

# **Chemistry 1250 - Sp22**

## **Solutions for Practice Final**

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Very large  $K_c$  ( $K_c > 10^{10}$ ) : “only” products (at equil.) - for all practical purposes (see below)

Very small  $K_c$  ( $K_c < 10^{-10}$ ) : “only” reactants (at equil.) - for all practical purposes (see below)

Large  $K_c$  ( $10^2 < K_c < 10^{10}$ ) : products predominate

Small  $K_c$  ( $10^{-10} < K_c < 10^{-2}$ ) : reactants predominate

$0.01 < K_c < 100$  : significant amounts of both reactants & products present at equil.  
(Roughly equal molar amounts depending on the form of  $K_c$ .)

$$K_c = \frac{[X][Y]}{[A][B]} = 9.5 \times 10^{-33} \quad \text{essentially only reactants}$$

Both numerator and denominator are squared (have same form). So if  $K \approx 1$  then there are roughly equal molar amounts of reactants and products.

Look at equilibrium tables starting with  $10^3$  M conc. of A & B (rather large conc.):

If  $K_c = 1 \times 10^{-10}$  you will get the following conc. for reactants & products at equil.

$[A] = [B] = 999.99999$  M and  $[X] = [Y] = 1.0 \times 10^{-5}$  M. Certainly **reactants predominate** but these conc. for [X] and [Y] are still very easily measurable.

If  $K_c = 1 \times 10^{-20}$  you will get the following conc. for reactants & products at equil.

$[A] = [B] = 999.9999999999999$  M and  $[X] = [Y] = 1.0 \times 10^{-10}$  M. These conc. for [X] and [Y] are much harder to measure and there are **essentially only reactants** at equilibrium.

Look at equilibrium tables starting with 1.0 M conc. of A & B (much more reasonable starting conc.) and the  $K_c$  given in the problem:

If  $K_c = 9.5 \times 10^{-33}$  you will get the following conc. for reactants & products at equil.

$[A] = [B] = 0.9999999999999999025$  M and  $[X] = [Y] = 9.7 \times 10^{-17}$  M. These conc. for [X] and [Y] are very difficult to measure and there are **essentially only reactants**.

Even for a  $K_c = 1 \times 10^{-10}$  you will get the following conc. for reactants & products at equil.

$[A] = [B] = 0.9999900001$  M and  $[X] = [Y] = 1 \times 10^{-5}$  M. Certainly reactants predominate but these conc. for [X] and [Y] are still easily measurable.

This is why I said the answer is essentially “ONLY” reactants exist. This was something I said in class on more than one occasion. I said when you have a really small K (around  $10^{-15}$  or smaller) you have essentially only reactants at equilibrium (reaction really doesn’t occur).

I said the following in class on more than one occasion.

If you have a really large K (around  $10^{15}$ ) you have “only” products (such as is the case for strong acids).

If you have a really small K (around  $10^{-15}$ ) you have “only” reactants.

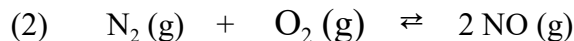
If you have a large K ( $> 10^2$ ) you have mostly products.

If you have a small K ( $> 10^{-2}$ ) you have mostly reactants.

2)

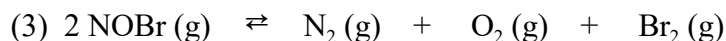


$$K_1 = \frac{[\text{NO}] [\text{Br}_2]^{1/2}}{[\text{NOBr}]}$$



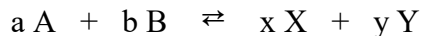
$$K_2 = \frac{[\text{NO}]^2}{[\text{N}_2] [\text{O}_2]}$$

Want K for



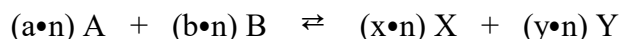
$K_{\text{rev}}$  for rev. rx is  $1/K_{\text{for}}$  (reciprocal of  $K_{\text{for}}$  for the forward rx)

Also, when multiply a rxn by some factor the K for the new rxn is equal to original K raised to the factor the rxn was multiplied by (multiplying by -1 reverses the rxn)

**Proof**

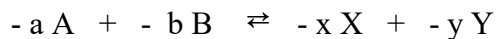
$$K_1 = \frac{[\text{X}]^x [\text{Y}]^y}{[\text{A}]^a [\text{B}]^b}$$

Multiply by n

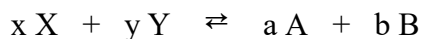


$$K_2 = \frac{[\text{X}]^{xn} [\text{Y}]^{yn}}{[\text{A}]^{an} [\text{B}]^{bn}} = \left( \frac{[\text{X}]^x [\text{Y}]^y}{[\text{A}]^a [\text{B}]^b} \right)^n = K_1^n$$

Multiply by -1 reverses rxn.



want (+) coeff - like in math switch reactants & products to other sides



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## 2) (cont.)

When you add reactions together to get another reaction the K for the overall reaction equals the K's from the added reactions multiplied together.



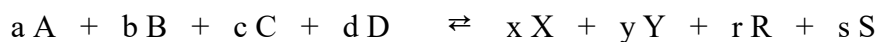
$$K_1 * K_2 = K_3$$

**Proof**

$$K_1 = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

$$K_2 = \frac{[R]^r [S]^s}{[C]^c [D]^d}$$

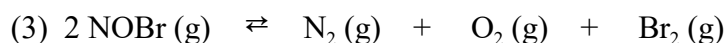
Add the two equations (reactions) to get a third equation (reaction)



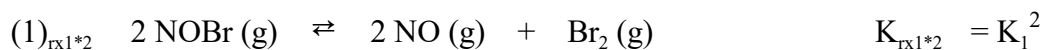
$$K_3 = \frac{[X]^x [Y]^y [R]^r [S]^s}{[A]^a [B]^b [C]^c [D]^d} = \left( \frac{[X]^x [Y]^y}{[A]^a [B]^b} \right) * \left( \frac{[R]^r [S]^s}{[C]^c [D]^d} \right)$$

$$K_3 = K_1 * K_2$$

To get reaction 3 for this question,



must multiply rxn 1 by 2 and reverse rxn 2 (multiply it by -1). Then add rxn 1 and rxn 2.



$$K_3 = K_{\text{rxn}1*2} * K_{\text{rev}_2} = K_1^2 * K_2^{-1}$$



use  $K_p = K_c (RT)^{\Delta n}$  ( $\Delta n$  = change in moles of **gas**)

$$\Delta n = 1 - 2 = -1$$

Do **NOT** include pure **solids**, **liquids** or **aqueous** when calculating  $\Delta n$ .

$$K_c = \frac{[\text{CO}_2]}{[\text{CO}]^2} \quad K_p = \frac{P_{\text{CO}_2}}{(P_{\text{CO}})^2}$$

$$R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K} \quad \text{NOT } 8.314 \text{ J/mol}\cdot\text{K}$$

$$T = 800^\circ\text{C} + 273 = 1073 \text{ K} \quad (\text{must be in } \underline{\text{kelvin}})$$

$$K_c = 7.14 \times 10^{-2}$$

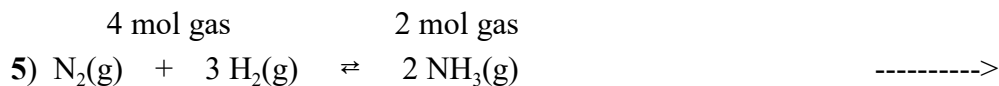
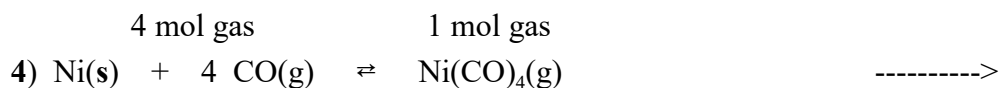
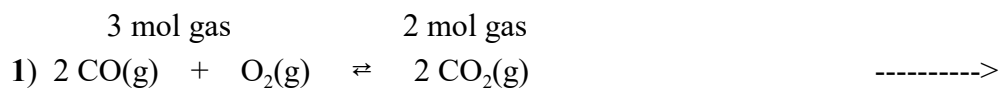
$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} = K_c (RT)^{-1} \\ &= (7.14 \times 10^{-2}) \{(0.0821) (1073)\}^{-1} \end{aligned}$$

$$K_p = 8.11 \times 10^{-4}$$

**B**

4)

For Pressure changes

**P inc** ==> **fewer** moles **gas****P dec** ==> **more** moles **gas**Changes in Pressure do **not** affect **liquids, solids** or **aqueous** (their conc. do not change w. P like conc. of gases do)If **no change** in **moles gas** changes in **P** have **no effect****INC Pressure** go towards **FEWER** moles **GAS****C** (1, 4, 5) can use stuff below but just remembering **Inc P** => **fewer mole gas** is easier

$$\Delta n = (\# \text{ mol gaseous products}) - (\# \text{ mol gaseous reactants})$$

$$\Delta n < 0 \text{ (i.e. \# mol gaseous products} < \text{\# mol gaseous reactants)}$$

Inc P shifts rx to rightDec P shifts rx to left

$$\Delta n > 0 \text{ (i.e. \# mol gaseous products} > \text{\# mol gaseous reactants)}$$

Inc P shifts rx to leftDec P shifts rx to right

$$\Delta n = 0 \text{ (i.e. \# mol gaseous products} = \text{\# mol gaseous reactants)}$$

Changing P has NO effect on the rx

5)

Want **reactant** formation **avored** (shift **left**) by **low P AND high T**

When changes in P and T are applied at the same time do temp. part first (easier than P changes).

**High T**, favors **reactant** (shifts **left**) for **EXO**thermic ( $\Delta H < 0$ )

Only (1), (3) & (4) are **exo**thermic ( $\Delta H < 0$ ). Only need to apply pressure rule to these reactions. However, I will do them all.

**Low P** favors **more** moles **gas**

<u>Low P</u>		<u>High T</u>
4 mol gas	2 mol gas	
<----- 1) $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{heat}$	$\Delta H = -91.8 \text{ kJ}$	<-----
2 mol gas	3 mol gas	
-----> 2) $\text{heat} + 2 \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO}(\text{g}) + \text{O}_2(\text{g})$	$\Delta H = + 566 \text{ kJ}$	----->
2 mol gas	3 mol gas	
-----> 3) $2 \text{O}_3(\text{g}) \rightleftharpoons 3 \text{O}_2(\text{g}) + \text{heat}$	$\Delta H = - 285 \text{ kJ}$	<-----
2 mol gas	2 mol gas	
NC 4) $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2 \text{HF}(\text{g}) + \text{heat}$	$\Delta H = - 541 \text{ kJ}$	<-----
3 mol gas	2 mol gas	
<----- 5) $\text{heat} + \text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$	$\Delta H = 66.4 \text{ kJ}$	----->

Only # 1 has **BOTH T** and **P** shifting left toward **reactant**.

**A**

6)

<u>Reactant</u>	<u>Product</u>	<u>Shift</u>
Add	Remove	Right
Remove	Add	Left

Move **AWAY** from what is **ADDED**

Move **TOWARD** what is **REMOVED**

**NOTE:** **K** remains **constant (Q changes)** for changes in conc. & pressure (Numerical value of K changes only for temp. changes)

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6) (cont.)

**NOTE:** Adding or Removing **Pure SOLIDS** of **LIQUIDS** (as long as some is present) does **NOT** **affect** the equil. (adding water to an aqueous rxn involving water can cause an affect due to dilution - changing the conc. of aqueous substances).

This is because the conc. of pure solids and liquids are essentially constant and do **NOT** appear in K (or Q).

You can see how Le Chatelier's Principle works by looking at the following:

Changing conc. changes the value or the **reaction quotient, Q**. We can see how it changes and compare it to K (qualitatively) to see which way the reaction shifts. See example below.

When the reaction is at equilibrium  $Q = K$ .

For example: **Remove a reactant:** (conc. of reactant dec.)

$Q = \frac{[P]}{[R]}$  denominator dec, so **Q inc** and  $Q > K$  (too much prod, not enough react to be at equil.)  
rx must **shift to left** to make  $Q = K$  again (inc. denominator & dec. numerator)

Shift **left** to make **more reactant** and **use product to reestablish a new equil.** (in which conc of reactants and products will be different than in the original equil. but the value of K will be the same).

1)  $\text{CO(g)} + 3 \text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$  **remove**  $\text{H}_2\text{O(g)}$ , **product**,  $Q = \frac{[P] \downarrow}{[R]}$ ,  $Q < K$ , shift **right**

2)  $\text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)} \rightleftharpoons 2 \text{NH}_3\text{(g)}$  **add**  $\text{NH}_3\text{(g)}$ , **product**,  $Q = \frac{[P] \uparrow}{[R]}$ ,  $Q > K$ , shift **left**

3)  $\text{H}_2\text{(g)} + \text{F}_2\text{(g)} \rightleftharpoons 2 \text{HF(g)}$  **add**  $\text{HF(g)}$ , **product**,  $Q = \frac{[P] \uparrow}{[R]}$ ,  $Q > K$ , shift **left**

4)  $\text{N}_2\text{(g)} + 2 \text{O}_2\text{(g)} \rightleftharpoons 2 \text{NO}_2\text{(g)}$  **remove**  $\text{NO}_2\text{(g)}$ , **product**,  $Q = \frac{[P] \downarrow}{[R]}$ ,  $Q < K$ , shift **right**

5)  $\text{BaO(s)} + \text{SO}_3\text{(g)} \rightleftharpoons \text{BaSO}_4\text{(s)}$  **add**  $\text{BaO(s)}$ , **solid** reactant, **NO shift**

**A** (1 & 4)



7) Reaction is ENDOthermic so the heat is a REACTANT.



**Raise T, add heat** ==> add reactant ==> shift **right** (forward direction)

**changing temp., changes** value of **K**

shift **right** (forward) ==> **inc. product** (dec. reactant)

$$K = \frac{[\text{Product}]}{[\text{Reactant}]}$$

↑  
↓

**K inc**

**Remember:**

**Exothermic rxn** ( $\Delta H < 0$ ) **Low T** favors **products**

T ↑ K ↓ and T ↓ K ↑

**Endothermic rxn** ( $\Delta H > 0$ ) **High T** favors **products**

T ↑ K ↑ and T ↓ K ↓

**C**

- 8) The reaction is starting with reactants and products. There are two steps to this problem.

First it must be determined what direction the reaction is proceeding by calculating the reaction quotient,  $Q$  using the starting concentrations.

$$[I_2]_0 = [Br_2]_0 = 0.400 \text{ mol}/2.00 \text{ L} = 0.200 \text{ M}$$

$$[IBr]_0 = 2.10 \text{ mol}/2.00 \text{ L} = 1.05 \text{ M}$$

$$Q_c = \frac{[IBr]^2}{[I_2][Br_2]} = \frac{(1.05)^2}{(0.200)(0.200)} = 27.\underline{5}6 \text{ (only 3 s.f.)}$$

$$Q_c (27.6) < K_c (110.25)$$

$Q_c < K_c$  **numerator** ([prod]) is **too small**, need to **inc numerator (products)**

Reaction must be **proceeding** to the **RIGHT**.

Set up an equilibrium (ICE) table (in molarity):

	$I_2$	+	$Br_2$	$\rightleftharpoons$	$2 IBr$
initial	0.200		0.200		1.05
change	- x		- x		+ 2x
<hr/>					
equil	$0.200 - x$		$0.200 - x$		$1.05 + 2x$

$$K = \frac{[IBr]^2}{[I_2][Br_2]} = \frac{(1.05 + 2x)^2}{(0.200 - x)(0.200 - x)} = \frac{(1.05 + 2x)^2}{(0.200 - x)^2} = 11\underline{0}.25$$

$$\frac{(1.05 + 2x)^2}{(0.200 - x)^2} = 11\underline{0}.25 \text{ perfect square (take square root of both sides)}$$

$$\frac{(1.05 + 2x)}{(0.200 - x)} = 10.5$$

$$(1.05 + 2x) = (10.5)(0.200 - x); \quad (1.05 + 2x) = (2.10 - 10.5x);$$

$$(12.5)x = 1.05 \quad x = 0.0840 \text{ M}$$

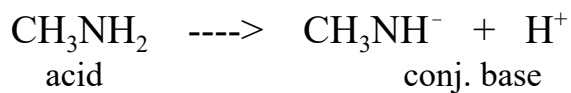
$$[I_2] = [Br_2] = 0.200 - x = 0.200 - 0.0840 = 0.116 \text{ M};$$

$$[IBr] = 1.05 + 2x = 1.05 + 2(0.0840) = 1.2\underline{1}8 \text{ M} = 1.22 \text{ M}$$

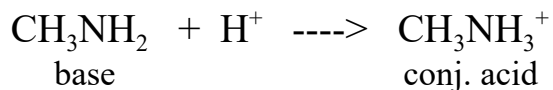
**A** (0.116, 1.22)

9)

Want the conjugate base of methylamine,  $\text{CH}_3\text{NH}_2$ . Treat it as an acid so it will lose an  $\text{H}^+$ . The conjugate base of an acid has 1 fewer proton (1 less H and a more negative charge)



If you want the conjugate acid of methylamine,  $\text{CH}_3\text{NH}_2$ , treat it as a base and add  $\text{H}^+$  to it. The conjugate acid of a base has 1 extra proton (an extra H and a more positive charge)

**E**

10) Use the definition of  $K_w$ .

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

For a neutral solution (pure water),  $[H^+] = [OH^-]$ . This is true no matter what the temp and the value of  $K_w$ .

At 25°C

$$K_w = [H^+] [OH^-] = 1.0 \times 10^{-14}$$

$$[H^+] = [OH^-] = 1.00 \times 10^{-7} \quad \text{pH} = 7.00 \quad \text{neutral}$$

$$[H^+] > 1.00 \times 10^{-7} \quad \text{pH} < 7.00 \quad \text{acidic}$$

$$[H^+] < 1.00 \times 10^{-7} \quad \text{pH} > 7.00 \quad \text{basic}$$

At 37°C

$$K_w = [H^+] [OH^-] = 2.40 \times 10^{-14}$$

even at 37°C for a neutral solutions  $[H^+] = [OH^-]$

$$x^2 = 2.40 \times 10^{-14} \quad x = 1.549 \times 10^{-7}$$

$$[H^+] = [OH^-] = 1.549 \times 10^{-7} \quad \text{for a neutral solution}$$

$$\text{pH} = -\log [H^+] = 6.81 \quad \text{for a neutral solution at 37°C}$$

At 37°C a solution with **pH = 7.00** is **basic**.

The definition of a basic solution is one in which the pH is greater than that for a neutral solution at a particular temperature. The definition of an acidic solution is one in which the pH is less than that for a neutral solution at a particular temperature.

At 37°C a solution with **pH = 6.81** is **neutral**

**pH < 6.81** is **acidic**

**pH > 6.81** is **basic**

11) Given the pH of a solution of 0.10 M  $\text{NH}_4\text{Cl}$  containing 0.10 M  $\text{NH}_3$  as 9.20 and want  $[\text{H}_3\text{O}^+]$

First of all remember that  $\text{H}_3\text{O}^+ \equiv \text{H}^+$  (i.e.  $\text{H}^+$  is shorthand for  $\text{H}_3\text{O}^+$ , hydronium ion)

$$\text{pH} = -\log [\text{H}^+] \qquad \text{pOH} = -\log [\text{OH}^-]$$

$$[\text{H}^+] = 10^{-\text{pH}} \qquad [\text{OH}^-] = 10^{-\text{pOH}}$$

It doesn't matter what the solution is, you are given the pH so the problem is quite straight forward

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-9.20} = 6.3 \times 10^{-10}$$

C

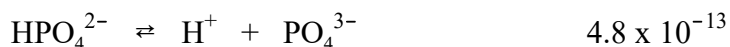
12)

Remember the following:

Larger  $K_a \implies$  smaller  $\text{p}K_a \implies$  stronger acid  $\implies$  weaker conjugate base

Larger  $K_b \implies$  smaller  $\text{p}K_b \implies$  stronger base  $\implies$  weaker conjugate acid

$K_a \times K_b = K_w$  for a conjugate acid-base pair.



$K_a$  for  $\text{HS}^- < K_a$  for  $\text{HPO}_4^{2-}$  :  $\text{HS}^-$  weaker than  $\text{HPO}_4^{2-}$

Since  $\text{HPO}_4^{2-}$  is the stronger acid its conjugate base,  $\text{PO}_4^{3-}$ , will be weaker.

$$K_b(\text{S}^{2-}) = 8.3 \times 10^{-2} \qquad K_b(\text{PO}_4^{3-}) = 2.1 \times 10^{-2}$$

$\text{HS}^-$	weaker acid	$\text{S}^{2-}$	stronger base
$\text{HPO}_4^{2-}$	stronger acid	$\text{PO}_4^{3-}$	weaker base

C (Weaker, Stronger)

$[H_3O^+] \approx [H^+]$ 

no unauthorized use allowed

13. What is the ionization constant of an acid if the hydronium ion concentration of a 0.500 M solution is  $1.70 \times 10^{-4} \text{ M}$ ?

a)  $3.62 \times 10^{-7}$

b)  $2.89 \times 10^{-8}$

c)  $5.80 \times 10^{-8}$

d)  $1.16 \times 10^{-7}$

e)  $1.70 \times 10^{-3}$

$$[H^+] = 1.70 \times 10^{-4} \text{ M}$$

$$[HA] = .500 \text{ M}$$



$.500$	$0$	$0$
$-x$	$+x$	$+x$
$.500 - x$	$x$	$x$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{.500 - x}$$

$$K_a = \frac{(1.70 \times 10^{-4})^2}{(.500 - 1.70 \times 10^{-4})}$$

$$= 5.80 \times 10^{-8}$$

14. A 0.010 M solution of  $\text{HNO}_2$  is 19% ionized. What is the  $K_a$ ?

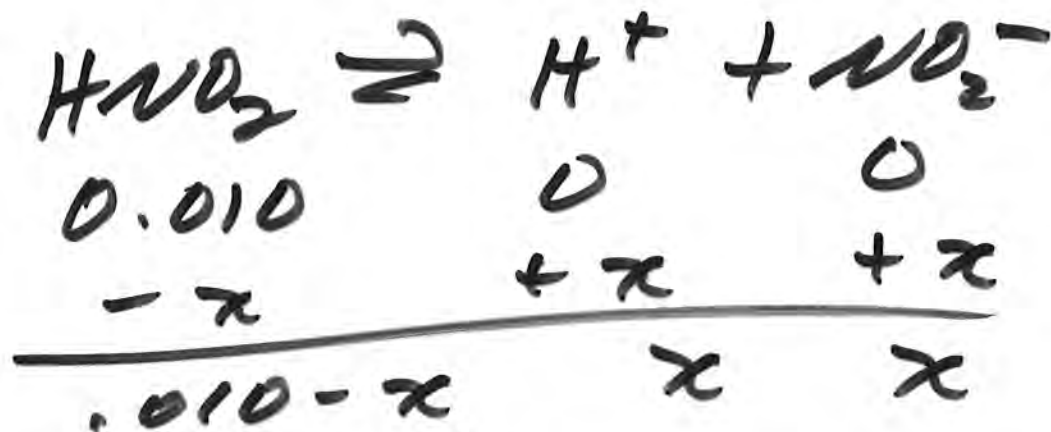
a)  $4.4 \times 10^{-4}$

b)  $3.9 \times 10^{-4}$

c)  $3.6 \times 10^{-4}$

d)  $5.0 \times 10^{-4}$

e)  $5.4 \times 10^{-4}$



$$K_a = \frac{x^2}{0.010 - x} \quad x = [\text{H}^+]$$

$$\% \text{ ion} = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HNO}_2]_0} \times 100\%$$

$$\begin{aligned}
 x = [\text{H}^+] &= \left( \frac{\% \text{ ion}}{100} \right) [\text{HNO}_2]_0 \\
 &= \left( \frac{19\%}{100} \right) (0.010 \text{ M}) \\
 &= 1.9 \times 10^{-3} \text{ M}
 \end{aligned}$$

$$K_a = \frac{(1.9 \times 10^{-3})^2}{(0.01 - 1.9 \times 10^{-3})}$$
$$= 4.4 \times 10^{-4}$$

---

$$\frac{K_a}{[HA]_0} < 10^{-3}$$

% error  $< 5\%$   
assump.  $x$  can be ignored  
is ok

$$[HA]_0 \geq 10^{-3}$$

$$K_a \leq 10^{-6}$$



15. What is the pH of a 0.20 M  $\text{NH}_4^+$  solution ( $K_b: \text{NH}_3 = 1.8 \times 10^{-5}$ )?

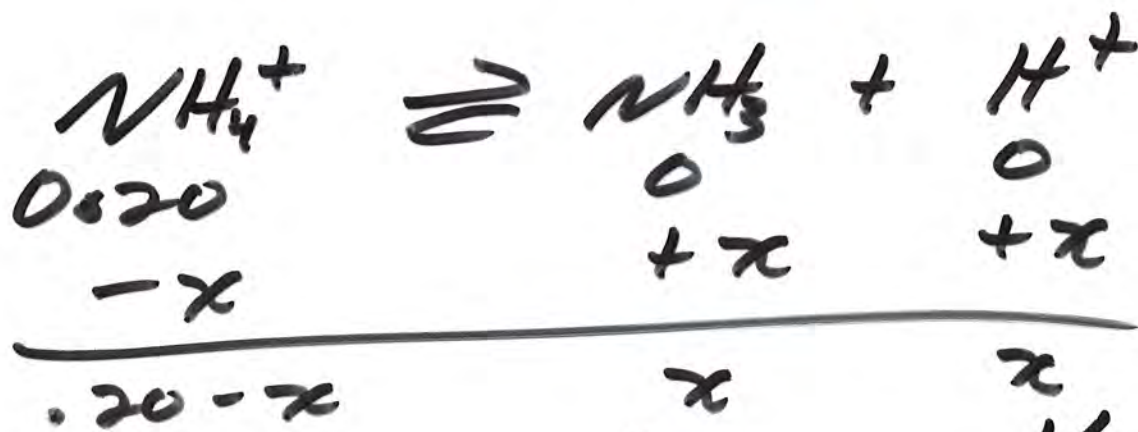
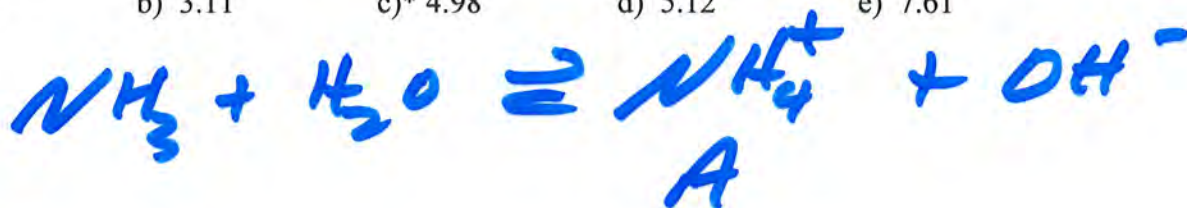
a) 2.72

b) 3.11

c)\* 4.98

d) 5.12

e) 7.61



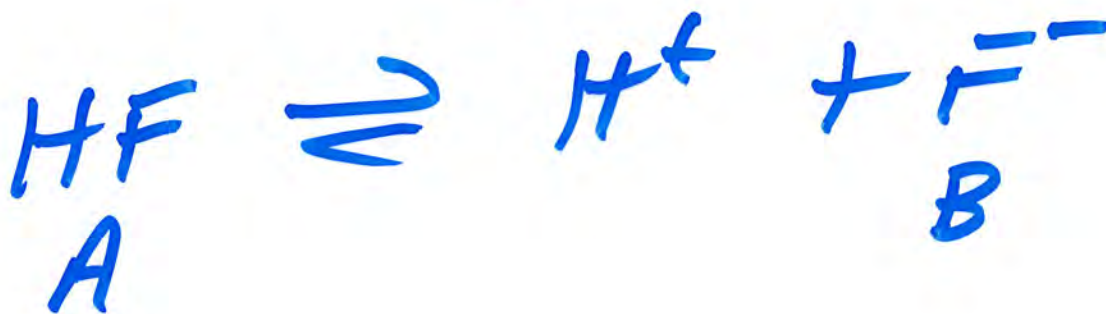
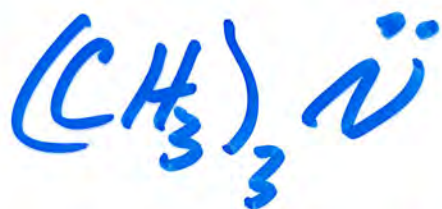
$$K_{a\text{NH}_4^+} = \frac{x^2}{.20 - x} = \frac{K_w}{K_{b\text{NH}_3}}$$

$$K_a \cdot K_b = K_w$$

$$\frac{x^2}{.20 - x} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$\begin{aligned} x &= [\text{H}^+] = 1.05 \times 10^{-5} \\ \text{pH} &= -\log(1.05 \times 10^{-5}) \\ &= 4.98 \end{aligned}$$

## Weak Bases



$$K_{\text{b F}^-} = \frac{K_{\text{w}}}{K_{\text{a HF}}}$$



16. A 1.50 g sample of Vitamin C is dissolved in 100.0 mL of water and titrated with 0.250 M NaOH to the methyl orange equivalence point. The volume of the base used is 34.1 mL. What is the molecular weight of Vitamin C assuming one dissociable proton per molecule?

a)\* 176

b) 164

c) 152

d) 146

e) 139

mw  $M = \frac{g}{\text{mol}} = \frac{1.50g}{? \text{mol}}$



$$\text{mol HC} = \text{mol NaOH}$$

$$\text{mol H}^+ = \text{mol OH}^-$$

$$? \text{ mol NaOH} \quad \text{mol} = M \cdot V_L$$

$$? \text{ mol NaOH} = 34.1 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.250 \text{ mol NaOH}}{1 \text{ L soln}}$$

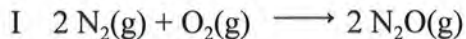
$\underbrace{\hspace{10em}}_{L_{\text{soln}} \cdot M}$

$$= 8.525 \times 10^{-3} \text{ mol NaOH}$$

$$\text{mol HC} = 8.525 \times 10^{-3} \text{ mol}$$

$$M = \frac{1.50g}{8.525 \times 10^{-3} \text{ mol}} = 176g/\text{mol}$$

17. Predict which of the following reactions has a positive entropy change.

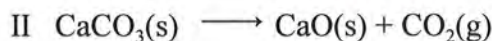


3 mol

2 mol gas

less disorder

$$\Delta S < 0$$



$$S \rightarrow S + g \quad \Delta S > 0$$



$$S + a g \rightarrow a g + g \quad \Delta S > 0$$

gas

a) I

b) II

c) III

d) I and II

e)\* II and III

Entropy: measure of disorder  
(randomness)

$$\Delta S = S_f - S_i > 0$$

$S_f > S_i$  more disorder



18. Calculate the  $\Delta S$  (J/mol·K) of fusion for ethane which melts at  $-183^\circ\text{C}$ . The heat of fusion is 2.86 kJ/mole.

a) 21.4      b)\* 31.8      c) 15.6      d) 28.1      e) 34.3



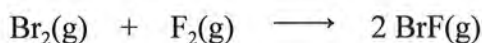
$$\Delta G = \Delta H - T\Delta S = 0 \text{ eq.}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{2.86 \text{ kJ/mol}}{90 \text{ K}}$$

$$= 3.177 \times 10^{-2} \text{ kJ/mol}\cdot\text{K}$$

$$= 31.8 \text{ J/mol}\cdot\text{K}$$

19. Calculate the entropy change (J/mole·K) of the reaction. The molar entropies are given below each substance.



$$\Delta S \approx 0$$

$S^\circ$  (J/K mole)      245.5      202.8      229.0

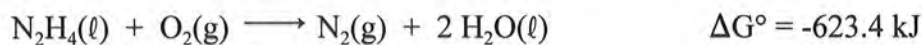
a)\* 9.7      b) -9.7      c) +15.3      d) -219.3      e) -126.3

$$\Delta S^\circ = \sum n S^\circ_{\text{prod}} - \sum n S^\circ_{\text{react.}}$$

$$= 2(229.0) - [245.5 + 202.8]$$

$$= 9.7 \text{ J/K}$$

20. The standard free energy of formation of  $\text{H}_2\text{O}(\ell)$  is  $-237.1 \text{ kJ/mol}$ . Using the data for the following reaction, calculate the free energy of formation,  $\Delta G_f^\circ$ , for  $\text{N}_2\text{H}_4(\ell)$  (in  $\text{kJ/mol}$ ).



a) 623.4

b)\* 149.2

c) 386.3

d) 193.2

e) 860.5



$$\Delta G_f^\circ \quad ? \quad \phi \quad \phi \quad -237.1$$

$$\Delta G_{\text{rxn}}^\circ = [1(0) + 2(-237.1)] - [\Delta G_f^\circ \text{ for } \text{N}_2\text{H}_4 + \phi]$$

$$-623.4 = -474.2 - \Delta G_f^\circ \text{ for } \text{N}_2\text{H}_4$$

$$\Delta G_f^\circ \text{ for } \text{N}_2\text{H}_4 = 149.2 \text{ kJ}$$



21. Consider the  $\Delta G_f^\circ$  and  $\Delta H_f^\circ$  (kJ/mole) for the following oxides. Which oxide can be **most easily decomposed** to form the metal and oxygen gas.

	$\Delta G_f^\circ$	$\Delta H_f^\circ$
a) PbO	-187.9	-217.3
b) ZnO	-318.4	-348.3
c)* Ag <sub>2</sub> O	-11.2	-31.1
d) CdO	-228.4	-258.2

$\Delta G^\circ_{rev}$   
187.9

318.4

11.2

228.4

$\Delta G^\circ_f$



$\Delta S < 0$

22. From the following  $\Delta H^\circ$  and  $\Delta S^\circ$  values predict which of reactions I, II, and III would be spontaneous at 25°C.

	$\Delta H^\circ$ (kJ)	$\Delta S^\circ$ (J/K)
I	-5.0	-20
II	-10.0	-10
III	-25.0	+75

$\Delta G^\circ$   
0.96

-7.02

-47.35

- a) I      b) II      c) III      d) I and II      e)\* II and III

$\Delta G^\circ < 0$  spont

$\Delta G^\circ > 0$  nonspont

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   
-20 J  $\Rightarrow$  kJ  
-.020

23. The  $K_p = 2.47 \times 10^{-29}$  at  $25^\circ\text{C}$  for the following reaction. Calculate  $\Delta G^\circ$  (kJ).



a) 157

b)\* 163

c) 169

d) 172

e) 175

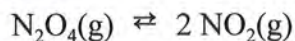
$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = - (8.314 \times 10^{-3} \text{ kJ/K}) (298 \text{ K}) \ln (2.47 \times 10^{-29})$$

$$= 163 \text{ kJ}$$

nonspont at std. st. cond.  
(nonspont to prod.)

24. The  $K_p = 0.113$  at  $25^\circ\text{C}$  and  $\Delta H^\circ = +57.2 \text{ kJ}$  for the following reaction. Calculate the temperature ( $^\circ\text{C}$ ) where  $K_p = 1.00$



a) 45

b)\* 56

c) 65

d) 70

e) 76

$$\ln K = \frac{-\Delta H_{\text{rxn}}^\circ}{R} \left( \frac{1}{T} \right) + C$$

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H_{\text{rxn}}^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$\Delta H^\circ = 57.2 \text{ kJ}$$

$$T \Rightarrow K$$

$$\begin{array}{c} \text{Endo} \\ \hline T \uparrow \quad K \uparrow \end{array}$$



25. For the following reaction, calculate the value of  $\Delta G$  (kJ) at  $25^\circ\text{C}$  in a solution when  $[\text{Co}^{3+}] = 0.0050\text{ M}$ ,  $[\text{NH}_3] = 0.10\text{ M}$ , and  $[\text{Co}(\text{NH}_3)_6^{3+}] = 1.00\text{ M}$ .



- a) -47.4                  b) +20.5                  c)\* +5.7                  d) -20.5                  e) -5.7

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

$$Q = Q_c = \frac{[\text{Co}(\text{NH}_3)_6^{3+}]}{[\text{Co}^{3+}][\text{NH}_3]^6} = \frac{(1.00)}{(0.0050)(0.10)^6} = 2.0 \times 10^8$$

$$\Delta G = -41.7 \text{ kJ} + (8.314 \times 10^{-3} \text{ kJ/K})(298.15 \text{ K}) \ln(2.0 \times 10^8)$$

$$\Delta G = -41.7 \text{ kJ} + 47.37 \text{ kJ}$$

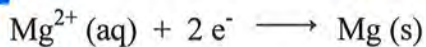
$$\Delta G = +5.67 \text{ kJ} = +5.6 \text{ kJ}$$

spont

no unauthorized use allowed

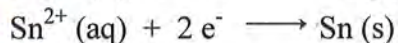
26. From the listed standard electrode potentials, what is  $E^\circ$  for a voltaic cell made from the following electrodes?

A



$$E^\circ = -2.363 \text{ V}$$

C



$$E^\circ = -0.136 \text{ V}$$

a)  $+2.227$

b)  $2.499$

c)  $-2.227$

d)  $-2.499$

e)  $+1.113$

$$E^\circ_{\text{cell}} \Rightarrow 0 \quad (+)$$

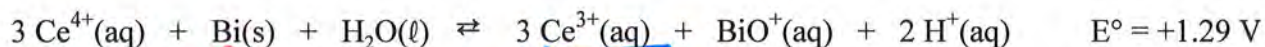
$$E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}} > 0$$

$$E^\circ_{\text{C}} > E^\circ_{\text{A}}$$

$$E^\circ_{\text{cell}} = (-0.136 \text{ V}) - (-2.363 \text{ V})$$

$$= +2.227 \text{ V}$$

27. The  $E^\circ = 1.29 \text{ V}$  for the following reaction. The standard electrode potential for  $\text{Ce}^{4+}$  as written is  $+1.61 \text{ V}$ . What is the standard electrode potential for the reduction of  $\text{BiO}^+$ ?



A



C



a)  $-0.32$

b)  $+0.32$

c)  $+2.90$

d)  $-2.90$

e)  $-1.45$

$$E^\circ_{\text{cell}} = E^\circ_{\text{C}} - E^\circ_{\text{A}}$$

$$1.29 \text{ V} = 1.61 - E^\circ_{\text{A}}$$

$$E^\circ_{\text{A}} = 0.32 \text{ V}$$

most easily red (best ox. agt)  
 27<sup>+</sup> no unauthorized use allowed

28. Consider the following half-cell reactions and associated standard half-cell potentials and determine which species is the **best reducing agent**.

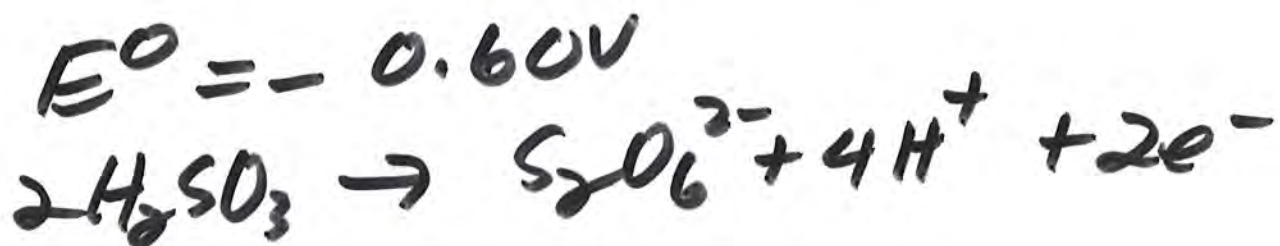
	$E^\circ$
$\text{S}_2\text{O}_6^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{SO}_3(\text{aq})$	+0.60 V
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.771 V
$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\ell)$	+1.00 V
$\text{N}_2\text{O}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O}(\ell)$	+1.77 V

a)  $\text{Fe}^{2+}$ b)  $\text{H}_2\text{SO}_3$ c)  $\text{N}_2$ d)  $\text{VO}^{2+}$ e)  $\text{VO}_2^+$ 

Best red. agt. : most easily  
 ox

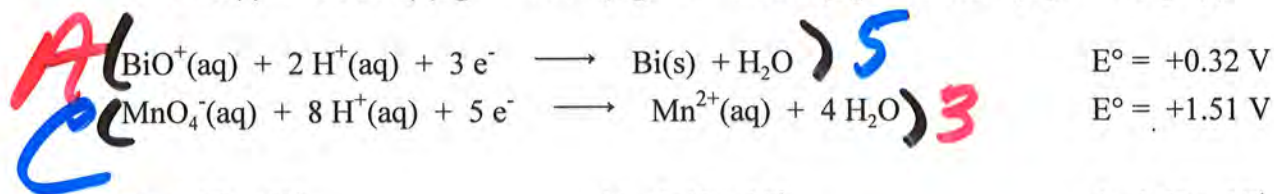
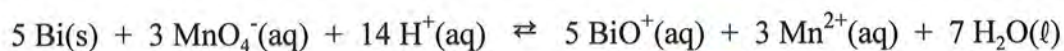
$\text{N}_2\text{O}$  most easily red  
 (best ox. agt)  
 most (+)  $E^\circ$

$\text{H}_2\text{SO}_3$  most easily ox  
 (strongest red. agt)  
 least (+)  $E^\circ$





29. Use the following  $E^\circ$  for the electrode potentials, calculate  $\Delta G^\circ$  in kJ for the indicated reaction.



a)  $-1.72 \times 10^2$

b)  $-1.42 \times 10^2$

c)  $-1.20 \times 10^4$

d)\*  $-1.72 \times 10^3$

e)  $-1.42 \times 10^3$

$$\Delta G^\circ = -n F E^\circ$$

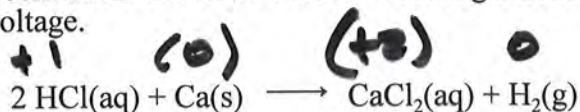
$$\begin{aligned}
 E_{\text{cell}}^\circ &= E_c^\circ - E_a^\circ \\
 &= 1.51 - 0.32 \\
 &= 1.19 \text{ V}
 \end{aligned}$$

$$n = 15 \text{ e}^- \text{ trans}$$

$$\begin{aligned}
 \Delta G^\circ &= -n F E^\circ \\
 &= - (15 \text{ mole e}^-) \left( \frac{96,500 \text{ C}}{\text{mole e}^-} \right) (1.19 \text{ V}) \\
 &= -1.7225 \times 10^6 \text{ C} \cdot \text{V} \\
 &= -1.7225 \times 10^6 \text{ J}
 \end{aligned}$$

$$\Delta G^\circ = -1.72 \times 10^3 \text{ kJ}$$

30. Consider an electrochemical cell in which the following reaction occurs and predict which changes will increase the cell voltage.



- I increase the amount of Ca(s)  
 II decrease the pressure of H<sub>2</sub>(g)  
 III decrease the [HCl(aq)]

a) I

b)\* II

c) III

d) I &amp; II

e) II &amp; III

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

$$E = E^\circ - \frac{0.0592}{2} \log \left( \frac{[\text{CaCl}_2] P_{\text{H}_2}}{[\text{HCl}]^2} \right)$$

I) inc amt Ca(s)  
 Nothing - not in Q

II) dec P<sub>H<sub>2</sub></sub>  
 Q ↓ num dec.  
 log Q dec.  
 E° - smaller # E ↑

III) dec [HCl]  
 denom dec Q ↑ (log Q) ↑  
 E° - larger # E ↓ ← rev



31. Which of the following is characteristic of the **anode** in an electrolysis cell?

- a) It is where reduction occurs.
- b)\* It attracts negative ions.
- c) It receives electrons from the wire.
- d) It may gain weight during electrolysis.
- e) More than one of the above is correct.

Voltaic  
Spont  
 $E > 0$

Anode: OX



Cathode: red



A: —

C: +

Electrolytic

Non Spont

$E < 0$

OX

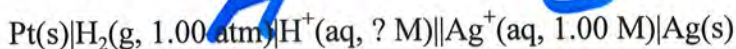
red

A: +

C: —

Battery pumps  
 $e^{-}$  onto Cat.  
& pulls  $e^{-}$   
from An.

32. The standard electrode potential of  $\text{Ag}^+$  is 0.800. The measured voltage of the following cell is 0.900 V at 25°C. Calculate the pH of the solution.



a)\* 1.69

b) 3.38

c) 1.12

d) 2.15

e) 2.78



$E = 0.900 \text{ V}$

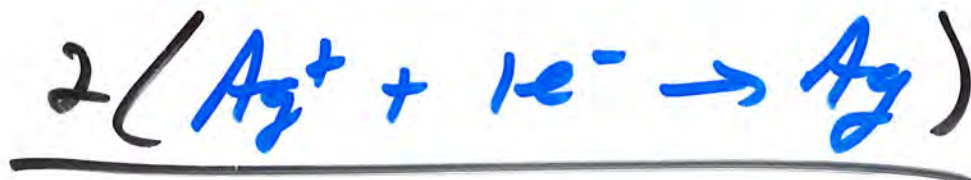
$E = E^\circ - \frac{0.0592}{n} \log Q$



$E^\circ = 0$



$E^\circ = 0.800$



$n = 2 \text{ e}^- \text{ trans}$

$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}} - E^\circ_{\text{H}_2}$

$= 0.800 - 0 = 0.800 \text{ V}$

$$Q = \frac{[H^+]^2}{P_{H_2} [A_5^+]^2}$$

$$Q = \frac{[H^+]^2}{(1)(1)^2} = [H^+]^2$$

$$E = E^0 - \frac{0.0592}{2} \log [H^+]^2$$

$$= E^0 - \frac{2(0.0592)}{2} \log [H^+]$$

$$E = E^0 - 0.0592 \log [H^+]$$

$$E = E^0 + (0.0592)(-\log [H^+])$$

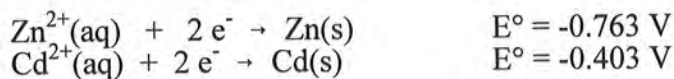
$$\frac{E - E^0}{0.0592} = -\log [H^+] = pH$$

$$pH = \frac{0.900 - 0.800}{0.0592}$$

$$= 1.69$$



33. Using standard electrode potentials, calculate the  $\Delta G$  (kJ) for the following electrochemical cell



a) 67.0

b) -69.5

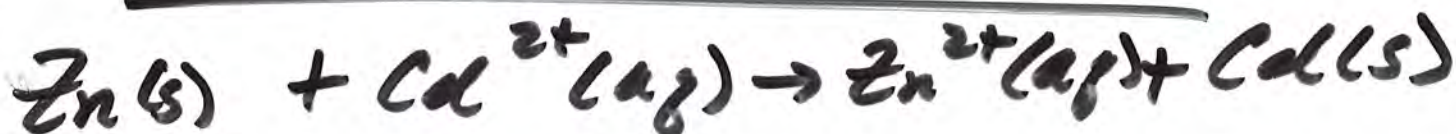
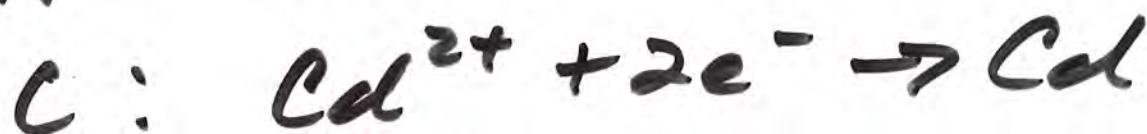
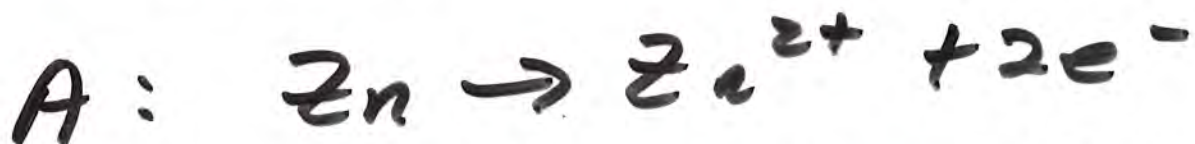
c)\* -73.4

d) -65.0

e) 71.5

$$\Delta G = -nFE$$

$$E = E^\circ - \frac{0.0592}{n} \log Q$$



$$n = 2$$

$$E^\circ = E^\circ_{\text{C}} - E^\circ_{\text{A}}$$

$$= (-0.403) - (-0.763)$$

$$= 0.36 \text{ V}$$

$$E = E^\circ - \frac{0.0592}{2} \log \left( \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} \right)$$

$$= 0.36 \text{ V} - \frac{0.0592}{2} \log \left( \frac{0.010}{0.050} \right)$$

$$= 0.3806 \text{ V} = 0.38 \text{ V}$$

$$\Delta G = -n F E$$

$$= - (2) \underset{\substack{\text{mol} \\ e^-}}{196,500} \underset{\substack{\text{C/mol} e^-}}{(0.38 \text{ V})}$$

~~500~~

$$= - 73,340 \quad \text{C}\cdot\text{V}$$

$$= - 73.3 \text{ kJ}$$

$$1 \text{ J} = 1 \text{ C}\cdot\text{V}$$

34. How many minutes will it take an electric current of 3.64 A to deposit all the copper from 740 mL of 0.250 M  $\text{CuSO}_4(\text{aq})$ ? (atomic weight: Cu = 53.55)

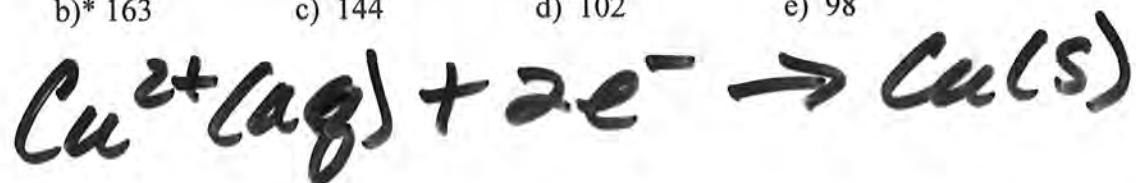
a) 182

b)\* 163

c) 144

d) 102

e) 98



$$? \text{ C} = 0.740 \frac{\text{L}}{\text{soln}} \times \frac{0.250 \text{ mol Cu}^{2+}}{1 \text{ L soln}} \times \frac{2 \text{ mole}^{-}}{1 \text{ mol Cu}^{2+}} \times \frac{96,500 \text{ C}}{1 \text{ mole}^{-}}$$

$$= 3.57 \times 10^4 \text{ C}$$

$$A = C / \Delta$$

$$? \Delta = \frac{3.57 \times 10^4 \text{ C}}{3.64 \text{ A}}$$

$$= 9.81 \times 10^3 \Delta$$

$$= (163 \text{ min})$$