NATIONAL MATH + SCIENCE INITIATIVE

THERMODYNAMICS
Enthalpy, Entropy, Free Energy, & Equilibrium

What I Absolutely Have to Know to Survive the AP Exam
The following might indicate the question deals with thermochemistry and thermodynamics: calorimeter; enthalpy (ΔH); specific heat (C_p); endothermic; exothermic; heat (q); heat capacity (C); heat transfer; bond energy; entropy (ΔS); Gibb's free energy (ΔG); spontaneous; state function

Laws of Thermodynamics	
Zeroth Law:	Heat flows from hot to cold
First Law:	Energy and matter are conserved
Second Law:	Matter tends towards chaos
Third Law:	Entropy of a pure crystal at 0K is zero

Thermodynamic Terms			
What does each term tell us?			
Enthalpy (ΔH)	Energy content	+ endothermic	− exothermic
Entropy (ΔS)	Disorder	+ increase in the dispersal of matter	− decrease in the dispersal of matter
Free energy (ΔG)	Thermodynamically favored or not favored	+ not thermodynamically favored	− thermodynamically favored
Equilibrium (K)	Extent of reaction	>1 reaction favors products	<1 reaction favors reactants

Internal Energy (ΔE) and Heat Flow
- Refers to all of the energy contained within a chemical system.
- Heat flow between the system and its surroundings involves changes in the internal energy of the system. It will either increase or decrease
  - Increases in internal energy may result in a
    - temperature increase
    - chemical reaction starting
    - phase change
  - Decreases in internal energy may result in a
    - a decrease in temperature
    - phase change
  - Note: even though the change in internal energy can assume several different forms, the amount of energy exchanged between the system and the surroundings can be accounted for ONLY by heat (q) and work (w)
    - $\Delta E = q + w$
  - Work (w) refers to a force acting on an object; in chemical processes this acting force is done **by** a gas through expansion or **to** a gas by compression.
    - This is referred to as "pressure/volume" work
    - Thus, $w = -P\Delta V$
    - Where P is constant external pressure (atm) and ΔV (L) is the change in volume of the system

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Calculating Heat (q)

- Heat (q) gained or lost by a specific amount of a known substance can be calculated using the heat capacity of the substance and the change in temperature the system undergoes.
- Calorimetry
    - The process of experimentally measuring heat by determining the temperature change when a body absorbs or releases energy as heat.

- <u>Coffee-cup calorimetry</u> –use a Styrofoam cup, mix reactants that begin at the same temperature and look for change in temperature; the heat transfer is calculated from the change in temp.

$$q = mC\Delta T$$

- q = quantity of heat (Joules)
- ΔT is the change in temperature
    - $\Delta T = T_f - T_i$ (final – initial)
        - watch the sign; if the system loses heat to the surroundings then the $\Delta T = -$
- Cp = specific heat capacity (J/g°C)
- m = mass in grams
- the specific heat of water (liquid) = 4.184 J/g°C

Also note:
- $q = -\Delta H$ at constant pressure

Enthalpy (ΔH)

Enthalpy
- Heat content; ΔH
- Endothermic (+) or Exothermic (−)
- Calculating Enthalpy 5 Ways
- Calorimetry (see above)
- Enthalpy of formation, ΔH_f° (using table of standard values)
- Hess's Law
- Stoichiometry
- Bond Energies

ΔH_f° – Enthalpy of Formation

- Production of **ONE MOLE** of compound FROM ITS ELEMENTS in their standard states (°)
- Zero (0) for ELEMENTS in standard states: 25°C (298 K), 1 atm, $1M$

Big Mamma Equation: $\Delta H°_{rxn} = \Sigma \Delta H°_{f\,(products)} - \Sigma \Delta H°_{f\,(reactants)}$

$$3\,Al(s) + 3\,NH_4ClO_4(s) \rightarrow Al_2O_3(s) + AlCl_3(s) + 3\,NO(g) + 6\,H_2O(g)$$
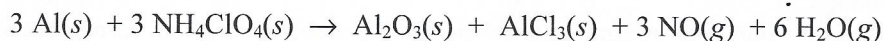
| Substance	ΔH_f° (kJ/mol)
$NH_4ClO_4(s)$	−295
$Al_2O_3(s)$	−1676
$AlCl_3(s)$	−704
$NO(g)$	90.0
$H_2O(g)$	−242

Hess's Law
- Enthalpy is not dependent on the reaction pathway. If you can find a combination of chemical equations that add up to the desired *overall* equation, you can sum up the ΔH_{rxn}'s for the individual reactions to get the overall ΔH_{rxn}.
- Remember this:
    - First decide how to rearrange equations so reactants and products are on appropriate sides of the arrows.
    - If equations had to be reversed, change the sign of ΔH
    - If equations had be multiplied to get a correct coefficient, multiply the ΔH by the coefficient
    - Check to ensure that everything cancels out to give you the correct equation.
    - **Hint** It is often helpful to begin working backwards from the answer that you want!**

$$C_2H_6(g) + \frac{7}{2} O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

$2\ C(s) + 3\ H_2(g) \rightarrow C_2H_6(g)$	$\Delta H° = -84.68\ kJ\ mol^{-1}$
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H° = -394\ kJ\ mol^{-1}$
$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$	$\Delta H° = -286\ kJ\ mol^{-1}$
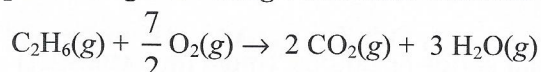
Using Stoichiometry to Calculate ΔH
- Often questions are asked about the enthalpy change for specific quantities in a reaction
- Use a little stoichiometry to solve these; just remember the $\Delta H°_{rxn}$ is per mole and convert to the unit and quantity given

How much heat is released when 1.00 g iron is reacted with excess O_2?

$$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s) \qquad \Delta H°_{rxn} = -1652\ kJ/mol\ rxn$$
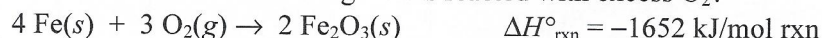
$$heat\ released = \frac{-1652kJ}{4\,mol\ Fe} \times \frac{1.00g}{55.85\dfrac{g}{mol}} = -7.39\ kJ\ per\ gram\ of\ Fe$$

- the (−) represents the LOSS or release of heat
- can also write 7.39 kJ released per gram of Fe

Using Bond Energy to Calculate ΔH
- Be able to use individual Bond Energy data to calculate the overall enthalpy change for a reaction

$$\Delta H°_{rxn} = Sum\ of\ Bonds\ Broken - Sum\ of\ Bonds\ Formed$$
$$H_2(g) + F_2(g) \rightarrow 2\ HF(g)$$
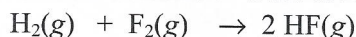
Bond Type	Bond Energy
H–H	432 kJ/mol
F–F	154 kJ/mol
H–F	565 kJ/mol

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Entropy (ΔS)

Entropy
▪ Dispersal of matter
▪ Less dispersal (−) or More dispersal (+)
▪ Calculating Entropy
▪ Table of standard values
▪ Hess's Law

- ▪ Entropy increases when:
    - ▪ Gases are formed from solids or liquids (most important!!!!)
        - ▪ $H_2O(\ell) \rightarrow H_2O(g)$
        - ▪ $C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$
    - ▪ A solution is formed
    - ▪ Volume is increased in a gaseous system (energy is more efficiently dispersed)
    - ▪ More complex molecules are formed

Big Mamma Equation II: $\Delta S^\circ_{rxn} = \Sigma\ \Delta S^\circ_{(products)} - \Sigma\ \Delta S^\circ_{(reactants)}$

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$
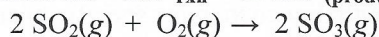
Substance	S° (J K^{-1} mol^{-1})
$SO_{2(g)}$	248.1
$O_{2(g)}$	205.3
$SO_{3(g)}$	256.6

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Free Energy (ΔG)

Free Energy
▪ Thermodynamic favorability of the reaction
▪ Thermodynamically favorable ($-\Delta G°$) or thermodynamically unfavorable ($+\Delta G°$)
▪ Calculate:
▪ Table of standard values
▪ Hess's Law

Big Mamma Equation III: $\Delta G°_{rxn} = \Sigma \Delta G°_{(products)} - \Sigma \Delta G°_{(reactants)}$

- $\Delta H°$, $\Delta S°$, and $\Delta G°$ may all be calculated from tables of standard values, from Hess' Law or from the Gibb's equation:

Connections to $\Delta H°$ and $\Delta S°$:

Granddaddy of Them All: $\Delta G° = \Delta H° - T\Delta S°$

Caution on units: $\Delta H°$ and $\Delta G°$ are typically given in kJ mol^{-1} whereas $\Delta S°$ typically given as J K^{-1}mol^{-1}

Conditions of ΔG

ΔH	ΔS	ΔG
−	+	Spontaneous (−) at all temp
+	+	Spontaneous (−) at high temp
−	−	Spontaneous (−) at low temp
+	−	Non-spontaneous (+) at all temp

Free Energy, Equilibrium, and Cell Potential

$\Delta G°$	K	$E°$
0	at equilibrium	0
negative	>1, products favored	+
positive	<1, reactants favored	−

- Connecting $\Delta G°$ to K
  - $\Delta G° = -RT \ln K$

- Connecting $\Delta G°$ to E
  - $\Delta G° = -n\mathfrak{I}E°$

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Endothermic v. Exothermic

PROBLEM STRATEGY

You should be able to determine if the reactions are endothermic or exothermic and possibly determine the value of the $\Delta H°$ if the diagram has energy values given. For kinetics you will be asked to label the activation energy, E_a. CAUTION. Make sure to read carefully as questions are often asked about the **reverse** reaction.

Potential Energy vs. Reaction Pathway

E_a

Reactants

$\Delta H = (-)$

Products

Reaction Pathway

Potential Energy vs. Reaction Pathway

E_a

Products

$\Delta H = (+)$

Reactants

Reaction Pathway
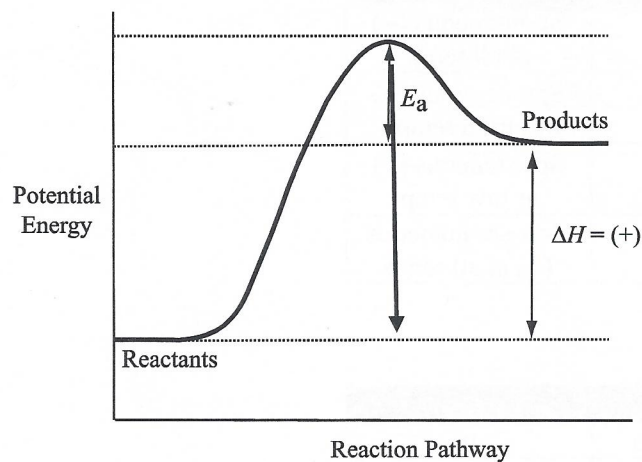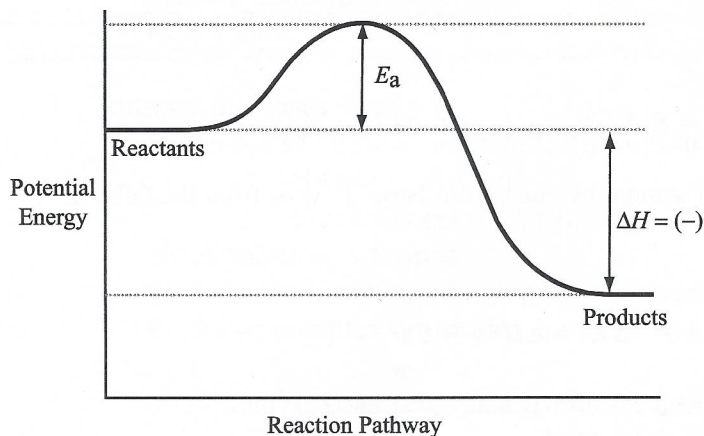
Thermochemistry Cheat Sheet

Relationships

$q = mC_p\Delta T$	$\Delta G = \Delta H - T\Delta S$
$q = \Delta H$ (when pressure is constant/coffee cup)	$\Delta S_{rxn} = \sum\Delta S_{prod} - \sum\Delta S_{react}$
$(-)\ q_{lost} = q_{gained}$ (same value; opp. sign)	$\Delta G_{rxn} = \sum\Delta G_{prod} - \sum\Delta G_{react}$
$\Delta H_{rxn} = \sum\Delta H_{prod} - \sum\Delta H_{react}$	$\Delta G° = -RT\ln K$ (use 8.31×10^{-3} kJ/molK for R) and watch your units for ΔG: they will be in kJ
$\Delta H_{rxn} = \sum bonds_{broken} - \sum bonds_{formed}$	$\Delta G° = -n\mathfrak{I}\,E°$ (96,500 for $\mathfrak{I}$)
$-\Delta H$ is exothermic; $+\Delta H$ is endothermic	$\Delta S = \dfrac{\Delta H}{T}$ at equilibrium (including phase change)
	$\Delta G = 0$ at equilibrium and direction change
Be cautious of which system component is losing heat and which is gaining heat. Assign +/– signs accordingly.	Use $\Delta G = \Delta H - T\Delta S$ equation to justify thermodynamic favorability. Discuss ΔH "overtaking" the $T\Delta S$ term and vice versa.

Connections

Kinetics – reaction diagrams	Electrochem: $\Delta G = -n\mathfrak{I}\,E°$
Stoichiometry – Energy values are usually kJ/mol so if you have other than 1 mole adjust accordingly	Equilibrium: $\Delta G = -RT\ln K$

Potential Pitfalls

ΔH_{rxn} is usually in kJ mol^{-1} (that's per mol of rxn) ΔH_f is usually in kJ mol^{-1} C_p = J/g°C (specific heat units)	ΔS is in J/K not in kJ like ΔH and ΔG ΔG must be negative for thermodynamic favorability Watch your signs and know what they mean
UNITS CAUTION: this calculation gives w in units of (L·atm) not Joules (or kJ)!!!! 1 atm = 101,325 $\dfrac{N}{m^2}$ and 1 L = 0.001 m^3 1 L·atm = 101.3 N·m = 101.3 J ALL $P\Delta V$ calculations for work need to be $\times$ 101.3 to convert to Joules, J	

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GENERAL EQUILIBRIUM
K_c, K_p, Le Châtelier, and K_{sp}

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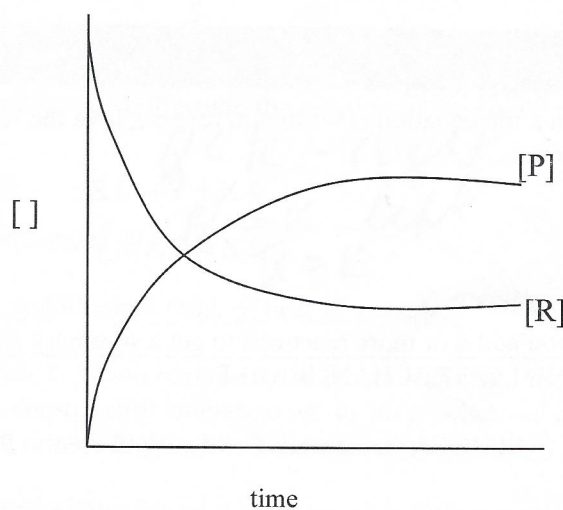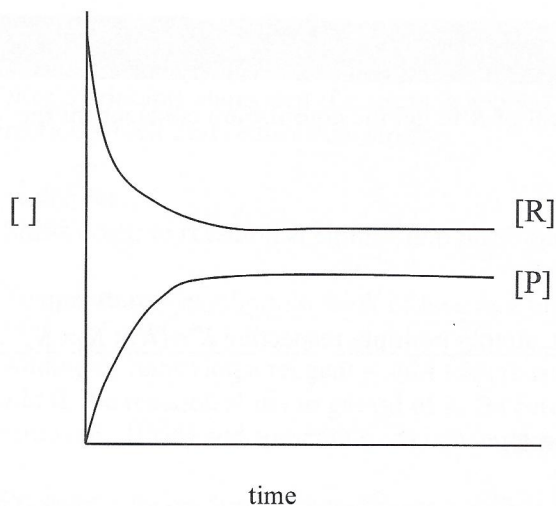
Factors that affect the equilibrium position:
- Initial concentrations of reactants: more collisions, more effective collisions, possibly more products i.e. a faster reaction (kinetics again)
- Energy: Energies of the reactants and products (favor minimum energy – thermodynamics, enthalpy)
- Order/disorder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

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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
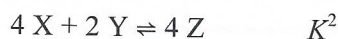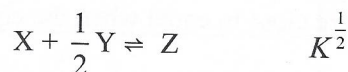
For the reaction: $aA + bB \rightleftharpoons cC + dD$
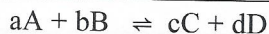
Equilibrium Constant Expression: $K_c = \dfrac{[\text{Products}]^{\text{coefficients}}}{[\text{Reactants}]^{\text{coefficients}}}$ $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

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.

$$2\,X + Y \rightleftharpoons 2\,Z \qquad\qquad K$$
$$X + \frac{1}{2}\,Y \rightleftharpoons Z \qquad\qquad K^{\frac{1}{2}}$$
$$4\,X + 2\,Y \rightleftharpoons 4\,Z \qquad\qquad K^2$$

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

$$2\,X + Y \rightleftharpoons 2\,Z \qquad\qquad K$$
$$2\,Z \rightleftharpoons 2\,X + Y \qquad\qquad \frac{1}{K}$$
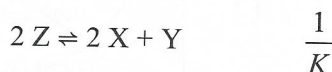
ADDING EQUATIONS
- If you add 2 or more reactions to get a summary reaction, simply multiply respective K's ($K_1 \times K_2 \times K_3 \dots$)

K_c & K_p ARE NOT INTERCHANGEABLE

<u>MUST KNOW FORMULA</u> (remember **P**olitically **C**orrect – 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 = *I*nitial 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 = *C*hange 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 **C**hanges stoichiometrically!!!!

    E = *E*quilibrium 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 **C**hanges 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.

*[handwritten: $Q < K$ – right; $Q > K$ left; $Q = K$]*

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*.

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Solubility Product: *It's Ksp!*

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.

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq) \quad K_{sp} = [Pb^{2+}][I^-]^2$$
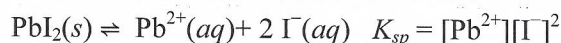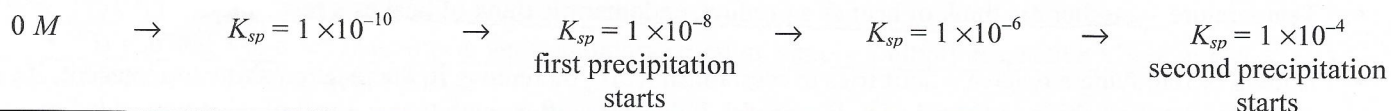
What is K_{sp} telling you?
1. The maximum amount of ions that dissolve as a poorly solubility salt is added to water to form a solution
2. The minimum concentration of ions necessary in a solution for precipitation to begin
   - Note: solids don't appear in the K expression
   - Be aware of the coefficients
      - the 1:2 ratio is important when determining concentrations of the ions present
      - the 2 results in an expression of $[I^-]^2$

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

$0\ M \quad \rightarrow \quad K_{sp} = 1 \times 10^{-10} \quad \rightarrow \quad K_{sp} = 1 \times 10^{-8} \quad \rightarrow \quad K_{sp} = 1 \times 10^{-6} \quad \rightarrow \quad K_{sp} = 1 \times 10^{-4}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ first precipitation $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ second precipitation

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ starts $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ starts
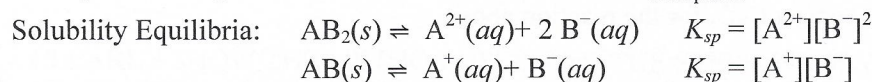
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General and Solubility Equilibrium Cheat Sheet

Relationships

Equilibrium Expression

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

Solubility Equilibria: $AB_2(s) \rightleftharpoons A^{2+}(aq) + 2\,B^-(aq)$ $K_{sp} = [A^{2+}][B^-]^2$

$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$ $K_{sp} = [A^+][B^-]$

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; ½ 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: $E_{\text{cell}} = E^\circ_{\text{table}} - \dfrac{0.0592}{n}\log Q$
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.