Equilibrium

Equilibrium can be thought of as equality or balance. **Dynamic equilibrium** refers to a balance between 2 opposing forces. Some chemical and physical changes can reach equilibrium. These symbols represent equilibrium; ↔, ⇔, ⇀↽ .

When equilibrium exists, the rate of the forward process equals the rate of the reverse process.

What is true about the rate of the forward and reverse process during equilibrium?

_____.

Equilibrium can exist for both chemical or physical processes.

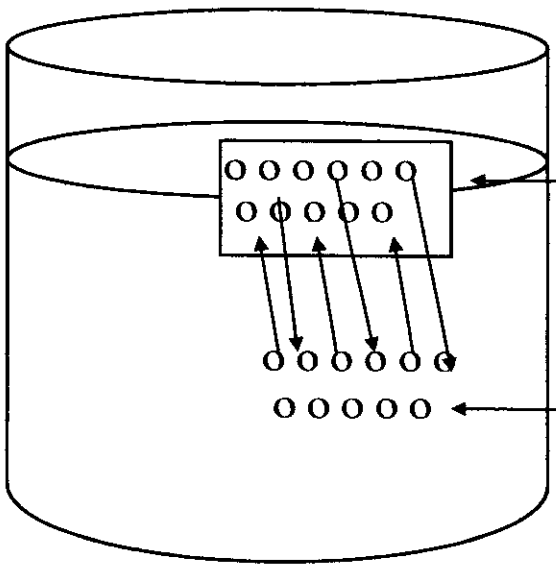
The measurable quantities of reactants and products remain constant at equilibrium.

What is true about the measurable amounts of products and reactants at equilibrium?

_____.

Phase Equilibrium. A phase equilibrium is an equilibrium between phases. **Liquid/solid**. Liquid ↔ Solid. The equilibrium between liquid and solid is a **phase equilibrium.** It can only exist at a substance's melting/freezing point. The temperature at which liquid and solid water can be in equilibrium is **0°C or 273 K**. You may see this equilibrium expressed as $H_2O_{(l)} \leftrightarrow H_2O_{(s)}$, In phase equilibrium the individual particles, in this case water molecules, may change phases. However; the measurable amounts of solid water molecules and liquid water molecules remain the same.

For equilibrium to exist between **solid and liquid** water the temperature must be constant at **0° C (273 K).**



Liquid/Solid equilibrium: Individual water molecules may change phase from liquid to solid or solid to liquid, but the ratio remains unchanged. If 10 liquid water molecules freeze then 10 solid water molecules must melt.

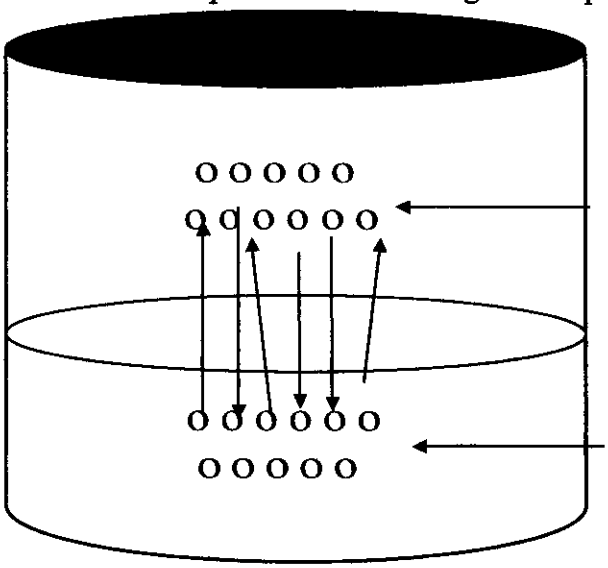
1. What temperature is required for $H_2O_{(l)} \leftrightarrow H_2O_{(s)}$ to exist? _____°C or _____K

2. What 2 phase changes occur during the above equilibrium?

Liquid/Gas equilibrium: The equilibrium between liquid and gas is a **phase equilibrium.** Equilibrium between a liquid and a gas can only occur in a sealed container. Let's examine the equilibrium between water vapor and liquid water in a sealed container. **$H_2O_{(l)} \leftrightarrow H_2O_{(g)}$.**

The equilibrium between liquid and gas can occur over a wide range of temperatures since water can evaporate at a wide range of temperatures.

For equilibrium to exist between gas and liquid water it must be in a sealed container to avoid evaporation out of the container.



Individual water molecules may change phase from liquid to gas or gas to liquid, but the ratio remains unchanged. If 10 liquid water molecules evaporate then 10 vapor water molecules must condense.

3. Is a specific temperature required for $H_2O_{(l)} \leftrightarrow H_2O_{(g)}$ to occur? Why?

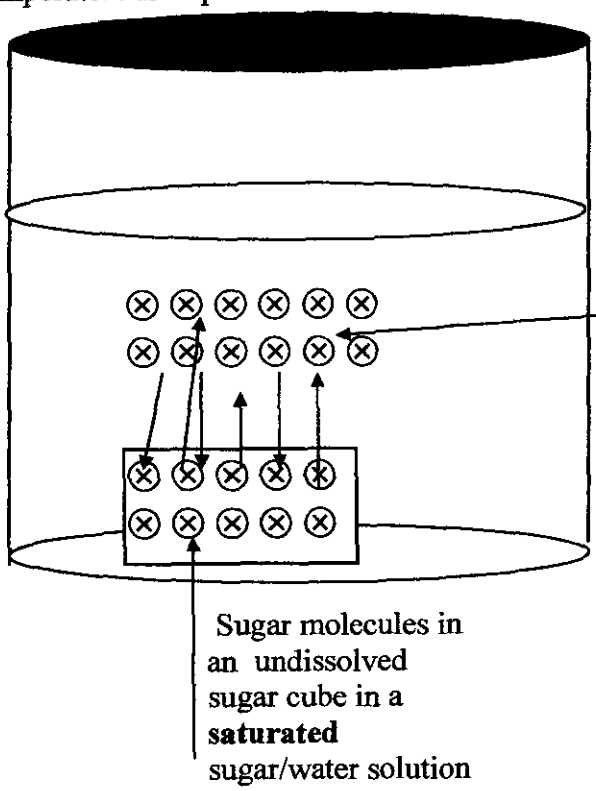
4. What 2 phase changes occur during the above equilibrium?

5. Is a sealed container necessary for the above equilibrium?

Solution Equilibrium: Solution equilibrium is a physical equilibrium. Solution equilibrium between a dissolved solid (solute) and the dissolving liquid (solvent) can only occur if the solution is **saturated** (full of solute).

Solid solute ↔ Aqueous solute $Sugar_{(s)} \leftrightarrow Sugar_{(aq)}$.

Solution equilibrium can occur over a wide range of temperatures. **No** specific temperature is required.



The container must be sealed to avoid evaporation out of the container.

Dissolved sugar molecules in a **saturated** sugar/water solution.

Sugar molecules in an undissolved sugar cube in a **saturated** sugar/water solution

Some sugar molecules may crystallize and precipitate (leave the solution). Some sugar molecules may dissolve, but the ratio remains unchanged. If 10 sugar molecules dissolve then 10 sugar molecules must precipitate.

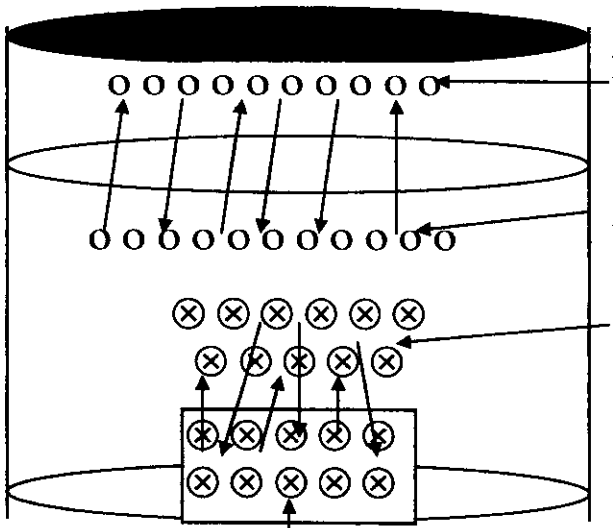
6. Is a specific temperature required for the above equilibrium to occur?

7. Compare the rate of dissolving to crystallizing in a **saturated** solution.

8. Compare the rate of dissolving to crystallizing in an **unsaturated** solution.

The following diagram of a sealed container combines the first 2 diagrams. Both phase equilibrium and solution equilibrium exist in this container.

The container must be sealed to avoid evaporation out of the container.



$H_2O_{(g)}$ gas water molecules.

$H_2O_{(l)} \leftrightarrow H_2O_{(g)}$.

$H_2O_{(l)}$ liquid water molecules.

Dissolved sugar molecules in a saturated sugar/water solution.

$Sugar_{(s)} \leftrightarrow Sugar_{(aq)}$

Sugar molecules in an undissolved sugar cube in a **saturated** sugar/water solution

Individual water molecules may change phase from liquid to gas or gas to liquid, but the ratio remains unchanged. If 10 liquid water molecules evaporate then 10 vapor water molecules must condense.

Some sugar molecules may crystallize and precipitate (leave the solution). Some sugar molecules may dissolve, but the ratio remains unchanged. If 10 sugar molecules dissolve then 10 sugar molecules must precipitate.

Chemical Equilibrium occurs in reversible chemical reactions.
Many chemical reactions run in both the forward and reverse directions. This type of **reversible reaction** may appear to stop but the reaction continues in equilibrium.
The **rate** of the **forward** reaction **equals** the **rate** of the **reverse** reaction.
An equilibrium reaction may be expressed as: A + B ↔ C + D.
When a chemical reaction has reached equilibrium **the ratio of products to reactants remains constant** (unchanging).

1. **Chemical Equilibrium** occurs in _____ chemical reactions.

2. In a chemical equilibrium the _____ of the **forward** reaction **equals** the _____ of the **reverse** reaction.

3. When a chemical reaction has reached equilibrium **the** _____ **of products to reactants remains constant** (unchanging).

Le Chatlier's Principle: Most chemical reactions in equilibrium will respond to changes in concentration, pressure, or temperature. A change in concentration, pressure, or temperature is referred to as a **stress.** A chemical reaction in equilibrium reacts to **stress** (change) to minimize the **stress**. The reaction will **shift the equilibrium** to minimize the **stress**. A new equilibrium will reestablish at a different point. Shifting the equilibrium means to produce more products or reactants to **relieve** the **stress**.

Shifting the equilibrium to the left means to produce more of the items to the left of the reversible arrow ↔.

Shifting the equilibrium to the right means to produce more of the items to the right of the reversible arrow ↔.

4. Most chemical reactions in equilibrium will respond to changes in _____,

_____, or _____.

5. A change in concentration, pressure, or temperature is referred to as a _____.

6. The reaction will _____ the _____ to minimize the **stress.**

7. Shifting the equilibrium to the left means to produce more of the items to the _____ of the reversible arrow ↔.

8. Shifting the equilibrium to the right means to produce more of the items to the _____ of the reversible arrow ↔.

Rules to predict how a reaction will react to stress factors:

The stress factors are: **temperature, pressure, or concentration.**
Things to know about stress factors.

1. **Pressure:** A change in **pressure** only affects reactions that have unequal numbers of moles of gas on each side of the arrow. Reactions that do not involve gas or have equal amounts of gas on each side of the arrow are not affected by a change in pressure. An increase in pressure will shift the equilibrium towards the side that has less moles of gas. A decrease in pressure will shift the equilibrium towards the side that has more gas. An increase in pressure will result in less moles of gas. A decrease in pressure will result in more gas

What types of equilibrium reactions will not react to a change in pressure? _____

Ex: How will an increase in pressure affect the following reaction?
$N_{2(g)} + 2\ O_{2(g)} \leftrightarrow 2NO_{2(g)}$

To solve: Determine the number of moles of gas on each side of the arrow.

1 2 2
$N_{2(g)} + 2O_{2(g)} \leftrightarrow 2NO_{2(g)}$

There are **3** moles of gas on the left side and **2** moles of gas on the right side. The left Side has more moles of gas than the right side.
An increase in pressure will shift the equilibrium towards the side with less gas (to the right). An increase in pressure will cause more $NO_{2(g)}$ to be produced.
The forward reaction is favored.

Now you try one!
How would an increase of pressure affect the following reaction?

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

Which way will the equilibrium shift?

Will the forward or reverse reaction be favored?

Try another one!

What will be the effect of an increase in pressure on the following system?

$CO_{2(s)} \leftrightarrow CO_{2(g)}$

Which way will the equilibrium shift?

Will the forward or reverse reaction be favored?

2. **Temperature:** An **increase in temperature** will shift the equilibrium towards the **endothermic** direction (favor the endothermic reaction).
A **decrease in temperature** will shift the equilibrium towards the **exothermic** direction (favor the exothermic reaction).
Rule: An increase in temperature favors the endothermic reaction.
Ex: How will a decrease in temperature affect the following reaction?
$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2NH_{3(g)}$
To solve:
Use Table I to determine if the reaction is endothermic or exothermic.
This reaction has a - **ΔH** therefore it, is **exothermic**. Exothermic reactions produce heat, therefore heat is a product and appears on the product side.
$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2NH_{3(g)} + 91.8\ kJ$
A decrease in temperature shifts the equilibrium towards the exothermic direction. Therefore, the forward reaction will be favored and more $NH_{3(g)}$ will be formed.
Now you try one!
How will a decrease in temperature affect the following reaction?
$N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)}$
a) Which way will the equilibrium shift?

b) Which items will increase in concentration?

c) Which items will decrease in concentration?

Try another one!
How will an increase in temperature affect the following reaction?

3. **Concentration:** A change in **concentration** of a reactant or product will shift the equilibrium to maintain the original balance (equilibrium). Concentration can be expressed as [ ].

Ex: $[Cl^-]$ means concentration of chloride ion.
Adding a reactant will produce more product. Removing a product will produce more product.
Remember! Soluble ionic compounds dissolve to form + and - ions.
Ex: How will the addition of $NaCl_{(aq)}$ to a saturated solution of $AgCl_{(aq)}$ affect the concentration of $AgCl_{(s)}$ and the concentration of Ag^{+1}
$AgCl_{(s)} \leftrightarrow Ag^{+1}{}_{(aq)} + Cl^{-1}{}_{(aq)}$
To solve: $NaCl_{(aq)}$ contains Na^{+1} ions and Cl^{-1} ions. Therefore, Cl^{-1} ions are being added. Product is being added, therefore, the equilibrium will shift towards the left and produce more $AgCl_{(s)}$. Ag^{+1} will be consumed in the production of $AgCl_{(s)}$ resulting in less Ag^{+1}.
Now you try one!
For the following equilibrium reaction.
$N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)}$
How will an increase in $[N_{2(g)}]$ affect $[O_{2(g)}]$ and $[NO_{(g)}]$?

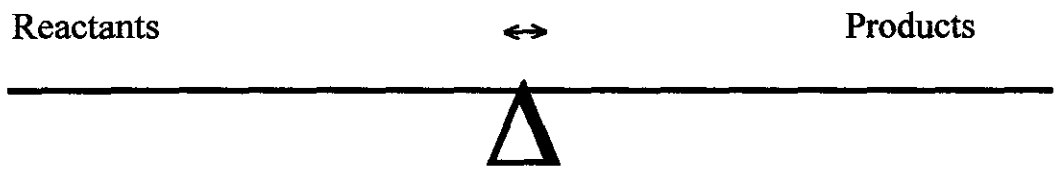
4. **Catalyst:** The presence of a **catalyst** does **not** change or shift equilibrium. A catalyst **speeds up the rate of both the forward and reverse** reaction but does not affect the amount of product or reactant.
   Ex: How does the addition of a catalyst affect the equilibrium of the following reaction? Why?
   $N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2NH_{3(g)} + 91.8\ kJ$

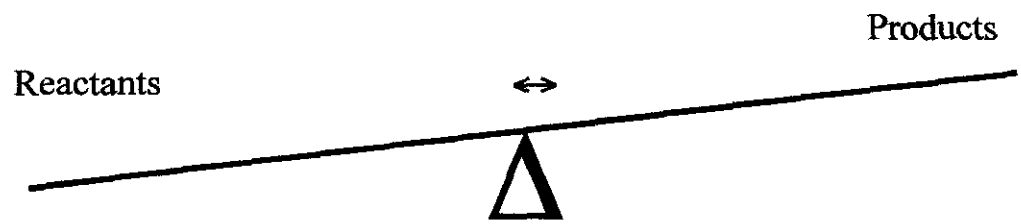
   Answer: There will be no effect. A catalyst does not shift equilibrium.

Try using this **Analogy** to help answer equilibrium reaction questions.
You might find it useful to compare an equilibrium reaction to a see-saw.
The reactants begin in equilibrium with the products "level see-saw".

Le Chatlier's Principle states that an equilibrium reaction will respond to a stress in order to maintain the original equilibrium (balance). If something is added or removed from one side, the reaction will produce more of the items necessary to restore the balance.

Raising the temperature can be thought of as adding heat. An exothermic reaction has heat as a product.
Lowering the temperature can be thought of as removing heat. An endothermic reaction has heat as a reactant.
Increasing the pressure can be thought of as adding gas to the side with the most moles of gas.





You can see which side will need more to restore the balance.

LE CHATELIER'S PRINCIPLE

Name _____

Le Chatelier's Principle states that when a system at equilibrium is subjected to a stress, the system will shift its equilibrium point in order to relieve the stress.

Complete the following chart by writing left, right or none for equilibrium shift, and decreases, increases or remains the same for the concentrations of reactants and products,

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) + 91.8\ kJ$$

Stress	Equilibrium Shift	$[N_2]$	$[H_2]$	$[NH_3]$	
1. Add N_2	right	———	decreases	increases	
2. Add H_2			———		
3. Add NH_3				———	
4. Remove N_2		———			
5. Remove H_2			———		
6. Remove NH_3				———	
7. Increase Temperature					
8. Decrease Temperature					
9. Increase Pressure					
10. Decrease Pressure					

LE CHATELIER'S PRINCIPLE CONTINUED

Name _____

$53\ kJ + H_2(g) + I_2(g) \leftrightarrow 2HI(g)$

Stress	Equilibrium Shift	$[H_2]$	$[I_2]$	$[HI]$	
1. Add H_2	right	———	decreases	increases	
2. Add I_2			———		
3. Add HI				———	
4. Remove H_2		———			
5. Remove I_2			———		
6. Remove HI				———	
7. Increase Temperature					
8. Decrease Temperature					
9. Increase Pressure					
10. Decrease Pressure					

$NaOH(s) \leftrightarrow Na^+(aq) + OH^-(aq) + 44.5\ kJ$

Stress	Equilibrium Shift	Amount NaOH(s)	$[Na^+]$	$[OH^-]$	
1. Add NaOH(s)		———			
2. Add NaCl (Adds Na^+)			———		
3. Add KOH (Adds OH^-)				———	
4. Add H^+ (Removes OH^-)				———	
5. Increase Temperature					
6. *Decrease* Temperature					
7. Increase Pressure					
8. Decrease Pressure					