

# REACTION EQUILIBRIUM

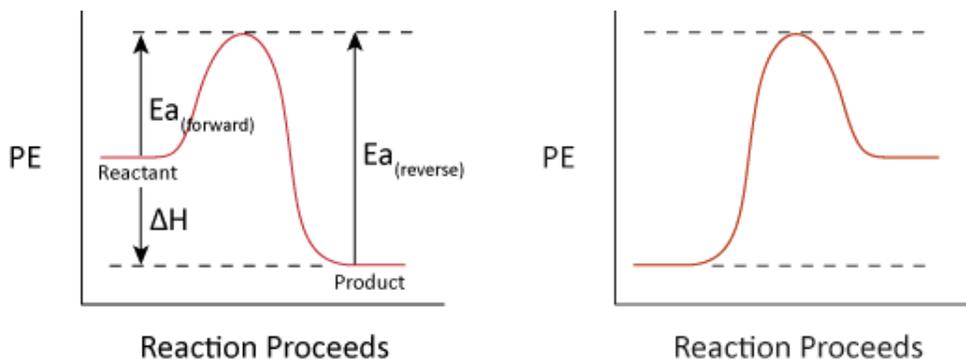
## A. REVERSIBLE REACTIONS

1. In most spontaneous reactions the formation of products is greatly favoured over the reactants and the reaction proceeds to completion (one direction). In some reactions the **product is only slightly favoured over the reactants and can proceed in both directions.**

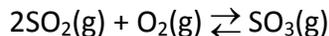
**REVERSIBLE REACTION = reactions that proceed in the forward (R → P) and reverse (P → R) direction SIMULTANEOUSLY.**

Reversible reactions involve two competing reactions that occur at the same time:

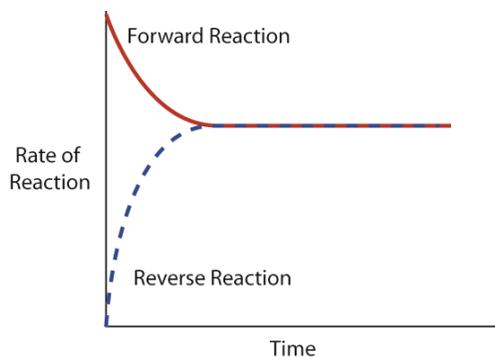
- **FORWARD REACTION** – the conversion of **reactants to products**
- **REVERSE REACTION** – the conversion of **products to reactants**



2. Consider the following reversible reaction:



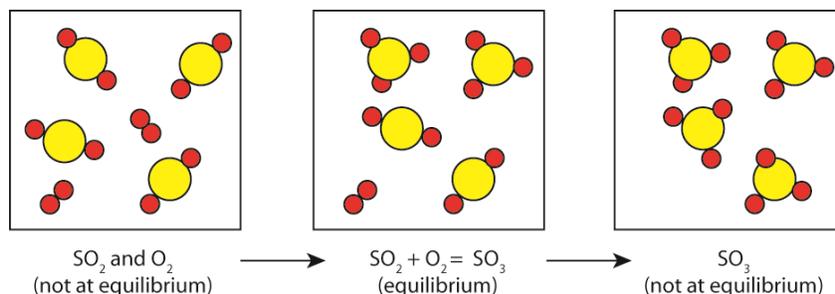
- The **DOUBLE ARROW (  $\rightleftharpoons$  )** indicates that the reaction is reversible.
- When a reversible reaction begins, **only the forward reaction occurs (if starting from the reactants).**
- As the reaction proceeds the forward reaction slows and the **reverse reaction speeds up.**
- Eventually the system reaches **equilibrium.**



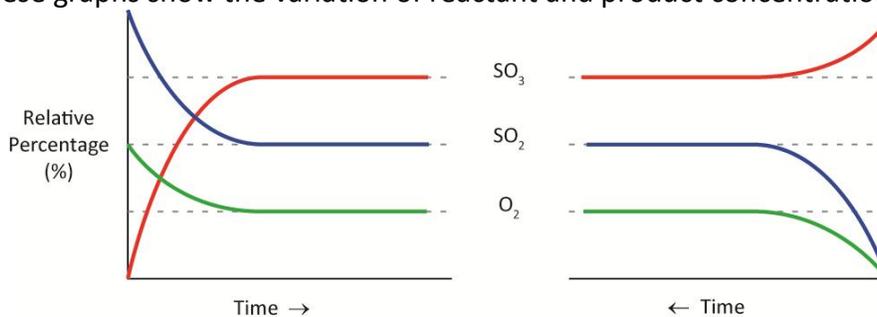
A reversible reaction is said to be at **EQUILIBRIUM** when the rate of the forward reaction **EQUALS** the rate of the reverse reaction.

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

3. A reversible reaction will achieve equilibrium **regardless of the direction from which it is approached**.



- These graphs show the variation of reactant and product concentration with time.

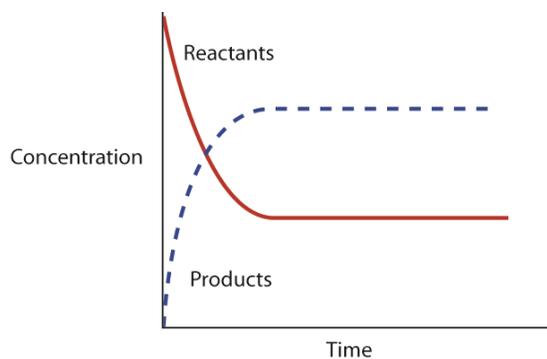
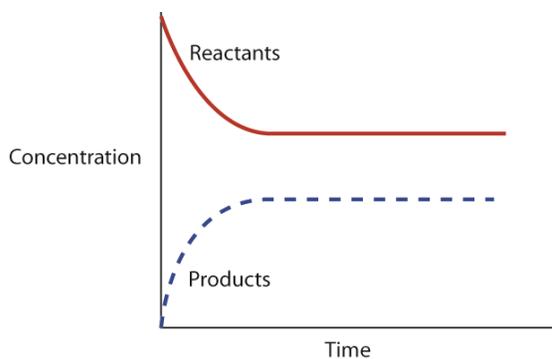
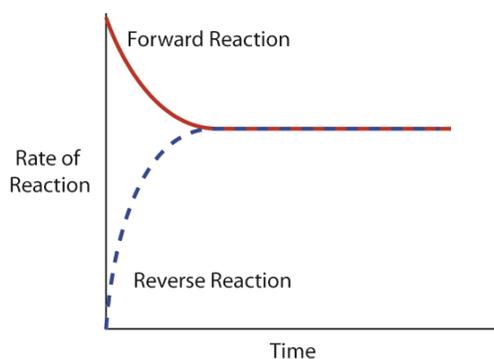


- At equilibrium, the concentrations of **reactant and product do not change** and the **relative amounts** of reactants and products are the **same** regardless of whether the reaction began from the reactants or products.

Chemical equilibrium are said to be:

**DYNAMIC** = forward and reverse reactions continue to occur although there is no net change in **MACROSCOPIC** properties.

4. When a reaction reaches equilibrium all **MACROSCOPIC** properties (*measurable*) are constant.
- These properties include **colour intensity, concentration, and pressure**.
  - Note that when a system reaches equilibrium, the **rates of the forward and reverse reactions are equal but the concentrations of reactants and products are not**.



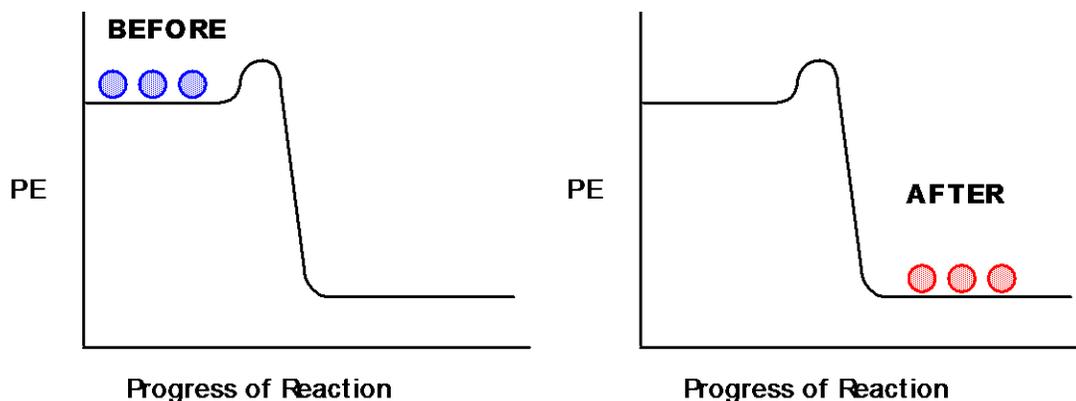
5. Systems at equilibrium are characterized by the following:
- a) the system is **closed, no material enters or leaves**;



- b) opposite reactions occur at the **same rate**;
- c) equilibrium was reached by **starting with either reactants or products**;
- d) the **temperature** is constant;
- e) **no change in macroscopic properties**.

## B. PREDICTING SPONTANEOUS REACTIONS

1. A **SPONTANEOUS** reaction is a reaction that will occur by itself without outside assistance. Spontaneous reactions can occur when the **activation energy barrier is low**.



- Reactions tend to favour the side of the reaction having **lower energy (ENTHALPY,  $\Delta H$ )**.
- **EXOTHERMIC** reactions result in a decrease in energy, **products are favoured**.
- **ENDOTHERMIC** reactions result in an increase in energy, **reactants are favoured**.

**EXOTHERMIC** reactions (forward or reverse) are favoured because of the tendency to move towards **MINIMUM ENTHALPY ( $\Delta H$ )**.

2. From energy stand point, exothermic reactions are favoured; however, some endothermic reactions, such as chemical ice packs, will occur spontaneously.

- Tendency for reactions to increase **disorder or randomness (ENTROPY,  $\Delta S$ )**.
- When entropy **increases** in the forward direction, **products** are favoured.
- When entropy **decreases** in the forward direction, **reactants** are favoured.

Reactions that produce the **greatest amount of randomness** are favoured because of the tendency to move towards **MAXIMUM ENTROPY ( $\Delta S$ )**.

- Entropy can be predicted by examining the phases of the reactants and products:

**GASES (g) >> SOLUTIONS (aq) > LIQUIDS (l) >> SOLIDS (s)**

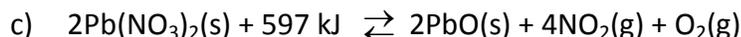
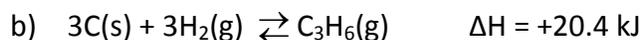
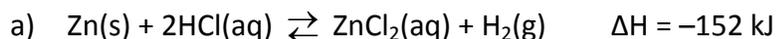
- In general, highly random states are more probable than highly ordered states. **Endothermic** reactions can be spontaneous when the difference in randomness between reactants and products is so great that it **overcomes** the tendency towards minimum enthalpy — these reactions are said to be “**DRIVEN**” by the entropy of the system.

There are two “drives” or “tendencies” for reactions:

- tendency for a reaction to **increase RANDOMNESS (MAXIMUM ENTROPY,  $\Delta H$ )**.
- tendency for a reaction to **lower ENERGY (MINIMUM ENTHALPY,  $\Delta S$ )**.

### EXAMPLE 2.1 – PREDICTING SPONTANEOUS REACTIONS

Based on changes in enthalpy and entropy, predict whether each of the following reactions will be spontaneous, non-spontaneous, or reach equilibrium.



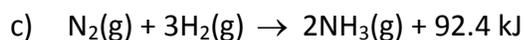
*a) Enthalpy decreases (exothermic) → favours products  
Entropy increases (gas on product side) → favours products  
**SPONTANEOUS***

*b) Enthalpy increases (endothermic) → favours reactants  
Entropy decreases (3 moles gas vs. 1 mole gas) → favours reactants  
**NON-SPONTANEOUS***

*c) Enthalpy increases (endothermic) → favours reactants  
Entropy increases (5 moles gas on product side) → favours products  
**EQUILIBRIUM***

**SAMPLE 2.1 – PREDICTING SPONTANEOUS REACTIONS**

Based on changes in enthalpy and entropy, predict whether each of the following reactions will be spontaneous, non-spontaneous, or reach equilibrium.



*a) Enthalpy increases (endothermic) → Reactants  
Entropy decreases (6 moles liquid form 1 mole solid) → Reactants  
Non-spontaneous*

*b) Enthalpy increases (endothermic) → Reactants  
Entropy increase (2 moles gas form 4 moles gas) → Products  
Equilibrium*

*c) Enthalpy decreases (exothermic) → Products  
Entropy decreases (4 moles gas form 2 moles gas) → Reactants  
Equilibrium*

### C. LE CHATELIER'S PRINCIPLE

1. Changes in factors such as temperature, pressure, concentration, and catalyst can **upset the balance in rates** of the forward and reverse reactions of a system in equilibrium.

Factors that upset an equilibrium system are referred to as **STRESSES**

- Stresses cause **changes to the reactant and product concentrations**.
- Net increase in [product] is called a **"shift to the right"**.
- Net increase in [reactant] is called a **"shift to the left"**.
- Henry Louis Le Châtelier (1850–1936), studied the effects of changing conditions on equilibrium systems.

#### LE CHATELIER'S PRINCIPLE

when a **stress** is applied to a system **at equilibrium**, the system readjusts to **relieve or offset** the stress and the system reaches a **new state of equilibrium**.

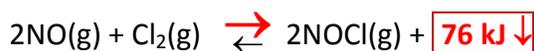
- In other words, **whatever we do to an equilibrium, the equilibrium will try to undo**.
2. Consider the following reaction:



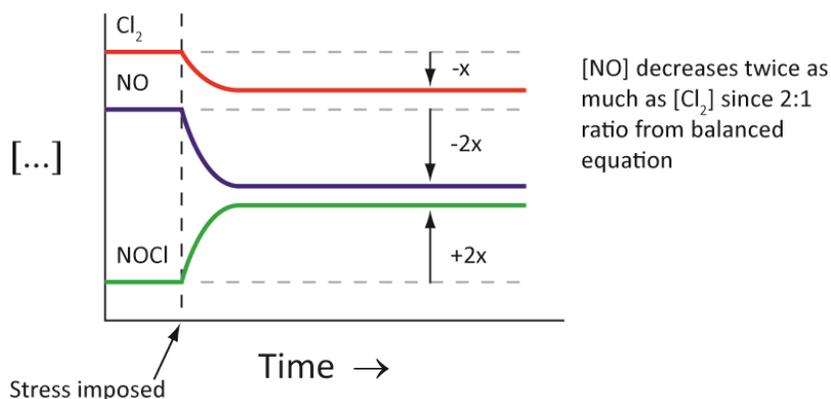
The effects of various stresses on a system at equilibrium can be summarized as follows:

#### a) TEMPERATURE

- If the temperature of the equilibrium is decreased, Le Chatelier's Principle predicts that the equilibrium **shifts to the right**.



- Exothermic reaction **shifts" to the right** to produce more heat.
- In terms of reaction rate, **the reverse rate initially experiences a greater decrease** because heat is a **"reactant"** in the reverse reaction.
- As equilibrium is re-established, the reverse rate increases and the forward rate decreases. The net change however, is that both forward and reverse rates will decrease.

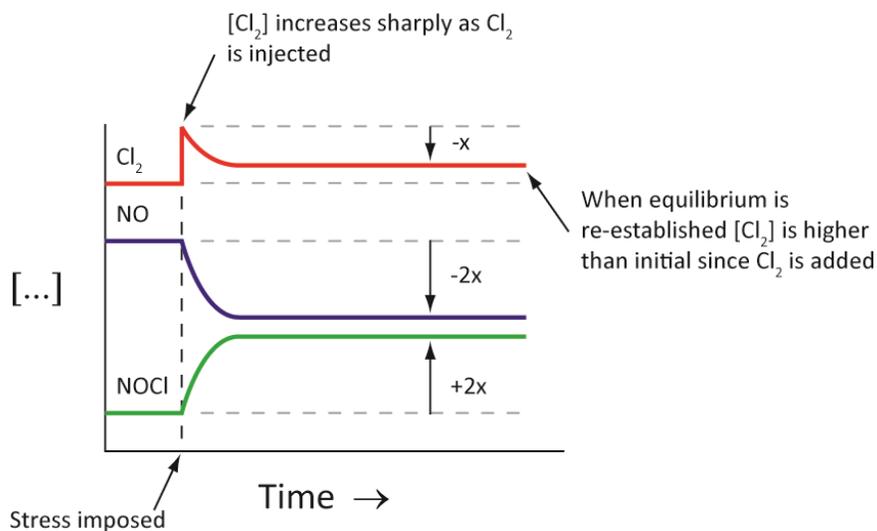


b) **CONCENTRATION**

- If the concentration of  $\text{Cl}_2$  increases, Le Chatelier's Principle predicts that the equilibrium will **shift to the right to use up the added  $\text{Cl}_2$** .



- In terms of reaction rate,  $\text{Cl}_2$  is a reactant in the forward reaction. Increase  $[\text{Cl}_2]$  increases forward reaction rate initially.
- As equilibrium is re-established, forward rate decreases and reverse rate increases. Overall, both rates will increase.

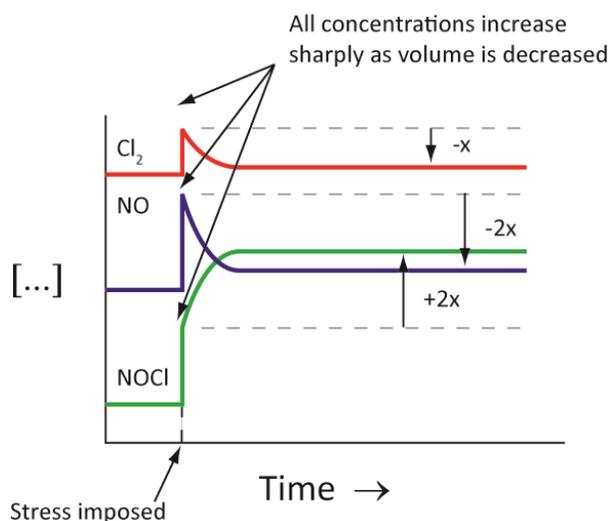


c) **PRESSURE**

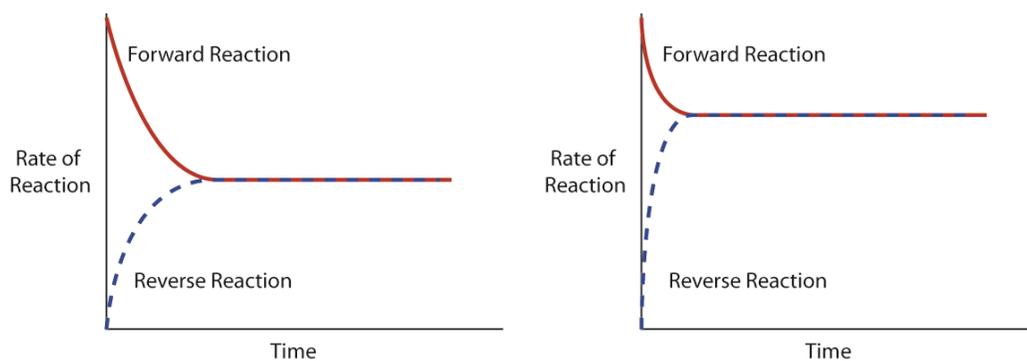
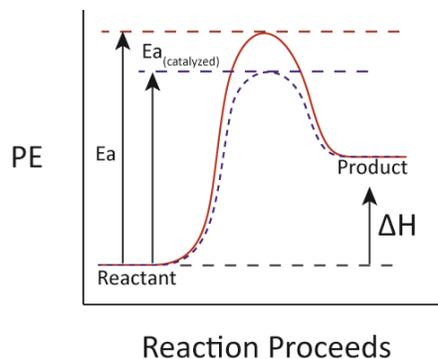
- Increasing the partial pressure of gas has the **same effect as increasing its concentration**.
- Pressure can also be increased by **decreasing the volume of the container**.
- A **decrease** in volume simultaneously **increases** the partial pressure and **concentration of ALL gases present in the system**.
- Shift to reduce the overall pressure — this results in a shift towards the side of the reaction with the **fewest moles of gas present**.



- The direction that involves the greater number of gas will experience a greater increase in rate initially. For this reaction, the forward reaction rate would increase initially. As equilibrium is re-established, forward rate decreases and reverse rate increases.
- When the number of **MOLES OF GAS are equal** on both sides of the equilibrium, **no shift is observed**.

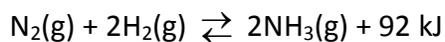
d) **CATALYST**

- A catalyst lowers the activation energy for a reaction, however it decreases the activation energy of both the forward and reverse reactions and **speeds up the forward and reverse rate by an equivalent amount**.
- Adding a catalyst to a reaction already **at equilibrium** will increase the rates of both forward and reverse reactions but will have **no effect on reactant and product concentrations**.
- Adding a catalyst to a reaction that is not at equilibrium will allow it to be **reached faster**.



### SAMPLE 2.2 – USING LE CHATELIER'S PRINCIPLE TO PREDICT SHIFTS IN EQUILIBRIUM

Consider the following reaction:



Predict the direction of shift and the effect on the amount of  $\text{H}_2(\text{g})$  resulting from the following stresses:

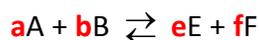
- increase  $[\text{N}_2]$
- increase  $[\text{NH}_3]$
- increase temperature
- increase volume

- right,  $\text{H}_2$  decreases*
- left,  $\text{H}_2$  increases*
- left,  $\text{H}_2$  increases*
- right,  $\text{H}_2$  increases*

## D. EQUILIBRIUM EXPRESSIONS AND EQUILIBRIUM CONSTANT

1. When a system is at equilibrium, the [reactants] and [products] remain constant. Experimentally, it is found that the **ratio of [product] to [reactant] is constant at a particular temperature.**

- Even though the **[reactants] and [products] may change** as result of a shift in equilibrium, the **ratio remains constant.**
- For an **EQUILIBRIUM EQUATION** with the general form:



experimentally, it is found that:

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

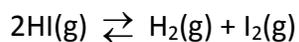
- This expression of concentrations is called the **EQUILIBRIUM EXPRESSION** and its numerical value,  $K_{eq}$ , is called the **EQUILIBRIUM CONSTANT.**
2. The equilibrium constant is the ratio of product concentration terms to reactant concentration terms.

$$K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

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

**EXAMPLE 2.2 – WRITING EQUILIBRIUM EXPRESSIONS**

Write the  $K_{eq}$  expression for the following equilibrium:



*The equilibrium expression is:*

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

**EXAMPLE 2.3 – CALCULATING  $K_{EQ}$  FROM EQUILIBRIUM CONCENTRATION**

Consider the following equilibrium



What is the value of  $K_{eq}$  if the equilibrium concentrations of HI,  $\text{H}_2$ , and  $\text{I}_2$  are 0.250 M, 0.120 M, and 0.120 M respectively

*The equilibrium expression is:*

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

*Substituting into  $K_{eq}$  expression:*

$$K_{eq} = \frac{(0.120)(0.120)}{(0.250)^2}$$

$$K_{eq} = \mathbf{0.230}$$

**EXAMPLE 2.4 – CALCULATING EQUILIBRIUM CONCENTRATION GIVEN  $K_{\text{EQ}}$** 

Consider the following equilibrium



If the value of  $K_{\text{eq}} = 0.230$  at a particular temperature, what is the equilibrium  $[\text{HI}]$  if the  $[\text{H}_2] = 0.075 \text{ M}$  and  $[\text{I}_2] = 0.320 \text{ M}$ ?

*The equilibrium expression is:*

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

*Substituting into  $K_{\text{eq}}$  expression:*

$$0.230 = \frac{(0.075)(0.320)}{[\text{HI}]^2}$$

$$[\text{HI}] = \sqrt{\frac{(0.075)(0.320)}{(0.230)}}$$

$$[\text{HI}] = \mathbf{0.323 \text{ M}}$$

3. The following substances are not included in the equilibrium expression because their concentrations are essentially constant:
- SOLIDS** cannot be compressed appreciably and hence their concentrations cannot be changed. The concentration of a solid is determined by the **density of the solid**.
  - PURE LIQUIDS** cannot be compressed appreciably and hence their concentrations cannot be changed. However, if there are two or more liquids present they may mix and are no longer pure and the concentrations may be change due to dilution. **Liquids are only pure if there is only one liquid present in the equilibrium equation.**

**SAMPLE EXERCISES 2.3 – WRITING EQUILIBRIUM CONSTANT EXPRESSIONS**

Write the  $K_{\text{eq}}$  expression for the following equilibrium:

- a)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   
 b)  $\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$   
 c)  $\text{Si}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{SiO}_2(\text{s})$   
 d)  $\text{CH}_3\text{COCH}_3(\text{l}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{COCH}_2\text{Cl}(\text{l}) + \text{HCl}(\text{g})$

4. The equilibrium constant,  $K_{\text{eq}}$ , is a ratio of  $\frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$ , so numerically, if  $K_{\text{eq}}$  is large the products are favoured and if  $K_{\text{eq}}$  is small the reactants are favoured.

$$\text{Large } K_{\text{eq}} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

$$\text{Small } K_{\text{eq}} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

$K_{\text{eq}} > 1$  then products **GREATER THAN** reactants

$K_{\text{eq}} < 1$  then products **LESS THAN** reactants

$K_{\text{eq}} = 1$  products **EQUAL** reactants

**SAMPLE EXERCISES 2.4 – RELATING EXTENT OF REACTION TO THE VALUE OF THE EQUILIBRIUM CONSTANT,  $K_{\text{EQ}}$** 

Predict the relative amount of reactants and products at equilibrium.

- a)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$   $K_{\text{eq}} = 6.3 \times 10^{-11}$   
 b)  $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$   $K_{\text{eq}} = 5 \times 10^3$   
 c)  $\text{Si}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{SiO}_2(\text{s})$   $K_{\text{eq}} = 2 \times 10^{-9}$

## E. DEPENDENCE OF $K_{eq}$ ON TEMPERATURE

- The value of  $K_{eq}$  remains constant even when the concentration, pressure, or surface area is changed; however, **changing temperature affects the value of  $K_{eq}$ .**
  - Changes in concentration, pressure, or surface area result in change in the number of reacting molecules per liter. The equilibrium counteracts these changes (stresses) by shifting to **re-distribute the change and re-establish a new equilibrium.** The ratio of **[PRODUCT]/[REACTANT]** and the **value of  $K_{eq}$  remains the same.**
  - Changing temperature causes a shift in the equilibrium; however, the **number of reacting molecules does not change.** As a result, the ratio of **[PRODUCT]/[REACTANT]** changes and the **value of  $K_{eq}$  changes.**

**Varying temperature is the only factor that changes the value of  $K_{eq}$**

- Consider the reaction:



- For an **exothermic reaction, an increase in temperature** will cause a shift to the **left.** The **[PRODUCTS]** decreases while the **[REACTANTS]** increases, and since

$$K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}, \text{ the value of } K_{eq} \text{ decreases.}$$

- For an **endothermic reaction, an increase in temperature** will cause a shift to the **right.** The **[PRODUCTS]** increases while the **[REACTANTS]** decreases, and the **value of  $K_{eq}$  would increase.**



- If the value of  $K_{eq}$  is provided for two different temperatures at which the reaction occurs, it is possible to predict whether a reaction is endothermic or exothermic.

$K_{eq}$  **increases** when the temperature of an **endothermic** reaction is increased

$K_{eq}$  **decreases** when the temperature of an **exothermic** reaction is increased

**EXAMPLE 2.3 – PREDICTING ENERGY CHANGES FROM  $K_{\text{EQ}}$** 

Consider the following reaction:



Is the above reaction endothermic or exothermic if  $K_{\text{eq}}$  is 2.24 at 227°C and 33.3 at 487°C?

*The increase in  $K_{\text{eq}}$  indicates that the equilibrium is shifted to the right by an increase in temperature and hence the reaction is endothermic.*

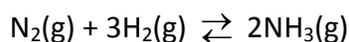
## F. EQUILIBRIUM CONSTANT CALCULATIONS

- Determining the value of  $K_{eq}$  requires information about the concentrations of the reactants and products when the system is at equilibrium. Such information can only be obtained by actually performing the experiment.

The following examples illustrate the various type of calculations which can be performed based on the equilibrium expression and some experimental data.

### EXAMPLE 2.4 – CALCULATING $K_{eq}$ FROM EQUILIBRIUM CONCENTRATIONS

Consider the following equilibrium system:



At 200°C, the concentration of nitrogen, hydrogen, and ammonia at **equilibrium** are measured and found to be  $[\text{N}_2] = 2.12$ ,  $[\text{H}_2] = 1.75$ , and  $[\text{NH}_3] = 84.3$ . Determine the value of  $K_{eq}$ .

*Determine the equilibrium expression for the reaction is:*

$$K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

*Substitute the **equilibrium concentrations** into the equilibrium expression:*

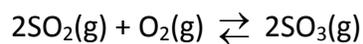
$$K_{eq} = \frac{(84.3)^2}{(2.12)(1.75)^3} = \frac{(7.11 \times 10^3)}{(2.12)(5.36)}$$

$$K_{eq} = \mathbf{626}$$

*\*Note: there are **no units** are no units associated with  $K_{eq}$  because they depend on the equilibrium system and are of little or no significance.*

**EXAMPLE 2.5 - CALCULATING CONCENTRATIONS FROM  $K_{\text{EQ}}$** 

The equilibrium concentrations of  $\text{SO}_2$  and  $\text{O}_2$  are each 0.0500M and  $K_{\text{eq}} = 85.0$  at  $25^\circ\text{C}$  for the reaction



Calculate the equilibrium concentration for  $\text{SO}_3$  at this temperature.

*The equilibrium expression for the reaction is*

$$K_{\text{eq}} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

*Let  $x$  equal the concentration of  $\text{SO}_3$  at equilibrium.*

*Substituting into the value of  $K_{\text{eq}}$  given and the equilibrium concentrations you have*

$$85.0 = \frac{(x)^2}{(0.0500)^2(0.0500)}$$

$$x^2 = 0.0106$$

$$x = \mathbf{0.103}$$

*therefore  $[\text{SO}_3]_{\text{eq}}$  is 0.103 M.*

**EXAMPLE 2.6 – CALCULATING  $K_{\text{EQ}}$  FROM INITIAL CONCENTRATIONS**

Suppose that 4.00 moles of HI(g) is placed into a 2.00 L flask at 425°C react to produce H<sub>2</sub> and I<sub>2</sub> according to the equation:



At equilibrium the concentrations of H<sub>2</sub> and I<sub>2</sub> are found to each be 0.214 mol/L. Calculate the value of  $K_{\text{eq}}$ .

*First, determine the equilibrium expression:*

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

*Next, calculate the concentrations of the reactants and products:*

$$[\text{HI}(\text{g})]_{\text{initial}} = \frac{4.00 \text{ mol}}{2.00 \text{ L}} = 2.00 \text{ mol/L}$$

$$[\text{H}_2(\text{g})]_{\text{equil'm}} = [\text{I}_2(\text{g})]_{\text{equil'm}} = 0.214 \text{ mol/L}$$

*Initial concentration is involved an “Initial – Change – Equilibrium” (ICE) table must be used. Variable “x” to represent the change in concentration of H<sub>2</sub> and setup an ICE table as follows:*

	$2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$		
<i>initial</i>	<i>2.00 M</i>	<i>0.00 M</i>	<i>0.00 M</i>
<i>change</i>	<i>- 2x</i>	<i>+ x</i>	<i>+ x</i>
<i>equilibrium</i>	<i>2.00 - 2x</i>	<i>x</i>	<i>x</i>

*At equilibrium,*

$$[\text{H}_2] = [\text{I}_2] = x = 0.214 \text{ mol/L}$$

$$[\text{HI}] = 2.00 - 2x = 2.00 - 2(0.214) = 1.57 \text{ mol/L}$$

*Finally, use the equilibrium concentrations to calculate the value of  $K_{eq}$ :*

$$[H_2] = 0.214 \text{ mol/L}; [I_2] = 0.214 \text{ mol/L}; [HI] = 1.57 \text{ mol/L}$$

$$K_{eq} = \frac{(0.214)(0.214)}{(1.57)^2} = \mathbf{1.86 \times 10^{-2}}$$

**EXAMPLE 2.7 – CALCULATING INITIAL CONCENTRATIONS FROM  $K_{\text{EQ}}$** 

A certain amount of  $\text{NO}_2(\text{g})$  was placed into a 5.00 L bulb and reacted according to the equation:  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ . When equilibrium was reached, the concentration of  $\text{NO}(\text{g})$  was 0.800 M. If  $K_{\text{eq}}$  has a value of 24.0, how many moles of  $\text{NO}_2$  were originally placed into the bulb.

*Since an initial concentration is involved we need to setup an ICE table.*

$$[\text{NO}]_{\text{equilibrium}} = 0.800 \text{ M and } [\text{NO}_2]_{\text{initial}} = y$$

	$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$		
<i>initial</i>	0.00 M	0.00 M	y
<i>change</i>	+2x	+x	-2x
<i>equilibrium</i>	2x	x	y - 2x

*At equilibrium,*

$$[\text{NO}] = 2x = 0.800 \text{ M} \quad [\text{O}_2] = x = \frac{0.800 \text{ M}}{2} = 0.400 \text{ M}$$

$$[\text{NO}_2] = y - 2x = y - 0.800 \text{ M}$$

*The equilibrium expression for the reaction is*

$$K_{\text{eq}} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

*Substituting into the equilibrium expression gives:*

$$24.0 = \frac{(y - 0.800)^2}{(0.800)^2(0.400)}$$

$$24.0 = \frac{(y - 0.800)^2}{0.256}$$

$$(y - 0.800)^2 = 6.144$$

$$y - 0.800 = 2.479$$

$$y = 3.279 \text{ M} = [\text{NO}_2]_{\text{initial}}$$

*The problem requires number of moles of  $\text{NO}_2$  which were originally placed into the 5.00 L bulb, so moles of  $\text{NO}_2 = 3.279 \text{ mol/L} \times 5.00 \text{ L} = \mathbf{16.4 \text{ mol}}$*

**EXAMPLE 2.8 – DETERMINING [EQUILIBRIUM] FROM [INITIAL]  $K_{\text{EQ}}$** 

$K_{\text{eq}} = 3.5$  for the reaction:  $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$ . If 4.0 mol of  $\text{SO}_2(\text{g})$ , 4.0 mol of  $\text{NO}_2(\text{g})$  are put into a 5.0 L bulb and allowed to come to equilibrium, what concentration of all species will exist at equilibrium?

*First, write out the equilibrium expression:*

$$K_{\text{eq}} = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]}$$

*Next, setup an ICE table,*

	$\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$			
<i>initial</i>	<i>0.80 M</i>	<i>0.80 M</i>	<i>0.00 M</i>	<i>0.00 M</i>
<i>change</i>	<i>- x</i>	<i>- x</i>	<i>+ x</i>	<i>+ x</i>
<i>equilibrium</i>	<i>0.80 - x</i>	<i>0.80 - x</i>	<i>x</i>	<i>x</i>

*Since we don't know any equilibrium concentrations we need to use the variables and substitute them into the equilibrium expression:*

$$K_{\text{eq}} = \frac{(x)(x)}{(0.80 - x)(0.80 - x)}$$

$$3.5 = \frac{x^2}{(0.80 - x)^2} \quad (\text{this is a perfect square})$$

$$1.87 = \frac{x}{(0.80 - x)}$$

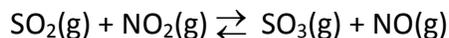
$$x = 0.52 \text{ M}$$

$$[\text{SO}_3] = [\text{NO}] = x = \mathbf{0.52 \text{ M}}$$

$$[\text{SO}_2] = [\text{NO}_2] = 0.80 - x = 0.80 - 0.52 = \mathbf{0.28 \text{ M}}$$

**EXAMPLE 2.9 – DETERMINING [EQUILIBRIUM] AFTER A SHIFT**

A 1.0 L reaction vessel contained 1.0 mol of  $\text{SO}_2$ , 4.0 mol of  $\text{NO}_2$ , 4.0 mol of  $\text{SO}_3$ , and 4.0 mol of  $\text{NO}$  at equilibrium according to the reaction:



If 3.0 mol of  $\text{SO}_2$  is added to the mixture what will the new concentration of  $\text{NO}$  be when equilibrium is re-established?

*The unknown is the final  $[\text{NO}]$  when equilibrium is re-established.*

*All other concentrations can be easily calculated and the value of  $K_{\text{eq}}$  is needed.*

*$K_{\text{eq}}$  is not given but we know the concentrations of each gas previously at equilibrium, so  $K_{\text{eq}}$  can be calculated.*

$$K_{\text{eq}} = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{(4.0)(4.0)}{(1.0)(4.0)} = 4.0$$

*Since the temperature does not change, the value of  $K_{\text{eq}}$  will remain the same.*

*Next, setup an ICE table,*

	$\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$			
<i>initial</i>	<i>1.0 + 3.0</i>	<i>4.0</i>	<i>4.0</i>	<i>4.0</i>
<i>change</i>	<i>- x</i>	<i>- x</i>	<i>+ x</i>	<i>+ x</i>
<i>equilibrium</i>	<i>4.0 - x</i>	<i>4.0 - x</i>	<i>4.0 + x</i>	<i>4.0 + x</i>

*Substituting into the equilibrium expression:*

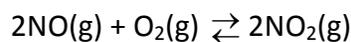
$$K_{\text{eq}} = \frac{(4.0 + x)^2}{(4.0 - x)^2} = 4.0$$

$$2.0 = \frac{(4.0 + x)}{(4.0 - x)}$$

$$x = 1.33$$

$$[\text{NO}] = 4.0 + x = 4.0 + 1.33 = \mathbf{5.3 \text{ M}}$$

2. For some problems, a numerical **answer is NOT required but rather a DECISION must be made.**
- For example, which way will the reaction shift in order to reach equilibrium or how will the concentration of reactants and product change in order to reach equilibrium.
  - For these decision type problems a **REACTION QUOTIENT (Q) or Trial  $K_{eq}$** , is used.
  - Consider the following equation:



the reaction quotient is:

$$Q = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

- Notice that the reaction quotient is the same as the equilibrium expression except that we will **use initial concentrations to solve for Q instead of equilibrium concentrations which are used for  $K_{eq}$** .
- Our decision can be based upon comparing the reaction quotient, Q, to the equilibrium constant,  $K_{eq}$ .

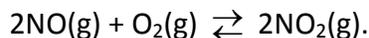
If  $Q = K_{eq}$ , then the system is at **EQUILIBRIUM** and no shift will occur

If  $Q < K_{eq}$ , then  $\frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$  is **TOO SMALL** and shift right, more **PRODUCTS**

If  $Q > K_{eq}$ , then  $\frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$  is **TOO BIG** and shift left, more **REACTANTS**

**EXAMPLE 2.10 – DETERMINING THE DIRECTION OF SHIFT, TRIAL  $K_{\text{EQ}}$** 

$K_{\text{eq}} = 49$  for the equilibrium:



If 2.0 mol of NO(g), 0.20 mol of O<sub>2</sub>(g), and 0.40 mol of NO<sub>2</sub>(g) are put into a 2.0 L bulb, which way will the reaction shift in order to reach equilibrium? Support your answer with the appropriate calculations.

*First of all, this question is **NOT** asking for a numerical value. Asking for a **DECISION**. We will base our decision on comparing the **Reaction Quotient, Q**, to the  $K_{\text{eq}}$ .*

$$Q = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} \quad (\text{where } Q = \text{the } \mathbf{REACTION QUOTIENT})$$

*Calculate the initial concentrations:*

$$[\text{NO}]_{\text{initial}} = \frac{2.0 \text{ mol}}{2.0 \text{ L}} = 1.0 \text{ M} \quad [\text{O}_2]_{\text{initial}} = \frac{0.20 \text{ mol}}{2.0 \text{ L}} = 0.10 \text{ M}$$

$$[\text{NO}_2]_{\text{initial}} = \frac{0.40 \text{ mol}}{2.0 \text{ L}} = 0.20 \text{ M}$$

*Now substitute the initial concentrations into reaction quotient:*

$$Q = \frac{(0.20)^2}{(1.0)^2(0.10)} = 0.40$$

*Since  $Q < K_{\text{eq}}$ , the reaction must shift right to produce more **PRODUCTS**.*