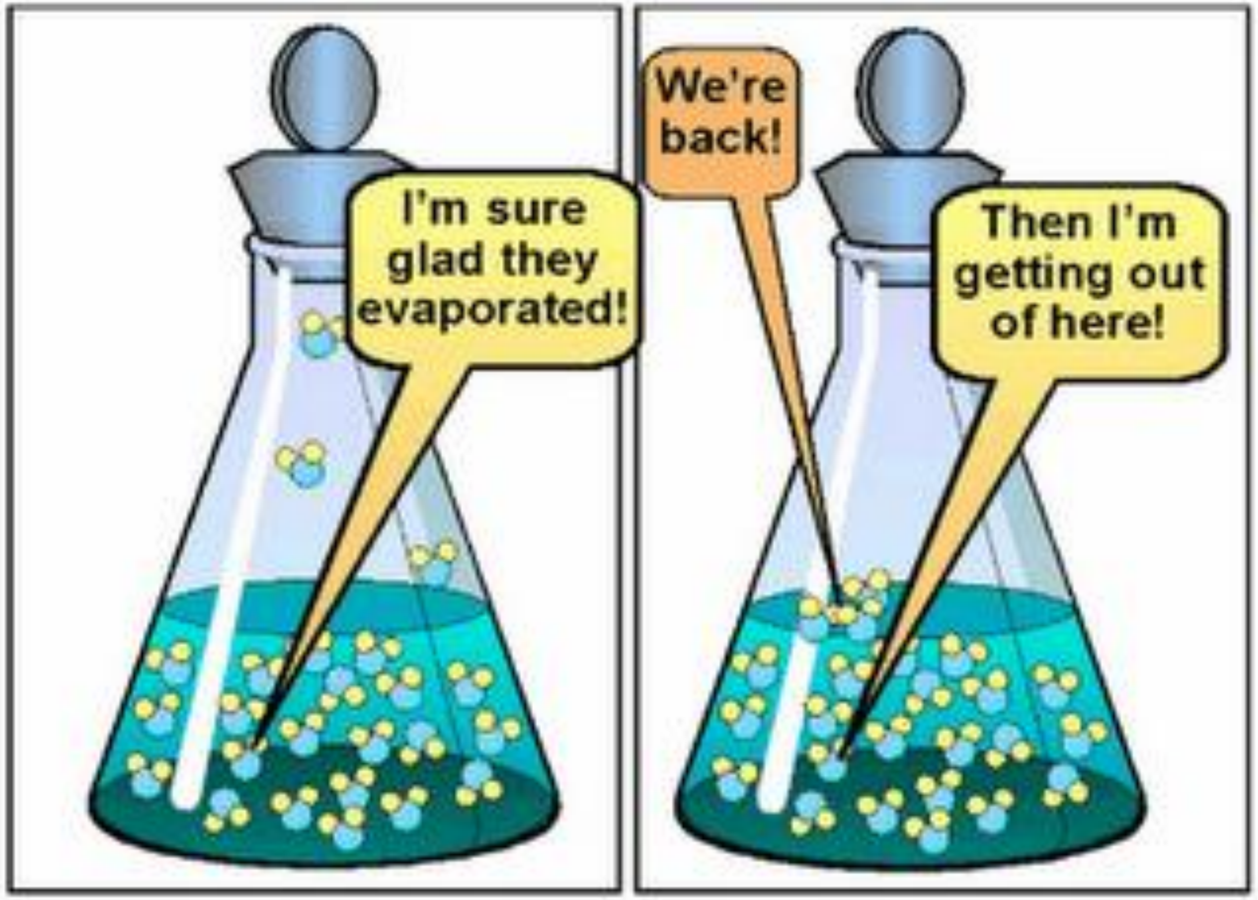
Physical Equilibria



http://equilibriumstudyguide.blogspot.ca/2009/05/types-of-equilibrium.html

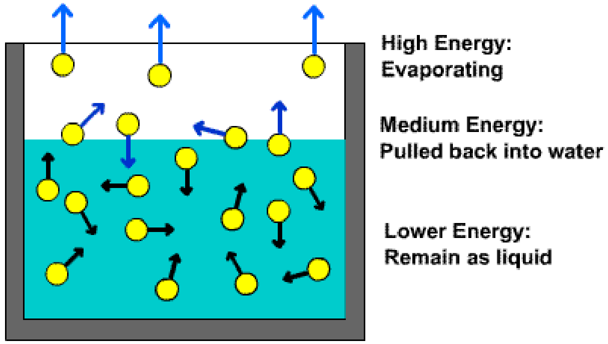
Outcome:

Relate the concept of equilibrium to physical and chemical systems. Include conditions necessary for equilibrium.

<u>Recall From Chem 30S:</u>

1. Evaporation:

- *Some molecules on the surface of a liquid possess enough energy to overcome* **<u>INTERMOLECULAR FORCES</u>** *and escape to become* **<u>VAPOUR</u>**.

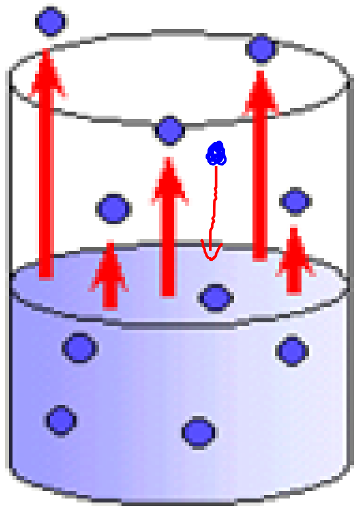


2. Condensation:

- *Water* **<u>VAPOUR</u>** *that hits the surface of a liquid, can also be converted to a* **<u>LIQUID</u>**.

In an open container…

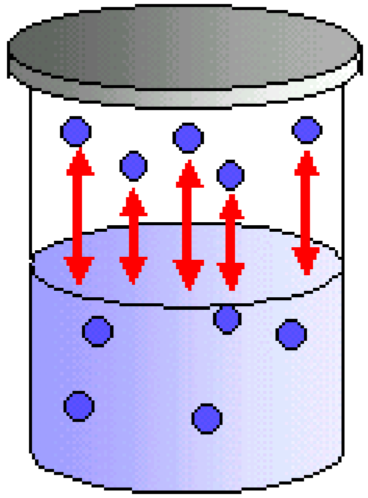
The water will eventually **EVAPOURATE** since the number of molecules **EVAPORATING** exceeds those **CONDENSING**.



Open Container

In a closed container…

- Molecules on the surface will also **EVAPORATE**, but will stay in the container creating **VAPOUR PRESSURE.**
- As **EVAPORATION** increases, so does **VAPOUR PRESSURE**.
- As more molecules **VAPOURIZE**, more will **CONDENSE**, until there is a balance between **EVAPORATION and CONDENSATION**.
- This balance is called a **DYNAMIC (LIQUID-VAPOUR) EQUILIBRIUM.**



Closed Container

Dynamic Equilibrium:

- When the rate of the **FORWARD PROCESS** is equal to the rate of the **REVERSE PROCESS**.
- There is no **APPARENT CHANGE** to the number of molecules in either state, but on a **MOLECULAR LEVEL**, particles are constantly changing states.
- We denote an equilibrium with a **DOUBLE ARROW** (the reaction is reversible)

In a system at equilibrium, the reaction proceeds in **BOTH DIRECTIONS** simultaneously.

Ex) Number of players in a **HOCKEY GAME** doesn't change, but is dynamic because players constantly go **ON AND OFF.**

Physical Equilibria:

Any **REVERSIBLE** physical process where the rate of the forward process is equal to the rate of the reverse.

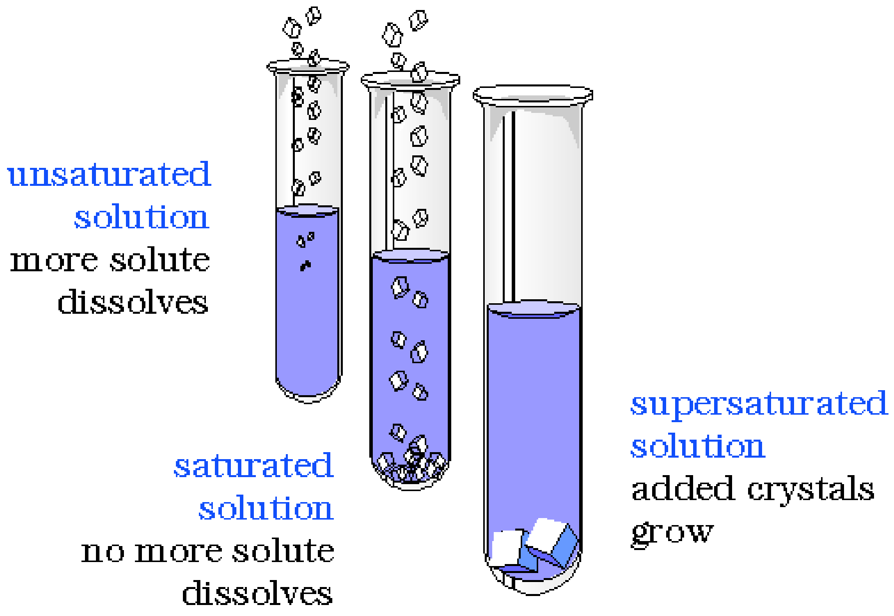
Examples:

- **SOLID-LIQUID**
- **LIQUID-VAPOUR**
- **SOLID-VAPOUR**
- **SOLUBILITY**

Solutions Review:

1. **Saturated Solution:**
   - Has the **MAXIMUM** amount of **SOLUTE IN SOLVENT** under given conditions.

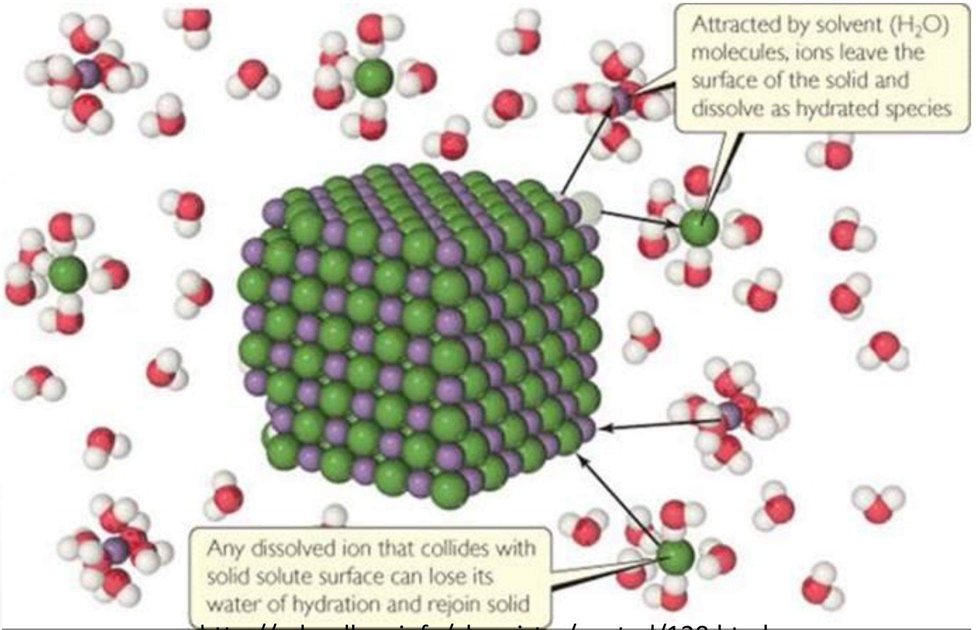
2. **Unsaturated Solution:**
   - Is capable of dissolving **MORE SOLUTE** under given conditions.



http://resource2.rockyview.ab.ca/science8/Sci8%20U1%20MixFlow/Sci8U1%20Lessons/Sci8U1L3.html

Solubility Equilibria:

- When a solute is dissolved in a solvent, the rate of dissolving is **FAST** at the start, and gradually **SLOWS** as **THE SOLUTE IS USED UP**.
- The rate of **PRECIPITATION** is slow at the start, but **SPEEDS UP** as the amount of **DISSOLVED SOLUTE** increases.
- Eventually these two processes will reach **EQUILIBRIUM**, and their **RATES** will stay constant. (see graph)
- Equilibrium is reached at the **SATURATION POINT**.



http://schoolbag.info/chemistry/central/120.html

Solution Equilibrium - AgCl

Example:

Dissolving sugar in water:

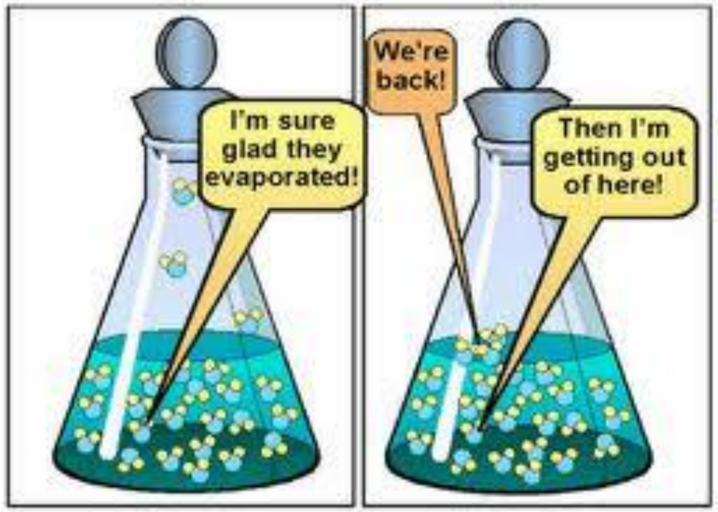
$$C_6H_{12}O_{6(s)} \leftrightarrow C_6H_{12}O_{6(aq)}$$

SOLUBILITY – Graphic Representation

Rate of Dissolving & Rate of Recrystallization

Phase Equilibria:

- Similar to solubility equilibria, but with **PHASE** changes.
- Initially a liquid's rate of **EVAPORATION** will be **FAST**, but will **SLOW** as the **VAPOUR PRESSURE** increases (**LESS ROOM FOR VAPOUR**)
- Initially, the rate of **CONDENSATION** will be **SLOW**, but will **INCREASE** as the amount of **VAPOUR INCREASES**.
- Eventually an **EQUILIBRIUM** will be reached, and the **RATES** will remain constant. (see graph)



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Example:

Water evaporating and condensing:

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

VAPOUR PRESSURE – Graphic Representation

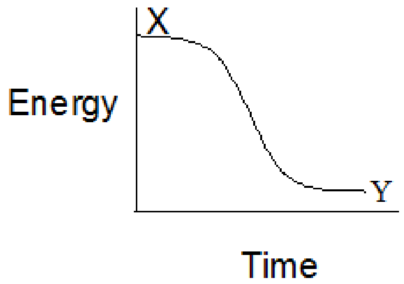
Rate of Evaporation vs. Rate of Condensation

<u>Chemical Equilibrium:</u>

In order for chemical reactions to reach a state of equilibrium, 2 basic requirements must be met:

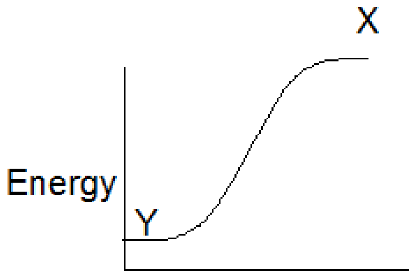
1. **<u>REACTION MUST BE REVERSIBLE</u>**
   - in principle <u>all</u> chemical reactions are **<u>REVERSIBLE</u>** (sometimes the reverse reaction is **<u>KINETICALLY INHIBITED</u>** or inhibited by **<u>ENTROPY</u>**

Example:



<u>X</u> ⇨ **<u>Y + ENERGY</u>**

If we added enough energy we could get the reaction to reverse:



<u>Y + ENERGY</u> ⇨ **<u>X</u>**

Chemical Equilibrium:

2. **REACTION MUST BE IN A CLOSED SYSTEM**
   - A 3-dimensional space that cannot exchange either **ENERGY** or **MATTER** with its surroundings.

Two Requirements must be met for a system to be closed.

1. **MUST BE SEALED**
   - Prevents **MATTER** from being exchanged with the outside environment.
   - Also keeps **PRESSURE** constant.

2. **MUST BE INSULATED**
   - Temperature must be **CONSTANT**

Example:

- NO_2 is produced by **CAR EXHAUST**, and is converted to N_2O_4 by **UV** light from the **SUN**. This is a major source of **SMOG**, since NO_2 is a **BROWN** gas (N_2O_4 is **COLOURLESS**).

$$NO_2 \rightarrow N_2O_4$$

Example:

$$NO_2 \rightarrow N_2O_4$$

- If NO_2 is placed in a sealed container, the brown colour will **FADE**, but not **COMPLETELY**. There will be a **BROWN TINT,** as long as conditions are kept constant.

- The fading is caused by the production of **N_2O_4**, but the brown tint remains since there is still some **NO_2**.

- Therefore, the reaction does not go completely to the **PRODUCTS**, but rests somewhere **IN BETWEEN**.

→***equilibrium*** **– CONSTANT CONCENTRATIONS OF BOTH REACTANTS AND PRODUCTS**

Chemical Equilibrium:

- As we have seen, the equilibrium state is characterized by ***constant*** **MACROSCOPIC PROPERTIES**.
  - →That is, the system **APPEARS** to be **STATIC, or UNCHANGING**.
- As the concentration of **N_2O_4** increases, it becomes converted back to **NO_2**.
- According to the collision theory, the rate of conversion to **REACTANTS** is increased as the **PRODUCT CONCENTRATION** increases.
- Eventually, the rate of **N_2O_4** production (the **FORWARD REACTION**) equals the rate of **NO_2** production (the **REVERSE REACTION**).
- This reaction is then written as follows:

$$2\,NO_2(g) \longleftrightarrow N_2O_4(g)$$

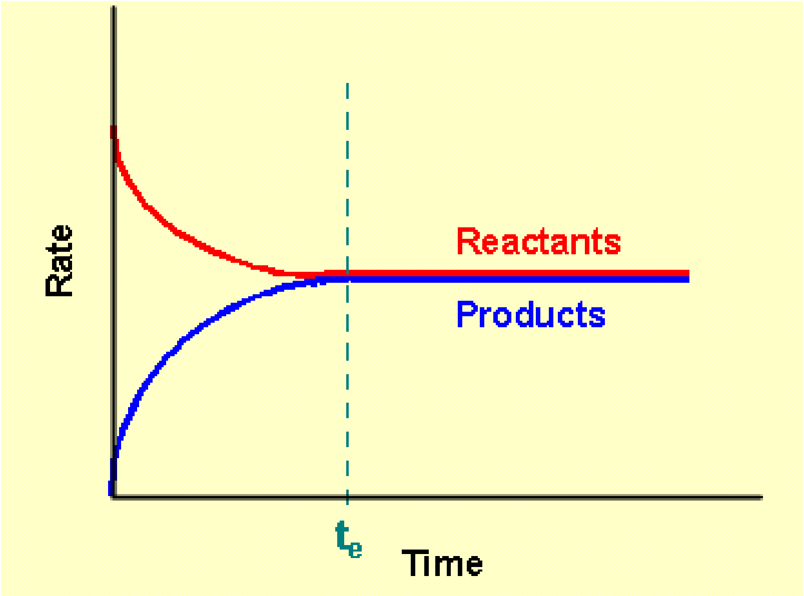
- The double arrow indicates the reaction is **REVERSIBLE**.

Chemical Equilibrium:

Therefore, ***chemical equilibrium*** is when the **RATE** of the forward reaction **EQUALS** the **RATE** of the reverse reaction.

- ***In our example, as one molecule of N_2O_4 is produced, one molecule of N_2O_4 is decomposed, simultaneously.***

→ A graph of **RATE VS. TIME** would look like:



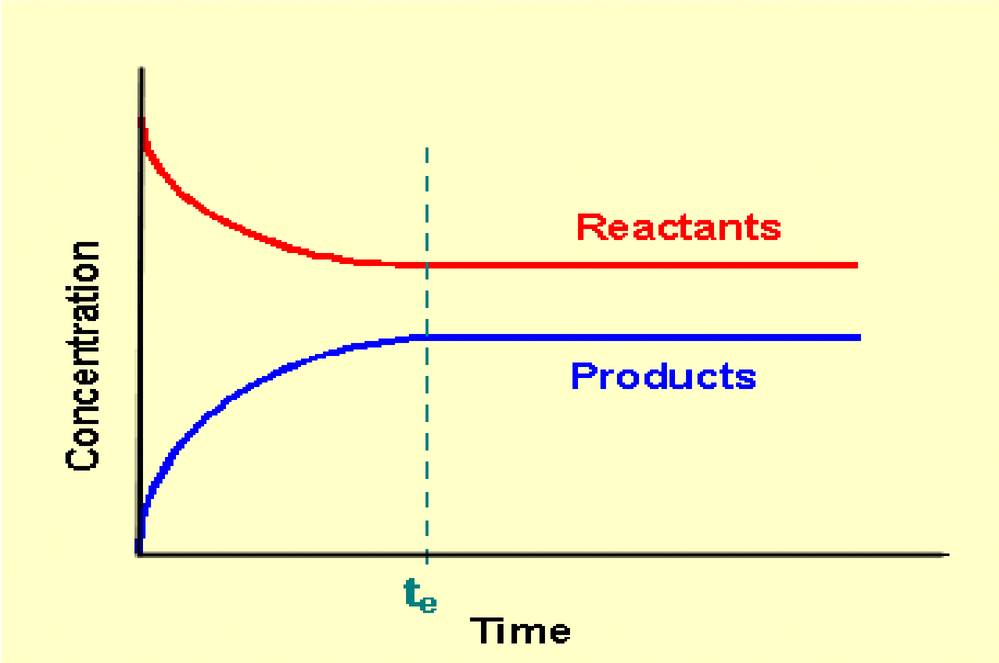
At time t_e, the **RATES** of both forward and reverse reactions are **EQUAL**

Chemical Equilibrium:

At equilibrium, the **CONCENTRATIONS** of both reactants and products **REMAIN CONSTANT** indefinitely.

- Note that concentrations of reactants and products are **NOT NECESSARILY EQUAL**.

A graph of **CONCENTRATION VS. TIME** ***could*** look like:



Summary:

Characteristics of a System at Equilibrium

1. The **RATE** of the **FORWARD** reaction = The **RATE** of the **REVERSE** reaction

2. **CONCENTRATIONS** of all reactants and products are **CONSTANT**

3. **MICROSCOPIC** processes (the forward and reverse reaction) continue in a **BALANCE** which yields **NO MACROSCOPIC CHANGES**. (so nothing **APPEARS** to be happening.)

4. The system is **CLOSED** and the **TEMPERATURE** is **CONSTANT** and **UNIFORM** throughout.

5. The equilibrium can be approached from the **LEFT** (starting with **REACTANTS**) or from the **RIGHT** (starting with **PRODUCTS**).