Review Probs for Exam 2 - Answers

1. $pK_a = 3.9$ at a pH of 3.9, it will be equal amts acid+base form. At a lower pH, it will be mostly acid form. At higher pH, mostly base form. At pH 5.0, mostly base form: blue

2. First find initial pH. buffer K_a of conj acid $= 6.4\times10^{-5}$

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a \quad \text{so } [H_3O^+] = K_a\left(\frac{\text{mol HA}}{\text{mol A}^-}\right) = 6.4\times10^{-5}\left(\frac{0.020\ HC_2O_4^-}{0.050\ C_2O_4^{2-}}\right)$$

$$[H_3O^+] = 2.56\times10^{-5}\ M \qquad pH = 4.59$$

a) To change pH to 3.80, must add acid ($HC_2O_4^-$)
find new ratio needed. $10^{-3.80} = 1.585\times10^{-4}$ M H_3O^+

$$\frac{K_a}{[H_3O^+]} = \frac{A^-}{HA} = \frac{6.4\times10^{-5}}{1.585\times10^{-4}} = \frac{0.4038\ A^-}{1\ HA} \text{ needed}$$

$$\frac{0.4038\ A^-}{1\ HA} = \frac{0.050\ C_2O_4^{2-}}{0.020 + X\ HC_2O_4^-}$$

$$0.4038(0.020+X) = 0.050$$

$$0.008076 + 0.4038X = 0.050$$

$$-0.008076 \qquad -0.008076$$

$$\frac{0.4038X}{0.4038} = \frac{0.041924}{0.4038} \qquad X = 0.1038 \text{ mol } HC_2O_4^- \text{ needed}$$

$$(0.1038 \text{ mol } NaHC_2O_4)\left(\frac{112.0\text{ g}}{1\text{ mol}}\right) = 11.6 \text{ g } NaHC_2O_4 \qquad 12\text{ g}$$

b. Must add HCl to change pH from 4.59 to 3.80. HCl reacts w/ A^-: $C_2O_4^{2-}$

$C_2O_4^{2-}$	+ H_3O^+	$\longrightarrow$ $HC_2O_4^-$	+ H_2O	
0.050 mol	Y	0.020 mol		(ofs
−Y	−Y	+Y		
0.050−Y	0	0.020+Y		

let Y = mol HCl to add

needed: $\frac{0.4038\ A^-}{1\ HA} = \frac{0.050-Y}{0.020+Y}$

$$0.4038(0.020+Y) = 0.050-Y)$$

$$0.008076 + 0.4038Y = 0.050 - Y$$

$$-0.008076 \quad +Y \qquad -0.008076 + Y$$

$$\frac{1.4038Y}{1.4038} = \frac{0.041924}{1.4038} \qquad Y = 0.02986 = 0.030 \text{ mol HCl}$$

$$(0.02986 \text{ mol HCl})\left(\frac{1\text{ L}}{2.00\text{ mol}}\right) = 0.01493 \text{ L} = 15 \text{ mL}$$

2.00 M HCl

3. $(0.0700\,L)(0.100\,\frac{mol}{L}) = 0.00700$ mol HCl $(0.0500\,L)(0.100\,\frac{mol}{L}) = 0.00500$ mol Na_3PO_4

	H_3O^+	+ PO_4^{3-}	$\longrightarrow$ HPO_4^{2-}	+ H_2O
	0.007	0.005 mol	0	lots
	-0.005	-0.005	+0.005	
	0.002	0	0.005 mol	

what's left? HPO_4^{2-} amphiprotic and H_3O^+, strong acid will react!

	H_3O^+	+ HPO_4^{2-}	$\longrightarrow$ $H_2PO_4^-$	+ H_2O
	0.002	0.005 mol	0	lots
	-0.002	-0.002	+0.002	
	0	0.003 mol	0.002 mol	

what's left? A buffer.
$H_2PO_4^-$, HPO_4^{2-}
$K_a = 6.2\times10^{-8}$

$K_a = [H_3O^+]\left(\frac{mol\,A^-}{mol\,HA}\right)$ $[H_3O^+] = K_a\left(\frac{mol\,HA}{mol\,A^-}\right) = 6.2\times10^{-8}\left(\frac{0.002}{0.003}\right) = 4.1\times10^{-8}$ M H_3O^+

pH = 7.38

4. H_3PO_4 $K_{a1} = 7.5\times10^{-3}$ $pK_{a1} = 2.12$
$K_{a2} = 6.2\times10^{-8}$ $pK_{a2} = 7.21$ * use this. $HA = H_2PO_4^-$, $A^- = HPO_4^{2-}$
$K_{a3} = 4.2\times10^{-13}$ $pK_{a3} = 12.38$

$\frac{K_a}{[H_3O^+]} = \frac{A^-}{HA} = \frac{6.2\times10^{-8}}{1.0\times10^{-7}} = \frac{0.62\,A^-}{1\,HA} = \frac{0.62\,HPO_4^{2-}}{1\,H_2PO_4^-}$ ← least conc = 0.10 mol

$(0.50\,L)(0.20\,\frac{mol}{L}) = 0.10$ mol least conc

$\frac{0.62}{1} = \frac{0.10\,mol}{X\,mol}$ $0.62X = 0.10$
$X = \frac{0.10}{0.62} = 0.161$ mol

① Mix 0.10 mol HPO_4^{2-} and 0.16 mol $H_2PO_4^-$
② Mix A^- (HPO_4^{2-}) and HCl

	HPO_4^{2-}	+ H_3O^+	$\longrightarrow$ $H_2PO_4^-$	+ H_2O
	A	B	0	
	-B	-B	+B	
	A-B	0	B	

A-B = 0.10 mol B = 0.16 mol
A = 0.10 + 0.16 = 0.26 mol

Mix 0.26 mol HPO_4^{2-} with 0.16 mol HCl

3 Mix HA ($H_2PO_4^-$) and NaOH

$H_2PO_4^-$	+ OH^-	→ HPO_4^{2-}	+ H_2O
X	Y	0	lots
−Y	−Y	+Y	
X−Y	0	Y	

X−Y = 0.16 mol Y = 0.10 mol = mol OH^-

X = 0.16 + 0.10 = 0.26 mol

Mix 0.26 mol $H_2PO_4^-$ with 0.10 mol OH^-

(Next - calc #g or #mL needed...)

5. a. $CH_3NH_2 + H_3O^+ \longrightarrow CH_3NH_3^+ + H_2O$ $K_a = \frac{K_w}{K_b} = 2.0\times10^{-11}$

at the 1/4 way point, 1/4 of CH_3NH_2 converted to $CH_3NH_3^+$, and 3/4 CH_3NH_2 left. buffer.

$K_a = \frac{[H_3O^+][A^-]}{(HA)}$ $[H_3O^+] = K_a\left(\frac{\text{mol HA}}{\text{mol A}^-}\right) = 2.0\times10^{-11}\left(\frac{1/4}{3/4}\right) = 6.67\times10^{-12}$ M H_3O^+

pH = 11.18

3/4 way point:

3/4 of CH_3NH_2 converted to $CH_3NH_3^+$

1/4 CH_3NH_2 left.

$[H_3O^+] = K_a\left(\frac{\text{mol HA}}{\text{mol A}^-}\right) = 2.0\times10^{-11}\left(\frac{3/4}{1/4}\right) = 6.0\times10^{-11}$ M H_3O^+ pH = 10.22

b. at eq. point - all CH_3NH_2 converted to $CH_3NH_3^+$, a weak acid.

calc new conc. $(0.025\text{ L})(0.10\frac{\text{mol}}{\text{L}}) = 0.0025$ mol CH_3NH_2 to start

0.0025 mol HBr needed to react $(0.0025\text{ mol HBr})\left(\frac{1\text{ L}}{0.10\text{ mol}}\right) = 0.025$ L HBr needed

$V_{tot} = 50$ mL

CH_3NH_2	+ H_3O^+	→ $CH_3NH_3^+$	+ H_2O
0.0025	0.0025	0	
−0.0025	−0.0025	+0.0025	
0	0	0.0025 mol	

$\frac{0.0025\text{ mol}}{0.050\text{ L}} = 0.050$ M $CH_3NH_3^+$

for 5c, 5d see P.11

$CH_3NH_3^+$	+ H_2O	⇌ CH_3NH_2	+ H_3O^+
0.050M	lots	0	0
−x		+x	+x
0.050−x		x	x

$K_a = \frac{x^2}{0.050-x} = 2.0\times10^{-11}$ neglect x

$x = \sqrt{(K_a)(0.050)} = 1.0\times10^{-6}$

pH = 6.00

6. $(0.10\text{ L})(0.10\frac{\text{mol}}{\text{L}}) = 0.010$ mol Na_2CO_3

add HCl: $CO_3^{2-} + H_3O^+ \longrightarrow HCO_3^- + H_2O$ K_{a2} $H_2CO_3 = 5.6\times10^{-11}$

Ka of HCO_3^-

want pH = 10.00

$$\frac{K_a}{[H_3O^+]} = \frac{A^-}{HA} = \frac{5.6\times10^{-11}}{1.0\times10^{-10}} = \frac{0.56\ A^-\ (CO_3^{2-})}{1\ HA\ (HCO_3^-)}$$ need this ratio.

CO_3^{2-}	+ H_3O^+	→ HCO_3^-	+ H_2O
0.010 mol	X	0	
−X	−X	+X	
0.010−X mol	0	X	

$$\frac{0.56\ CO_3^{2-}}{1\ HCO_3^-} = \frac{0.010-X \text{ mol } CO_3^{2-}}{X \text{ mol } HCO_3^-}$$

$$0.56X = 0.010 - X$$
$$+X \qquad +X$$
$$\frac{1.56X}{1.56} = \frac{0.010}{1.56}$$

X = 0.00641 mol HCl to add

$$(0.00641 \text{ mol HCl})\left(\frac{1\text{ L}}{0.20\text{ mol}}\right) = 0.032\text{ L} = 32\text{ mL}$$

7. Will ppt when Q = K_{sp}

Ag_2SO_4 $K_{sp} = [Ag^+]^2[SO_4^{2-}]$

$$[SO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1.4\times10^{-5}}{(0.010)^2} = 0.14\text{ M } SO_4^{2-}$$

$BaSO_4$ $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$$[SO_4^{2-}] = \frac{K_{sp}}{[Ba^{2+}]} = \frac{1.1\times10^{-10}}{0.010}$$

$[SO_4^{2-}] = 1.1\times10^{-8}$ M SO_4^{2-}

$BaSO_4$ will ppt first

what is $[Ba^{2+}]$ when $[SO_4^{2-}] = 0.14$M?

$$[Ba^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{1.1\times10^{-10}}{0.14} = 7.9\times10^{-10}\text{ M } Ba^{2+}$$

8. $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$ $K_{sp} = 1.8\times10^{-10}$

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$ $K_f = 1.5\times10^7$

$AgCl_{(s)} + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+{}_{(aq)} + Cl^-_{(aq)}$ $K = K_{sp}K_f = 0.0027$

Some	5.0 M	0	0
−X	−2x	+X	+X
Some−x	5.0−2x	x	x

$$K = \frac{x^2}{(5.0-2x)^2} = 0.0027$$

√ each side

$$\frac{x}{5.0-2x} = \sqrt{0.0027} = 0.05\bar{1}96$$

$$x = (5.0-2x)(0.05\bar{1}96)$$
$$x = 0.2\bar{5}98 - 0.1039x$$
$$+0.1039x \qquad +0.1039x$$
$$\frac{1.1039x}{1.1039} = \frac{0.2\bar{5}98}{1.1039}$$

$x = 0.2\bar{3}53$ M AgCl

$$\left(0.2\bar{3}53\ \frac{\text{mol}}{\text{L}}\ AgCl\right)\left(\frac{143.35\text{g}}{1\text{ mol}}\right) = 3\bar{3}.7\text{ g/L} = 34\text{ g/L}$$

9. $MgC_2O_4 \rightleftharpoons Mg^{2+} + C_2O_4^{2-}$ $\quad K_{sp} = 8.5\times10^{-5}$

$C_2O_4^{2-} + H_3O^+ \rightleftharpoons HC_2O_4^- + H_2O$ $\quad K = \frac{1}{K_a\ HC_2O_4^-} = \frac{1}{K_{a2}} = \frac{1}{6.4\times10^{-5}}$

$HC_2O_4^- + H_3O^+ \rightleftharpoons H_2C_2O_4 + H_2O$ $\quad K = \frac{1}{K_a\ H_2C_2O_4} = \frac{1}{K_{a1}} = \frac{1}{5.9\times10^{-2}}$

$MgC_2O_{4(s)} + 2H_3O^+ \rightleftharpoons Mg^{2+} + H_2C_2O_4 + 2H_2O$ $\quad K = \frac{8.5\times10^{-5}}{(6.4\times10^{-5})(5.9\times10^{-2})} = 22.51$

$K = 23$

10. $\frac{(0.0500L)(0.20\frac{mol}{L})}{(0.100L)} =$ ~~0.010 mol~~ $0.10\ M\ MgSO_4$

$= 0.10\ M\ Mg^{2+},\ 0.10\ M\ SO_4^{2-}$ – spectator

$\frac{(50.0mL)(0.20M)}{(100mL)} = 0.10\ M\ Na_3AsO_4 \Rightarrow 0.30\ M\ Na^+$ – spectator, $0.10\ M\ AsO_4^{3-}$

Ppt will form if $Q > K_{sp}$ $\quad Mg_3(AsO_4)_2$ $\quad K_{sp} = [Mg^{2+}]^3[AsO_4^{3-}]^2$

$Q = (0.10)^3(0.10)^2 = 1.0\times10^{-5}$ $\quad Q > K_{sp}$ will ppt.

	$3Mg^{2+}$	$+\ 2\ AsO_4^{3-}$	$\rightarrow Mg_3(AsO_4)_2$
	0.10 M	0.10 M	0
	$-3x$	$-2x$	$+x$
	$0.10-3x$	$0.10-2x$	x

Need $\frac{3Mg^{2+}}{2AsO_4^{3-}} = \frac{1.5\ Mg^{2+}}{1\ AsO_4^{3-}}$

have $\frac{0.10}{0.10} = \frac{1\ Mg^{2+}}{1\ AsO_4^{3-}}$

not enough Mg^{2+} – LR

LR $= 0$

$0.10 = 3x$ $\quad 0.10 - 2(0.0333) = 0.0333M$

$x = \frac{0.10}{3} = 0.03\bar{3}3\ M$

	$Mg_3(AsO_4)_{2(s)}$	$\rightleftharpoons 3Mg^{2+}$	$+\ 2AsO_4^{3-}$
	some	0	0.0333M
	$-x$	$+3x$	$+2x$
	some $-x$	$3x$	$0.03\bar{3}3 + 2x$

neglect

$[Na^+] = 0.30\ M$

$[SO_4^{2-}] = 0.10\ M$

$[AsO_4^{3-}] = 0.03\ M$

$[Mg^{2+}] = 3\times10^{-6}M$

$K_{sp} = [Mg^{2+}]^3[AsO_4^{3-}]^2$

$2\times10^{-20} = (3x)^3(0.03\bar{3}3)^2$ $\quad (3x)^3 = 27x^3$

$x = \sqrt[3]{\frac{2\times10^{-20}}{(0.03\bar{3}3)^2(27)}} = x = 8.736\times10^{-7}$

$[Mg^{2+}] = 3x = 2.62\times10^{-6}M$

11. $PbI_{2(s)} \rightleftharpoons Pb^{2+} + 2I^-$

Some	0	0.50 M
$-x$	$+x$	$+2x$
Some $-x$	x	$0.50+2x$

$K_{sp} = (x)(0.50+2x)^2 = x(0.50)^2 = 4.1\times10^{-8}$

neglect

$x = \frac{4.1\times10^{-8}}{(0.50)^2} = 1.64\times10^{-7}$ M dissolves

$\left(1.64\times10^{-7}\frac{mol}{L}\right)\left(\frac{461 g}{mol}\right) = 7.56\times10^{-5}$ g/L

7.6×10^{-5} g/L

In H_2O: $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$

Some	0	0
$-x$	$+x$	$+2x$
Some $-x$	x	$2x$

$K_{sp} = (x)(2x)^2 = 4x^3 = 4.1\times10^{-8}$

$x = \sqrt{\frac{4.1\times10^{-8}}{4}} = 2.17\times10^{-3}$ M

$\left(2.17\times10^{-3}\frac{mol}{L}\right)\left(\frac{461 g}{mol}\right) = 1.0$ g/L

12. a. Need $\Delta H^\circ, \Delta S^\circ$ (not 25°C) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ = (-74.6 - 241.83) - (3(0) - 110.5) = -205.93$ kJ/mol

$\Delta S^\circ = (186.3 + 188.835) - (3(130.68) + 197.7) = -214.605$ J/K mol

$\Delta G^\circ = (-205.93 \text{ kJ/mol}) - (423 K)(-0.214605 \text{ kJ/K mol})$

$-205.93 \quad + 90.7779 \quad = -115.152$ kJ yes spont $\Delta G^\circ \ominus$

b. Enthalpy-driven (ΔH is $\ominus$)

c. Both ΔH° and ΔS° are $\ominus$. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ($\ominus - \ominus = \oplus$)

lower T (smaller $\oplus$ term)

** Better determination: exothermic, so favored by low temp.

d. $\Delta G^\circ = -RT\ln K$

$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{+115152 \text{ J/mol}}{(8.314 \text{ J/mol K})(423 K)} = 32.743$

$K = e^{32.743} = 1.66\times10^{14}$ or 2×10^{14}

e. $\Delta G = \Delta G^\circ + RT\ln Q$ $\quad Q = \frac{P_{CH_4}P_{H_2O}}{P_{H_2}^3 P_{CO}} = \frac{(5.0)(5.0)}{(0.010)^3(0.010)} = 2.5\times10^9$

$\Delta G = -115152 J + (8.314 \text{ J/mol K})(423 K)\underbrace{\ln 2.5\times10^9}_{21.639556}$

$\Delta G = -115152 J + 76102 J$

$\Delta G = -39049$ J/mol will go forward $\Delta G -$

f. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ std. cond. becomes spont when $\Delta G^\circ = 0$

so $\Delta H^\circ = T\Delta S^\circ$ $T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-205930 \text{ J/mol}}{-214.605 \text{ J/mol·K}} = 959.6 \text{ K}$

-273 687 °C

g. $\Delta G = \Delta G^\circ + RT \ln Q$

$0 = \Delta G^\circ + RT \ln Q$

$\frac{-\Delta G^\circ}{RT} = \ln Q = \frac{+115152 \text{ J/mol}}{(8.314 \text{ J/mol·K})(423 \text{ K})} = 32.743$ $Q = e^{32.743} = 1.66 \times 10^{14}$

$P_{CO} \cdot Q = \frac{P_{CH_4} P_{H_2O}}{P_{H_2}^3 P_{CO}} \cdot P_{CO}$ $P_{CO} = \frac{P_{CH_4} P_{H_2O}}{P_{H_2}^3 Q} = \frac{(5.0)(5.0)}{(0.010)^3(1.66 \times 10^{14})}$

$P_{CO} = 1.5 \times 10^{-7}$ atm $\approx 2 \times 10^{-7}$ atm

13. a. condensation - gives off heat, so $\Delta H^\circ \ominus$. Increase in order, so $\Delta S^\circ \ominus$

b. enthalpy-driven

c. Reverse: $\Delta H \oplus$, $\Delta S \oplus$ entropy-driven.

d. nbp - bp at 1 atm pressure acetone$_l$ → acetone$_{(g)}$ $K = P_{acetone}$

$K = 1$ so $\Delta G^\circ = \emptyset$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $T = \frac{\Delta H^\circ}{\Delta S^\circ}$

$\Delta H^\circ = (-216.6) - (-247.6) = 31.0$ kJ/mol

$\Delta S^\circ = (294.9) - (200.04) = 94.86$ J/mol·K

$T = \frac{31000 \text{ J/mol}}{94.86 \text{ J/mol·K}} = 327 \text{ K} = 54°C$

e. $\Delta G^\circ = -RT \ln K$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 31000 \text{ J/mol} - (303 \text{K})(94.86 \text{ J/mol·K})$

$= 31000 - 28742.58$

$= 2257.42$

$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-2257.42 \text{ J/mol}}{(8.314 \text{ J/mol·K})(303 \text{ K})}$

$\ln K = -0.896$

$e^{-0.896} = 0.408 = K = P_{acetone} = 0.41$ atm

$(0.408 \text{ atm})\left(\frac{760 \text{ mmHg}}{1 \text{ atm}}\right) = 310$ mmHg

f. non std. not 25°C

$\Delta G = \Delta G^\circ + RT \ln Q$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G = \Delta H^\circ - T\Delta S^\circ + RT \ln Q$ becomes spont when $\Delta G = 0$

$0 = \Delta H^\circ - T\Delta S^\circ + RT \ln Q$ solve for T $(600. \text{ torr})\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.7895$ atm

$-\Delta H^\circ = -T\Delta S^\circ + RT \ln Q$

$-\Delta H^\circ = T(-\Delta S^\circ + R \ln Q)$

$T = \frac{-\Delta H^\circ}{-\Delta S^\circ + R \ln Q} = \frac{-31000 \text{ J}}{-94.86 \text{ J/K} + (8.314) \ln 0.7895} = \frac{-31000}{-96.825} = 320 \text{ K}$

47°C

14. $\Delta H \oplus \ \Delta S \oplus$ $\quad \Delta G = \underset{\oplus}{\Delta H} - \underbrace{T\Delta S}_{\ominus}$ $\quad$ spont @ high T
$|T\Delta S|$ larger than $|\Delta H|$

15. Entropy of a perfect crystal at 0 K = 0
everything else has <u>more</u> disorder!

16. $\Delta S \ominus$ getting more ordered $\quad$ K ↘ as T ↗ $\quad \Delta H \ominus$ also.

$\Delta G^\circ = -RT \ln K$

$\Delta G^\circ = -(8.314\ J/mol\,K)(298)\ln \overset{13.286}{5.89\times10^5} = -32917\ J$ @ 25°C

$\Delta G^\circ = -(8.314\ J/mol\,K)(773)\ln \underset{-9.58576}{6.87\times10^{-5}} = +61605\ J$ @ 500°C

subtract

$$\begin{aligned} -32917\ J &= \ominus\Delta H^\circ - \oplus(298K)(\Delta S^\circ) \\ +61605\ J &= \Delta H^\circ - (773K)(\Delta S^\circ) \\ \hline \frac{94522\ J}{-475} &= \frac{-475\ \Delta S^\circ}{-475} \end{aligned}$$

$\Delta S^\circ = -199\ J/mol\,K$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = 61605\ J + (773)(-199) = -92222\ J/mol = -92\ kJ/mol$

17. $Li^+ + e^- \longrightarrow Li \quad E^\circ = -3.05\ V$ $\quad$ Reducing agent - gets oxidized.
Li^+ <u>can't</u> be oxidized! ox # can't ↗ increase. reduction potential
and it's very hard to reduce!

18. Can't tell - depends on what it's combined with. ½ rxn isn't enough info! All we can say is it's harder to reduce Ni^{2+} than it is to reduce H^+ (SHE $E^\circ = 0\ V$)

19.

$$12H_2O + 3\underset{0}{P_4} + \underset{0}{P_4} + 12OH^- \longrightarrow \overset{12}{\cancel{4}}\,H_2\underset{+1}{P}\underset{+1}{O_2}^{-2} + 4\,P\underset{-3}{H_3}$$

$0 \to +4$: $4e^- \times 3$ $\quad$ $0 \to -12$: $12e^-$

12 H $\quad$ 12 − $\quad$ 24 H + 12 H = 36 H

overall $\quad 4P_4 + 12OH^- + 12H_2O \rightarrow 12\,H_2PO_2^- + 4PH_3$

can ÷ all by 4 $\quad P_4 + 3OH^- + 3H_2O \rightarrow 3H_2PO_2^- + PH_3$

20. $2\,MnO_4^- + 5\,C_2O_4^{2-} + 16H^+ \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$

(+7) (−2) (+3) (−2) (+2) (+4) (−2)

(5e⁻)2 (2e⁻)5

−2 − 10 = −12 +4

Mn is reduced. C is oxidized

MnO_4^- is ox. agent. $C_2O_4^{2-}$ is red. agent.

21.

	E°
$Na^+ + e^- \rightarrow Na$	−2.71 V
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.065 V
$Co^{2+} + 2e^- \rightarrow Co$	−0.277 V
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.440 V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771 V
$2H^+ + 2e^- \rightarrow H_2$	0 V
$Au^{3+} + 3e^- \rightarrow Au$	+1.498 V

Best ox agent: easiest to reduce. Most ⊕ reduction potential. Au^{3+}

Best red agent - easiest to oxidize. Most ⊕ ox potential (reverse all ½ rxns) $Na_{(s)}$ $Na \rightarrow Na^+ + e^-$ $E^\circ = +2.71V$

22. Does Fe react w/ H^+?

$Fe \rightarrow Fe^{2+} + 2e^-$ $E^\circ = +0.440V$

$2H^+ + 2e^- \rightarrow H_2$ $E^\circ = 0V$

$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$ $E^\circ = +0.440V$ ⊕ so spontaneous yes.

Does Au react w/ acid?

$Au \rightarrow Au^{3+} + 3e^-$ $E^\circ = -1.498V$

$2H^+ + 2e^- \rightarrow H_2$ $E^\circ = 0V$

$2Au + 6H^+ \rightarrow 2Au^{3+} + 3H_2$ $E^\circ = -1.498V$

⊖ NO not spontaneous

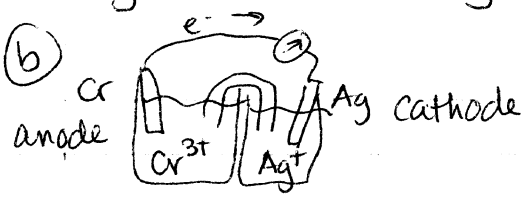
23. (a) Reverse Cr half cell

$3Ag^+ + 3e^- \rightarrow 3Ag \quad E^\circ = +0.799V$

$Cr \rightarrow Cr^{3+} + 3e^- \quad E^\circ = +0.740V$

$3Ag^+ + Cr \rightarrow Cr^{3+} + 3Ag \quad E^\circ = 1.539V$

(b)



← anions
cations →

(c) To make voltage higher (more ⊕, more spontaneous/favorable) increase $[Ag^+]$, decrease $[Cr^{3+}]$

(d) $E = E^\circ - \frac{0.0257V}{n} \ln Q \qquad Q = \frac{[Cr^{3+}]}{[Ag^+]^3}$

$Q = 1.0 \times 10^{11}$

$E = 1.539V - \frac{0.0257V}{3} \ln \underbrace{\frac{0.80}{(2.0\times10^{-4})^3}}_{25.3\bar{2}84}$

$E = 1.539\ V - 0.21\bar{6}98\ V = 1.322\ V$

(e) $\Delta G^\circ = -nFE^\circ = -3(96485 \frac{C}{mole^-})(1.322 \frac{J}{C}) = -3.82\bar{6}6 \times 10^5\ J/mol$
$= -382.7\ kJ/mol$

$E^\circ = \frac{0.0257}{n} \ln K$

$\ln K = \frac{E^\circ n}{0.0257V} = \frac{(1.539V)(3)}{(0.0257\ V)} = 179.65 \qquad K = e^{179.65}$

$K = 1 \times 10^{78}$
huge! (no sf)

(f) $E = E^\circ - \frac{0.0257}{n} \ln Q$

$1.413V = 1.539V - \frac{0.0257V}{3} \ln Q$
$-1.539 \qquad -1.539$

$-0.126\ V = -\frac{0.0257}{3} \ln Q$

$\frac{(-0.126V)(3)}{-0.0257V} = 14.\bar{7}08 = \ln Q$

$Q = e^{14.708} = \bar{2}.4416 \times 10^6$

$Q = \frac{[Cr^{3+}]}{[Ag^+]^3} \qquad [Ag^+] = \sqrt[3]{\frac{[Cr^{3+}]}{Q}}$

$[Ag^+] = \sqrt[3]{\frac{0.50}{\bar{2}.4416\times10^6}} = \bar{5}.89 \times 10^{-3} M$
$= 6 \times 10^{-3} M$

24. Yes - ΔG° ⊕ means its nonspont under standard conditions, where you start with all Reactants and products at 1M or 1atm. If you start with just reactants, it must go forward at least a little to form some products!

5c. $(0.0250\ L)(0.10\ \frac{mol}{L}\ CH_3NH_2) = 0.0025\ mol\ CH_3NH_2$
$(0.0300\ L)(0.10\ \frac{mol}{L}\ HBr) = 0.0030\ mol\ HBr$

	CH_3NH_2 +	H_3O^+	$\longrightarrow$ $CH_3NH_3^+$	+ H_2O
Start	0.0025 mol	0.0030 mol	Ø	lots
	− 0.0025	− 0.0025	+ 0.0025	
	Ø	0.0005 mol	0.0025 mol	

what's left? a strong acid and a weak acid, the weak acid won't contribute much to the pH of the solution. The leftover strong acid is what determines the pH of the solution.

$[H_3O^+] = \frac{mol}{L} = \frac{0.0005\ mol\ H_3O^+}{0.0550\ L} = 0.00\bar{9}09\ M\ H_3O^+$
(1 sf)

$V_{total} = 25.0 + 30.0\ mL = 55.0\ mL$

$pH = 2.\bar{0}4 = 2.0$

5d. pH at equivalence point = 6.00
choose an indicator with a pKa close to 6.00.
looking at the indicator color table:
litmus has the closest pKa (6.5) but it's not ideal because the color change range is pretty wide.
methyl red (pKa 5.0) or bromothymol blue (pKa 7.1) would probably both work.

25. $(0.050\ L)(0.65\ \frac{mol}{L}) = 0.03\bar{2}5$ moles HCl added

HCl - SA - reacts with the base in the buffer.

	HPO_4^{2-}	+ H_3O^+	→ $H_2PO_4^-$	+ H_2O
i	0.266 mol	$0.03\bar{2}5$ mol	0.153 mol	lots
Δ	$-0.03\bar{2}5$	$-0.03\bar{2}5$	$+0.03\bar{2}5$	
end	$0.233\bar{3}5$ mol	Ø	$0.185\bar{5}$ mol	

what's left? A buffer. Use buffer shortcut.

$K_a = \frac{[H_3O^+][A^-]}{[HA]}$ $\quad [H_3O^+] = K_a\left(\frac{mol\ HA}{mol\ A^-}\right) = (6.2\times10^{-8})\left(\frac{0.185\bar{5}\ mol\ H_2PO_4^-}{0.233\bar{3}5\ mol\ HPO_4^{2-}}\right)$

$[H_3O^+] = 4.\bar{9}25\times10^{-8}\ M$

pH = 7.31

26. $PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$ $\quad \Delta H^\circ \oplus$, $\Delta S^\circ \ominus$

$\Delta G^\circ = \frac{\Delta H^\circ - T\Delta S^\circ}{-RT} = \frac{-RT\ln K}{-RT}$

$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

Sign of ΔH° is what really matters!

endothermic - favored at higher temps.

if ΔH° is $\oplus$, the $\frac{-\Delta H^\circ}{RT}$ term is negative, and if T ↗, then the $\frac{-\Delta H^\circ}{RT}$ gets smaller in magnitude.

If you subtract a smaller $\ominus$ number, ln K gets larger and K gets larger.

Larger K = more products at equilibrium so more soluble.