Chemistry 1250 - Sp22
Solutions for Practice Final

1) $A + B \rightleftarrows X + Y$ $K_c = 9.5 \times 10^{-33}$ at 472 K

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.)

$$K_c = \frac{[X]\,[Y]}{[A]\,[B]} = 9.5 \times 10^{-33}$$ 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.
$[A] = [B] = 999.9999999999$ 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 <u>only</u> 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 <u>only</u> 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.

<u>**E**</u>

2)

(1) $NOBr\ (g) \rightleftarrows NO\ (g) + \frac{1}{2} Br_2\ (g)$

$$K_1 = \frac{[NO]\,[Br_2]^{1/2}}{[NOBr]}$$

(2) $N_2\ (g) + O_2\ (g) \rightleftarrows 2\ NO\ (g)$

$$K_2 = \frac{[NO]}{[N_2]\,[O_2]}$$

Want K for

(3) $2\ NOBr\ (g) \rightleftarrows N_2\ (g) + O_2\ (g) + Br_2\ (g)$

K_{rev} for rev. rx is $1/K_{for}$ (reciprocal of K_{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

$a\,A + b\,B \rightleftarrows x\,X + y\,Y$

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

Multiply by n

$(a\cdot n)\,A + (b\cdot n)\,B \rightleftarrows (x\cdot n)\,X + (y\cdot n)\,Y$

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

Multiply by -1 reverses rxn.

$-a\,A + -b\,B \rightleftarrows -x\,X + -y\,Y$

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

$x\,X + y\,Y \rightleftarrows a\,A + b\,B$

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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.

Rxn 1 + Rxn 2 = Rxn 3

$K_1 * K_2 = K_3$

Proof

(1) $a\,A + b\,B \rightleftarrows x\,X + y\,Y$ and (2) $c\,C + d\,D \rightleftarrows r\,R + s\,S$

$$K_1 = \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b} \qquad K_2 = \frac{[R]^r\,[S]^s}{[C]^c\,[D]^d}$$

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

$a\,A + b\,B + c\,C + d\,D \rightleftarrows x\,X + y\,Y + r\,R + s\,S$

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

$K_3 = K_1 * K_2$

To get reaction 3 for this question,

(3) $2\,NOBr\,(g) \rightleftarrows N_2\,(g) + O_2\,(g) + Br_2\,(g)$

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

$(1)_{rx1*2}$ $2\,NOBr\,(g) \rightleftarrows 2\,NO\,(g) + Br_2\,(g)$ $K_{rx1*2} = K_1^{\,2}$

$(2)_{rev\_1}$ $2\,NO\,(g) \rightleftarrows N_2\,(g) + O_2\,(g)$ $K_{rev\_2} = K_2^{\,-1}$

$2\,NOBr\,(g) \rightleftarrows N_2\,(g) + O_2\,(g) + Br_2\,(g)$ K_3

$K_3 = K_{rx1*2} * K_{rev\_2} = K_1^{\,2} * K_2^{\,-1}$

A

3) $2\,CO(g) \rightleftarrows C(\mathbf{s}) + CO_2(g)$

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

$\Delta n = 1 - 2 = -1$ Do **<u>NOT</u>** include pure **solids**, **liquids** or **aqueous** when calculating Δn.

$$K_c = \frac{[CO_2]}{[CO]^2} \qquad K_p = \frac{P_{CO2}}{(P_{CO})^2}$$

R = 0.0821 L•atm/mol•K <u>NOT</u> 8.314 J/mol•K

$T = 800°C + 273 = 107\underline{\mathbf{3}}$ K (**must** be in **<u>kelvin</u>**)

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

$K_p = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{-1}$

$= (7.14 \times 10^{-2})\,\{(0.0821)\,(1073)\}^{-1}$

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

<u>B</u>

4)

For Pressure changes

P <u>inc</u> ==> **<u>fewer</u>** moles **<u>gas</u>**

P <u>dec</u> ==> **<u>more</u>** moles **<u>gas</u>**

Changes in Pressure do **<u>not</u> affect liquids**, **solids** or **aqueous** (their conc. do not change w. P like conc. of gases do)

If **<u>no</u> <u>change</u>** in **moles gas** changes in **P** have **<u>no</u> effect**

<u>INC</u> Pressure go **towards <u>FEWER</u>** moles **GAS**

3 mol gas 2 mol gas
1) $2\,CO(g) + O_2(g) \rightleftarrows 2\,CO_2(g)$ ---------->

2 mol gas 2 mol gas
2) $2\,NO(g) \rightleftarrows N_2(g) + O_2(g)$ No Change (no change in moles gas)

1 mol gas 2 mol gas
3) $N_2O_4(g) \rightleftarrows 2\,NO_2(g)$ <----------

4 mol gas 1 mol gas
4) Ni(**s**) + $4\,CO(g) \rightleftarrows Ni(CO)_4(g)$ ---------->

4 mol gas 2 mol gas
5) $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$ ---------->

<u>C</u> (1, 4, 5) can use stuff below but just remembering **Inc P => fewer mole gas** is easier

Δn = (# mol gaseous products) - (# mol gaseous reactants)

Δn < 0 (i.e. # mol gaseous products < # mol gaseous reactants)

<u>Inc</u> <u>P</u> shifts rx to <u>right</u>
<u>Dec</u> <u>P</u> shifts rx to <u>left</u>

Δn > 0 (i.e. # mol gaseous products > # mol gaseous reactants)

<u>Inc</u> <u>P</u> shifts rx to <u>left</u>
<u>Dec</u> <u>P</u> shifts rx to <u>right</u>

Δn = 0 (i.e. # mol gaseous products = # mol gaseous reactants)

Changing P has NO effect on the rx

5)

Want **reactant** formation **favored** (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 (**ΔH < 0**)

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

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

Low **P**			High **T**
<------	4 mol gas 2 mol gas 1) $N_2(g) + 3 H_2(g) \rightleftarrows 2 NH_3(g)$ + **heat**	ΔH = -91.8 kJ	<--------
------>	2 mol gas 3 mol gas 2) **heat** + $2 CO_2(g) \rightleftarrows 2 CO(g) + O_2(g)$	ΔH = + 566 kJ	-------->
------>	2 mol gas 3 mol gas 3) $2 O_3(g) \rightleftarrows 3 O_2(g)$ + **heat**	ΔH = - 285 kJ	<--------
NC	2 mol gas 2 mol gas 4) $H_2(g) + F_2(g) \rightleftarrows 2 HF(g)$ + **heat**	ΔH = - 541 kJ	<--------
<------	3 mol gas 2 mol gas 5) **heat** + $N_2(g) + 2 O_2(g) \rightleftarrows 2 NO_2(g)$	ΔH = 66.4 kJ	-------->

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

A

6)

Reactant	**Product**	**Shift**
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.)

$Q = \frac{[P]}{[R]\downarrow}$ 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) $CO(g) + 3\,H_2(g) \rightleftarrows CH_4(g) + H_2O(g)$ **remove** $H_2O(g)$, **product**, $Q = \frac{[P]\downarrow}{[R]}$, Q < K, shift **right**

2) $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$ **add** $NH_3(g)$, **product**, $Q = \frac{[P]\uparrow}{[R]}$, Q > K, shift **left**

3) $H_2(g) + F_2(g) \rightleftarrows 2\,HF(g)$ **add** HF(g), **product**, $Q = \frac{[P]\uparrow}{[R]}$, Q > K, shift **left**

4) $N_2(g) + 2\,O_2(g) \rightleftarrows 2\,NO_2(g)$ **remove** $NO_2(g)$, **product**, $Q = \frac{[P]\downarrow}{[R]}$, Q < K, shift **right**

5) $BaO(\mathbf{s}) + SO_3(g) \rightleftarrows BaSO_4(\mathbf{s})$ **add** BaO(**s**), **solid** reactant, **NO shift**

A (1 & 4)

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

$$2\,H_2O(g) \quad + \quad Cl_2(g) \quad + \quad \textbf{heat} \quad \rightleftarrows \quad 4\,HCl(g) \quad + \quad O_2(g)$$

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

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

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

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

K inc

Remember:

Exothermic rxn	(ΔH < 0)	**Low T** favors **products**
T ↑ K ↓	and	T ↓ K ↑
Endothermic rxn	(ΔH > 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.

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

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

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

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

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

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

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

	I_2	+	Br_2	$\rightleftarrows$	2 IBr
initial	0.200		0.200		1.05
change	- x		- x		+ 2x
equil	0.200 - x		0.200 - x		1.05 + 2x

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

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

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

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

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

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

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

<u>A</u> (**0.116, 1.22**)

9)

Want the <u>conjugate</u> **<u>base</u>** of methylamine, CH_3NH_2. Treat it as an acid so it will lose an H^+. The conjugate base of an acid has 1 fewer proton (1 less H and a more negative charge)

$$\underset{\text{acid}}{CH_3NH_2} \;\; \text{---->} \;\; \underset{\text{conj. base}}{CH_3NH^-} + H^+$$

If you want the <u>conjugate</u> **<u>acid</u>** of methylamine, CH_3NH_2, treat it as a base and add H^+ to it. The conjugate acid of a base has 1 extra proton (an extra H and a more positive charge)

$$\underset{\text{base}}{CH_3NH_2} + H^+ \;\; \text{---->} \;\; \underset{\text{conj. acid}}{CH_3NH_3^+}$$

<u>E</u>

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

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

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

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

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

At 37°C

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

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

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

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

$pH = -\log[H^+] = 6.81$ 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**

D

11) Given the pH of a solution of 0.10 M NH_4Cl containing 0.10 M NH_3 as 9.20 and want $[H_3O^+]$

First of all remember that $H_3O^+ \equiv H^+$ (i.e. H^+ is shorthand for H_3O^+, hydronium ion)

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

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

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

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

C

12)

Remember the following:

Larger K_a ==> smaller pK_a ==> stronger acid ==> weaker conjugate base

Larger K_b ==> smaller pK_b ==> stronger base ==> weaker conjugate acid

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

	K_a
$HS^- \rightleftarrows H^+ + S^{2-}$	1.2×10^{-13}
$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}$	4.8×10^{-13}

K_a for HS^- < K_a for HPO_4^{2-} : HS^- weaker than HPO_4^{2-}

Since HPO_4^{2-} is the stronger acid its conjugate base, PO_4^{3-}, will be weaker.

$K_b(S^{2-}) = 8.3 \times 10^{-2}$ $K_b(PO_4^{3-}) = 2.1 \times 10^{-2}$

HS^-	weaker acid	S^{2-}	stronger base
HPO_4^{2-}	stronger acid	PO_4^{3-}	weaker base

C (Weaker, Stronger)

K_a $[H_3O^+]$ or $[H^+]$

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

a) 3.62×10^{-7} b) 2.89×10^{-8} c)* 5.80×10^{-8}

d) 1.16×10^{-7} e) 1.70×10^{-3}

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

$[HA] = .500$ M

$$HA \rightleftharpoons H^+ + A^-$$

HA	H^+	A^-
.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 HNO_2 is 19% ionized. What is the K_a?

a)* 4.4×10^{-4} b) 3.9×10^{-4} c) 3.6×10^{-4}

d) 5.0×10^{-4} e) 5.4×10^{-4}

$$\begin{array}{ccccc} HNO_2 & \rightleftharpoons & H^+ & + & NO_2^- \\ 0.010 & & 0 & & 0 \\ -x & & +x & & +x \\ \hline .010-x & & x & & x \end{array}$$

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

$$\%\,ion = \frac{[H^+]_{eq}}{[HNO_2]_0} \times 100\%$$

$$x = [H^+] = \left(\frac{\%\,ion}{100}\right)[HNO_2]_0$$

$$= \left(\frac{19\%}{100}\right)(0.010\,M)$$

$$= 1.9 \times 10^{-3}\,M$$

$$K_a = \frac{(1.9\times10^{-3})^2}{(0.01 - 1.9\times10^{-3})}$$

$$= 4.4\times10^{-4}$$

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

% 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 NH_4^+ solution (K_b: $NH_3 = 1.8 \times 10^{-5}$)?

a) 2.72 b) 3.11 c)* 4.98 d) 5.12 e) 7.61

$$NH_3 + H_2O \rightleftharpoons \underset{A}{NH_4^+} + OH^-$$

$$\begin{array}{ccccc} NH_4^+ & \rightleftharpoons & NH_3 & + & H^+ \\ 0.20 & & 0 & & 0 \\ -x & & +x & & +x \\ \hline .20-x & & x & & x \end{array}$$

$$K_{a_{NH_4^+}} = \frac{x^2}{.20-x} = \frac{K_w}{K_{b_{NH_3}}}$$

$$K_a \cdot K_b = K_w$$

$$\frac{x^2}{.20-\cancel{x}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}6 \times 10^{-10}$$

$$x = [H^+] = 1.05 \times 10^{-5}$$

$$pH = -\log(1.05 \times 10^{-5})$$

$$= 4.98$$

Weak Bases

$:NH_3$ CH_3NH_2

$(CH_3)_3\ddot{N}$

$$\underset{A}{HF} \rightleftharpoons H^+ + \underset{B}{F^-}$$

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

$$K_{b_{F^-}} = \frac{K_w}{K_{a_{HF}}}$$

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 $\mathcal{M} = \frac{g}{mol} = \frac{1.50g}{?\,mol}$

$$HC + NaOH \rightarrow NaC + H_2O$$

mol HC = mol NaOH

mol H^+ = mol OH^-

$mol = M \cdot V_L$

? mol NaOH

$$?\,mol\ NaOH = 34.1\,mL\ NaOH \times \underbrace{\frac{1L}{10^3\,mL} \times \frac{.250\,mol\ NaOH}{1\,L\ soln}}_{L_{soln} \cdot M}$$

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

mol HC = 8.525×10^{-3} mol

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

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

I $2\,N_2(g) + O_2(g) \longrightarrow 2\,N_2O(g)$ less disorder

3 mol 2 mol gas

$\Delta S < 0$

II $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

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

III $Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

$s + aq \rightarrow aq + g$ $\Delta S > 0$

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 ΔS (J/mol•K) of fusion for ethane which melts at -183°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

$$C_2H_6(s) \rightleftarrows C_2H_6(l)$$

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

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

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

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

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

$$Br_2(g) + F_2(g) \longrightarrow 2\,BrF(g)$$

$\Delta S \approx 0$

S° (J/K mole) 245.5 202.8 229.0

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

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

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

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

20. The standard free energy of formation of $H_2O(\ell)$ is -237.1 kJ/mol. Using the data for the following reaction, calculate the free energy of formation, $\Delta G_f°$, for $N_2H_4(\ell)$ (in kJ/mol).

$$N_2H_4(\ell) + O_2(g) \longrightarrow N_2(g) + 2\ H_2O(\ell) \qquad \Delta G° = -623.4\ \text{kJ}$$

a) 623.4 b)* 149.2 c) 386.3 d) 193.2 e) 860.5

$\Delta G^\circ_{f\,N_2H_4(\ell)}$: $N_2(g) + 2H_2(g) \rightarrow N_2H_4(\ell)$

ΔG_f° ? Φ Φ -237.1

$$\Delta G^\circ_{rxn} = [1(0) + 2(-237.1)] - [\Delta G^\circ_{f\,N_2H_4} + \Phi]$$

$$-623.4 = -472.2 - \Delta G^\circ_{f\,N_2H_4}$$

$$\Delta G^\circ_{f\,N_2H_4} = 149.2\ \text{kJ}$$

21. Consider the ΔG°_f and ΔH°_f (kJ/mole) for the following oxides. Which oxide can be **most easily** **<u>decomposed</u>** to form the metal and oxygen gas.

	ΔG_f°	ΔH_f°	ΔG°_{rev}
a) PbO	-187.9	-217.3	187.9
b) ZnO	-318.4	-348.3	318.4
[✓ c)* Ag_2O]	-11.2	-31.1	[✓ 11.2]
d) CdO	-228.4	-258.2	228.4

ΔG°_f

~~Δ~~

$$Pb(s) + \frac{1}{2} O_2(g) \rightarrow PbO(s) \quad -187.9$$

$$PbO \rightarrow Pb + \frac{1}{2} O_2$$

$$\Delta S < 0$$

22. From the following ΔH° and ΔS° values predict which of reactions I, II, and III would be spontaneous at 25°C.

	ΔH°(kJ)	ΔS°(J/K)	ΔG°
I	-5.0	-20	0.96
II	-10.0	-10	-7.02
III	-25.0	+75 spont	-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

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

$-20J \Rightarrow kJ$

$-.020$

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

$$\frac{3}{2} O_2(g) \longrightarrow O_3(g)$$

a) 157 b)* 163 c) 169 d) 172 e) 175

$$\Delta G° = -RT \ln K$$

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

$$= 163\ kJ$$

non spont at std. st. cond

(nonspont to prod.)

24. The $K_p = 0.113$ at 25°C and $\Delta H° = +57.2$ kJ for the following reaction. Calculate the **temperature** (°C) where $K_p = 1.00$

$$N_2O_4(g) \rightleftarrows 2\,NO_2(g)$$

a) 45 b)* 56 c) 65 d) 70 e) 76

$$\ln K = -\frac{\Delta H°_{rxn}}{R}\left(\frac{1}{T}\right) + C$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H°_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$R = 8.314\ J/mol \cdot K$

$\Delta H° = 57.2\ kJ$

$T \Rightarrow K$

Endo

T↑ K↑

25. For the following reaction, calculate the value of ΔG (kJ) at 25°C in a solution when $[Co^{3+}] = 0.0050$ M, $[NH_3] = 0.10$ M, and $[Co(NH_3)_6^{3+}] = 1.00$ M.

$Co^{3+}(aq) + 6\ NH_3(aq) \rightleftarrows Co(NH_3)_6^{3+}(aq)$ $\Delta G^\circ = -41.7$ kJ

a) −47.4 b) +20.5 c)* +5.7 d) −20.5 e) −5.7

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

$$Q = Q_C = \frac{[\ Co(NH_3)_6^{3+}]}{[Co^{3+}]\ [NH_3]^6} = \frac{(1.00)}{(0.0050)\ (0.10)^6} = 2.0 \times 10^8$$

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

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

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

spont

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

$Mg \rightarrow Mg^{2+} + 2e^-$

A $Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$ E° = -2.363 V

C $Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$ E° = -0.136 V

a)* +2.227 b) 2.499 c) -2.227 d) -2.499 e) +1.113

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

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

$$E^\circ_C > E^\circ_A$$

$$E^\circ_{cell} = (-0.136V) - (-2.363V)$$
$$= +2.227V$$

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

$\underline{3\,Ce^{4+}(aq)} + Bi(s) + H_2O(\ell) \rightleftarrows \underline{3\,Ce^{3+}(aq)} + BiO^+(aq) + 2\,H^+(aq)$ E° = +1.29 V

A $BiO^+(aq) + 2\,H^+(aq) + \boxed{3\,e^-} \longrightarrow Bi(s) + H_2O(\ell)$ E° = ?

C $(Ce^{4+}(aq) + \boxed{1\,e^-} \longrightarrow Ce^{3+}(aq))3$ E° = +1.61 V

a) -0.32 b)* +0.32 c) +2.90 d) -2.90 e) -1.45

$$E^\circ_{cell} = E^\circ_C - E^\circ_A$$

$$1.29\,V = 1.61 - E^\circ_A$$

$$E^\circ_A = 0.32V$$

most easily red (best ox agt)

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

	E°
$S_2O_6^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \rightarrow 2\,H_2SO_3(aq)$	+0.60 V
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.771 V
$VO_2^+(aq) + 2\,H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(\ell)$	+1.00 V
$N_2O(aq) + 2\,H^+(aq) + 2\,e^- \rightarrow N_2(g) + H_2O(\ell)$	+1.77 V

a) Fe^{2+} b)* H_2SO_3 c) N_2 d) VO^{2+} e) VO_2^+

Best red. agt. : most easily ox

N_2O most easily red (best ox. agt) most (+) E°

H_2SO_3 most easily ox (strongest red. agt) least (+) E°

$E^\circ = -0.60V$

$2H_2SO_3 \rightarrow S_2O_6^{2-} + 4H^+ + 2e^-$

29. Use the following E° for the electrode potentials, calculate ΔG° in kJ for the indicated reaction.

$$5\,Bi(s) + 3\,MnO_4^-(aq) + 14\,H^+(aq) \rightleftarrows 5\,BiO^+(aq) + 3\,Mn^{2+}(aq) + 7\,H_2O(\ell)$$

A $(BiO^+(aq) + 2\,H^+(aq) + 3\,e^- \longrightarrow Bi(s) + H_2O)\,5$ E° = +0.32 V

C $(MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O)\,3$ E° = +1.51 V

a) -1.72 x 10^2 b) -1.42 x 10^2 c) -1.20 x 10^4

d)* -1.72 x 10^3 e) -1.42 x 10^3

$$\Delta G^\circ = -nFE^\circ$$

$$E^\circ_{cell} = E^\circ_C - E^\circ_A$$

$$= 1.51 - 0.32$$

$$= 1.19\ V$$

$n = 15\ e^-$ trans

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

$$= -(15\ \cancel{mole}\,e^-)\left(\frac{96{,}500\ C}{\cancel{mole}\,e^-}\right)(1.19\ V)$$

$$= -1.72235 \times 10^6\ C \cdot V$$

$$= -1.72235 \times 10^6\ J$$

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

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

$$\overset{+1}{2\,HCl(aq)} + \overset{(0)}{Ca(s)} \longrightarrow \overset{(+2)}{CaCl_2(aq)} + \overset{0}{H_2(g)}$$

I increase the amount of $Ca(s)$
II decrease the pressure of $H_2(g)$
III decrease the $[HCl(aq)]$

a) I b)* II c) III d) I & II e) II & III

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

$$E = E^\circ - \frac{0.0592}{2}\log\left(\frac{[CaCl_2]\,P_{H_2}}{[HCl]^2}\right)$$

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

II) dec P_{H_2}
Q ↓ num dec.
log Q dec.
$E^\circ -$ smaller # E ↑
for →

III) dec [HCl]
denom dec Q ↑ (log Q) ↑
$E^\circ -$ 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	Electrolytic
Spont	Non Spont
$E > 0$	$E < 0$
Anode: ox $Cu \rightarrow Cu^{2+} + 2e^-$	ox
Cathode: red $Cu^{2+} + 2e^- \rightarrow Cu$	red
A: −	A: +
C: +	C: −
	Battery pumps e^- onto Cat. & pulls e^- from An.

32. The standard electrode potential of 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 C

$$Pt(s)|H_2(g, 1.00\ atm)|H^+(aq, ?\ M)||Ag^+(aq, 1.00\ M)|Ag(s)$$

a)* 1.69 b) 3.38 c) 1.12 d) 2.15 e) 2.78

E°

$Ag^+ + 1e^- \rightarrow Ag(s)$ 0.800

$E = 0.900\ V$

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

E°

A: $2H^+ + 2e^- \rightarrow H_2$ 0

C: $Ag^+ + 1e^- \rightarrow Ag$ 0.800

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$\underline{2(Ag^+ + 1e^- \rightarrow Ag)}$$

$$H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s)$$

$n = 2\ e^-$ trans

$$E^\circ_{cell} = E^\circ_{Ag} - E^\circ_{H_2}$$

$$= 0.800 - 0 = 0.800\ V$$

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

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

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

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

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

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

$$\frac{E - E^\circ}{.0592} = -\log[H^+] = pH$$

$$pH = \frac{0.900 - 0.800}{.0592}$$

$$= 1.69$$

33. Using standard electrode potentials, calculate the ΔG (kJ) for the following electrochemical cell

A C

$Zn(s)|Zn^{2+}(aq, 0.010\ M)||Cd^{2+}(aq, 0.050\ M)|Cd(s)$

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E° = -0.763 V
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ E° = -0.403 V

a) 67.0 b) -69.5 c)* -73.4 d) -65.0 e) 71.5

$$\Delta G = -nFE$$

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

$$A:\ Zn \rightarrow Zn^{2+} + 2e^-$$

$$C:\ \underline{Cd^{2+} + 2e^- \rightarrow Cd}$$

$$Zn(s) + Cd^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cd(s)$$

$$n = 2$$

$$E^\circ = E^\circ_C - E^\circ_A$$

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

$$= 0.36V$$

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

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

$$= 0.3\underline{8}06V = 0.38V$$

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

$$= -\underset{\text{mol } e^-}{(2)}\,\underset{C/\text{mole}^-}{(96,500)}\,(0.38V)$$

$$= -73,340 \qquad C\cdot V$$

$$= -73.3\ kJ$$

$$1\ J = 1\ C\cdot V$$

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 $CuSO_4$(aq)? (atomic weight: Cu = 53.55)

a) 182 b)* 163 c) 144 d) 102 e) 98

$$\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$$

$$?\,\mathrm{C} = 0.740\,\cancel{\mathrm{L}}\ \cancel{\mathrm{soln}} \times \frac{.250\,\mathrm{mol}\,\cancel{\mathrm{Cu^{2+}}}}{1\,\cancel{\mathrm{L\,soln}}} \times \frac{2\,\cancel{\mathrm{mol}}\,\mathrm{e^-}}{1\,\cancel{\mathrm{mol\,Cu^{2+}}}} \times \frac{96{,}500\,\mathrm{C}}{1\,\cancel{\mathrm{mol}\,\mathrm{e^-}}}$$

$$= 3.57 \times 10^{4}\,\mathrm{C}$$

$$\mathrm{A = C/s}$$

$$?\,\mathrm{s} = \frac{3.57 \times 10^{4}\,\mathrm{C}}{3.64\,\mathrm{A}}$$

$$= 9.81 \times 10^{3}\,\mathrm{s}$$

$$= (163\,\mathrm{min})$$