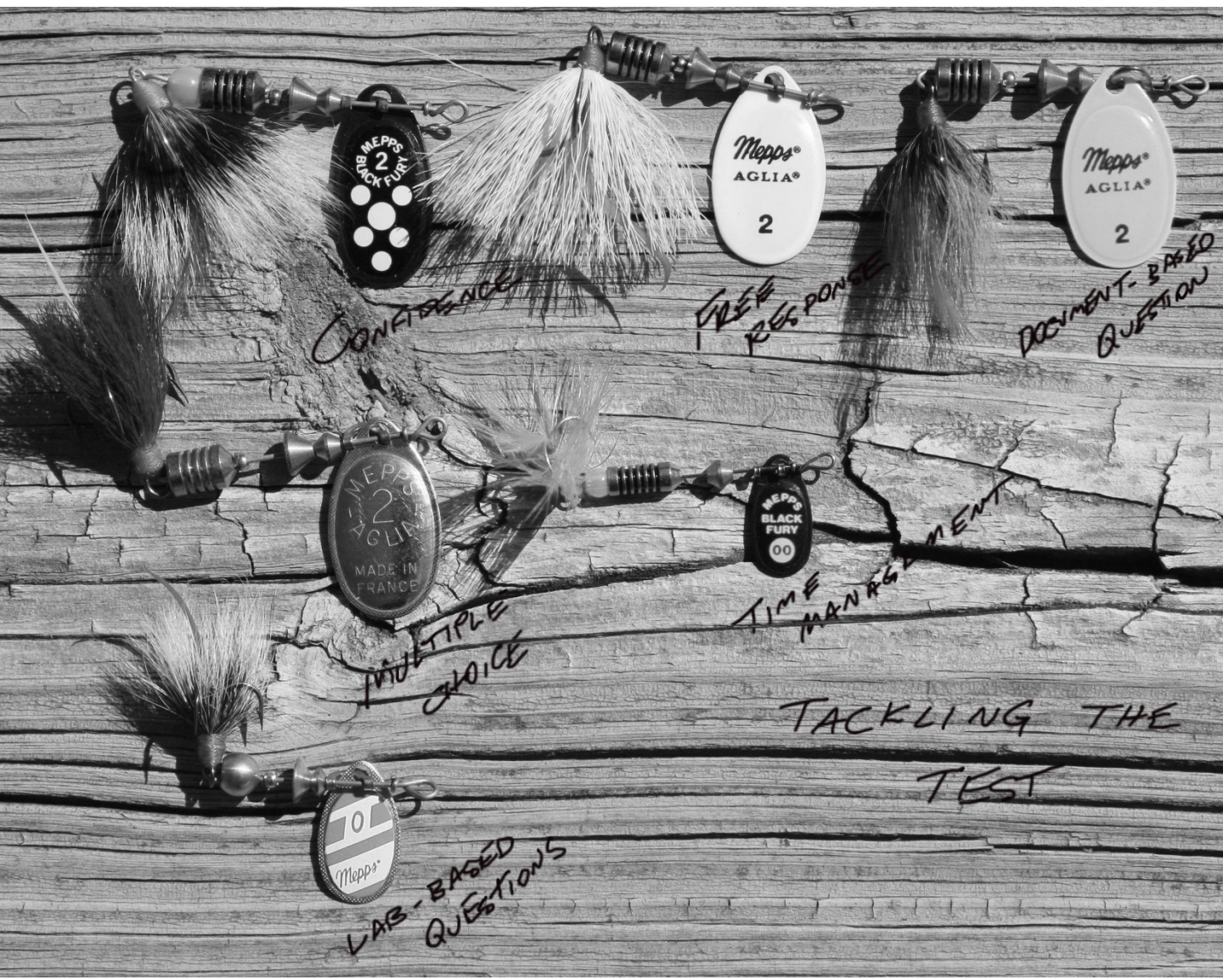


Chemistry

General Equilibrium and K_{sp}



Periodic Table of the Elements

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012															9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30															17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)	§Not yet named					

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

*Lanthanide Series:

†Actinide Series:

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$
$$= K_a \times K_b$$

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

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

1 atm = 760 mm Hg

$$= 760 \text{ torr}$$

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

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

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, $F = 96,485$ coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



What I Absolutely Have to Know to Survive the AP Exam

The following might indicate the question deals with equilibrium and solubility equilibrium:
Initial concentrations and/or pressures; original concentration and/or pressures; placed in a container; at equilibrium;
LeChâtelier's principle (reaction shift direction); K ; K_c ; K_p ; equilibrium concentration; percent dissociation; equilibrium
expression; law of mass action; molar solubility, precipitation, ; K_{sp} ; ; Q_{sp} ; poorly soluble, when does precipitation
form...

Equilibrium: *It's Dynamic!*

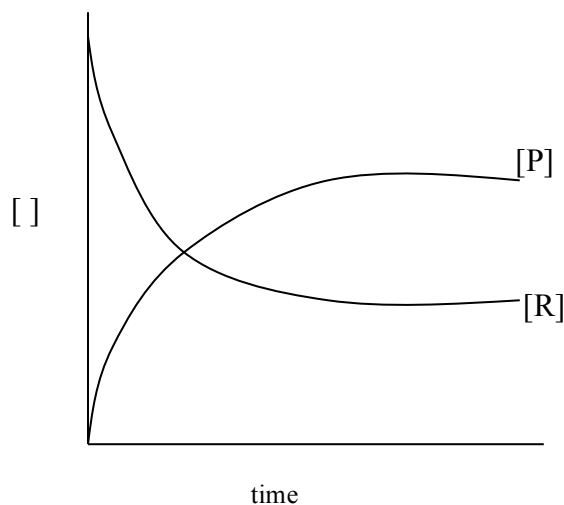
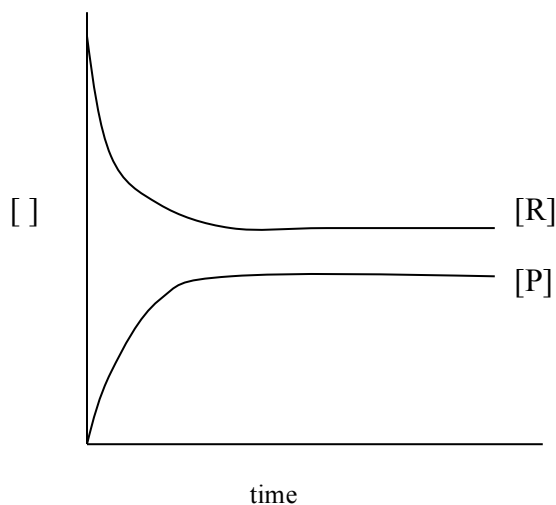
Equilibrium is the state where the concentrations of all reactants and products remain constant with time.
Reactions are reversible. This is indicated by double arrows...

Dynamic means that the reaction is proceeding in the *forward* and in the *reverse* directions; even when equilibrium is established (i.e. the concentration of the reactants and products remain constant) the forward and reverse reactions continue. The reaction concentrations do not change because the rate of the forward and reverse reactions are equal (remember kinetics?).

The Equilibrium Position: *Where is it?*

Reactions that reach equilibrium do so with:

- The concentration of reactants greater than products – the reaction “lies far to the left” or “the reaction favors reactants” and “the equilibrium constant K is less than 1.”
- The concentration of products greater than reactants – the reaction “lies far to the right” or “the reaction favors products” and “the equilibrium constant K is greater than 1.”
- The concentrations of reactants and products are close to equal when the equilibrium constant K is close to 1.



Factors that affect the equilibrium position:

- Initial concentrations of reactants: more collisions, more effective collisions, possibly more products i.e. a faster reaction (kinetics again)
- Energy: Energies of the reactants and products (favor minimum energy – thermodynamics, enthalpy)
- Order/disorder of reactants and products (favor maximum disorder – thermodynamics, enthalpy)
- Really a combination of all these issues...

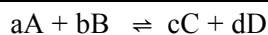


The Equilibrium Expression: *Law of Mass Action!*

The equilibrium expression: ratio of concentration/pressure of products to reactants at the equilibrium position

- Regardless of the initial conditions at a given temperature, a reaction will reach its equilibrium position with the same ratio of products to reactants, i.e. the ratio will be the same...
- It is temperature dependent – change the temperature; change the ratio... i.e. the reaction reaches equilibrium at a different position

For the reaction:



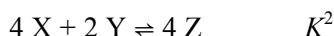
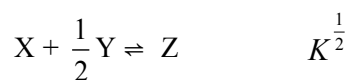
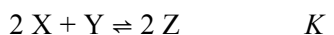
Equilibrium Constant Expression: $K_c = \frac{[\text{Products}]^{\text{coefficients}}}{[\text{Reactants}]^{\text{coefficients}}} \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

Where...

- [] indicates concentration in Molarity, M
- K_c – indicates concentrations; can be used for (aq) or (g) reactants and products as long as they are measured in terms of molarity, M .
- K_p – is for partial pressure; all species in the expression must be gases and measured in pressure units (usually atmospheres)
- Pure solids – do not appear in expression as their “concentrations” are not changed effectively
- Pure liquids – do not appear in expression

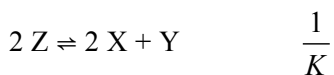
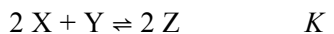
STOICHIOMETRIC COEFFICIENTS

- Different stoichiometric coefficients in a reaction result in a different ratio, or value for K .
 - When the coefficients of the balanced equation are multiplied by some factor, the equilibrium constant, K is raised to the power of that factor.



REVERSING EQUATIONS

- When the equation is written in reverse, take the reciprocal of K to get the equilibrium constant for the reaction.



ADDING EQUATIONS

- If you add 2 or more reactions to get a summary reaction, simply multiply respective K 's ($K_1 \times K_2 \times K_3 \dots$)

K_c & K_p ARE NOT INTERCHANGEABLE

MUST KNOW FORMULA (remember Politically Correct – P before C)

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

Δn = total moles gas prod. – total moles gas reactants

R = universal gas law constant 0.0821 L atm/mol K

T = temperature in Kelvin

EXAM TIME SAVER ALERT

- $K_c = K_p$ if the number of moles of gaseous product = number of moles of gaseous reactants because $\Delta n = 0$

$$K_p = K_c(RT)^0$$

$$K_p = K_c(1)$$

$$K_p = K_c$$



Calculating with the Equilibrium Expression

You **MUST** have a balanced equation.

If the amounts are given in moles **BE WARY** – you must convert to M (molarity)

Write the Equilibrium Constant Expression for K_c or K_p

Set up **RICE TABLE**

R = Balanced Reaction

I = Initial concentrations

If nothing about the products are mentioned then the reaction hasn't started so there are no initial concentrations for products; if they are put them in but you are in the land of Q (more on that later)

C = Change in concentration

If the products are initially zero (0) then the reactants lose (–) and the products gain (+); if there are products present initially as well as reactants then you must enter the land of Q to determine who gains (+) and who loses (–). Remember: Everything Changes stoichiometrically!!!!

E = Equilibrium concentrations

These are the concentrations (pressures) of all species at equilibrium

Hints:

- Look for very small K values (where $K < 10^{-5}$ or $M = 1000 \times K$) the “ $-x$ ” in the change may be negligible and the need for the quadratic equation is no more.... If “ $-x$ ” is necessary, then see if the problem may be a perfect square and thus, ease the steps of solving.
- If none of the initial concentrations are zero, then Q must be calculated first to determine the direction of the shift (who gains and loses) before calculating the equilibrium concentrations.
- Watch for being given one of the equilibrium concentrations in the problem. If so there is no need for (x) because there is no unknown; you can work backwards.
- Everything Changes stoichiometrically!!!!

Le Châtelier's Principle

Le Châtelier's Principle states that if a stress is applied to a system at equilibrium, the position of the equilibrium will shift in the direction which best reduces the stress.

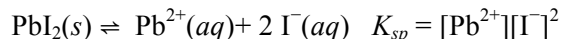
What to watch for...

- Shifts occur to reestablish equilibrium positions. Think about Q !
- Temperature – exothermic think of heat as a product; endothermic think of heat as a reactant.
- Adding or removing a reagent – shift tries to reestablish K . If you remove it, the reaction shifts to replace it; if you add it, the reaction shifts to get rid of it. Be careful, it doesn't shift enough to use up all of what you added or removed. If you add something, its concentration will remain higher than before it was added.
- Pressure – Increasing pressure favors a shift to the side with the fewest # of moles of gas; the converse is true.
- Volume – same effect as pressure; remember Boyle's Law... pressure and volume are inversely related, thus increasing the volume is the same as decreasing the pressure and vice versa...
- Catalysts – **NO EFFECT** on K ; just gets to equilibrium faster (kinetics moment)!
- **REMEMBER** – nothing but a change in temperature will change the **VALUE** of K .



Solubility Product: *It's K_{sp}!*

When solids are first added to water no salt ions are present. As dissolution occurs, the ions dissolve in the water until equilibrium is established and a saturated solution is formed. The extent to which a substance dissolves in the solvent is the solubility. The equilibrium constant, K_{sp} , is the product of all ions in solution.



What is K_{sp} telling you?

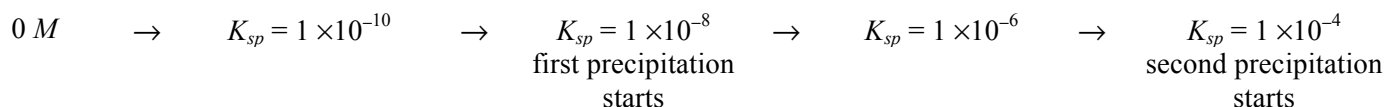
1. The maximum amount of ions that dissolve as a poorly solubility salt is added to water to form a solution
2. The minimum concentration of ions necessary in a solution for precipitation to begin
 - Note: solids don't appear in the K expression
 - Be aware of the coefficients
 - the 1:2 ratio is important when determining concentrations of the ions present
 - the 2 results in an expression of $[\text{I}^{-}]^2$

A precipitate is an insoluble compound formed when two soluble solutions are mixed. To determine whether a precipitate will form the reaction quotient will need to be calculated.

- $Q < K$ unsaturated solution is formed as the reaction has not reach the equilibrium position; no ppt
- $Q = K$ a saturated solutions is made; no ppt
- $Q > K$ a supersaturated solution is formed the concentration of ions are greater than allowed; a ppt will form

There are essentially 3 types of problems you will encounter with solubility equilibria

1. Calculate K_{sp}
 - Plug in concentrations to K_{sp} expression
 - Apply ratios of coefficients as needed
2. Calculate "x"
 - Use x and $2x$ type variables for concentrations of salt ions and solve for x
 - If a "COMMON ION" is mentioned use its concentration and x or $2x$ variable for concentration of the other salt ion and solve for x
3. Conditions for a precipitation to occur
 - How much must be added for a precipitation to start – solve for x in the K_{sp} expression
 - Which salt will precipitate first?
 - The smaller the K_{sp} the quicker it will precipitate; think time line



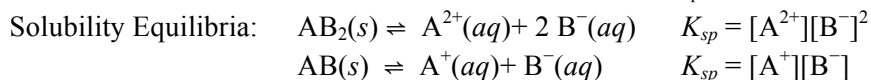


General and Solubility Equilibrium Cheat Sheet

Relationships

Equilibrium Expression

$$K_c = \frac{[\text{Products}]^{\text{coefficients}}}{[\text{Reactants}]^{\text{coefficients}}} \quad K_p = \frac{(\text{Products } P_{\text{atmospheres}})^{\text{coefficient}}}{(\text{Reactants } P_{\text{atmospheres}})^{\text{coefficient}}} \quad \text{Either setup for } Q$$



Converting between K_p and K_c : $K_p = K_c(RT)^{\Delta n}$

Be sure to leave out any solids and liquids and realize that changing their amounts can in no way affect the position of the equilibrium – they are not variables that are included in the equilibrium expression.

Manipulating K for different versions of the same reaction: reverse rxn = $1/K$; double coefficients = K^2 ; $1/2$ the coefficients = $K^{1/2}$
 Adding reactions = multiply K values

If K is >1 then reaction favors products because K ratio is “top heavy”

If K is <1 then reaction favors reactants because K ratio is “bottom heavy”

LeChâtelier’s Principle: If a system at equilibrium is stressed the system will shift direction until equilibrium is re-established.

A LeChâtelier’s shift will result in different concentration/pressure values for the individual members of the reaction but the VALUE of K will not change without a change in the temperature.

$Q < K$ unsaturated solution is formed as the reaction has not reach the equilibrium position; no ppt
 $Q = K$ a saturated solutions is made; no ppt

$Q > K$ a supersaturated solution is formed the concentration of ions are greater than allowed; a ppt will form

Connections

Thermodynamics: $\Delta G = \Delta H - T\Delta S$

Electrochem: $E_{\text{cell}} = E^{\circ}_{\text{table}} - \frac{0.0592}{n} \log Q$

The easiest question you can be asked is “What is the value of ΔG or E_{cell} when the system is at equilibrium?”
 Answer: ZERO

Potential Pitfalls

No units on K – you finally get to ignore units – just don’t do it with other stuff!!!!

LeChâtelier’s tricky questions:

- Only temperature will change the value of K ; no shifting can affect value of K
- Amounts of solids and liquids that are not in the K expression can not change position or size of K
- Adding an inert gas (He, Ar, Ne...) to a gaseous equilibrium has NO EFFECT since it is not represented in the K expression.

In general equilibrium don’t forget that these equations may have 1:2 ratios or other ratios [i.e. $(2x)^2$ terms]

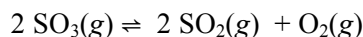
Be on the lookout for “perfect squares”.

Neglecting the “ $-x$ ” will be OK. You should never have to use the quadratic equation on the AP exam. Always show the original equilibrium expression with the $-x$ first then show the approximation without the $-x$.

For solubility be aware of the COEFFICIENTS!

- Don’t get confused by when to use x and $2x$ and when to apply the exponent.
- If either $[X]$ and $[Y]$ are given as numbers, use the number in the appropriate $[]$ and remember to square/cube it if necessary. USE “ x ” for the unknown concentration.
- If $[X]$ and $[Y]$ are both unknown to you THEN apply the coefficient ratio and use “ x ” and “ $2x$ ” in the appropriate $[]$. Remember to square/cube them if necessary.

NMSI Super Problem



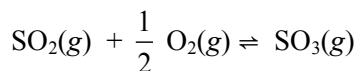
A 5.00 mol sample of sulfur trioxide, SO_3 is placed into a 5.00 L reaction vessel and allowed to decompose at 400 K according to the reaction above. Once equilibrium is established, 3.00 mol of sulfur dioxide, SO_2 , is present.

- Write the expression for the equilibrium constant, K_c , for the reaction above.
- Calculate
 - the initial molar concentration of SO_3
 - the equilibrium concentrations of O_2 , SO_2 , and SO_3
- Calculate the equilibrium constant, K_c for this reaction.
- Calculate the equilibrium constant, K_p for this reaction.

The reaction vessel above is cooled from 400 K to 298 K. The mixture reestablishes equilibrium with fewer moles of sulfur dioxide and oxygen gas at the new temperature.

- Is the forward reaction endothermic or exothermic? Justify your answer.
- Predict the sign of the standard entropy change, ΔS° , for the reaction. Explain.
- The value of the standard free energy change, ΔG° , for the reaction is $+141.8 \text{ kJ mol}^{-1}$. Calculate the value of the equilibrium constant, K , at 298 K.
- Determine whether the number of moles of SO_3 will increase, decrease, or stay the same after each of the following disturbances. Justify each response.
 - The temperature of the equilibrium mixture is decreased.
 - The volume of the reaction container is increased.

In a different experiment, sulfur dioxide and oxygen gases were added to a reaction vessel at 400 K and the following reaction occurred and equilibrium was established.



- Calculate the equilibrium constant, K_c for this reaction at 400. K.

2003 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

CHEMISTRY

Section II

(Total time—90 minutes)

Part A

Time—40 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

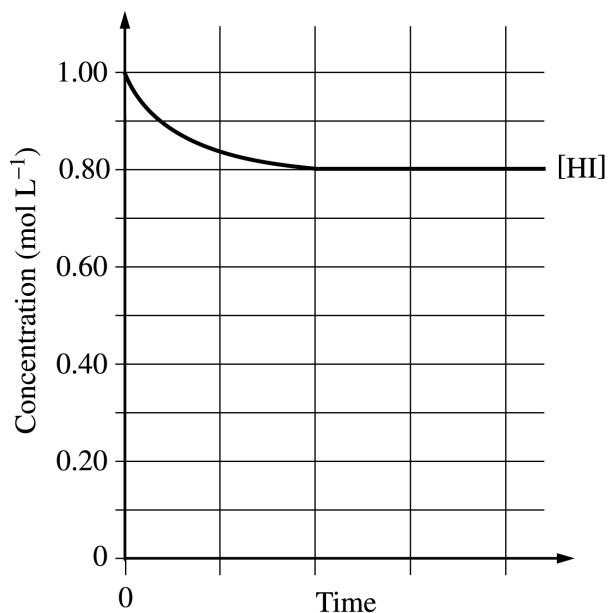
CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the goldenrod cover. Do NOT write your answers on the lavender insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.



1. After a 1.0 mole sample of $\text{HI}(g)$ is placed into an evacuated 1.0 L container at 700. K, the reaction represented above occurs. The concentration of $\text{HI}(g)$ as a function of time is shown below.



- (a) Write the expression for the equilibrium constant, K_c , for the reaction.
- (b) What is $[\text{HI}]$ at equilibrium?

2003 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

- (c) Determine the equilibrium concentrations of $\text{H}_2(g)$ and $\text{I}_2(g)$.
- (d) On the graph above, make a sketch that shows how the concentration of $\text{H}_2(g)$ changes as a function of time.
- (e) Calculate the value of the following equilibrium constants at 700. K.
- K_c
 - K_p
- (f) At 1,000 K, the value of K_c for the reaction is 2.6×10^{-2} . In an experiment, 0.75 mole of $\text{HI}(g)$, 0.10 mole of $\text{H}_2(g)$, and 0.50 mole of $\text{I}_2(g)$ are placed in a 1.0 L container and allowed to reach equilibrium at 1,000 K. Determine whether the equilibrium concentration of $\text{HI}(g)$ will be greater than, equal to, or less than the initial concentration of $\text{HI}(g)$. Justify your answer.