

Chemistry 12

Unit II – Dynamic Equilibrium

Notes

II.1 – The Concept of Dynamic Equilibrium

- A reversible reaction is a chemical reaction where products can react to form the reactants.
A reversible reaction is represented by a *double arrow* (\rightleftharpoons)
- It results when there are two opposing reactions, formation of products and the reformation of reactants.
- Dynamic: always changing to adapt. Equilibrium refers to balance.
- ***A reversible reaction is said to be at equilibrium when the rate of the forward reaction is equal to the rate of the reverse reaction.***
- ***Dynamic equilibrium:*** an equilibrium situation in which microscopic changes occur, but macroscopic changes do not.

Macroscopic = visible or large scale changes; as opposed to *microscopic* changes which occur at the atomic or molecular level

- To recognize when equilibrium has been reached, a *constant property* of the system must be observed. Colour intensity, concentration, and pressure are examples of macroscopic (*measurable*) properties that can be used to decide when equilibrium has been reached.
- If a reaction forms products, but the products are able to escape from the reaction vessel, then the products will not be available for the reverse reaction. Therefore, in order for equilibrium to exist, there must be a **closed system**.
- ***Closed system:*** system in which nothing can enter or leave.

Examples:

1. January 1998

Chemical equilibrium is said to be dynamic because

- A. the reaction proceeds quickly.
- B. the mass of the reactants is decreasing.
- C. the macroscopic properties are constant.
- D. both forward and reverse reactions are occurring.

2. April 2001

In an equilibrium system, continuing microscopic changes indicate that the equilibrium is

- A. dynamic.
- B. complete.
- C. exothermic.
- D. spontaneous.

*****Do Hebden Questions #2, pg37*****

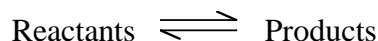
- From doing Equilibrium Exercises #2, we can draw the following conclusions:
 - ① Temperature affects equilibrium.
 - ② A new equilibrium is attained at a new temperature.
 - ③ Since both the hot and cold tubes become the same colour at room temperature, we must get the same equilibrium whether we start with an excess of reactants, or an excess of products.
 - ④ When a system is at equilibrium, **no MACROSCOPIC changes occur**. (Macroscopic = visible, or large scale as opposed to microscopic changes which occur at the atomic or molecular level.)

II.2 – The Characteristics of Equilibrium

- A system in equilibrium shows the following characteristics:
 - a) The system is closed
 - b) Opposite reactions occur at the same rate
 - c) Equilibrium was reached by starting with either reactants or products
 - d) The temperature is constant.
- When these conditions are met, all properties of a system in equilibrium will be constant even though the forward and reverse reactions continue to occur.
- Chemical equilibrium is said to be **dynamic** because both forward and reverse reactions continue to occur even though there is no net change because the **rates are equal**.

$$\text{rate}_{(\text{forward})} = \text{rate}_{(\text{reverse})}$$

- Since the rate of the forward reaction is equal to that of the reverse reaction, “reactants” are formed just as fast as “products”.

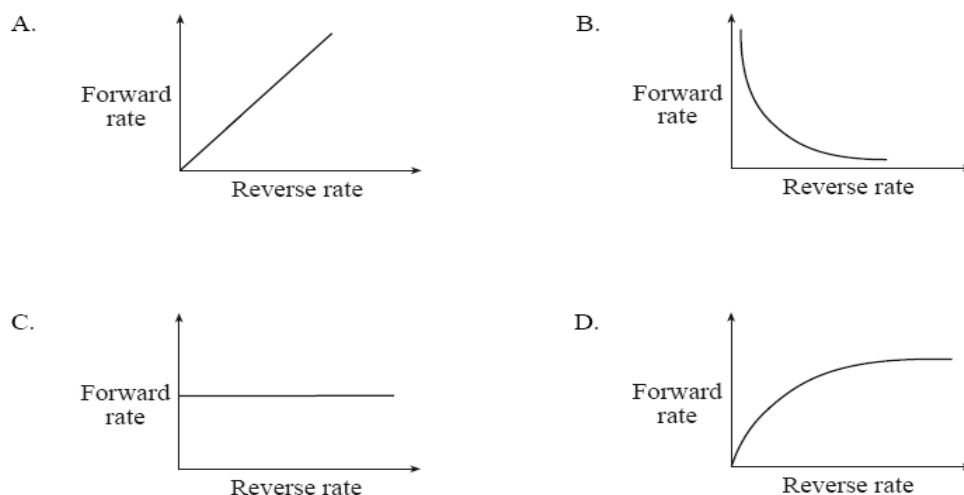


- At equilibrium (constant temperature) we find:
 1. In a closed system
 2. Concentrations of products and reactants are **CONSTANT**, but not necessarily equal.
 3. Macroscopic properties remain constant
 4. the forward rate = the reverse rate
 5. System which is not at equilibrium will tend to move toward a position of equilibrium
- As you get close to equilibrium, the rate slows down.
- Activation energy (E_a) is **NOT** affected by equilibrium. Only a **CATALYST** can affect E_a

Examples:

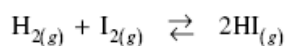
1. August 1999

At different conditions, the relationship between the forward and reverse rates of reaction in an equilibrium system can be represented by



2. January 2004

Two experiments were performed involving the following equilibrium. The temperature was the same in both experiments.



In experiment A, 1.0 M H_2 and 1.0 M I_2 were initially added to a flask and equilibrium was established. In experiment B, 2.0 M HI was initially added to a second flask and equilibrium was established. Which of the following statements is always true about the equilibrium concentrations?

- A. $[\text{H}_2]$ equals $[\text{HI}]$ in experiment A.
- B. $[\text{HI}]$ equals $2[\text{H}_2]$ in experiment A.
- C. $[\text{HI}]$ in experiment A equals $[\text{HI}]$ in experiment B.
- D. $[\text{HI}]$ in experiment A equals $\frac{1}{2}[\text{I}_2]$ in experiment B.

3. August 2001

All chemical equilibria must have

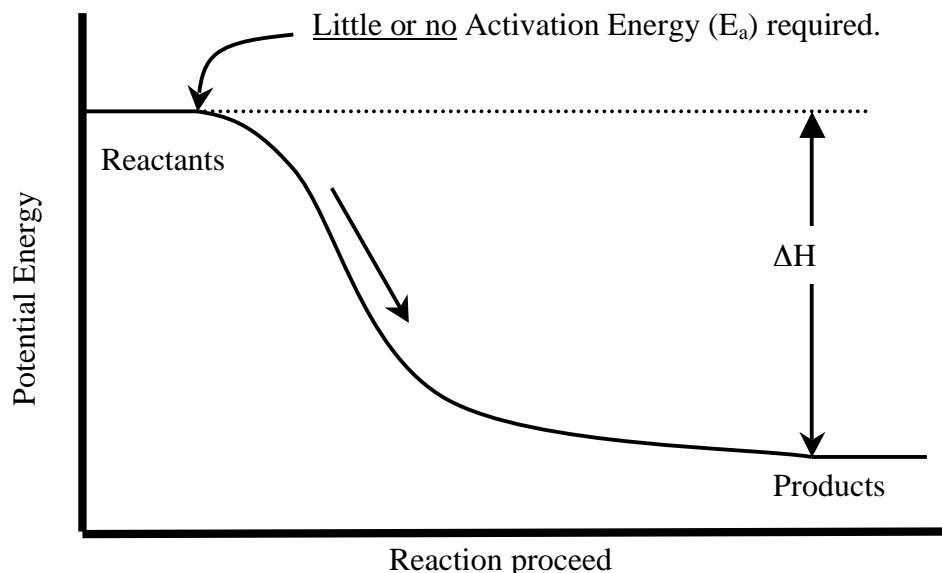
- A. $K_{eq} = 1$
- B. $[\text{reactants}] = [\text{products}]$.
- C. rate forward = rate reverse.
- D. mass of reactants = mass of products.

*****Do Hebden Questions #6 - 13, pg37*****

II.3 – Predicting Whether A Reaction is Spontaneous or Not

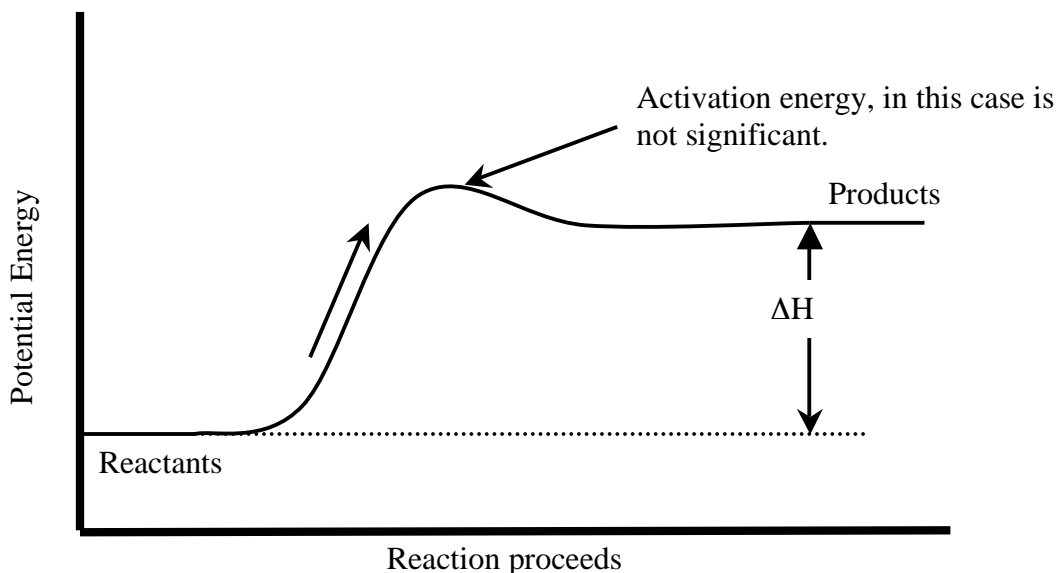
- **Spontaneous** change is a change that occurs by itself.
- When the energy barrier (activation energy) is low enough, a reaction is expected to move spontaneously to the side of the reaction having the **minimum energy (minimum enthalpy)**.

Potential Energy diagram of a spontaneous reaction.



- Most spontaneous reactions, as the one above are **exothermic**. There are however, many **endothermic** reactions that are spontaneous. Why does this seem unlikely?

*Potential Energy diagram of a spontaneous **endothermic** reaction.*



- In the above graph, we can see that a reaction can be spontaneous even though it is endothermic and needs energy.
- There must be another factor at work beside just enthalpy. The other factor is **RANDOMNESS**.
- Highly **RANDOM** states are favoured over highly **ORDERED** states because there are more random states possible.

- The amount of randomness in a system is **ENTROPY**. In general, we can say: **Entropy tends to a maximum value**. In other words, “things tend to become jumbled up as time passes”.
- S is the symbol for entropy. ΔS means “change in entropy”. If entropy has increased we say that ΔS is positive and vice versa.
- Two recap; there are **TWO** factors that determine spontaneity, **ENTHALPY** and **ENTROPY**.
- The tendency to minimum enthalpy favours going to the side of the reaction containing the “heat” term.
That would be the **PRODUCT** side in **EXOTHERMIC** reactions and the **REACTANT** side in **ENDOTHERMIC** reactions.

- **Conclusion:**

Two “drives” or “tendencies” exist in any reaction:

- a) The tendency for a reaction to go to the side with the **maximum randomness**. (maximum entropy)
 - b) The tendency for a reaction to go to the side with the **minimum energy** (minimum enthalpy)
- Levels of Randomness:
 1. Gases are more random than aqueous which is more random than liquids, which is more random than solids.

Gases >> Aqueous >> Liquids >> Solids
 (Random) (Highly ordered)
 2. If we are dealing **with only a single phase through an entire reaction**, the side of the reaction having the **most molecules** is the most random side.
 3. If we have more than one phase present in a reaction, then the side having the most random phase is the side with maximum randomness.
 4. If both sides contain particles having equally random phases, then the side having the greater number of particles of the most random phase will have the maximum randomness.

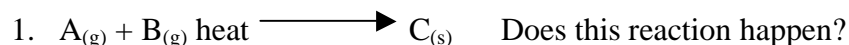
Once you have decided on which phase is the most random, there is no need to consider any other phase.

To summarize...

The side of a reaction equation favoured by the tendency to maximum randomness (maximum entropy) is the side containing **THE MOST PARTICLES OF THE MOST RANDOM PHASE**.

- We examine some examples below to see how the tendencies to minimum enthalpy and maximum entropy combine to determine the OVERALL tendency for a reaction to occur.

Examples:



Which is the most random side? (What side does ENTROPY favour?)

Which side is the heat term on? (What side has minimum energy?)

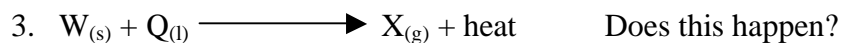
_____ because both enthalpy and entropy favour the _____



Which is the most random side? (What side does ENTROPY favour?)

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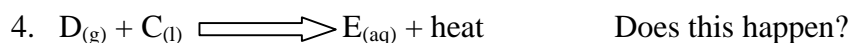
_____ because both enthalpy and entropy favour the _____



Which is the most random side? (What side does ENTROPY favour?)

Which side is the heat term on? (What side has minimum energy?)

Both favour the _____, therefore reaction goes to _____.



Which is the most random side? (What side does ENTROPY favour?)

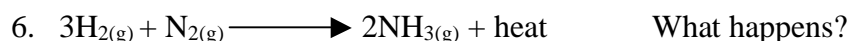
Which side is the heat term on? (What side has minimum energy?)

Opposing forces (Enthalpy favours _____, Entropy favours _____) = _____



Because we are at equilibrium, driving forces must oppose each other. What side does entropy favour?

If entropy favours _____, then enthalpy must favour _____. Thus, the heat term is on the _____.



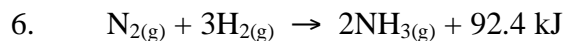
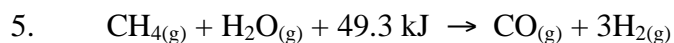
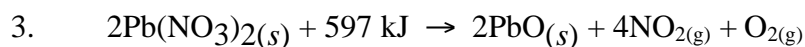
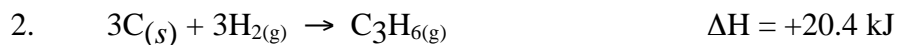
Enthalpy favours the _____... What side does entropy favour? Both sides have gases?

Entropy favours the _____ because there are more molecules (moles) of gas on that side. (4 molecules on the reactants side and only 2 on the product side.)

Opposing forces, therefore... _____

Try these...

Predict whether each of the following reactions is spontaneous, non-spontaneous, or reaches equilibrium.



*****Do Hebden Questions #14 - 16, pgs 48 - 49***

II.4 - Le Châtelier's Principle

- **Le Châtelier's Principle:** If a closed system at equilibrium is subjected to a change, processes will occur that tend to counteract that change.

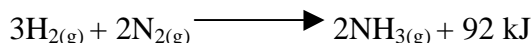
or

“Whatever we do, nature tried to undo”

- Le Châtelier's Principle gives us the ability to quickly and easily predict the effect that any change of conditions will have on equilibrium.
- Anything that changes the equilibrium is referred to as a **Stress**. Stresses are factors that affect the *position* of an equilibrium (*i.e. whether the equilibrium favours the reactants or products.*)
- The term *stress* refers to any imposed factor, *temperature, pressure, concentration etc.*, which upsets the balance in rates of the forward and reverse reactions.

*****Note: Catalysts DO NOT affect the position of an equilibrium.*****

For example:



[H₂] is increased:

[N₂] is decreased:

Temperature is increased:

Pressure is decreased:

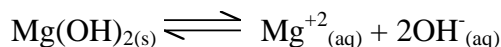
Temperature decreased:

Pressure is increased:

[NH₃] is decreased:

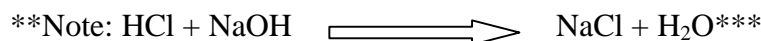
Volume is increased:

What about this one...



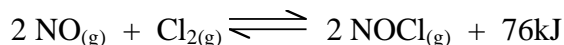
[Mg⁺²] is increased:

Add HCl:



Le Châtelier and Graphs

Consider the following equilibrium system:

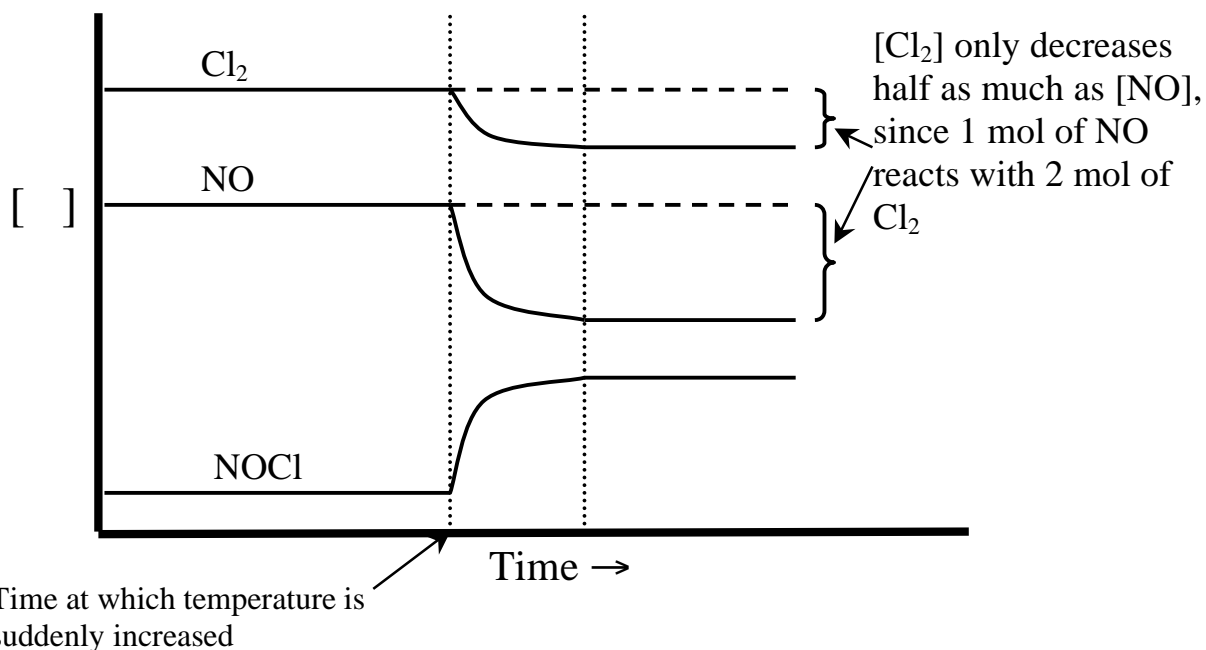


We will use Le Chatelier's Principle to predict the effect of changing the temperature, concentration and pressure conditions of this equilibrium.

1. The Effect of Temperature Changes

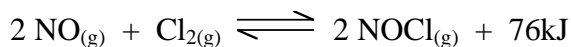
- If we decrease the amount of heat energy, the reaction “shifts” so as to produce more heat.
- In our example, since heat is on the product side, the reaction will shift to the product side to produce more heat.

Graph of Concentration vs. Time for a reaction at equilibrium that was stressed by a decrease in temperature.



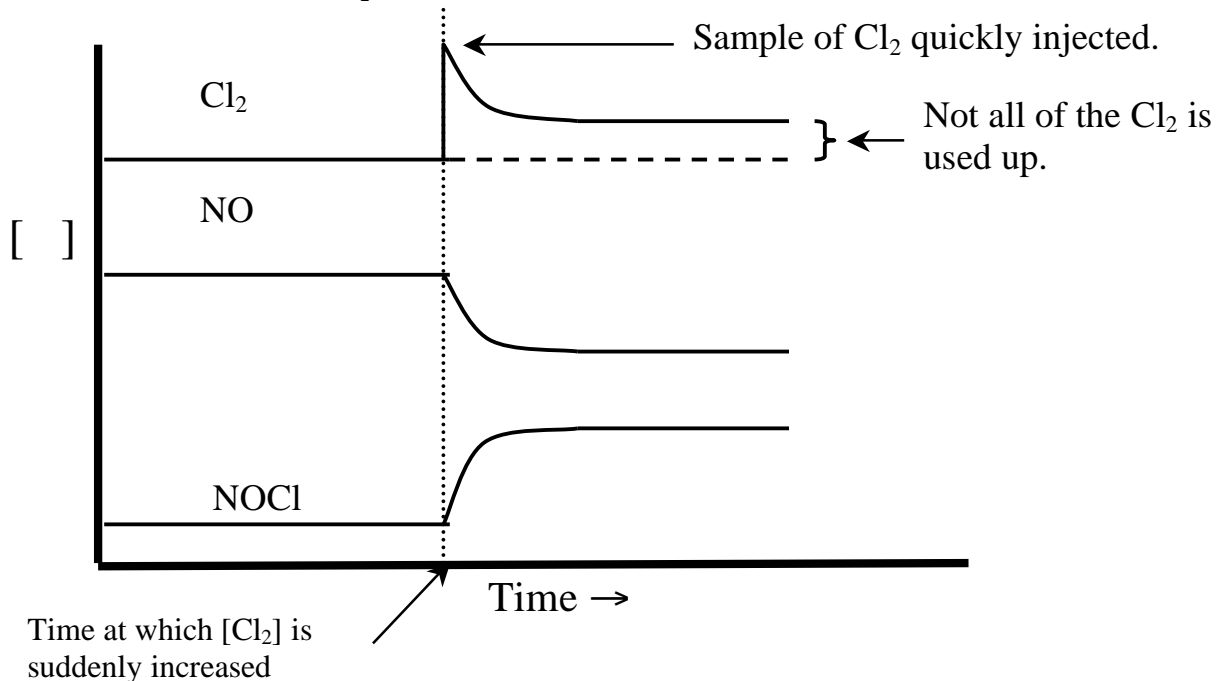
2. The Effect of Concentration Changes

Staying with the same example,



- If we increase the [Cl₂], the reaction shifts so as to partly decrease the amount of added Cl₂. This can be illustrated as follows:

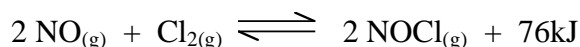
Graph of Concentration vs. Time for a reaction at equilibrium that was stressed by an increase in Cl₂ concentration.



3. The Effect of Pressure Changes

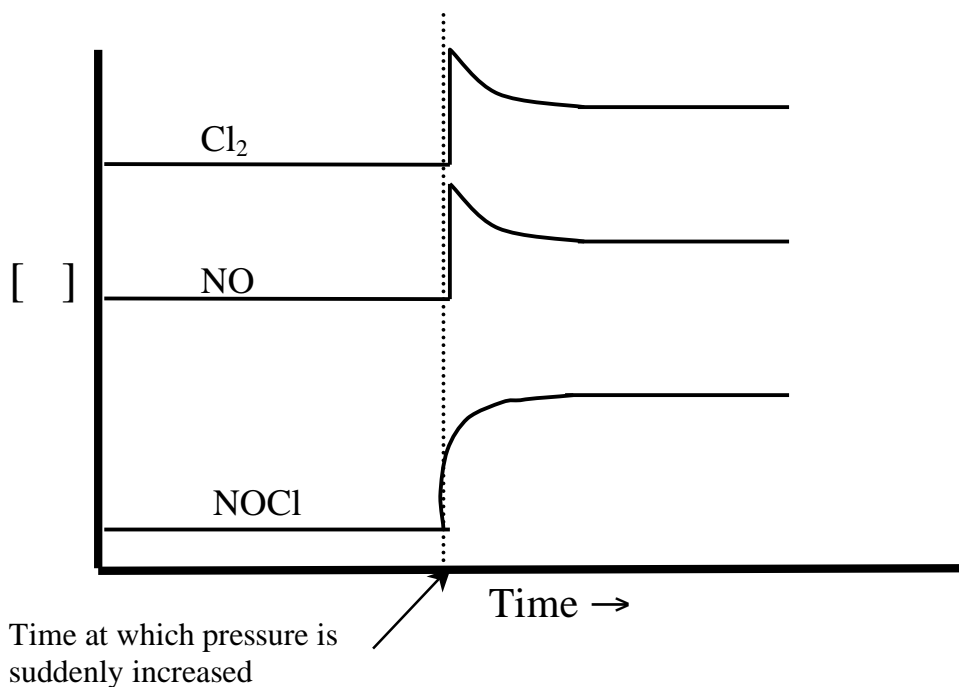
- A decrease in volume will increase pressure and simultaneously increase the concentration of ***all gaseous species present***. According to Le Chatelier's Principle, the reaction will shift in response to this change in a way that will lower the overall pressure.

Consider the reaction:



- An increase in pressure will result in an equilibrium shift towards the side that has the fewest moles of gas. This is illustrated as follows:

Graph of Concentration vs. Time for a reaction at equilibrium that was stressed by a decrease in volume (increase in pressure).



- Unlike the illustration above, an increase in volume (decrease in pressure) will result in the equilibrium shifting towards the side with the greater number of moles.
- If reactants and products have the same number of particles there is **no shift** in equilibrium.
- If the overall pressure is increased by adding a **non-reactive** gas such as helium, the ***concentration of the reacting gases is unaffected*** and hence there is ***no change in the equilibrium***. The volume is not changed so there is still the same number of moles of reactant and product gases in the same volume.

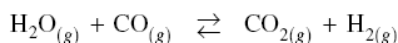
4. The Effect of Adding a Catalyst

- The addition of a catalyst has **NO effect** on the position of equilibrium; however, it does allow equilibrium to be reached faster.
- Recall from section I.11 in unit I, ***adding a catalyst speeds up the forward and reverse rates by an equal amount, so that a reaction at equilibrium remains at equilibrium.***

Examples:

1. August 2003

Consider the following system at equilibrium:



This equilibrium will shift right as the result of the addition of some extra H_2O . How will this shift affect the concentrations of the other gases?

	[CO]	[CO ₂]	[H ₂]
A.	increases	decreases	decreases
B.	increases	increases	decreases
C.	decreases	increases	increases
D.	decreases	decreases	increases

2. August 2004

Consider the following equilibrium:



Which of the following will cause a shift to the left?

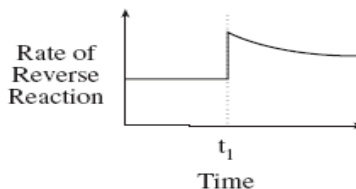
- A. adding more O_2
- B. adding more KCl
- C. removing some KClO_3
- D. increasing the temperature

3. August 2004

Consider the equilibrium:



The following diagram represents the rate of the reverse reaction.



Which of the following stresses explains what happened at t_1 ?

- A. $[\text{H}_2]$ increased.
- B. $[\text{N}_2]$ decreased.
- C. $[\text{NH}_3]$ increased.
- D. $[\text{NH}_3]$ decreased.

*****Do Hebden Questions #17 - 28, pgs 54 - 55*****

II.5 - Industrial Applications of Equilibrium Principles

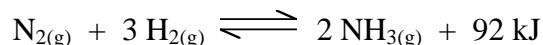
- Equilibrium concepts are widely used in the manufacturing of chemicals. By changing pressure, concentration, or temperature we can shift a given reaction and cause it to produce more of a desired.

The following are only two of many examples:

1. The Haber process for Making Ammonia

In 1910, the German chemist, Fritz Haber (1868-1934), developed a process that combines nitrogen and hydrogen to make ammonia. Ammonia is used as a raw material for fertilizer, explosives and other important chemicals.

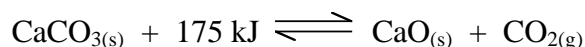
The process that makes ammonia occurs by the following equilibrium:



It can be seen that the reaction is **exothermic**, energy is liberated as indicated by the +92.4 kJ.

2. Making Cement From Limestone

Limestone, CaCO_3 , can be used to produce “quicklime”, CaO , according to the reaction:

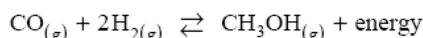


The quicklime can then be added to a mixture of sand, clay, iron oxide and gypsum (CaSO_4) to make Portland cement powder.

Examples:

1. June 1999

Methanol, CH_3OH , can be produced by the following:

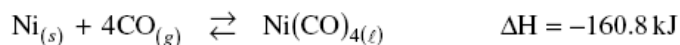


The conditions that are necessary to maximize the equilibrium yield of CH_3OH are

- A. low temperature and low pressure.
- B. high temperature and low pressure.
- C. low temperature and high pressure.
- D. high temperature and high pressure.

2. June 2001

Consider the following equilibrium:



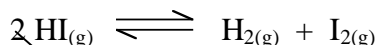
Which of the following will cause this equilibrium to shift to the left?

- A. add some CO
- B. decrease the volume
- C. remove some $\text{Ni}(\text{CO})_4$
- D. increase the temperature

*****Do Hebden Questions #29 - 30, pg 56*****

II.6 - The Equilibrium Expression and the Equilibrium Constant

- Each equilibrium reaction *at a particular temperature* will have a constant ratio of [products] to [reactants]. This ratio of [products] to [reactants] is called the “**equilibrium constant**” and is often represented by the symbol K_{eq} .
- K_{eq} is a ratio of $\frac{[\text{products}]}{[\text{reactants}]}$
- Consider the following equilibrium at 423°C



The equilibrium constant would be found as follows:

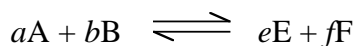
$$K_{eq} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}][\text{HI}]}$$

However, instead of writing $[\text{HI}][\text{HI}]$, which reads “concentration of hydrogen iodide times the concentration of hydrogen iodide,” we can write $[\text{HI}]^2$.

$$K_{eq} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

In the K_{eq} expression, the power to which each of the concentrations is raised is equal to its **coefficient** in the balanced equation.

In other words, for the reaction with the general form:

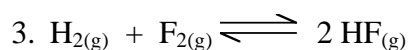
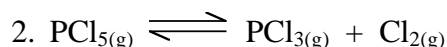
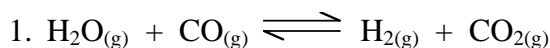


the K_{eq} expression can be written as:

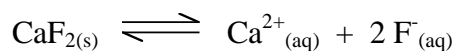
$$K_{eq} = \frac{[\text{E}]^e [\text{F}]^f}{[\text{A}]^a [\text{B}]^b}$$

Examples:

Write the equilibrium equations for the following equilibrium equations:



- There is one other important thing to know about writing equilibrium expressions. Consider the following equilibrium expression:



We would expect to write the equilibrium expression as:

$$K_{\text{eq}} = \frac{[\text{Ca}^{2+}_{(aq)}][\text{F}^{-}_{(aq)}]}{[\text{CaF}_{2(s)}]}$$

However, $\text{CaF}_{2(s)}$ is a solid and has a constant density and therefore a constant molar concentration. If the density of $\text{CaF}_{2(s)}$ is $3.18 \times 10^3 \text{ g/L}$, its molar concentration is:

$$[\text{CaF}_{2(s)}] = \frac{3.18 \times 10^3 \text{ g}}{\text{L}} \times \frac{1 \text{ mol}}{78.1 \text{ g}} = 40.7 \text{ M}$$

$$\text{If, } K_{\text{eq}} = 8.4 \times 10^{-13} = \frac{[\text{Ca}^{2+}_{(aq)}][\text{F}^{-}_{(aq)}]}{[\text{CaF}_{2(s)}]}$$

We have two constants in the expression:

$$K_{\text{eq}} = 8.4 \times 10^{-13} = \frac{[\text{Ca}^{2+}_{(aq)}][\text{F}^{-}_{(aq)}]}{40.7}$$

It is best to have only one constant in each equilibrium expression.

Therefore, the equilibrium expression that we will use is:

$$K_{\text{eq}} = 3.4 \times 10^{-11} = [\text{Ca}^{2+}_{(aq)}][\text{F}^{-}_{(aq)}]$$

When writing equilibrium expressions:

Eliminate any concentrations that have a constant value in the equilibrium expression.

- Substances that have a constant concentration that will not be included in equilibrium expressions are:

1. SOLIDS

Solids cannot be appreciably compressed therefore their density and molar concentrations are constant.

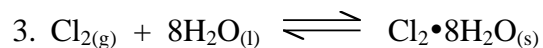
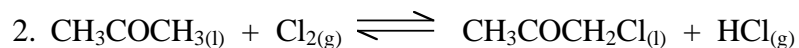
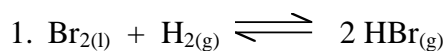
2. PURE LIQUIDS

Liquids cannot be appreciably compressed therefore their density and molar concentrations are constant. However, if there is another liquid present, which can *dilute* the first liquid, then the liquid is **not pure** and **can have its concentration changed by dilution**. Therefore, a liquid is said to be *pure if and only if it is the only liquid which exists on both sides of the entire equilibrium equation*.

- All other substances (other than solids and pure liquids) must be included in the equilibrium expression. Included will be: gases, aqueous ions, gases in solution, and multiple liquids.

Examples:

Write the equilibrium expressions for the following equilibrium equations:

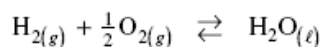


- The units for K_{eq} vary depending on the number of concentration terms in the numerator as compared to the denominator. These units do not have any particular importance so units for K_{eq} are generally ***not shown***.
- Because solids and pure liquids have a constant concentration, adding a reactant or product that is a solid or a pure liquid will have ***NO EFFECT*** on the equilibrium. That is, the equilibrium does not shift.

Examples:

1. August 2004

Consider the following equilibrium:



Which of the following represents the concentration of O_2 at equilibrium?

A. $[\text{O}_2] = \left(\frac{1}{K_{\text{eq}}[\text{H}_2]} \right)^2$

B. $[\text{O}_2] = K_{\text{eq}}[\text{H}_2]$

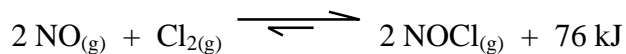
C. $[\text{O}_2] = \left(\frac{[\text{H}_2\text{O}]}{K_{\text{eq}}[\text{H}_2]} \right)^2$

D. $[\text{O}_2] = \sqrt{\frac{1}{K_{\text{eq}}[\text{H}_2]}}$

*****Do Hebden Questions #31 - 35, pg 60*****

II.7 - Le Chatelier's Principle and the Equilibrium Constant

- When the temperature is decreased and held at a certain value, the equilibrium will shift to the product side:



A decrease in temperature will then cause an increase in [PRODUCT] and a decrease in [REACTANT], and since:

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{then } K_{eq} \text{ is increased.}$$

****Only a temperature change can affect the value of K_{eq} .****

Changes in pressure and concentration or the addition of a catalyst have no effect on K_{eq} .

- Since

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

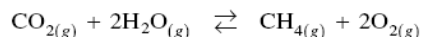
a **LARGE** value of K_{eq} implies that a **LARGE** amount of products (small amount of reactant) is present at equilibrium

a **SMALL** value of K_{eq} implies that a **SMALL** amount of products (large amount of reactant) is present at equilibrium

Examples:

1. January 2003

Consider the following equilibrium:



Which of the options below indicates that the reactants are favoured?

- A. K_{eq} is zero.
- B. K_{eq} is very large.
- C. K_{eq} is slightly less than 1.
- D. K_{eq} is slightly greater than 1.

2. August 2005

Which of the following describes how a K_{eq} value is related to the relative concentrations of reactants and products?

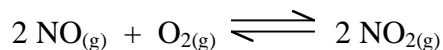
	K_{eq} value	Relative Concentration
I.	large	[products] > [reactants]
II.	large	[reactants] > [products]
III.	small	[products] > [reactants]
IV.	small	[reactants] > [products]

- A. I only
- B. IV only
- C. I and IV only
- D. II and III only

****Do Hebden Questions #36 - 46, pg 62****

II.8 - Equilibrium Calculations

- Consider the equilibrium:

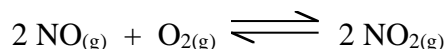


In order to consider the value of K_{eq} we must have accurate information on the concentrations of $\text{NO}_{(g)}$, $\text{O}_{2(g)}$ and $\text{NO}_{2(g)}$ when the system is at equilibrium. Such information cannot be obtained without actually doing an experiment.

In the following examples, we will see the various types of calculations that can be performed based on the equilibrium expression and some experimental data.

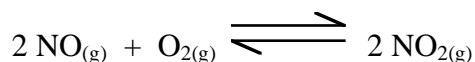
Example A:

A 2.0 L bulb contains 6.00 mol of $\text{NO}_{2(g)}$, 3.0 mol of $\text{NO}_{(g)}$ and 0.20 mol of $\text{O}_{2(g)}$ at equilibrium. What is K_{eq} for:



Example B:

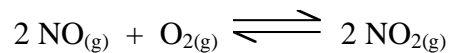
Into a 2.00 L bulb was introduced 4.00 mol of $\text{NO}_{2(g)}$. After a while equilibrium was attained according to the equation:



At equilibrium, 0.500 mol of $\text{NO}_{(g)}$ was found. Find the value of K_{eq} ?

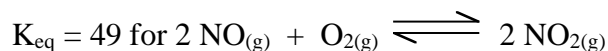
Example C:

A certain amount of $\text{NO}_{2(g)}$ was introduced into a 5.00 L bulb. When equilibrium was attained according to the equation,



the concentration of $\text{NO}_{(g)}$ was 0.800 M. If K_{eq} has a value of 24.0, how many moles of NO_2 were originally put into the bulb?

Example D:



If we introduce 2.0 mol of $\text{NO}_{(\text{g})}$, 0.20 mol of $\text{O}_{2(\text{g})}$, and 0.40 mol of $\text{NO}_{2(\text{g})}$ into a 2.0 L bulb, **which way** will the reaction **shift** in order to reach equilibrium?

Note: This question is not asking us to find a numerical value; it is asking for a decision. To make this decision we must make a simple comparison between two numbers. This comparison will tell us one of three things:

The reaction is,

- ① at equilibrium.
- Or ② going to shift right, towards the products.
- Or ③ going to shift left, towards the reactants.

One of the numbers that we will compare is K_{eq} , the other is Q .

$$Q = \frac{[\text{NO}_{2(\text{g})}]^2_{\text{initial}}}{[\text{NO}_{(\text{g})}]^2_{\text{initial}} [\text{O}_{2(\text{g})}]_{\text{initial}}}$$

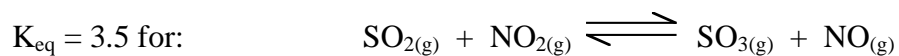
Q is the **REACTION QUOTIENT** (sometimes called a '*Trial K_{eq}* ') and is a "trial value" for K_{eq} .

If, $Q = K_{\text{eq}}$, the system is at equilibrium.

If, $Q < K_{\text{eq}}$, then $\frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$ is too small and the reaction must shift to produce more products.

If, $Q > K_{\text{eq}}$, then $\frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$ is too large and the reaction must shift to produce fewer products and more reactants.

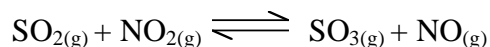
Example E



If 4.0 mol of $\text{SO}_{2(\text{g})}$ and 4.0 mol of $\text{NO}_{2(\text{g})}$ are placed in a 5.0 L bulb and allowed to come to equilibrium, what concentration of all species will exist at equilibrium?

Example F

A 1.0 L reaction vessel contained 1.0 mol of SO_2 , 4.0 mol of SO_3 and 4.0 mol of NO at equilibrium according to:



If 3.0 mol of SO_2 is added to the reaction mixture, what will be the new concentration of NO when equilibrium is re-attained?

Note: The unknown is the final $[\text{NO}]$ when equilibrium is re-established. Therefore, all other concentrations must be given or be readily calculated AND you must have the value of K_{eq} . But you are not given the value for K_{eq} . You are told the amount of each gas previously present at equilibrium. This information will allow you to calculate K_{eq} .