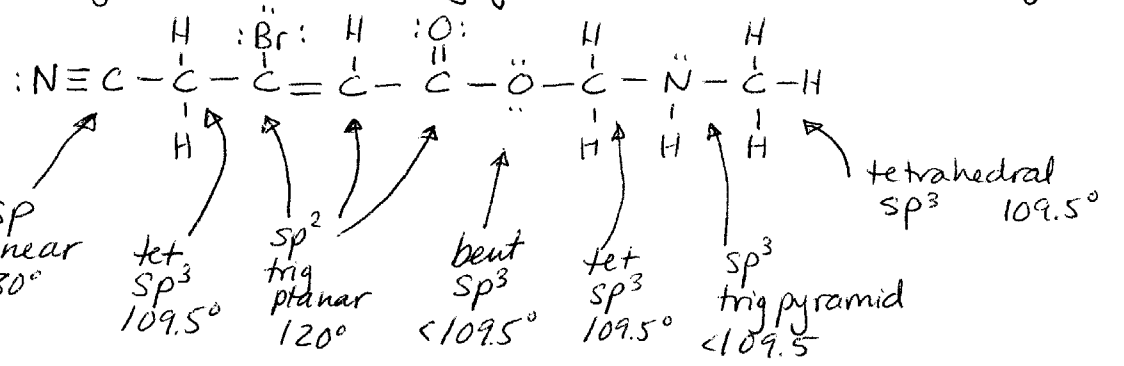
For a first order rxn, half life is constant!

16a) 



b) F is the most electronegative element. Presence of 3 F's withdraws electron density from the O-H bond. (more polar, easier to break.) The resulting negative ion is more stable than it would otherwise be. TFA is more acidic than acetic acid.

c) Stronger acid, weaker conjugate base. Acetate is the stronger base.

17. 


18. $H_3PO_4$ $pK_a = 2.12$ $\underbrace{H_2PO_4^-\ pK_a = 7.21}_{\text{closest to desired pH}}$ $HPO_4^{2-}$ $pK_a = 12.44$

desired $[H_3O^+] = 8.91\times10^{-8}$ M

buffer system $H_2PO_4^-$ / $HPO_4^{2-}$

$K_a = \frac{[H_3O^+][A^-]}{[HA]}$ $\frac{K_a}{[H_3O^+]} = \frac{A^-}{HA} = \frac{6.2\times10^{-8}}{8.91\times10^{-8}} = 0.696$

$\frac{0.696\ A^-}{1\ HA}$ ← least conc. $= 0.10\,M \times 1.5\,L = 0.15$ mol $HPO_4^{2-}$

$\frac{0.696}{1} = \frac{0.15}{x}$ $x = 0.2\bar{1}55$ mol $H_2PO_4^-$ in buffer

① Mix 0.15 mol $Na_2HPO_4$ $\left(\frac{141.96\,g}{1\,mol}\right) = 21$ g $Na_2HPO_4$
and $0.2\bar{1}55$ mol $NaH_2PO_4$ $\left(\frac{119.98\,g}{1\,mol}\right) = 26$ g $NaH_2PO_4$
add water until $V_{total} = 1.50$ L!

② Mix HCl with conj base.

| | $H_3O^+$ | + $HPO_4^{2-}$ | → $H_2O$ | + $H_2PO_4^-$ |
|---|---|---|---|---|
| | A | B | | 0 |
| | −A | −A | | +A |
| | 0 | 0.15 mol | | $0.2\bar{1}55$ mol |

A = $0.2\bar{1}55$ mol HCl
B = 0.15 + 0.2155
= $0.3\bar{6}55$ mol $HPO_4^{2-}$

18. $(0.2\bar{1}55\ mol)\left(\frac{1\ L}{2.00\ mol}\right) = 0.108$ 108 mL HCl

$(0.\bar{3}655\ mol)\left(\frac{141.96\ g}{mol}\right) = 52$ + 52 g $Na_2HPO_4$

add $H_2O$ until $V_{tot} = 1.5\ L$, Mix

(3) Mix NaOH w/ conj acid

| $OH^-$ + | $H_2PO_4^-$ → | $H_2O$ + | $HPO_4^{2-}$ |
|---|---|---|---|
| A | B | | 0 |
| −A | −A | | +A |
| | 0.2155 mol | | 0.15 mol |

A = 0.15 mol NaOH × $\left(\frac{1\ L}{2\ mol}\right)$ = 0.075 L (75 mL NaOH)

B = 0.2155 + 0.15 = 0.3655 mol $H_2PO_4$

$(0.\bar{3}655\ mol)\left(\frac{119.98\ g}{1\ mol}\right) = 44\ g\ NaH_2PO_4$

Mix 75 mL 2 M NaOH + 44 g $NaH_2PO_4$ + water so $V_{tot} = 1.50\ L$, Mix.

19. Have a buffer. Initial pH? $K_a = (H_3O^+)\left(\frac{mol\ A^-}{mol\ HA}\right)$

$H_3O^+ = K_a\left(\frac{mol\ HA}{mol\ A^-}\right) = 3.6\times10^{-13}\left(\frac{0.020\ mol\ HA}{0.030\ mol\ A^-}\right) = 2.4\times10^{-13}$ pH = 12.62

have to add NaOH to make it more basic

$OH^-$ will react w/ HA

| $HPO_4^{2-}$ + | $OH^-$ → | $PO_4^{3-}$ + | $H_2O$ |
|---|---|---|---|
| 0.020 mol | X mol | 0.030 mol | |
| −X | −X | +X | |
| 0.020 − X | 0 | 0.030 + X | |

final pH = 13.00

$\frac{K_a}{[H_3O^+]} = \frac{3.6\times10^{-13}}{1.0\times10^{-13}} = \frac{3.6\ A^-}{1\ HA}$

can't neglect X!

$\frac{3.6\ A^-}{1\ HA} = \frac{0.030 + X}{0.020 - X}$

$3.6(0.020 - X) = 0.030 + X$

$0.072 - 3.6X = 0.030 + X$

$-0.030 + 3.6X \quad -0.030 + 3.6X$

$0.042 = 4.6X$

X = 0.0091 mol $OH^-$

$(0.0091\ mol)\left(\frac{L}{3\ mol}\right) = 0.0030\ L$ = 3.0 mL NaOH