# UNIT 9 REVIEW GUIDE - KINETICS AND EQUILIBRIUM

#### **PART ONE - COLLISION THEORY AND REACTION RATES**

#### Notes:

Collision theory states that in order for a reaction to take place, there are three things that must happen. Particles must:

- 1) collide
- 2) with the right orientation and
- 3) with energy greater than the required activation energy.

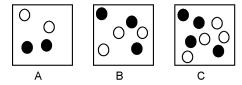
Collisions that meet these requirements should result in successful reaction from reactants to products, while other collisions that don't meet at least one of these requirements will fail to produce new products.

There are some factors that can be manipulated in order to speed up or slow down a chemical reaction through changing the number of successful collisions that take place over a certain period of time, its reaction rate. They are summarized in the table below and then explained in greater detail below the data table.

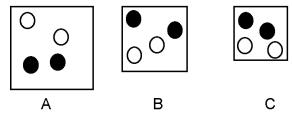
#### Factors that influence the rate of reaction:

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Reactant	Higher molarity <i>increases the chance of a collision</i> between reacting particles.		
Concentration			
Temperature	Higher temperature means that the particles are more likely to collide with <i>energy that is greater than the activation energy</i> . (They also move faster but this has less effect)		
Surface area	If solid particles (or something that forms an interface like immiscible liquids or gas/liquid) have more surface area (same amount but smaller particles or a larger interface) then there is a greater chance of the particles colliding.		
Catalysts	<ul> <li>Catalysts speed up chemical reactions in one of two ways</li> <li>Homogenous catalysts (same phase ex. Aqueous in aqueous or gas in gas) speed up reactions by providing an alternate pathway to complete the reaction that takes less activation energy.</li> <li>Heterogeneous catalysts (different phase ex. Solid with an aqueous solution) speed up reactions by altering the orientation of the molecules so that the correct sides of the reactants can collide. Leading to more effective collisions.</li> </ul>		

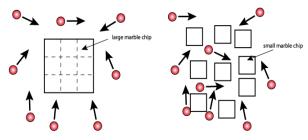
**Concentration:** Increasing the reactants' concentrations (shown in pictures from A to B to C) increases the frequency of collisions. Since the molecules are colliding more frequently, successful collisions should occur at a faster rate of reaction.



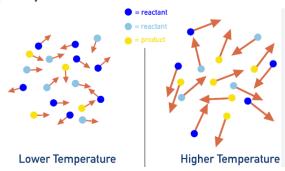
A similar effect is observed when increasing the pressure of a gaseous reaction. Increasing the pressure of a gas can also be achieved by adding additional molecules or by reducing its volume (shown in pictures below), even though the number of particles is the same.



**Surface area:** When a solid reacts only the particles on the surface are available for reaction. If the solid is broken up into smaller pieces its surface area gets larger. More particles are available for collision, therefore collision frequency increases, and the reaction rate increases.



**Temperature:** As the temperature is changed, the average kinetic energy of the particles changes as well. At a higher temperature, the average kinetic energies are greater, resulting in molecules that move at faster speeds. This has two major effects on the collisions between molecules: (1) a greater percentage of collisions will collide with greater energy, significantly increasing the number of collisions that possess energy equal to or greater than the activation energy, and (2) more overall collisions will also occur as molecules move more quickly and collide more frequently.



Catalysts: Catalysts are chemical species that are not consumed in chemical reaction. Their role in a chemical reaction then is to provide an alternate reaction route that requires <u>less activation</u> <u>energy</u>. By lowering the energy requirement of the reaction, collisions that did not possess enough energy to meet the higher

Energy Without catalyst

With catalyst

Product

a

activation energy are able to successfully meet the new lower energy requirement and successfully react. Common examples include enzymes in your body and demonstrations like elephant toothpaste that speed up the breakdown of hydrogen peroxide.

# **Collision Theory Problems**

1) Stu Dent wanted to figure out the rate of a reaction by measuring the rate that CO<sub>2</sub> gas was formed from the reaction between HCl and CaCO<sub>3</sub> according to the reaction below:

$$2\; HCl_{\,(aq)} + CaCO_{3\,(s)} \rightarrow H_2O_{\,(l)} + CO_{2\,(g)} + CaCl_{2\,(aq)}$$

		() ~()	- \-'/ -\D/ -\-''/
	$CaCO_{3(aq)}$	HCl <sub>(aq)</sub>	Temperature
	Small chips	0.0050 M	Warm water bath
Powdered 0.50 M		0.50 M	Ice Bath

- a) Which set of conditions will cause the reaction to go slower? Explain.
- b) Which set of conditions will cause the reaction to go fastest? Explain.
- 2) The overall reaction for the decomposition of bleach with a cobalt ion catalyst is shown below:

$$2\,Na^{1+}{}_{(aq)} + \,2Cl0^{1-}{}_{(aq)} \xrightarrow{Co^{2+}} 2\,Na^{1+}{}_{(aq)} + \,2Cl^{1-}{}_{(aq)} + O_{2(g)}$$

- a) In a test trial using 6% extra strength bleach at room temperature, 100.0 mL of oxygen gas was produced in 2.03 seconds. What would be the effect of the time the reaction would proceed in if it is run at 50°C?
- b) The reaction produced the gas too fast to record useful data. State two ways to slow down this reaction and explain how those factors cause the rate to decrease.
- 3) Three students performed the reaction below:

$$Zn_{\text{ (s)}} + 2 \text{ HCl}_{\text{ (aq)}} \rightarrow H_{2 \text{ (g)}} + ZnCl_{2 \text{ (aq)}}$$

Student 1	Student 2	Student 3
Powdered zinc	Zinc strips	Zinc strips
1.00 M HCl	1.00 M HCl	1.00 M H <sub>2</sub> SO <sub>4</sub>
25.0 °C	25.0 °C	35.0 °C

a) Which student's conditions will produce the hydrogen gas the SLOWEST?

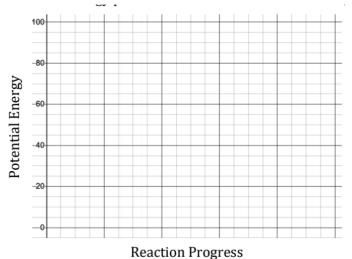
4) Given the following reaction, which set of reaction conditions will result in the highest reaction rate? Explain in terms of collision theory.

Experiment	Moles H <sub>2</sub>	Moles Cl <sub>2</sub>	Temperature (K)	Volume of Container (L)
1	1.00	1.00	298	2.00
2	2.00	2.00	298	4.00
3	1.00	1.00	298	1.00

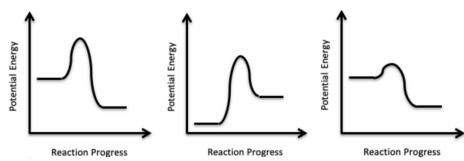
5) Given the reaction:  $2 \text{ NO}_{2 \text{ (g)}} \rightarrow \text{N}_2\text{O}_{4 \text{ (g)}}$ , the rate of reaction was too slow with 2.00 moles of  $\text{NO}_2$  in a 2.00 L container at 1.00 atm and 285 K. Suggest three ways to increase the rate of this reaction and explain, with reference to collision theory, how they alter the rate of reaction.

6) On the graph below, draw a reaction energy profile of a reaction with the following:

Compound	Energy (kJ/mol)
Reactants	75
Transition State	90
Products	10



- a) What is the activation energy for this reaction?
- b) What is the enthalpy change for this reaction?
- 7) Which two of the following reactions represent the same reaction, catalyzed and uncatalyzed? Label them.



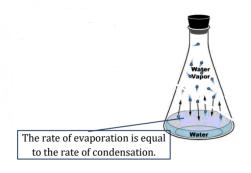
#### **PART TWO - EQUILIBRIUM CONCEPTS AND EXPRESSIONS**

#### Notes:

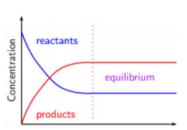
Many chemical reactions do not proceed in one direction (from reactants to products). Consider a sealed bottle of water: the water can both evaporate and condense within that bottle. We call reactions that can go in either direction reversible and a  $\rightleftharpoons$  arrow instead of a single directional arrow to describe them. There are many types of reversible reactions.

Type of Reaction	Example
Evaporation/condensation of water	$H_2O_{(1)} \rightleftharpoons H_2O_{(g)}$
Adsorption/desorption of a gas by a solid	Seen in hydrogenation of a hydrocarbon in
	heterogeneous catalysis
	$C_2H_{4(g)} + H_{2(g)} \stackrel{Pt}{\leftrightarrow} C_2H_{6(g)}$
Dissolution/precipitation of a solid in a solution	$PbCl_{2(s)} \rightleftharpoons PbCl_{2(aq)}$
Proton transfer in an acid base reaction	$HNO_{2(aq)} + NH_{3(aq)} \rightleftharpoons NO_{2^{-}(aq)} + NH_{4^{+}(aq)}$
Transfer of electrons in a redox reaction	$H_{2(g)} + I_{2(g)} \rightleftharpoons 2 HI_{(g)}$
	$Fe^{2+}_{(aq)} + Cu^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Cu^{+}_{(aq)}$

In a reaction that is reversible, it will eventually reach a state of <a href="dynamic">dynamic</a> equilibrium. Equilibrium is reached when the rate of the forward reaction is equal to the rate of the reverse reaction. It does NOT mean that the amounts of reactants and products are equal. When the rates of the forward and reverse reactions are equal, there is no net change to the amounts of reactants and products. The equilibrium is dynamic, which means that the system is in constant motion; but reactants and products are constantly being formed at equal rates.



We can graph the changes to the concentration of the reactants and products as a reaction proceeds to equilibrium. You can see that the reactants and products change rapidly at the beginning, and then the rate of reaction decreases as species are used up until the reaction reaches equilibrium. When the reaction reaches equilibrium, there is no change to the amount of reactants and products. We can graph the changes to the concentration of the reactants and products as a reaction proceeds to equilibrium. This can also be done through molecular level pictures or data tables.



Some reactions reach equilibrium when there are more products (favors products), while other reactions reach equilibrium with more reactants than products (favors reactants). The reaction quotient, Q, describes the relative concentrations of reaction species at any time. At equilibrium, this can be described as the equilibrium constant, K.

Q	Reaction Quotient	Relative concentrations of reaction species at ANY TIME	
K	Equilibrium Constant	Relative concentrations of reaction species at EQUILIBRIUM	

We can write the reaction quotient or equilibrium constant in terms of either concentrations or partial pressures. Solids and liquids are not included in the expression because they are pure substances and their concentrations do not change within the system. When writing a reaction quotient or equilibrium constant expression for a system with molarities of species, you can use concentrations and label the Q or K with a subscript of <sub>C</sub>. When writing a reaction quotient or equilibrium constant expression for a system of gases, you can also use partial pressures and label the Q or K with a subscript of <sub>P</sub>.

		<u> </u>
Q <sub>c</sub> , K <sub>c</sub>	System with solutions	Use concentrations, Molarity
Q <sub>p</sub> , K <sub>p</sub> System with gases Use partial pressures, atm, mmHg, kPa		

For a given reaction:  $aA + bB \rightleftharpoons cC + dD$ 

You write the Reaction Quotient/Equilibrium Constant expression:

For solutions: And for gases:

$$Q_c \text{ or } K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

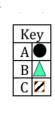
# **Concepts and Expressions Problems**

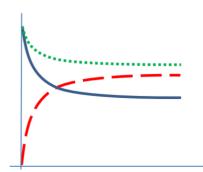
8) Given the reaction:  $2 A_{(aq)} + B_{(aq)} \longleftrightarrow 3 C_{(aq)}$ 

Look at the model and graph, and then answer the following questions:

- a) If the initial mixture contained A and B, label the substances on the graph as A, B, and C on the graph of concentrations vs. time.
- b) Explain how you knew which line was A and which line was B.
- c) Complete the model at equilibrium.
- d) Indicate where the graph reaches equilibrium on the graph.

Initial	Equilibrium



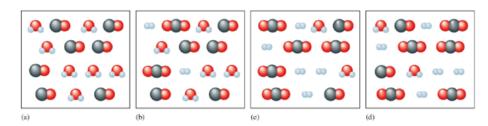


9) Given the reaction:  $2 A_{(g)} + B_{(g)} \longleftrightarrow C_{(g)}$ . The partial pressures of the three gases were collected over time as shown below.

			ı
Time (min)	A (atm)	B (atm)	C (atm)
0	0.1000	0.0900	0
1	0.0800	0.0800	0.0100
2	0.0700	0.0750	0.0150
3	0.0650	0.0725	0.0175
4	0.0625	0.0713	0.0188
5	0.0625	0.0713	0.0188
6	0.0625	0.0713	0.0188

- a) Did the reaction reach equilibrium? How do you know?
- b) If it did reach equilibrium, at what time did this happen?
- 10) Use the picture and reaction below to answer the following questions:

$$CO(g) + H2O(g) = CO2(g) + H2(g)$$



- a) Did the system reach equilibrium? If it did, in what picture was equilibrium FIRST established?
- b) Why does the system continue to have different molecules in different parts of the container throughout the reaction time? Explain how this relates to dynamic equilibrium.

11) Write equilibrium expressions or reaction quotients for each of the following reactions:

a) 
$$C_3H_{8\,(g)} + 5\ O_{2\,(g)} \longleftrightarrow 3\ CO_{2\,(g)} + 4\ H_2O_{(g)}$$

b) 
$$2 \text{ NO}_{(g)} + O_{2(g)} \longleftrightarrow 2 \text{ NO}_{2(g)}$$

c) 
$$2 \text{ Ca}_{(s)} + O_{2(g)} \longleftrightarrow 2 \text{ CaO}_{(s)}$$

d) 
$$NH_4NO_{3(s)} \longleftrightarrow N_2O_{(g)} + 2 H_2O_{(l)}$$

e) 
$$2 \text{ Al}(OH)_{3 \text{ (aq)}} + 3 \text{ K}_2CO_{3 \text{ (aq)}} \longleftrightarrow \text{Al}_2(CO_3)_{3 \text{ (s)}} + 6 \text{ KOH }_{\text{(aq)}}$$

f) 
$$HCl_{(aq)} + NaOH_{(aq)} \longleftrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

## PART THREE - EQUILIBRIUM CALCULATIONS (K AND Q)

# Notes:

Once the expression is written for the equilibrium constant or the reaction quotient, the value of these can be determined by plugging in equilibrium values (for K) or current experimental values (for Q), including the coefficients as exponents. Two examples are shown below:

Consider these examples:

$2 Cu^{2+}_{(aq)} + Pb^{2+}_{(aq)} \rightleftharpoons 2Cu^{+}_{(aq)} + Pb^{4+}_{(aq)}$	$N_{2(g)} + 3 H_{2(g)} \rightleftharpoons 2NH_{3(g)}$		
$K_{c} = \frac{[Cu^{+}]^{2}[Pb^{4+}]}{[Cu^{2+}]^{2}[Pb^{2+}]}$	$K_{p} = \frac{(P_{NH_3})^2}{(P_{N_2}) (P_{H_2})^3}$		
In an experiment, the following were combined:	The equilibrium constant for this reaction is 0.061* at		
$[Cu^+] = 2.00 \text{ M}$	500K. If the partial pressure of N <sub>2</sub> is 2.34 atm and the		
$[Pb^{4+}] = 3.00 \text{ M}$	partial pressure of H <sub>2</sub> is 4.56 atm, what is the partial		
$[Cu^{2+}] = 4.00 \text{ M}$	pressure of the NH <sub>3</sub> ?		
$[Pb^{2+}] = 5.00 \text{ M}$	$K_p = 0.061 = \frac{(P_{NH_3})^2}{(2.34 \text{ atm})(4.56 \text{ atm})^3}$		
Calculate the value for the <u>reaction quotient</u> :			
$O_{1} = [2.00  M]^{2} [3.00  M]$	$P_{NH_3} = 3.68 \text{ atm}$		
$Q_{\rm C} = \frac{[2.00  M]^2 [3.00  M]}{[4.00  M]^2 [5.00  M]}$	*Note: there are no units for reaction quotients or		
$Q_{\rm C} = 0.150 *$	equilibrium expressions. Use pressure units of atm		
	for K <sub>P</sub> calculations.		

Notice that whether you are solving for the reaction quotient (Q) or the equilibrium constant (K), the process is the same. The interpretation of the values, however, leads to different analyses.

When solving for the equilibrium constant, the value is usually compared to 1 (when there would be exactly equal amounts of reactants and products). Reactions with equilibrium constants that are greater than 1 are said to favor the products and those that are less than one favor the reactants. When the order of magnitude is very big or very small, we can say that there are almost all products or reactants since they are favored by a significant amount.

Value for K	K<<1	K<1	K>1	K>>1
	(Usually 0.001 or smaller)			(Usually 1000 or more)
Means that	The reaction barely	Reactants favored	Products Favored	Reaction goes to
	proceeds at all.			completion

When the values are not at equilibrium, comparing the value for Q to K can be used to predict the direction that the reaction will go to reach equilibrium.

- If Q is equal to K, then the reaction is at equilibrium.
- If Q is less than K, then the reaction currently has too many reactants and the ratio of products to reactants needs to increase, therefore the reaction will proceed towards products until Q = K.
- If Q is greater than K, then the reaction currently has too many products and the ratio of products to reactants needs to decrease, therefore the reaction will proceed towards reactants until Q = K.

Changes to the concentrations (or partial pressures) can change the value of Q, but not the value of K. The K will only change with a change in temperature.

# **Equilibrium Calculations Problems**

12) Given the following concentrations in an equilibrium system, calculate the value of the equilibrium constant  $(K_c)$ :

13) Calculate the reaction quotient based on the reaction and information below. Determine which way the reaction will proceed in order to reach equilibrium:

$$NaOH_{(s)} \leftrightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$$
  $K = 44.5$   
Current conditions  $\Rightarrow [Na^{+}] = 4.22 \text{ M}, [OH^{-}] = 6.41 \text{ M}$ 

14) The following reaction is at equilibrium at a certain temperature. At that temperature, the value of K<sub>p</sub>, the equilibrium constant, is 38,000. If the partial pressure of I<sub>2</sub> is 1.00 atm, determine the equilibrium partial pressure of I.

$$I_{2\,(g)} \longleftrightarrow 2\ I_{\,(g)}$$

15) What is K for  $Cu_{(s)} + 2 AgCl_{(aq)} \leftrightarrow CuCl_{2(aq)} + 2 Ag_{(s)}$  given 33.00 grams of copper, 187.2 g of silver chloride, 21.00 grams of copper (II) chloride, and 28.45 grams of silver metal in a 3.000-L container?

16) CO<sub>2 (g)</sub> + NaOH (aq) ←→ NaHCO<sub>3 (aq)</sub> has a K of 1.36 x 10<sup>-10</sup> at 25°C. Calculate the Q (reaction quotient) for the reaction <u>RIGHT NOW</u> given 1.43 x 10<sup>4</sup> moles of CO<sub>2</sub>, 3.22 x 10<sup>9</sup> moles of NaOH, and 2.21 x 10<sup>3</sup> moles of NaHCO<sub>3</sub> in a 5.00 L container? What does that tell us about where we are in the reaction? How could we get it to equilibrium?

## PART FOUR - LE CHATELIET'S PrINCIPLE

## Notes:

Le Châtelier's principle states that a system at equilibrium will restore or stay at equilibrium when a stress is applied. In other words, when a stress (such as changes in temperature, pressure, or concentration) is applied to a system at equilibrium, the reaction will respond in order to minimize the effect of that stress. Recall that the equilibrium constant for any reaction at equilibrium is mathematically determined by dividing the concentrations of the products raised to their stoichiometric coefficients by the concentrations of the reactants raised to their stoichiometric coefficients. For the general reaction:

2 A<sub>(aq)</sub> + B<sub>(aq)</sub> 
$$\rightleftharpoons$$
 C<sub>(aq)</sub> + 3 D<sub>(aq)</sub>  

$$K_{C} = \frac{[C] * [D]^{3}}{[A]^{2} * [B]}$$

As long as the temperature remains unchanged, the value of K will remain the same as well.

Le Châtelier's principle is useful in determining how a reaction at equilibrium will react to certain stresses that are applied.

**Adding species**: If additional material is added to one side of the reaction, the system will shift away from the added substance to relieve the stress. For example, if some of the reactant A is added, the concentration of [A] is increased; this disturbs the equilibrium of the reaction. In order to reestablish the equilibrium, the reaction will shift to favor the reaction that uses up A, the forward reaction. Another way to look at it is that the addition of A will cause the value of  $Q_c$  to decrease with additional reactants, so the reaction will shift towards the products to get back to the same  $K_C$  value. The reaction will decrease the concentrations of reactants and increase the concentrations of products. The same thing would happen in reverse if the concentration of a product is increased, as the value of Q would increase and cause a shift towards the reactants to alleviate the stress placed on the system.

**Removing species:** Removing a reactant/product or decreasing the concentration of one of the chemicals will cause the opposite effect; the reaction will shift to reform the missing (or lower amount) of the material. Often, the most effective way to remove material from the reaction was to <u>react</u> the species in a way that it selectively removes a specific reactant or product that will be reformed through a shift in the equilibrium system.

**Pressure/volume:** If we consider a gas-phase equilibrium reaction, the equilibrium is written in terms of the partial pressures of gases. For example:

2 NO<sub>2(g)</sub> 
$$\leftrightarrow$$
 N<sub>2</sub>O<sub>4(g)</sub> is  $K_P = \frac{(P_{N_2O_4})}{(P_{NO_2})^2}$ 

When you are working with systems that involve gases, changes in pressure can cause a shift in the reaction. If the pressure on the system is increased, the system will try to alleviate the stress by reducing the pressure; it does this by shifting to the side with fewer moles of gas (towards the products in the reaction above). The side with greater moles of gas gains additional stress from additional collisions, so the system moves to remove this stress. If the pressure is decreased, the side of the system with more moles of gas will be

similarly affected: since more collisions are removed from this side, the system will shift towards this side to reestablish the equilibrium system. A similar change can be made from changing the volume of the system. Pressure and volume have an inverse relationship; increasing the volume will decrease the pressure and decreasing the volume will increase the pressure. This will cause the same shifts explained above. If the reaction above is at equilibrium and the volume of the container increases, the pressure would decrease. The system would counteract that by shifting towards the reactants.

**Temperature:** The final type of stress on a system at equilibrium is a change in temperature. In an exothermic reaction like  $2 C_{(s)} + O_{2(g)} \longleftrightarrow 2 CO_{(g)} \Delta H = -111 \, kJ$ , heat is released in the reaction. If this reaction experiences an increase in temperature, the reverse reaction is favored, producing more of the reactants and consuming the products. Increasing the temperature in this case is similar to adding a product; it shift the reaction to the left. Decreasing the temperature would shift the reaction to the right in order to replace the energy that is removed from the equilibrium system. In general, heating or cooling the system will cause it to shift in the same manner as adding/removing a reactant or product. The side that the heat is placed on depends on whether the reaction is endothermic (reactants) or exothermic (products). Heating causes the system to shift away from the heat in the reaction, while cooling the system causes a shift towards the heat in the reaction. Since the ratio of reactants to products is altered with a change in temperature, the value of K WILL change when a system is heated or cooled.

**NO effect:** The addition of a catalyst to a system at equilibrium will not stress the system. Catalysts decrease the activation energies of the forward and reverse reactions, so adding a catalyst does not change the equilibrium composition of the system. Adding an inert gas to a reaction at equilibrium will have <u>no</u> effect as both sides of the reaction remain at their equilibrium pressures. Adding a solid or liquid has no effect on the equilibrium; since the addition of a solid or liquid does not affect or stress equilibrium, they will not cause a disturbance to the system.

Le Châtelier's principle also allows us to predict the effect that any stresses may have on any measurable properties. We can predict the effect on the amount of products or reactants, but we can also predict changes on the pH of a system that involves acids and bases and color changes for systems where one (or more) species are colored.

# Le Chatelier Problems

17) In an endothermic process, phosgene gas (COCl<sub>2</sub>) decomposes into carbon monoxide (CO) and chlorine gas (Cl<sub>2</sub>). The K for the reaction is 0.0071. Using Le Châtelier's principle, predict how the reaction will respond to each of the following stressors:

$$COCl_{2(g)} \longleftrightarrow CO_{(g)} + Cl_{2(g)}$$

- a) Adding more COCl<sub>2 (g)</sub>
- b) Removing CO<sub>(g)</sub>
- c) Increasing the pressure
- d) Decreasing the temperature

18) \_\_\_\_ Fe(OH)
$$_{2 \text{ (aq)}}$$
 + \_\_\_ AlCl $_{3 \text{ (aq)}}$   $\longleftrightarrow$  \_\_\_ FeCl $_{2 \text{ (aq)}}$  + \_\_\_ Al(OH) $_{3 \text{ (s)}}$   $\Delta$ H = - 1243 kJ/mol $_{rxn}$ 

Change	Shift	Effect on
Increase [AlCl <sub>3</sub> ]		[FeCl <sub>2</sub> ]
Add aluminum hydroxide		[Fe(OH) <sub>2</sub> ]
Remove FeCl <sub>2</sub>		[AlCl <sub>3</sub> ]
Add catalyst		[Fe(OH) <sub>2</sub> ]
Cool it down (remove heat)		[AlCl <sub>3</sub> ]

19) 
$$\mathbf{heat} + 2 \mathbf{SO}_{2 (g)} + \mathbf{O}_{2 (g)} \longleftrightarrow 2 \mathbf{SO}_{3 (g)}$$

Change	Shift	Effect on
Increase [SO <sub>2</sub> ]		[SO <sub>3</sub> ]
Add He gas		$[O_2]$
Increase volume		[SO <sub>3</sub> ]
Add SO <sub>3</sub>		[SO <sub>2</sub> ]
Add heat		[O <sub>2</sub> ]

- 20) The reaction:  $2 \text{ NO}_{2 \text{ (g)}} \longleftrightarrow \text{N}_2\text{O}_{4 \text{ (g)}}$  is an exothermic reaction.  $\text{NO}_2$  is brown while  $\text{N}_2\text{O}_4$  is colorless. If the reaction is light brown at equilibrium, predict the changes to the color of the reaction:
  - a) The reaction is heated
  - b) The gases are placed in a container of half the size
  - c) More  $N_2O_{4(g)}$  is added
  - d) An acid is added, which selectively reacts with NO<sub>2</sub>
- 21) Consider the reaction known as the Haber process:  $N_{2(g)} + 3 H_{2(g)} \leftrightarrow 2 NH_{3(g)}$ 
  - a) It is determined that increasing the temperature causes the equilibrium to shift toward the products. Is the reaction endothermic or exothermic? Explain your answer.
  - b) In order to maximize the yield of NH<sub>3</sub> (make the maximum amount of products), should the reaction be run at a high pressure or a low pressure? Explain your answer.

## PART FIVE - ICE EQUILIBRIUM PROBLEMS

## Notes:

Given the stoichiometry of a chemical reaction and the associated K value at a particular temperature, we can determine the concentrations of products or reactants for a reaction at equilibrium based on the initial values for the reacting species. The concept behind this is essentially stoichiometry for reactions that don't go to completion. This accounts for the nature of equilibrium being dynamic (forward and reverse reactions happening simultaneously) and allows us to determine the final amounts of reactants and products.

One way to approach solving these types of problems is to use an ICE table to organize the information given in an equilibrium problem. I stands for INITIAL, C stands for CHANGE, and E stands for EQUILIBRIUM. ICE tables are used whenever species are placed initially into a container and allowed to reach equilibrium.

**Example 1:** Given this reaction:  $A + 2 B \leftrightarrow 4 C$ 

If the initial concentration of A and B is 1.00 M and the equilibrium concentration of C is 0.120 M, what is the value for  $K_C$ ?

1) Start by writing the reactions and the K<sub>C</sub> expression. Fill in the table with information given in the problem.

$$\kappa_{\rm c} = \frac{[C]^4}{[A][B]^2}$$

- 2) Since you have no information about the initial value of C, we assume that there was none of that species initially. By filling in the initial value for C as zero, we can tell that the C must have increased by 0.120 M. This allows us to determine the change for C, and the x value.
- 3) The change is related stoichiometrically to all other parts of the equation, so we can use the mole ratio to deduce the changes to the other species in the reaction and determine their equilibrium concentrations.
- 4) We can then plug them into the equilibrium expression to determine its equilibrium constant.

	A	2B	4C
Initial	1.000 M	1.000 M	
Change			
Equilibrium			0.120 M

	A	2B	4C
Initial	1.000 M	1.000 M	0
Change			+0.120 M
Equilibrium			0.120 M

	A	2B	4C
Initial	1.000 M	1.000 M	0
Change	-0.030 M	-0.060 M	+0.120 M
Equilibrium	0.970 M	0.940 M	0.120 M

$$\kappa_{\rm c} = \frac{[0.120\,M]^4}{[0.970\,M][0.940\,M]^2} = 2.42\,\text{X}\,\text{10}^{-4}$$

Example 2: In another example, we are provided with the value for K and the initial concentrations and have to find the equilibrium concentrations. We can also use an ICE table to solve this type of problem. Given this reaction: A  $_{(aq)}$  + B  $_{(aq)} \leftarrow \rightarrow$  AB  $_{(aq)}$  with an equilibrium constant,  $K_c$ , of 3.4 x  $10^{-3}$  at  $50^{\circ}$  C. If 1.00 M A and 2.00 M B are allowed to reach equilibrium, what are the equilibrium concentrations of all species?

1) Start by writing the reaction and the K<sub>c</sub> expression. Fill in the table with information given in the problem.

Initial

Change

Initial

Change

Equilibrium

Equilibrium

1.00 M

Α

1.00 M

-X

1.00-X

2.00 M

В

2.00 M

2.00 -X

AB

AB

+x

X

$$K_{\rm C} = \frac{[AB]}{[A][B]} = 3.4 \text{ X10}^{-3}$$

- 2) Since there was no AB initially, we can include a value of zero for this initially.
- 3) We know that the reaction MUST proceed to the products, since you can't have a negative concentration. Since we don't know any changes, we again use x to represent the change. If there are coefficients, this change would stoichiometrically be shown as 2x or 3x, etc.

4)	We can add up the I and C lines to fill in
	the E line of the ICE table.

,	1
	the E line of the ICE table.
5)	Finally we can plug those equilibrium

Finally we can plug those equilibrium values into the equilibrium expression and solve to find the value of x, using those to give the equilibrium values.

$$K_{\rm C} = \frac{|x|}{[1.00-x][2.00-x]} = 3.4 \text{ X10}^{-3}$$

This can be solved using an equation solver, graphing, or the solver on your graphing calculator.

After finding the value of x, we need to use the x to solve for all equilibrium values.

	A	В	AB
Equilibrium	1.00-X	2.00 -x	X
	(0.99 M)	(1.99 M)	(0.0067 M)

Regardless of which type of problem you are given, the ICE table is a useful tool to keep track of species present throughout the reaction and to show the stoichiometric change of reactants and products.

## **ICE Problems**

22) Consider the reaction:  $I_{2(g)} + Cl_{2(g)} \longleftrightarrow 2ICl_{(g)} K_p = ?$ 

Enough ICl was added to reach a partial pressure of 2.45 atm in a previously evacuated vessel. After the reaction reaches equilibrium, the pressure of  $I_2$  was 0.30 atm. Determine the equilibrium constant,  $K_P$ .

23) Consider the reaction:  $N_2O_{4(g)} \longleftrightarrow 2 NO_{2(g)}$   $K_p = 0.36$ 

The reaction is carried out where the vessel initially contains only the reactant  $N_2O_4$  with a pressure of 0.0550 atm and none of the product. Determine the equilibrium partial pressures for  $N_2O_4$  and  $NO_2$ .

24) Consider the reaction:  $Cl_{2(g)} + F_{2(g)} \longleftrightarrow 2 ClF_{(g)} \quad K_p = ?$ 

The partial pressure is 2.00 atm for  $Cl_2$  and 4.00 atm for  $F_2$ . Upon reaching equilibrium, the partial pressure of ClF is 1.78 atm. Calculate the equilibrium pressures and use them to calculate the value of  $K_p$ .

25) Given the reaction:  $A_{3(g)} + 2 AB_{(g)} \longleftrightarrow A_{(g)} + 2 A_2B_{(g)}$  K= 0.25 Initially 5.00 atm of  $A_3$  and 4.00 atm of AB were added together, as shown in the box to the right. Calculate the equilibrium pressures for all species in the reaction and then complete the box to model species present at equilibrium.

