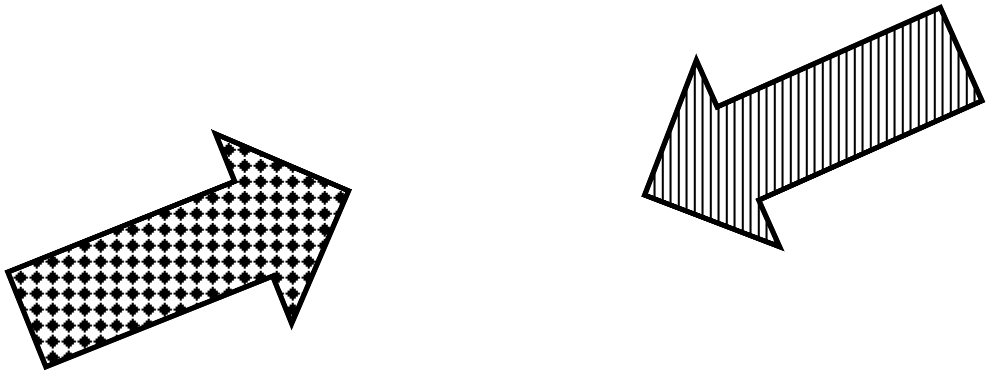
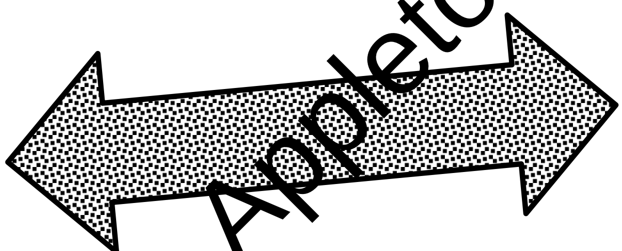
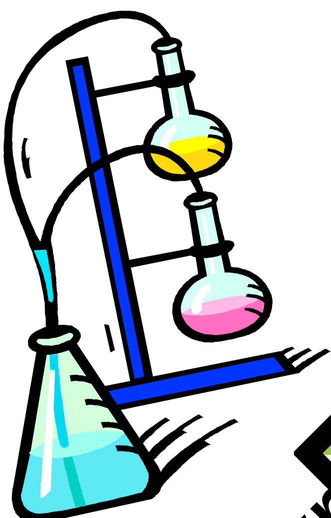
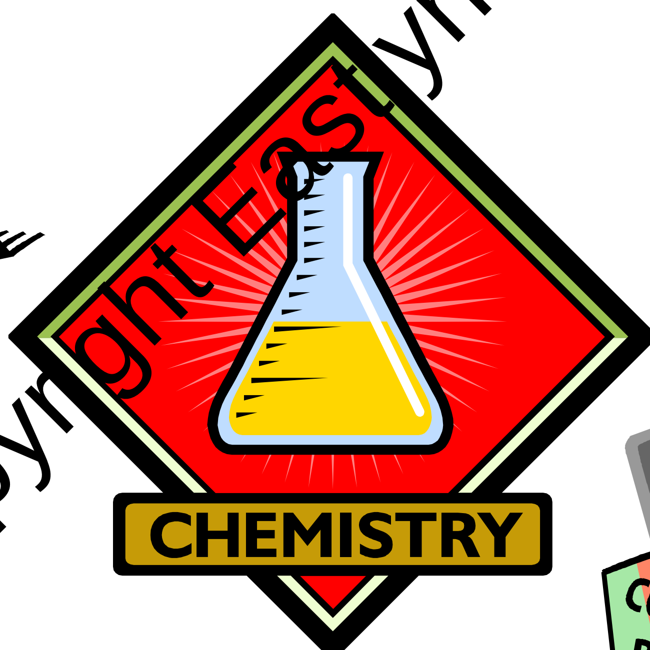


Equilibrium







Reversibility of Chemical Reactions

- Chemical reactions can either be reversible or not reversible:
  - Examples of irreversible chemical reactions:
    -
  - Examples of reversible chemical reactions:
    -

      (blue) *(white)*
    -
- The double arrow "⇌" indicates that a chemical reaction is ______________________________.

Equilibrium

- In a reversible reaction, when the forward step proceeds at the same rate as the reverse step, the reaction has reached ___________________________.
- Most physical changes are reversible, so many can exist at equilibrium.

Example: Water in a closed beaker can represent a system at equilibrium:

a. What is the forward 'reaction' that is occurring?

b. What is the reverse 'reaction' that is occurring?

c. What is the overall reaction that is occurring?

d. If the beaker was uncapped, equilibrium would not exist. Why?

- At equilibrium, the concentrations of all reactants and products remain ___________________________ with time as a result of the forward and reverse reactions occurring at equal rates.
- As reactants are consumed, the rate of the ___________________________ reaction decreases; as products are formed, the rate of the ___________________________ reaction increases.
- _______________________________ Equilibrium is where the reaction appears to have stopped because as products are made by reactants, reactants are being made by the products.
- A **steady state system** is where reactants are being added and products are being removed at the same rate. This may appear to be at equilibrium but it is not the same thing.

See Equilibrium Analogy Lab

As an example of **dynamic** equilibrium, think of bailing out a leaking rowboat. Water leaking into the boat is analogous to a forward reaction, and our pouring buckets of water overboard are analogous to the reverse reaction. As we bail water out, we reach a point of equilibrium at which the water is bailed out just as fast as it leaks in. The level of water in the boat remains constant, analogous to the constant concentration of reactants and products at equilibrium.

Equilibrium Reaction Example:

Change in the concentrations of N_2O_4 and NO_2 with time in two experiments at 25°C: $2NO_2 \rightleftharpoons N_2O_4$

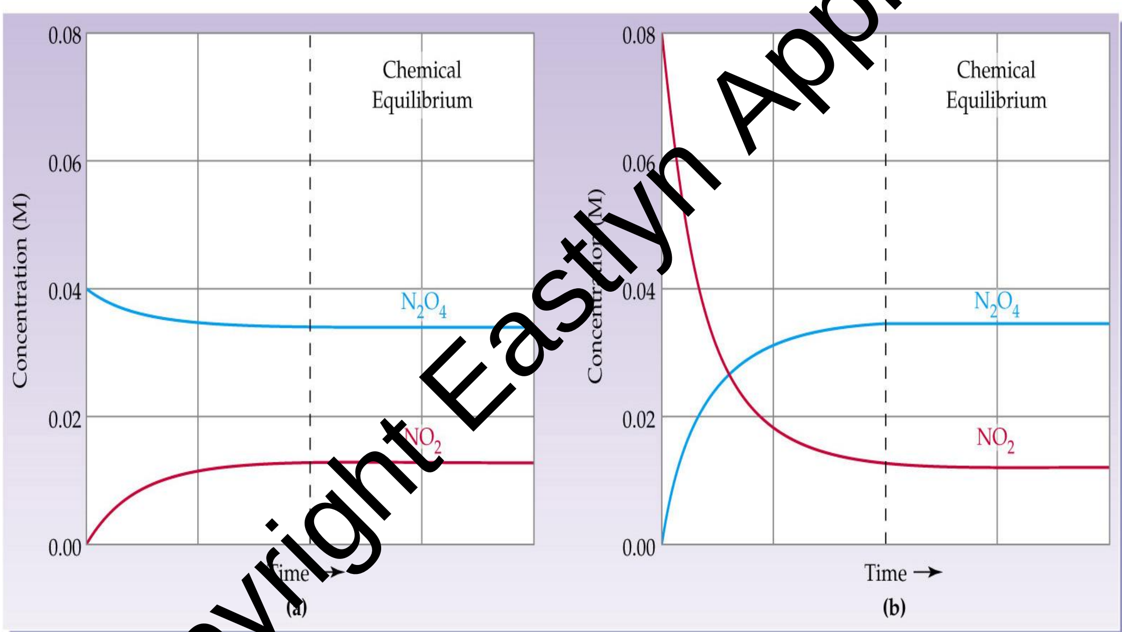
(a) Only N_2O_4 is present initially.

In experiment (a), $[NO_2]$ ______________________________ as $[N_2O_4]$ ______________________________.

(b) **only NO_2 is present initially.**

In experiment (b), $[N_2O_4]$ ______________________________ as $[NO_2]$ ______________________________.

In both experiments, a state of chemical equilibrium is reached when the concentrations level off at constant values: $[N_2O_4]$ = 0.0337 M; $[NO_2]$ = 0.0125 M.



How to Identify when Equilibrium Exists

There are two important characteristics of a system at equilibrium

1. The equilibrium can be approached from ___________________________ side of the reaction equation.
2. At equilibrium the concentration of the reactants and products do not ________________________.

Signs that a system is at equilibrium:

- It must be a ______________________________ system at a ______________________________ temperature
- Constant ______________________________ indicated by constant color, pressure, volume, and electrical conductivity.

The Equilibrium Constant Expression

- When equilibrium is established in a closed system there is a relationship between the concentrations of the reactants and the concentration of the products. This relationship is a constant ratio called the equilibrium ________________________ and represented by the symbol $\underline{K_{eq}}$.
- For the general reaction represented by the equation:

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

- The concentrations of reactants and products at equilibrium must conform to the equilibrium constant expression:

Where A, B, C, D are the ____________________________ (M) of the reactants and products and the exponents (a, b, c, d) are the ____________________________ in the balanced equation.

- K_{eq} is _________________________ and its value changes with the ________________________ of the system.

Example: Determine the value for K_{eq} for the reaction: $\mathbf{H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}}$ using the three trials shown below.

Five trials involving the reaction $H_{2(g)} + I_{2(g)} \longrightarrow 2\,HI_{(g)}$ ***(equilibrium concentrations)***				
Trial	***[HI]***	***[H_2]***	***[I_2]***	***K_{eq}***
1	0.156	0.0220	0.0220	
2	0.750	0.106	0.106	
3	1.00	0.820	0.0242	

- Equilibrium constant expressions do not include terms for any reactants or products present as pure __________________________ or pure ____________________________ because their concentrations do not change in a reaction.

Example: Write an equilibrium expression for the following: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

Example: Write the equilibrium expressions for each of the following:

a) $Fe_3O_{4(s)} + H_{2(g)} \rightleftharpoons 3\,FeO_{(s)} + H_2O_{(g)}$

b) $Ag_2S_{(s)} \rightleftharpoons 2\,Ag^{+}_{(aq)} + S^{2-}_{(aq)}$

See Calculating K_{eq} Assignment

Calculations with K_{eq}

Example: If the equilibrium concentrations of Cl_2 and $COCl_2$ are the same at 395°C, find the equilibrium concentration of CO in the reaction:

$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ $K_{eq} = 1.2 \times 10^3$ at 395°C

When we ____________________ the equation for a chemical reaction for which the equilibrium constant is K_{eq}, we ____________________ the equilibrium constant. That is, the reverse reaction has the equilibrium constant $1/K_{eq}$.

Example: If the equilibrium concentrations of Cl_2 and $COCl_2$ are the same, and the equilibrium constant is:

$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ $K_{eq} = 1.2 \times 10^3$ at 395°C

What is the value of K_{eq} at 395°C for the reaction $COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$ (The reverse reaction)?

When the ____________________ of an equation are ____________________ by a common factor n to produce a new equation, we ____________________ the original K_{eq} value to the ____________________ to obtain the new equilibrium constant.

Example: If the equilibrium concentrations of Cl_2 and $COCl_2$ are the same, and the equilibrium constant is:

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)} \qquad K_{eq} = 1.2 \times 10^3 \text{ at } 395°C$$

What is the value of K_{eq} at 395°C for the reaction $2\ CO_{(g)} + 2\ Cl_{2(g)} \rightleftharpoons 2\ COCl_{2(g)}$ (double rxn)?

Example: Solid ammonium carbamate, $NH_4CO_2NH_2$, decomposes as shown below:

$$NH_4CO_2NH_{2(s)} \rightleftharpoons 2\ NH_{3(g)} + CO_{2(g)}$$

At 40°C the equilibrium concentration of CO_2 is 4.7×10^{-3} M. Calculate the K_{eq} at this temperature.

Example: The white solid salt, ammonium chloride, decomposes on heating to form gaseous hydrogen chloride and ammonia.

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$

At 400 K, the K_{eq} = 6.0×10^{-9}. Calculate the equilibrium concentration of each gas at this temperature.

See Calculations using K_{eq} Assign

Example: At 430°C the K_{eq} for the following reaction is 1.84×10^{-2}

$$2\ HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

If 0.100 mol of hydrogen iodide is placed in a 1.00 L container and allowed to reach equilibrium at this temperature, find the concentrations of all the species at equilibrium.

K_{eq} = ____________________ = 1.84×10^{-2}

ICE Box Problems: *To fill in an ICE box, we write the* ________________________ *concentrations of all species in the first row. We use the balanced equation to determine the values in the middle* ________________________ *row. In this example, for every two moles of HI that are used up, one mole of H_2 and one mole of I_2 are created. We let the change in concentration equal x. To find the values in the bottom '*________________________ *row you add the 'initial' and 'change' values.*

Initial + Change = @ Equilibrium

	[HI]	***[H₂]***	***[I₂]***
Initial			
Change			
Equilibrium			

Example: In a 3.0L container, 0.69 moles of N2 and 6.87 moles of H2 are allowed to react and reach equilibrium. The concentration of H2 at equilibrium is 1.91M. Calculate the equilibrium constant for this reaction.

Example: At 727°C the K_{eq} for the dissociation of molecular iodine into iodine atoms is 3.80×10^{-5}

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

If the original concentration of molecular iodine is 0.200 M, calculate the concentration of atomic iodine at equilibrium.

K_{eq} =____________________ = 3.80×10^{-5}

The Magnitude of the K_{eq}

- K_{eq} > 1 favours formation of ______________________________, equilibrium lies to the _______________________
  - ex. The decomposition of ozone: $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

    At 298K the value of K_{eq} is 2.0×10^{57}. This means there is way more product than reactant. The equilibrium lies to the ______________________________ and favors the products.
- $K_{eq} \approx 1$, there are measurable quantities of ____________________________ reactants and products
  - ex. The production of hydrogen gas: $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

    At 700K the K_{eq} is 5.09. Since the K_{eq} is fairly close to 1, the concentrations of the reactants and products at equilibrium will be ______________________________ equal (slightly higher concentration of products than reactants).
- K_{eq} < 1, favours formation of ______________________________, equilibrium lies to the ________________________ (this means not a lot of reactants react)
  - ex. The combination of nitrogen and oxygen: $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

    At 298K the K_{eq} is 1.0×10^{-25}, which means the equilibrium lies to the ______________________________. This means at equilibrium, the concentration of the reactants is way ______________________________ than the products. This is good for us because if K_{eq} was really high, oxygen would combine with nitrogen in the atmosphere, and we would not be able to breathe.

See ICE box Assign

Le Châtelier's Principle

"If a system at equilibrium is subjected to an external stress, the equilibrium will shift so as to minimize the stress."

- By external stress, we generally mean a change in ______________________________ of a reactant or product, a change in ______________________________ or ______________________________, or a change in ______________________________.

Changes in Concentration of reactant or Product:

$H_2 + I_2 \rightleftharpoons 2\,HI$

↓ *Increase in H_2*

$\mathbf{H_2} + I_2 \rightleftharpoons 2\,HI$

↓ *Response of System*

$\mathbf{H_2} + I_2 \rightleftharpoons \mathbf{2\,HI}$

Adding hydrogen to this equilibrium results in an increase in ____and a decrease in ______________________________while the concentration of ______________________________ remains up slightly. If K_{eq} is to remain the same, an increase in $[H_2]$ must be accompanied by a decrease in $[I_2]$ or by an increase in [HI] or by both.

$H_2 + I_2 \rightleftharpoons 2\ HI$

↓ *Decrease in H_2*

$H_2 + I_2 \rightleftharpoons 2\ HI$

↓ *Response of System*

$H_2 + \mathbf{I_2} \rightleftharpoons 2\ HI$

If we increase the concentration of one of the reactants, the equilibrium will shift in the ______________________ direction, to use up the excess reactant. If we decrease the concentration of one of the components, the equilibrium will shift in the direction that tends to ______________________ that component.

Example: For the reaction below, predict the direction the equilibrium will shift.

$2\ NO_{2(g)} + 7\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)} + 4\ H_2O_{(g)}$

Given the following changes (assuming constant T and V):

a) addition of ammonia

b) removal of NO_2

c) removal of water vapour

d) addition of hydrogen

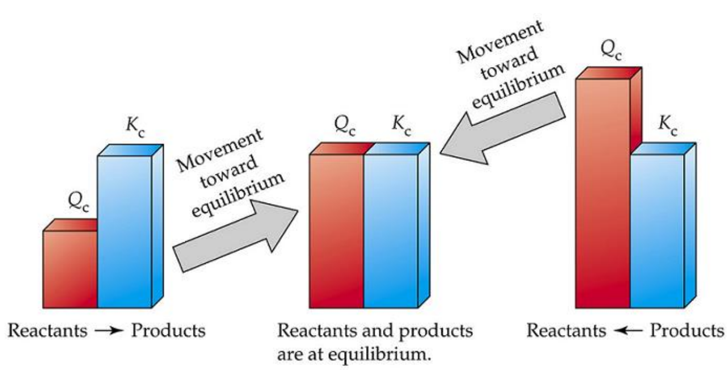
Note: *there are 3 symbols that are equivalent to K_{eq}. K_{eq} is general and refers to the equilibrium constant at a certain temperature. K_c refers to the equilibrium constant at a specific temperature, calculated using ______________________. K_p is the other symbol and is the same as the other two, but it is when you calculate K_{eq} using ______________________ (for gas states)*

Comparing initial values with Keq

Q= the reaction quotient and deals with ______________________ values (concentration or partial pressures)

K= ______________________ constant and deals with the values (concentration or partial pressures) at equilibrium

	Initial State	Net Change
Q = 0	Pure reactants	
Q < K	Mostly reactants	
Q = K	At Equilibrium	
Q > K	Mostly products	
Q = ∞	Pure products	



Example: At a particular temperature, the following reaction has an equilibrium constant value of 0.18.

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

Predict the direction in which the reaction shifts to establish equilibrium, in an experiment for which the starting concentration of each gas is 0.10 mol/L.

See Le Chatelier Assignment 1

Changes in Volume or Pressure

- A decrease in volume or an increase in pressure favours the side of the equation with ____________________________ numbers of moles of gas. These occupy a smaller volume, thus relieving the stress of the added pressure on the system.
- An increase in volume or a decrease in pressure favours the side of the reaction with the ____________________________ number of moles of gas.
- If there are equal numbers of gas molecules on each side of the equation, there will be ____________________________ in the position of the equilibrium, since changes in pressure or volume affect each side equally.
- The addition of an inert gas or gases to a constant volume system at equilibrium ____________________________ change the position of the equilibrium.

$N_2O_{4(g)} \rightleftharpoons 2NO_{(g)}$

$\downarrow$ *Increase in pressure/decrease volume*

$\mathbf{N_2O_{4(g)} \rightleftharpoons 2NO_{(g)}}$

$\downarrow$ *Response of System*

$\mathbf{N_2O_{4(g)}} \rightleftharpoons 2NO_{(g)}$

Example: The pressure on each of the following systems is increased by decreasing the volume of the container. Explain whether each system would shift in the forward direction, the reverse direction, or stay the same.

a) $2\ SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\ SO_{3(g)}$

b) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2\ HI_{(g)}$

c) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

d) $AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

Effect of Temperature on Equilibrium

- When you add heat to a system at equilibrium, there are 2 possible consequences of this temperature change:
  - First, according to Le Châtelier's principle, the equilibrium will shift in the direction that ______________________________ heat.
  - Second, the value of the K_{eq} changes, since K_{eq} is only constant at a specific temperature. The direction of the shift in equilibrium and the increase or decrease in the K_{eq} depends on whether the reaction is ______________________________ or ______________________________.

If you think of heat as a reactant or product, it makes it easier to determine how the equilibrium will shift.

Example:

$$N_2O_{4(g)} \rightleftharpoons 2\ NO_{2(g)} \qquad \Delta H^\circ = +58.0\,kJ$$

Since ΔH is positive, this reaction is _________________thermic.

This means that heat is ______________________________ when the reaction moves in the forward direction. We can write the reaction equation by including heat as one of the ______________________________:

$$N_2O_{4(g)} + \text{heat} \rightleftharpoons 2\ NO_{2(g)}$$

- If we add heat we are adding a ______________________________. The forward reaction is then favoured, partially compensating for the increased temperature.
- If we remove heat (decrease temperature) the ______________________________, or heat-producing reaction, is then favoured, partially compensating for the lowered temperature.

Example: For each of the following equilibria, predict whether the system will shift in the forward direction. Note the energy changes involved and assume that the volume remains constant.

a) heat removed from system: $A \rightleftharpoons B$ $\Delta H^\circ = +40.0$ kJ

b) heat removed from system: $A + B \rightleftharpoons 2\ C$ $\Delta H^\circ = -25.5$ kJ

c) heat added to system: $A + 2\ B \rightleftharpoons 3\ C$ $\Delta H^\circ = -32.0$ kJ

If the reaction is exothermic, the K_{eq} ______________________________ when the temperature is raised. When the temperature is increased during the reaction the equilibrium moves in the ______________________________ direction.

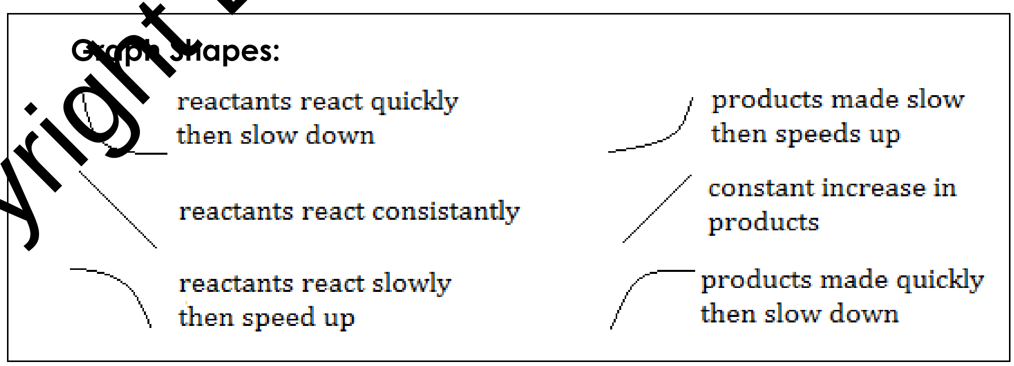
Adding a Catalyst

- A catalyst will not change the ______________________ of an equilibrium because it speeds up the reverse reaction as much as the forward reaction.
- The only thing a catalyst will do is make a reaction reach equilibrium ______________________.

Graphing Equilibrium Concentrations

Example: Reactants A and B are mixed, each at a concentration of 0.80M. A reaction occurs ($A + B \rightleftharpoons C + D$) and equilibrium is established in five minutes. If the equilibrium constant is 9, find the concentrations of C and D and graph the data.

	A	B	C	D
I				
C				
E				



Chemistry 12
Notes on Graphs Involving LeChatelier's Principle

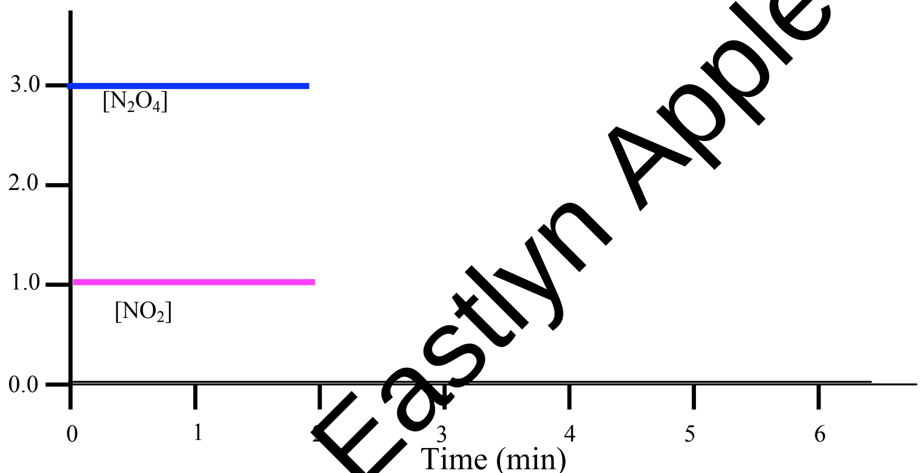
1. Temperature Changes

When a system adjusts due to a temperature change, there are no sudden changes in concentration of any species, so there are no vertical lines on the graph.

Look at the following example:

Given the equilibrium: $N_2O_{4\,(g)} + \text{heat} \rightarrow 2\,NO_{2\,(g)}$

Let's say that the system is at equilibrium at a certain temperature. We'll just pretend that the $[N_2O_4] = 3.0M$ and the $[NO_2] = 1.0M$ at this temperature.



At Time = 2 minutes, **the temperature is increased**.

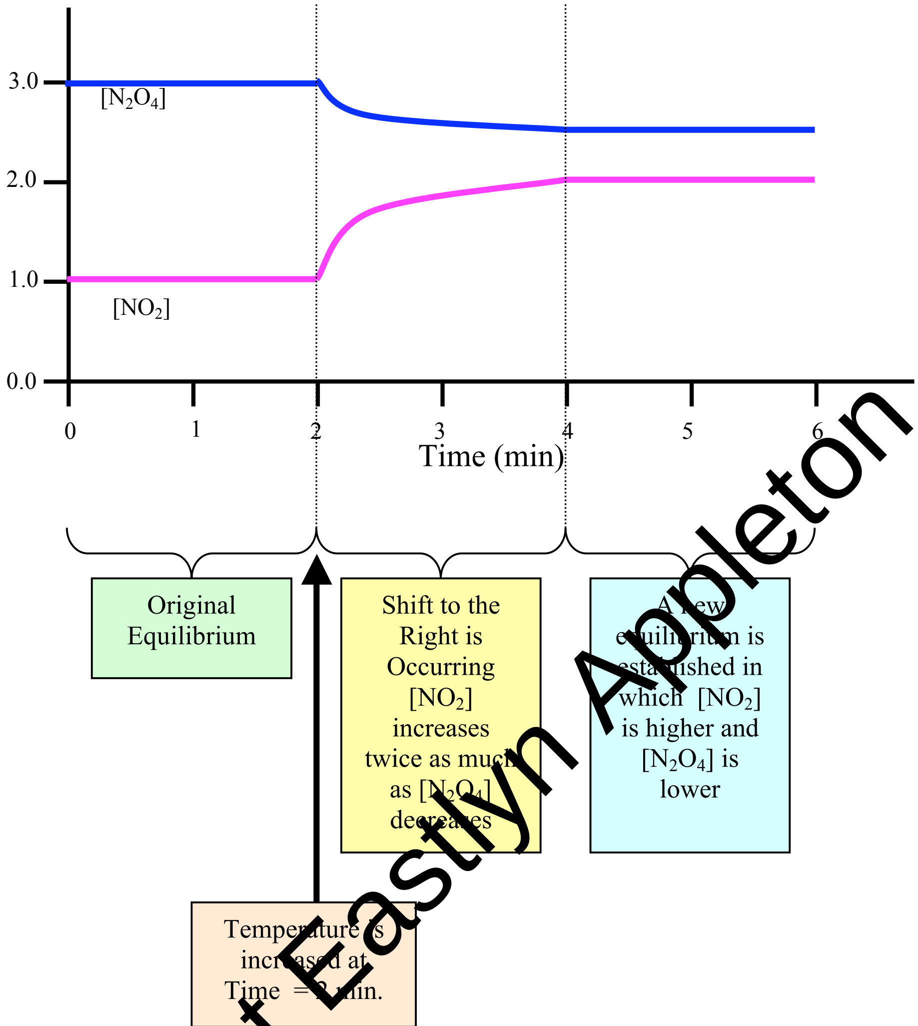
We know by LCP that the equilibrium: $N_2O_{4\,(g)} + \text{heat} \rightarrow 2\,NO_{2\,(g)}$ will shift to the **RIGHT**, away from the heat term in order to counteract the imposed change.

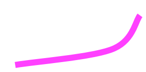
During this shift to the right, the $[N_2O_4]$ will **decrease** and the $[NO_2]$ will **increase**. This is not instant, but takes place gradually, until a NEW equilibrium is established.

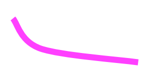
It is also VERY important to note that for every mole of N_2O_4 that is consumed in the shift that 2 moles of NO_2 will be formed (coefficients in balanced equation). So $[NO_2]$ will increase TWICE as much as the $[N_2O_4]$ decreases.

The graph on the next page shows what happens before, during and after this temperature increase and resulting shift. Study it carefully!

$N_2O_{4\,(g)} + \text{heat} \rightarrow 2\,NO_{2\,(g)}$

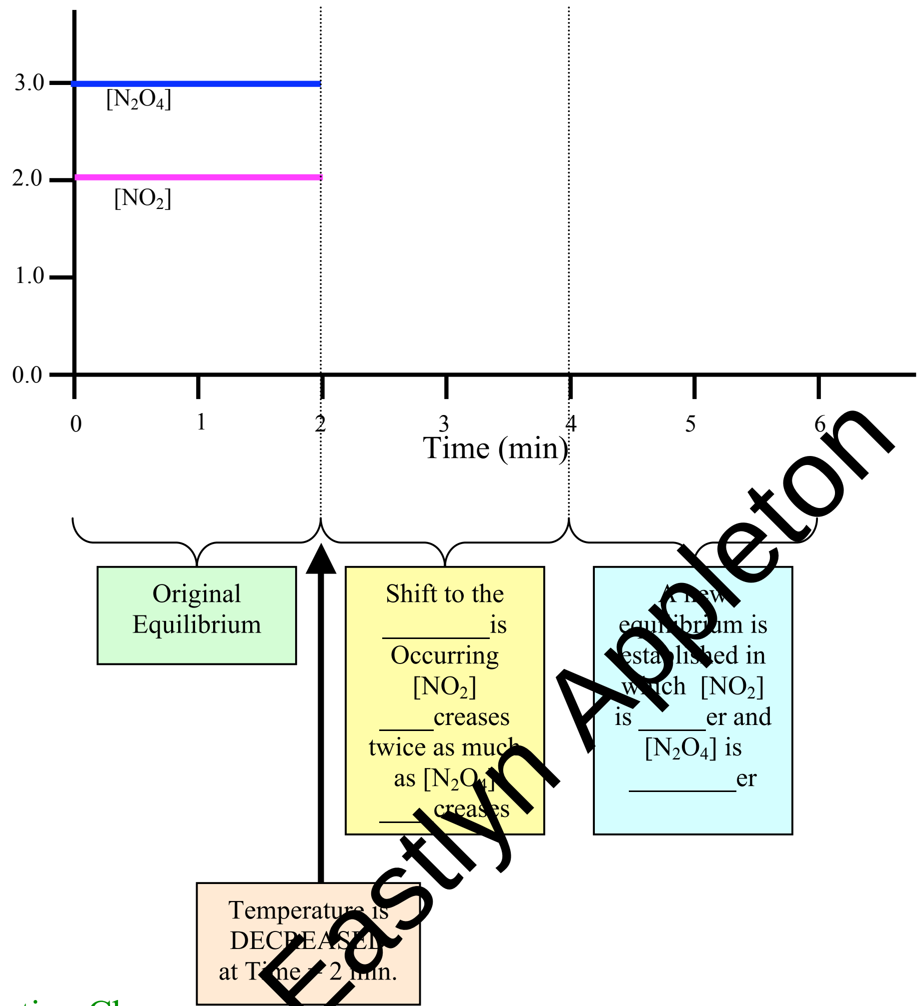


Notice that an increase in a concentration looks like  and **not** like 

Also, a decrease in concentration looks like  and **not** like 

Now it's your turn. On the next page, complete the graph showing the changes that would take place if originally $[N_2O_4]$ = 3.0M and the $[NO_2]$ = 2.0M and the temperature is suddenly DECREASED at Time = 2.0 min. Draw it so that the new equilibrium is achieved at Time = 4 min. Compare yours with the one your teacher does.

$$N_2O_{4\,(g)} + \text{heat} \rightarrow 2\,NO_{2\,(g)}$$

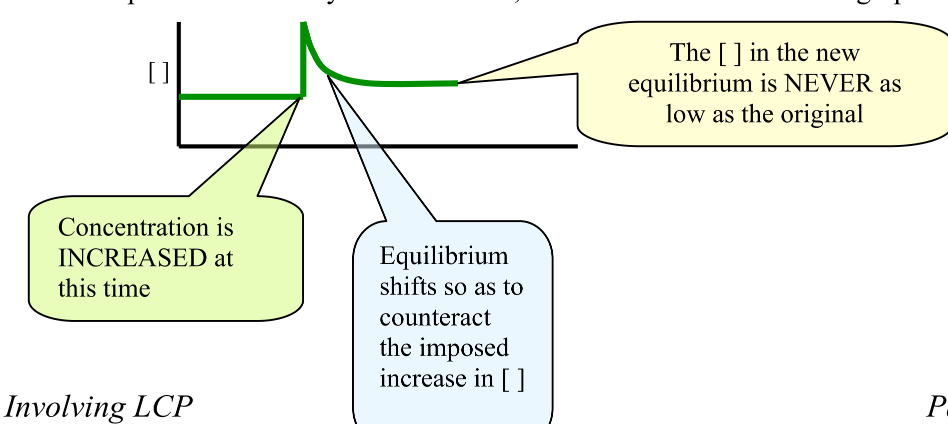


2. Concentration Changes

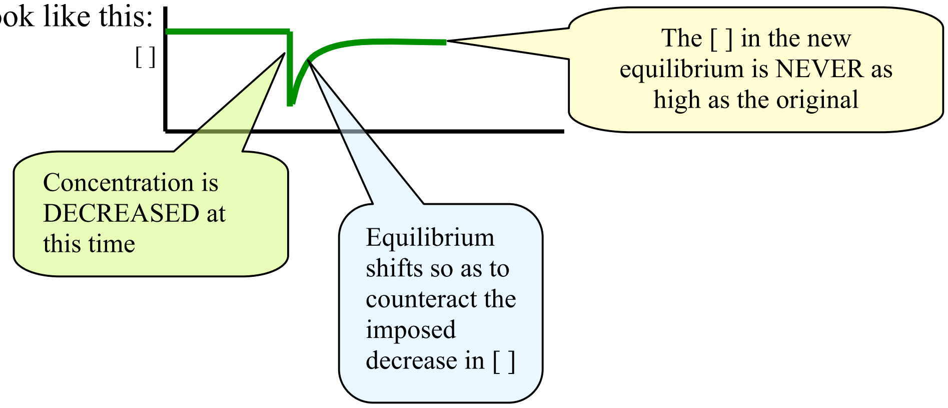
When a concentration is changed (or a substance is added or taken away), there will be a vertical line on the graph because there is a sudden change in concentration.

However, as soon as the change is imposed, the equilibrium will shift so as to counteract the change and eventually establish a new equilibrium.

It is important to note that in a shift, the concentration of any species only PARTIALLY compensates for the imposed change. THE CONCENTRATION NEVER RETURNS TO WHAT IS ORIGINALLY WAS.
If the concentration of a species is suddenly INCREASED, it's Concentration vs. Time graph will look like this:



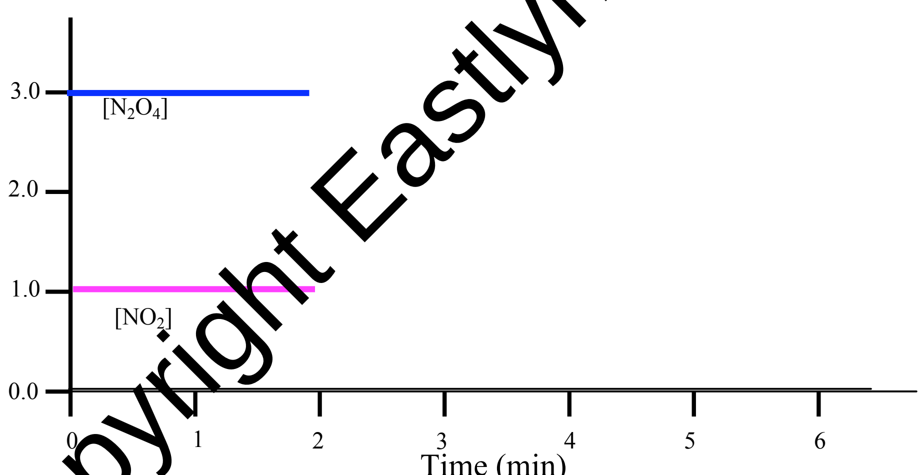
If the concentration of a species is suddenly DECREASED, it's Concentration vs. Time graph will look like this:



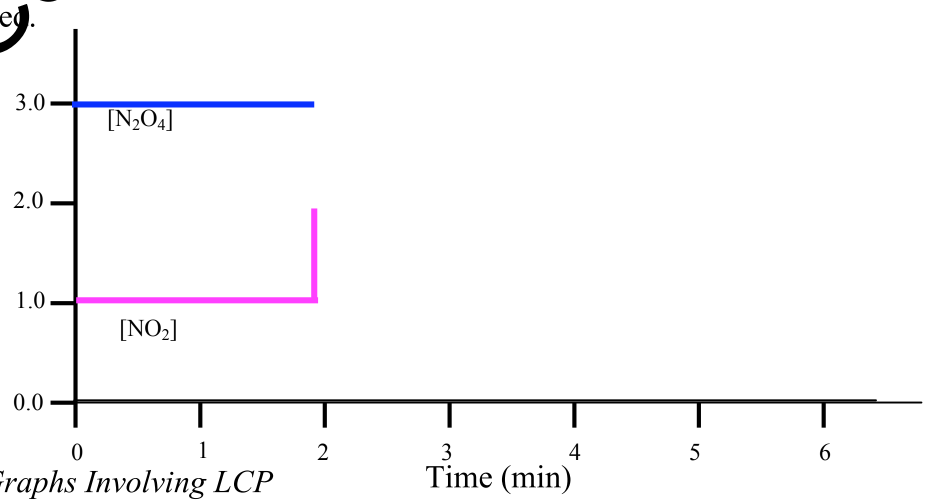
Again, the **extent** of increase or decrease in concentration of a substance during a shift is proportional to the **coefficient of that substance** in the balanced equation. Also, the ONLY substance with the "vertical line" is the one that the experimenter actually increased or decreased. Consider the situation …

Given the equilibrium: $N_2O_{4\,(g)}$ + heat $\rightarrow$ $2\ NO_{2\,(g)}$

Let's say that the system is at equilibrium in a closed container. We'll just pretend that the $[N_2O_4]$ = 3.0M and the $[NO_2]$ = 1.0M . The temperature will be kept constant.

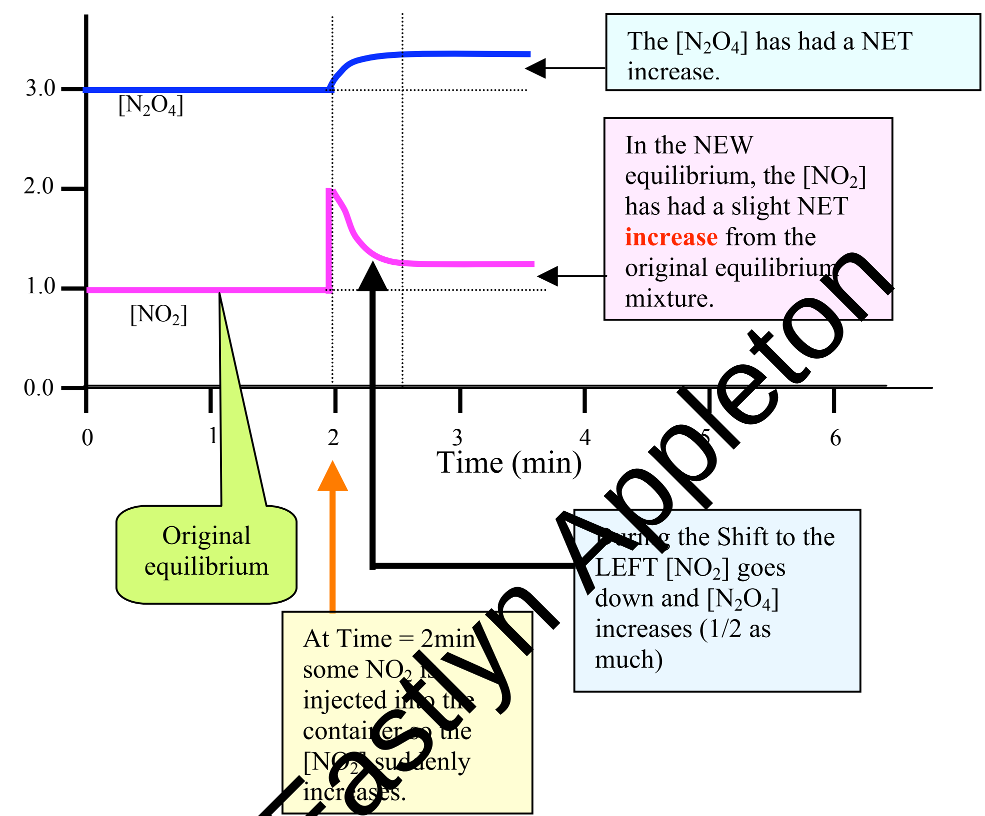


At Time = 2 minutes, more NO_2 is injected into the container. Thus the $[NO_2]$ is suddenly increased.



Now, of course the equilibrium $N_2O_{4\,(g)}$ + heat $\rightarrow$ 2 $NO_{2\,(g)}$ will shift to the **LEFT** in order to counteract the sudden increase in the $[NO_2]$. Thus $[NO_2]$ will **decrease** and the $[N_2O_4]$ will **increase** (but only **half as much** as the $[NO_2]$ decreases due to the 1:2 coefficient ratio!)

$$N_2O_{4\,(g)} + \text{heat} \rightarrow 2\,NO_{2\,(g)}$$



3. Changes in Total Pressure (caused by changing the volume of a closed container). Applies to Gaseous Systems.

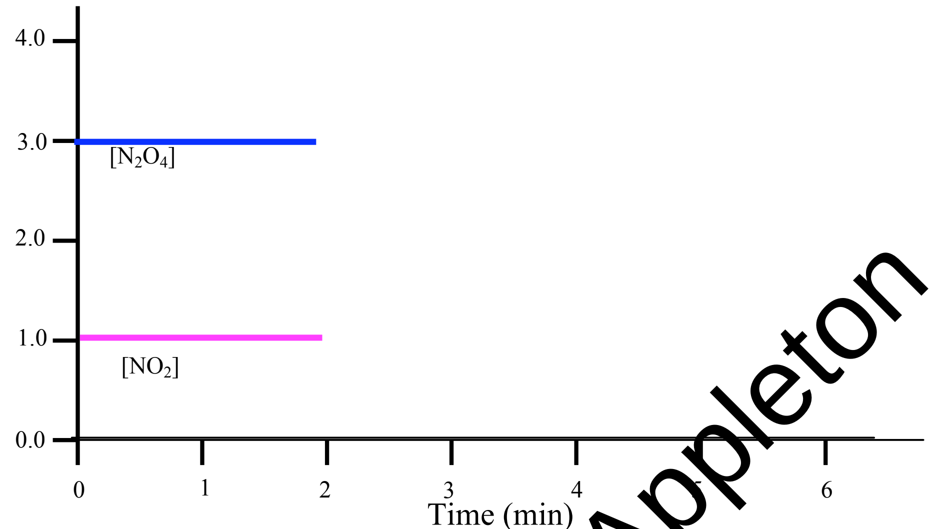
Recall, when the volume of a closed container is DECREASED, the TOTAL PRESSURE increases. When this happens THE CONCENTRATION OF EVERY GAS IN THE CONTAINER **INITIALLY** INCREASES. (# of moles per unit volume).

However, at this point LCP kicks in and the equilibrium will shift whichever way it needs to partially counteract the imposed stress.

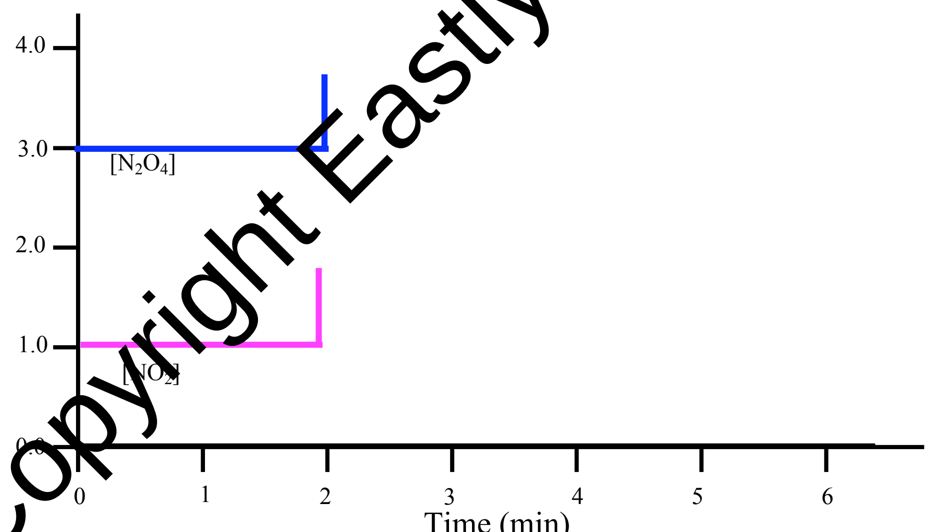
With PRESSURE (or VOLUME) changes **ALL substances** will have vertical lines on the graph at the time the imposed change takes place.

See the example on the next page…

Given the equilibrium: $N_2O_4\,_{(g)}$ + heat → $2\ NO_2\,_{(g)}$
Let's say that the system is at equilibrium in a **closed container**. We'll just pretend that the $[N_2O_4] = 3.0M$ and the $[NO_2] = 1.0M$. The temperature will be kept constant.

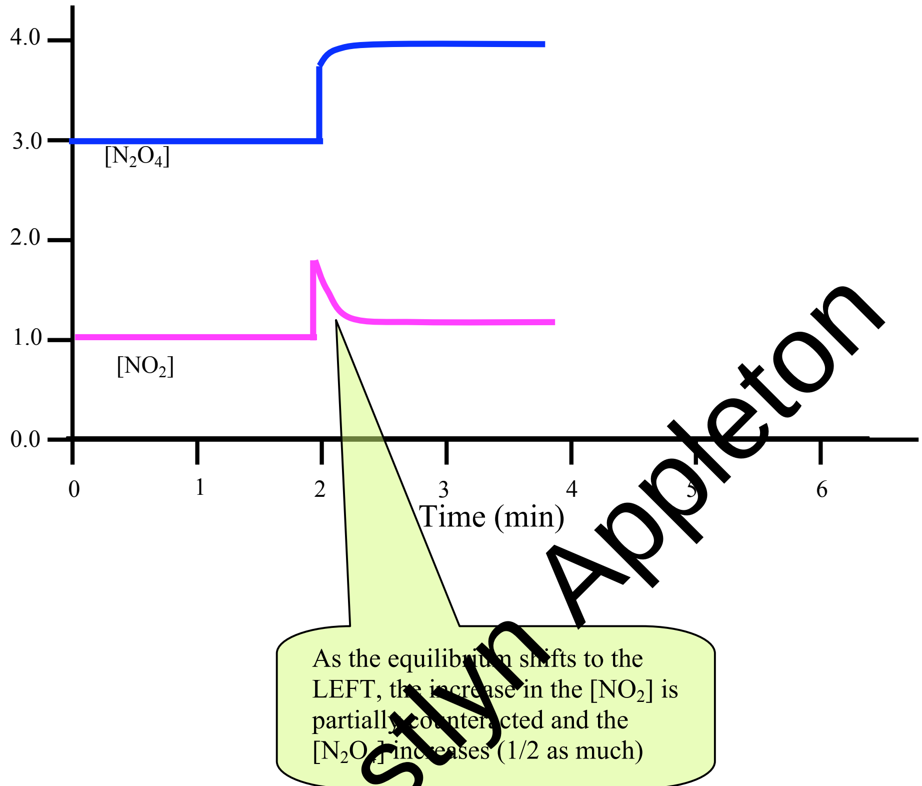


At Time = 2 minutes, the **volume** of the container is suddenly DECREASED. Thus the **concentrations of BOTH gases initially increase**.



Now, in order to counteract the imposed pressure increase, the equilibrium will shift to the side with LESS moles of gas: $N_2O_4\,_{(g)}$ + heat → $2\ NO_2\,_{(g)}$
In this case, this would be a shift to the LEFT where $[NO_2]$ will decrease and the $[N_2O_4]$ will increase. See the graph on the next page…

$$N_2O_{4\,(g)} + \text{heat} \rightarrow 2\,NO_{2\,(g)}$$



Now, lets say you were given the equilibrium: $NO_{2(g)} + CO_{(g)} \rightarrow CO_{2(g)} + NO_{(g)}$ in a closed system.

Initially $[NO_2]$ = 2.0M, [CO] = 3.0M, $[CO_2]$ = 4.0M and [NO] = 5.0M

At Time = 2 minutes, the volume of the container is suddenly decreased.
Draw and label a graph showing all that would happen in this case. Compare your answer with that of the teacher.

4. Catalysts

When you add a catalyst to a system at equilibrium, both the forward and the reverse reactions speed up, so there is no change in the concentrations of any of the species in the mixture. Adding a catalyst would have no effect on a graph of Concentration vs. Time!

An Analogy for an Equilibrium Reaction

Adapted from umanitoba.ca

Introduction:
Most of the reactions you have encountered so far proceed in only one direction. That is, when the reaction has stopped all of the reactants have been converted into products. This type of reaction is said to go to completion. This is not true of all reactions. Sometimes the products react with each other to reform the reactants. The reaction of the reactants to form the products is called the forward reaction. The reaction of the products to form the reactants is called the reverse reaction.
At some point in a chemical reaction, the rate of the forward reaction will equal the rate of the reverse reaction. When this occurs, the system is said to be in equilibrium. At this point, the number of molecules changing from reactants to products equals the number changing from products to reactants. At this point there will be no apparent visible (macroscopic) changes but there are still changes occurring at the molecular level, albeit they are the same in both directions.

Objectives:

1. To illustrate the experimental conditions necessary to have a system at experimental equilibrium.
2. To illustrate graphically the changes which lead to the establishment of equilibrium.

Materials:

2-25 mL graduated cylinders

2 drinking straws of different diameter

graph paper

Procedure: Simulating Equilibrium

1. Label a 25 mL graduated cylinder "A". Fill it to the 25.0 mL mark with water. This is the REACTANTS. Label a second 25 mL graduated cylinder "B". This is the PRODUCTS. This cylinder will begin empty. Why is it empty at this stage?
2. Obtain 2 straws of <u>different</u> diameter. Label these straws with "A" and "B". Be sure to keep straw "A" with cylinder "A" and straw "B" with cylinder "B".
3. With a partner, simultaneously lower the straws into each of the graduated cylinders. When the straws reach the bottom of the cylinder each partner will place an index finger over the opening of the straw and then transfer the contents to the opposite graduated cylinder and allow the water to drain.
4. Accurately record the volume of water in each of the REACTANTS and PRODUCTS cylinders on the "transfer #1" space in the data table attached.

***Note that in the first transfer some reactants changed to products but no products changed to reactants because there were none available.**

5. Repeat steps 3 and 4 until equilibrium is reached. Note that as some products start to form in the B cylinder they become available for becoming reactants through the reversible reaction. <u>Equilibrium will be reached when 5 successive transfers result in no</u>

further change in volume. (Note: Always return the same straw to its original graduated cylinder for refilling.) Even though there is no apparent change there are still changes occurring at the molecular level. Explain.

6. Plot this data on the graph paper provided by your teacher. Place the Volumes of Water in Cylinders "A" and "B" on the y-axis and the Transfer #'s on the x-axis.

Analysis:

1. In the transfer of water from cylinder to cylinder, what does the water represent in terms of a real chemical equation?
2. In relation to any of the simulations, what significance can be attributed to:
    a) any point where the two curves meet (if they do)? In other words, what is happening at the molecular level in the 'reaction' when this overlap occurs.
    b) the first flat portion of the two curves?
3. What is the evidence that equilibrium has been if:
    a) the data for the water transfers are observed?
    b) the plotted data are observed?
4. What factors control the relative volumes of water in each cylinder at equilibrium in this exercise?
5. Consult with other member of the class to see if their graphs are similar to or different from yours. Account for the differences you find.

Summary:
Reactions in nature occur in both the forward and reverse directions. When the rate of the forward reaction equals the rate of the reverse reaction, the reaction is in equilibrium. In this lab, we simulated concentration changes by adding or removing water from the "reactants". This would be analogous to increasing or decreasing the concentration of reactants (i.e., the number of reacting molecules in a real chemical reaction).

Data Table: Reactants ________________ straw, products ___________________straw

Transfer #	Volume of H_2O in "A" (mL)	Volume of H_2O in "B" (mL)	Transfer #	Volume of H_2O in "A" (mL)	Volume of H_2O in "B" (mL)
0	25.0	0.0	31		
1			32		
2			33		
3			34		
4			35		
5			36		
6			37		
7			38		
8			39		
9			40		
10			41		
11			42		
12			43		
13			44		
14			45		
15			46		
16			47		
17			48		
18			49		
19			50		
20			51		
21			52		
22			53		
23			54		
24			55		
25			56		
26			57		
27			58		
28			59		
29			60		
30			61		

Name____________________________

Calculating K_{eq} Assign

1. If the system represented by the following equation is found to be at equilibrium at a specific temperature, explain whether each of the following statements is true.

$$CO_{(g)} + H_2O_{(g)} \Longleftrightarrow CO_{2(g)} + H_{2(g)}$$

   a) all species must be present in the same concentration

   b) the rate of the forward reaction equals the rate of the reverse reaction

2. Write the equilibrium expression, K_{eq}, for each of the following reactions:

   a) $2\ NO_{(g)} + O_{2(g)} \rightleftharpoons 2\ NO_{2(g)}$

   b) $P_{4(s)} + 6\ Cl_{2(g)} \rightleftharpoons 4\ PCl_{3(l)}$

   c) $4\ HCl_{(g)} + O_{2(g)} \rightleftharpoons 2\ H_2O_{(g)} + 2\ Cl_{2(g)}$

   d) $AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

   e) $NOCl_{(g)} \rightleftharpoons NO_{(g)} + \frac{1}{2}\ Cl_{2(g)}$

   f) $(NH_4)_2Se_{(s)} \rightleftharpoons 2\ NH_{3(g)} + H_2Se_{(g)}$

   g) $Br_{2(g)} + 5\ F_{2(g)} \rightleftharpoons 2\ BrF_{5(g)}$

   h) $Ca_3(PO_4)_{2(s)} \rightleftharpoons 3\ Ca^{2+}_{(aq)} + 2\ PO_4^{3-}{}_{(aq)}$

3. For each of the following reversible chemical changes, write a balanced equation indicating the two-way nature of the reaction, then write an equilibrium constant expression.

    a) the condensation of steam

    b) the dissolving of silver bromide in water

    c) hydrogen gas passed over a heated iron oxide, Fe_3O_4, forms iron and steam

    d) hydrogen iodide gas decomposes into its gaseous elements

4. At the equilibrium point in the decomposition of phosphorus pentachloride the following concentrations are obtained: 0.010 M PCl_5, 0.15M PCl_3, 0.37 M Cl_2.

    Determine the equilibrium constant for the reaction. $PCl_{5(g)} \Longleftrightarrow PCl_{3(g)} + Cl_{2(g)}$

5. The following table gives some values for reactant and product equilibrium concentrations at 700 K for the Shift reaction, an important method for the commercial production of hydrogen gas. All concentrations are in mol/L.

$$CO_{(g)} + H_2O_{(g)} \Longleftrightarrow CO_{2(g)} + H_{2(g)}$$

Trial	$[CO_2]$	$[H_2]$	$[CO]$	$[H_2O]$
1	0.600	0.600	0.266	0.266
2	0.600	0.800	0.330	0.286
3	2.00	2.00	0.887	0.887
4	1.00	1.50	0.450	0.655
5	1.80	2.00	0.590	1.20

Using the data, show that the ratio of the concentration of the products to that of the reactants, is a constant value at equilibrium.

6. At 1000°C, methane reacts with water as follows:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3\ H_{2(g)}$$

In one experiment the equilibrium concentrations of the gases were $[CH_4] = 2.97 \times 10^{-3}$, $[H_2O] = 7.94 \times 10^{-3}$, $[CO] = 5.45 \times 10^{-3}$, and $[H_2] = 2.1 \times 10^{-3}$. Calculate K_{eq} at this temperature.

7. For the following process, the K_{eq} is 0.98.

$$2\ FeBr_{3(s)} \rightleftharpoons 2\ FeBr_{2(s)} + Br_{2(g)}$$

A 3.0 L reaction vessel contains 3.6 moles of iron(II) bromide, 1.2 moles of iron(III) bromide, and 2.1 moles of bromine gas at this temperature. Is the system at equilibrium? (Show your calculations).

8. Consider the following equilibrium process at 686°C:

$$CO_{2(g)} + H_{2(g)} \longleftrightarrow CO_{(g)} + H_2O_{(g)}$$

The equilibrium concentrations of the reacting species are $[CO] = 0.050\ M$, $[H_2] = 0.045\ M$, $[CO_2] = 0.086\ M$, and $[H_2O] = 0.040\ M$. Calculate K_{eq} for the reaction at 686 °C.

Name:______________________________

Calculations Using K_{eq}

1. At a particular temperature, $K_{eq} = 1.6 \times 10^{-2}$ for:

$$2\ H_2S_{(g)} \rightleftharpoons 2\ H_{2(g)} + S_{2(g)}$$

Calculate K_{eq} for each of the following reactions:

a) $H_{2(g)} + \frac{1}{2}\ S_{2(g)} \rightleftharpoons H_2S_{(g)}$

b) $5\ H_2S_{(g)} \rightleftharpoons 5\ H_{2(g)} + {}^{5}/_{2}S_{2(g)}$

2. The equilibrium constant for the equilibrium below is 302 at 600 K. What is the value of the equilibrium constant for the reverse reaction at the same temperature?

$$CO_{(g)} + H_2O_{(g)} \Longleftrightarrow CO_{2(g)} + H_{2(g)}$$

3. At 1200°C, hydrogen sulfide decomposes according to the following reaction:

$$2\ H_2S_{(g)} \rightleftharpoons 2\ H_{2(g)} + S_{2(g)}$$

The K_{eq} for this reaction is 4.22×10^{-4}. If the temperature remains constant, what is the K_{eq} for the following reaction?

$$3\ S_{2(g)} + 6\ H_{2(g)} \rightleftharpoons 6\ H_2S_{(g)}$$

4. For the reaction:

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}\ O_{2(g)} \qquad K_{eq} = 16.7 \text{ at } 1000\ K$$

What is the value of K_{eq} at 1000 K for the reaction?

$$2\ SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\ SO_{3(g)}$$

5. A reaction vessel contains NH_3, N_2, and H_2 at equilibrium at a certain temperature. The equilibrium concentrations are $[NH_3] = 0.25$ M, $[N_2] = 0.11$ M, and $[H_2] = 1.91$ M. Calculate the equilibrium constant for the synthesis of ammonia if the reaction is represented below.

a) $N_{2(g)} + 3\ H_{2(g)} \longrightarrow 2\ NH_{3(g)}$

b) $\frac{1}{2}\ N_{2(g)} + 3/2\ H_{2(g)} \longrightarrow NH_{3(g)}$

6. For the reaction below, at 700°C, $K_{eq} = 0.534$. Calculate the number of moles of H_2O formed at equilibrium if at equilibrium, there are 0.173mol of H_2 and 0.173mol of CO_2 at equilibrium at 700°C in a 10.0 L container.

$$H_{2(g)} + CO_{2(g)} \longleftrightarrow H_2O_{(g)} + CO_{(g)}$$

7. Equilibrium is established in the following reaction:

$$A + B \rightleftharpoons C + D \qquad K_{eq} = 10.0$$

At this point, which of the following must be true?

a) [C][D] = [A][B]

b) [C] = [A] and [D] = [B]

c) [A][B] = 0.10 × [C][D]

d) [A] = [B] = [C] = [D] = 10.0

8. At a high temperature the equilibrium constant for the reaction was found to be 0.15.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

what is the equilibrium concentration of carbon dioxide at this temperature?

9. Bromine chloride, BrCl, decomposes to form chlorine and bromine.

$$2\ BrCl_{(g)} \rightleftharpoons Cl_{2(g)} + Br_{2(g)}$$

At a certain temperature the equilibrium constant for the reaction is 11.1, and the equilibrium mixture contains 4.00 mol Cl_2. How many moles of Br_2 and BrCl are present in the equilibrium mixture?

10. Gaseous dinitrogen tetroxide, N_2O_4, is placed in a flask and allowed to reach equilibrium at 100°C.

$$N_2O_{4(g)} \Longleftrightarrow 2\ NO_{2(g)}$$

At the temperature of the reaction, the value of the K_{eq} is 0.212. The concentration of dinitrogen tetroxide at equilibrium is 0.155 mol/L. Calculate the concentration of nitrogen dioxide at equilibrium.

11. The decomposition of hydrogen iodide at 450°C produces an equilibrium mixture that contains 0.50 mol of hydrogen. The equilibrium constant is 0.020 for the reaction. How many ***moles*** of iodine and hydrogen iodide are present in the equilibrium mixture?

$$2\ HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Name:________________________________

ICE Box Assignment

1. Hydrogen iodide decomposes according to the reaction

$$2\ HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

A sealed 1.50 L container initially holds 0.00623 mol of H_2, 0.00414 mol of I_2, and 0.0244 mol of HI at 703 K. When equilibrium is reached, the concentration of H_2 is 0.00467 M. What are the concentrations of HI and I_2?

2. The first step in HNO_3 production is the catalyzed oxidation of NH_3. Without a catalyst, a different reaction predominates:

$$4\ NH_{3(g)} + 3\ O_{2(g)} \rightleftharpoons 2\ N_{2(g)} + 6\ H_2O_{(g)}$$

When 0.0150 mol of $NH_{3(g)}$ and 0.0150 mol of $O_{2(g)}$ are placed in a 1.00 L container at a certain temperature, the $N_{2(g)}$ concentration at equilibrium is 1.96×10^{-3} M. Calculate K_{eq}.

3. Phosphorus pentachloride decomposes via the reaction:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

A sample of phosphorus pentachloride of concentration 1.10 M was placed in a container. Once equilibrium was attained, it was found that the concentration of chlorine in the vessel was 0.330 M. Calculate K_{eq} for the reaction at this temperature. *(0.141)*

4. The colourless gas dinitrogen tetroxide and the brown-coloured air pollutant nitrogen dioxide exist in equilibrium as

$$N_2O_{4(g)} \Longleftrightarrow 2\ NO_{2(g)}$$

Assume that 0.125 mol of dinitrogen tetroxide gas is introduced into a 1.00 L container and allowed to decompose. When equilibrium with nitrogen dioxide is reached, the concentration of the dinitrogen tetroxide is 0.0750 M. What is the value of K_{eq} for this reaction?

5. For the following reaction the equilibrium constant has a value of 85.0 at 460°C:

$$SO_{2(g)} + NO_{2(g)} \Longleftrightarrow NO_{(g)} + SO_{3(g)}$$

If a mixture of sulfur dioxide and nitrogen dioxide is prepared, each with an initial concentration of 0.100 M, calculate the equilibrium concentrations of nitrogen dioxide and nitrogen monoxide at this temperature.

6. At 100°C the following reaction has an equilibrium constant value of 2.2×10^{-10}.

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

If 1.00 mol of phosgene, $COCl_2$, is placed in a 10.0 L flask, calculate the concentration of carbon monoxide at equilibrium.

7. A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00 L stainless steel flask at 430°C. Calculate the concentrations of H_2, I_2, and HI at equilibrium. The equilibrium constant K_{eq} for the reaction is 54.3 at this temperature.

$$H_{2(g)} + I_{2(g)} \longleftrightarrow 2\ HI_{(g)}$$

8. The equilibrium constant for the following reaction is 0.11.

$$2\ ICl_{(g)} \rightleftharpoons I_{2(g)} + Cl_{2(g)}$$

Calculate all the equilibrium concentrations if 0.33 mol of iodine chloride gas is placed in a 1.00 L vessel and the reaction is allowed to reach equilibrium.

9. The dissociation of ammonia at 27°C, has a K_{eq} value of 2.63×10^{-9}.

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$$

If 1.00 mol of ammonia is placed in a 1.00 L vessel, calculate the equilibrium concentration of nitrogen and hydrogen.

10. The following reaction takes place in a 1.00 L vessel at 500°C.

$$2\,HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Equilibrium concentrations were found to be 1.76 M HI and 0.20 M for H_2 and I_2. If an additional 0.500 mol of HI gas is introduced, what are the concentrations of all gases once equilibrium has again been reached?

11. The dissociation of ammonia at 400°C has a K_{eq} of 1.92.

$$2\ NH_{3(g)} \rightleftharpoons N_{2(g)} + 3\ H_{2(g)}$$

If 0.500 mol of ammonia is placed in a 500.0 mL container, determine the equilibrium concentrations of all gases.

12. The equilibrium constant, K_{eq}, for the following reaction is 85.0 at 460°C.

$$SO_{2(g)} + NO_{2(g)} \rightleftharpoons NO_{(g)} + SO_{3(g)}$$

If a mixture is prepared where the initial concentration of sulfur dioxide is 1.00 mol/L and that of nitrogen dioxide is 2.00 mol/L, calculate the equilibrium concentration of nitrogen monoxide and nitrogen dioxide at this temperature.

13. For each of the following reactions, state whether the value of the equilibrium constant favours the formation of reactants or products.

a) $I_{2(g)} + Cl_{2(g)} \Longleftrightarrow 2\ ICl_{(g)}$ $K_{eq} = 2 \times 10^{6}$

b) $H_{2(g)} + Cl_{2(g)} \Longleftrightarrow 2\ HCl$ $K_{eq} = 1.08$

c) $I_{2(g)} \Longleftrightarrow I_{(g)} + I_{(g)}$ $K_{eq} = 3.8 \times 10^{-7}$

14. The equilibrium constant for the decomposition of molecular chlorine at 298 K is 1.4×10^{-38}. Would many chlorine atoms result from the dissociation of the chlorine molecules at this temperature?

Name:____________________________

Le Chatlier Assignment 1

1. The dissociation of acetic acid in water has a K_{eq} value 1.8×10^{-5} at 25°C.

$$CH_3CO_2H_{(aq)} \rightleftharpoons CH_3CO_2^-{}_{(aq)} + H^+_{(aq)}$$

a. calculate the equilibrium concentration of H^+ in a solution that was originally 0.100 mol/L acetic acid

b. in which direction will this equilibrium move if H^+ ions from concentrated hydrochloric acid are added?

2. Consider the following equilibrium reaction

$$2\ NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2\ NOCl_{(g)}\quad K_{eq} = 6.5 \times 10^4 \text{ at } 35°C$$

In a certain experiment 2.0×10^{-2} mol NO, 8.3×10^{-3} mol Cl_2, and 6.8 mol NOCl are mixed in a 2.0 L flask. In which direction will the system proceed to reach equilibrium?

3. For the synthesis of ammonia

$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$$

the equilibrium constant at 200°C is 0.65. Starting with $[H_2]_0 = 0.76$ M, $[N_2]_0 = 0.60$ M, and $[NH_3]_0 = 0.48$ M, when this mixture comes to equilibrium, which gases will have increased in concentration and which will have decreased in concentration?

4. At some point during a reaction, the following concentrations are measured.

$$2\ ICl_{(g)} \rightleftharpoons I_{2(g)} + Cl_{2(g)} \qquad K_{eq} = 8.33 \times 10^{-4}$$

0.15 M   0.00125M   0.0075 M

Which of the following represents a true statement?

a) the reaction is at equilibrium
b) the reaction will proceed until all ICl is consumed
c) I_2 will be consumed in reaching equilibrium
d) the concentration of Cl_2 will increase in reaching equilibrium

5. At the start of a reaction, there are 0.249 mol N_2, 3.21×10^{-2} mol H_2, and 6.42×10^{-4} mol NH_3 in a 3.50 L reaction vessel at 200°C. If the equilibrium constant for the reaction is 0.65 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed. $N_{2(g)} + 3\ H_{2(g)} \longleftrightarrow 2\ NH_{3(g)}$

6. At 350°C, the K_{eq} for the reaction is 2.37×10^{-3} $N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$

In a certain experiment, the equilibrium concentrations are $[N_2] = 0.683$ M, $[H_2] = 8.80$ M, and $[NH_3] = 1.05$ M. Suppose some more NH_3 is added to the mixture so that its concentration is increased to 3.65 M.

a) Use Le Châtelier's principle to predict the direction that the net reaction will shift to reach a new equilibrium.

b) Confirm your prediction by calculating the reaction quotient Q and comparing its value to K_{eq}.

7. The following reaction occurs readily at 425°C: $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$

The equilibrium constant is 14.9 at this temperature. Predict the shift that the reaction would take to establish equilibrium for each of the following starting conditions:

a) all gases are at a concentration of 0.100 mol/L

b) all gases are at a concentration of 1.00 mol/L

c) $[NOCl] = 0.100$, $[NO] = 0.0500$, $[Cl_2] = 0.100$

Name:________________________________

Le Chatelier Assignment 2

1. Consider the following equilibrium systems:

   a) $2\ PbS_{(s)} + 3\ O_{2(g)} \longleftrightarrow 2\ PbO_{(s)} + 2\ SO_{2(g)}$

   b) $PCl_{5(g)} \longleftrightarrow PCl_{3(g)} + Cl_{2(g)}$

   c) $H_{2(g)} + CO_{2(g)} \longleftrightarrow H_2O_{(g)} + CO_{(g)}$

   Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature

2. In each of the following equilibria, would you increase or decrease the temperature to force the reaction in the forward direction?

   a) $CO_{2(g)} + H_{2(g)} \Longleftrightarrow CO_{(g)} + H_2O_{(g)}$ $\Delta H° = +41\ kJ$

   b) $2\ SO_{2(g)} + O_{2(g)} \Longleftrightarrow 2\ SO_{3(g)}$ $\Delta H° = -198\ kJ$

3. List three ways that the following equilibrium reaction could be forced to shift to the right:

   $$2\ NO_{2(g)} \Longleftrightarrow 2\ NO_{(g)} + O_{2(g)}$$

4. Given the following equilibrium reaction

   $$2\ C_{(s)} + O_{2(g)} \Longleftrightarrow 2\ CO_{(g)}$$

   what will be the effect of the following disturbances to the system?

   a) addition of carbon monoxide (at constant V and T)

   b) addition of oxygen (at constant V and T)

   c) addition of solid carbon (at constant V and T)

   d) decreasing the container volume (at constant T))

   e) addition of helium gas to the container (at constant V)

5. Describe the changes that occur after each stress is applied to the equilibrium.

$N_{2\,(g)}$ + $3H_{2\,(g)}$ ←→ $2NH_{3(g)}$ + 92 KJ

Change	Shift (to the reactants or products)
[N_2] is increased	
[H_2] is increased	
[NH_3] is increased	
Temp is increased	
[N_2] is decreased	
[H_2] is decreased	
[NH_3] is decreased	
Temp is decreased	

6. Consider the following equilibrium process:

$N_2F_{4(g)} \longleftrightarrow 2\ NF_{2(g)}$ $\Delta H = +38.5$ kJ

Predict the changes in the equilibrium (direction of shift and effect on K_{eq}) if:

a) the reacting mixture is heated at constant volume

b) $NF_{2(g)}$ is removed from the reacting mixture at constant temperature and volume

c) the pressure on the reacting mixture is decreased at constant temperature

d) an inert gas, such as helium, is added to the reacting mixture at constant volume and temperature

7. Why is the Haber Process carried out under high pressure?

$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$ (Δ H = -92.22 kJ·mol^{-1})

8. In which direction will the equilibrium shift, with the following changes:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad \Delta H = +179kJ$$

a) addition of nitrogen gas

b) removal of oxygen gas

c) addition of a catalyst

d) halving of the volume of the system

9. How would you adjust the volume of the container in order to maximize product yield in each of the following reactions?

a) $Fe_3O_{4(s)} + 4\ H_{2(g)} \rightleftharpoons 3\ Fe_{(s)} + 4\ H_2O_{(g)}$

b) $2\ C_{(s)} + O_{2(g)} \rightleftharpoons 2\ CO_{(g)}$

10. Predict the effect of increasing the temperature on the amounts of products in the following reactions:

a) $CO_{(g)} + 2\ H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$ $\quad \Delta H_{rxn} = -90.7$ kJ

b) $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$ $\quad \Delta H_{rxn} = 131$ kJ

c) $2\ NO_{2(g)} \rightleftharpoons 2\ NO_{(g)} + O_{2(g)}$ (endothermic)

d) $2\ C_{(s)} + O_{2(g)} \rightleftharpoons 2\ CO_{(g)}$ (exothermic)

11. The oxidation of SO_2 is the key step in H_2SO_4 production:

$SO_{2(g)} + ½\ O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad \Delta H_{rxn} = -99.2$ kJ

What qualitative combination of T and P maximizes SO_3 yield?

Name:________________________

Graphing Equilibrium

1. If the initial $[H_2]$ = 0.200 M, $[I_2]$ = 0.200 M and Keq = 55.6 at 250°C calculate the equilibrium concentrations of all molecules and sketch a graph.

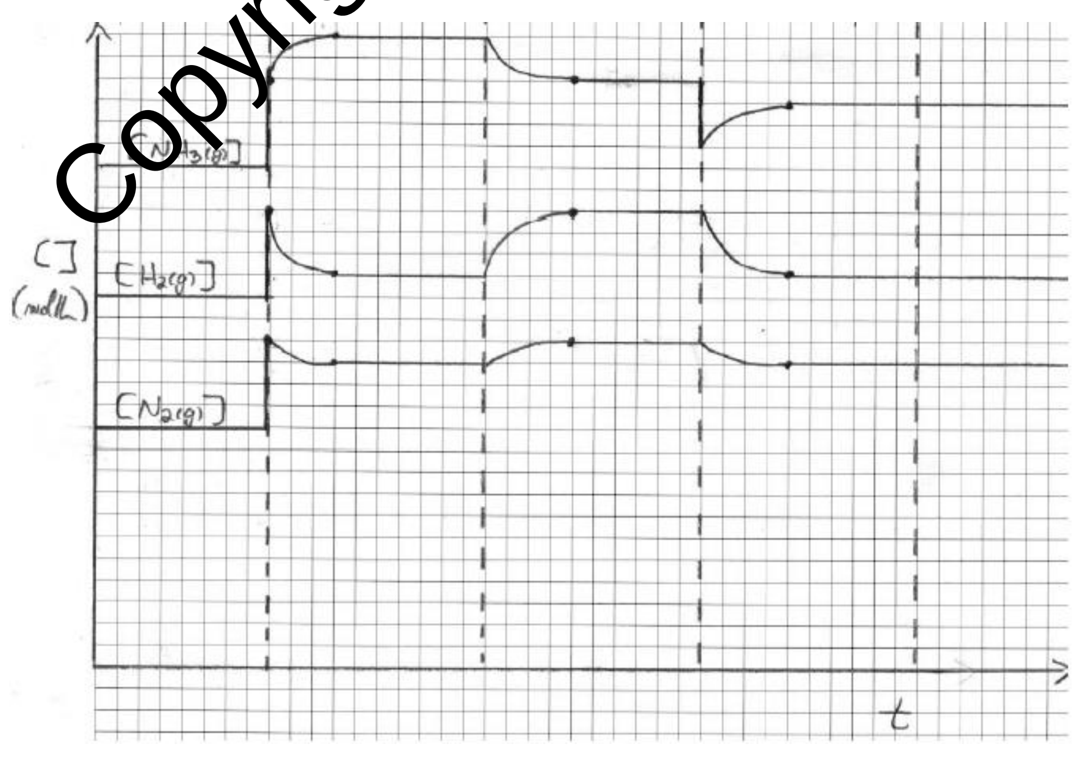
   H_2 (g) + I_2 (g) ← → 2HI (g)

2. Consider the following equilibrium system: $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ ΔH = -46 kJ/mol

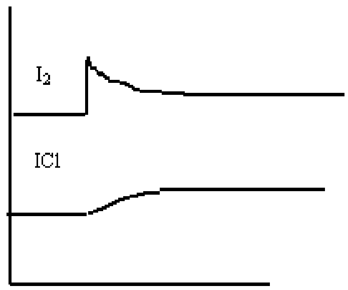
Below is a sketch a concentration versus time graph. Each vertical dashed line represents one of the following stresses:

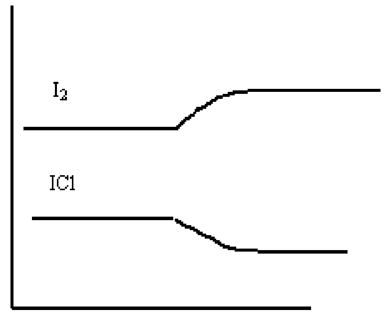
- Addition of a catalyst
- Increase in temperature
- Decrease in volume of container
- Remove some $NH_{3(g)}$

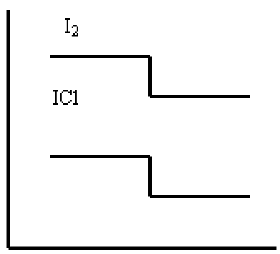
Label the vertical lines in the graph below with the appropriate stress that was applied

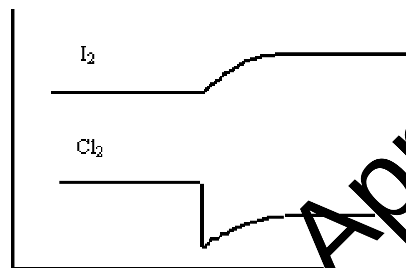


3. Label the graph that best represents each of the following stresses and shift:
   - Adding I_2
   - Increasing temperature
   - Decreasing pressure
   - Removing Cl_2









4. The graph below is represented by the following equilibrium equation. For each shift in equilibrium (ie. 4 min, 10 min, 14 min), state what stress you think could have been applied to the system.

$$COCl_2(g) \rightleftharpoons Cl_2(g) + CO(g) \quad \Delta H = +108 \text{ kJ}$$