Unit 5, Lesson 03: Reversible Reactions and Equilibrium

There are two "driving forces" behind a chemical reaction:

1. systems tend to move toward minimum enthalpy
2. systems tend to move toward maximum entropy

When the driving forces act in opposite directions, the reaction is reversible. The majority of reactions are reversible.

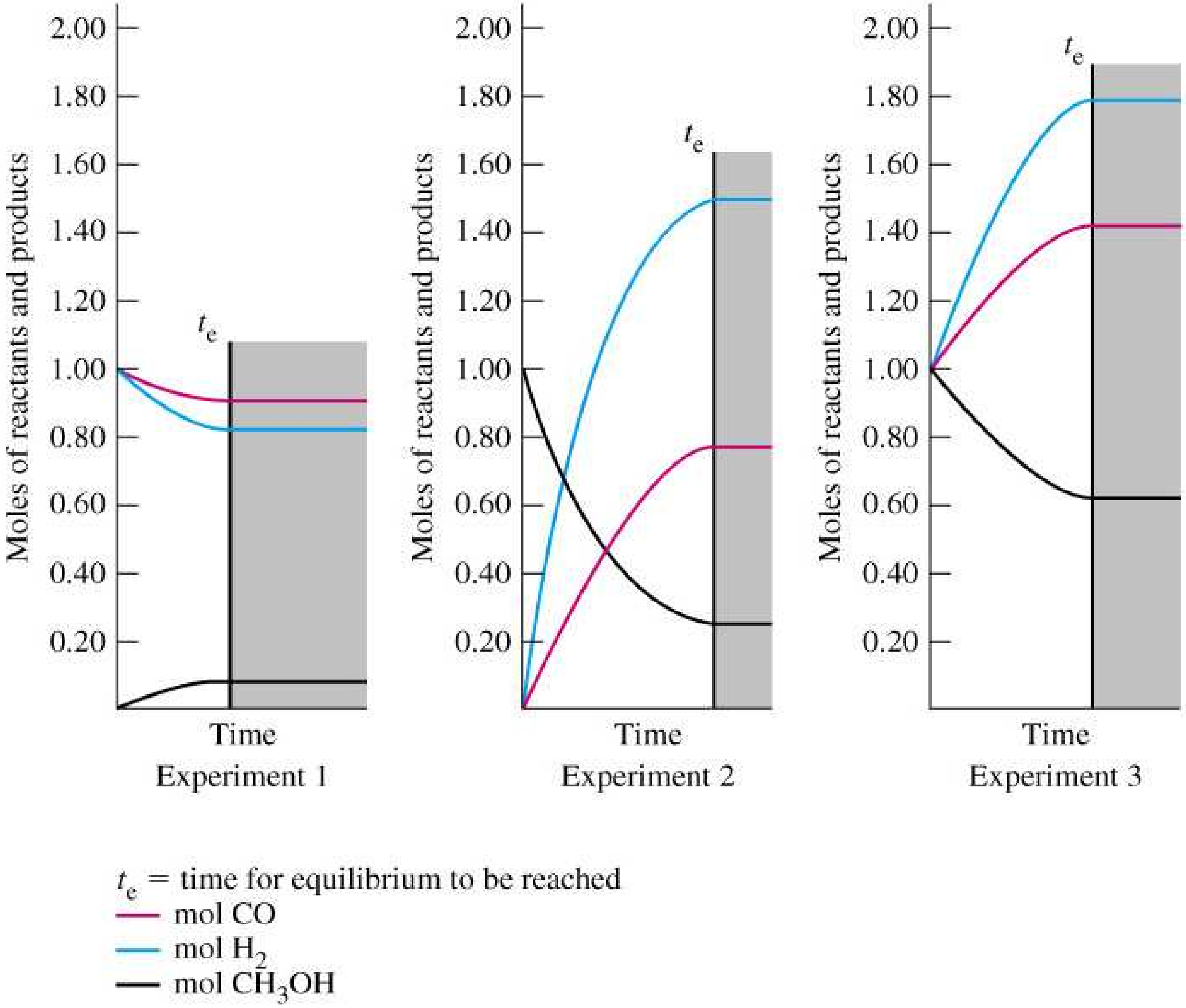
Animation to demonstrate equilibrium: http://www.dlt.ncssm.edu/TIGER/chem5.htm
http://www.dlt.ncssm.edu/TIGER/chem4.htm

Let's go back to the Collision Theory and think about what is happening as a reaction proceeds:

- When the reactants are first mixed, there are high concentrations of reactants and no products present yet.
- The collisions that occur are between reactant molecules, and if there is sufficient activation energy, the collisions will produce product. The rate of the forward reaction is high.
- As the reaction proceeds, more and more product molecules are present, while there are fewer and fewer reactant molecules as they get used up. The rate of the forward reaction slows down.
- Now there will be collisions between reactant and reactant, reactant and product, and product and product.
- Sometimes, as the product molecules collide with each other, they will convert back into reactant molecules, so the reverse reaction will occur (how often these collisions are effective depends on the activation energy of the reverse reaction). At first, the rate of the reverse reaction will be slow.
- As the concentration of product builds up, there are more and more collisions between product molecules and the rate of the reverse reaction increases.
- The reactions never stop happening- the particles in the system continue to move and collide forever. Sometimes the reactant molecules collide and produce product. Sometimes the product molecules collide and produce reactant.
- Eventually the forward reactions and reverse reactions are occurring at the same rate- the products are being produced at the same rate that the reactants are being reformed, so the concentrations of the products and reactants are constant. At this point, the system is said to be in "**equilibrium**".
- When the rate of the forward reaction is equal to the rate of the reverse reaction, the system does not appear to be changing- it has constant "macroscopic" properties (properties we can see with our eyes or feel with our hands). But, at the molecular level- both the forward and reverse reactions are happening continuously.
- Because the reactions never stop happening, we say that the system is in "**dynamic equilibrium**" (dynamic means "constant motion")

For the reversible reaction: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

The following graphs show what happens to the concentrations of the reactants and products as the reaction approaches equilibrium.
*Note that equilibrium **DOES NOT MEAN** that the concentrations of the reactants equals the concentrations of the products.
*Equilibrium **DOES MEAN** that the reactants are used up at the same rate that they are reformed so that the concentration does not change

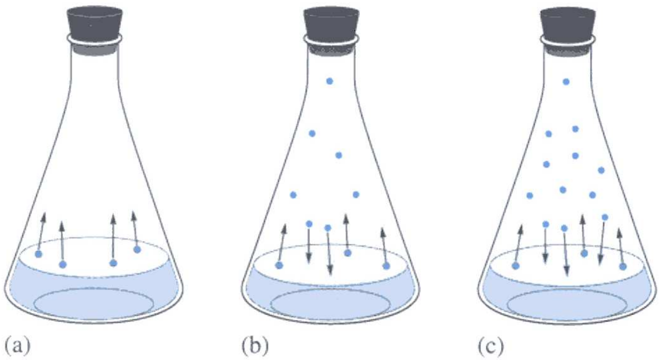


In order for a system to be able to reach equilibrium, it must meet the following conditions:

1. the reaction must be **reversible**

2. the system must be **closed** with respect to the reaction that you are considering (no reactants, products or energy may leave or enter the system)

eg. for the physical change: **H_2O (l) ↔ H_2O (g) ,** an open beaker of water can not reach equilibrium, because as the water evapourates, it leaves the system. On the other hand, a sealed jar of water can reach equilibrium with water molecules evapourating at the same rate that they re-condense back into liquid water



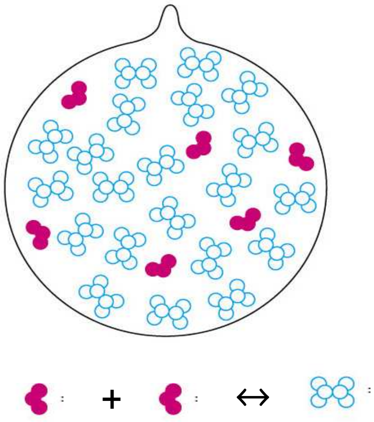
3. the observable (macroscopic) appearance of the system at equilibrium is constant. Once equilibrium is reached, its **properties are constant**

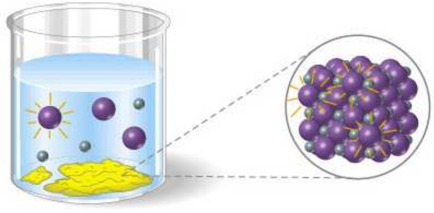
eg. referring back to our sealed jar of water, the water level will not change after equilibrium is reached

4. For a reaction, equilibrium can be reached from either direction: if we start with reactants and they react to form products, or we start with products and they form reactants, we will reach exactly the same equilibrium conditions.

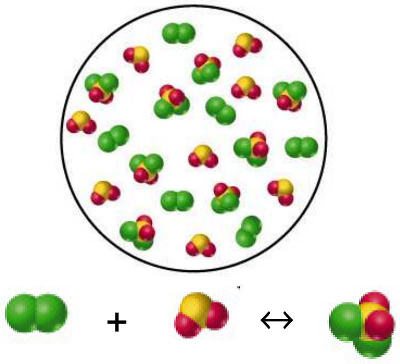
eg. If you fill a jar with steam and let it condense, or put liquid water in the jar and let it evaporate, it will reach exactly the same equilibrium point (as long as the system is closed with regard to the reactants and the products)

The following diagrams illustrate reversible reactions in closed systems that have reached equilibrium:



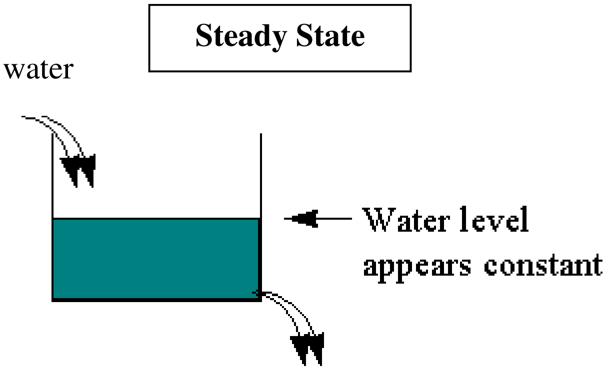


Al^{3+} (aq) + N^{3-} (aq) ↔ AlN (S)



Some open systems may have constant properties, but they are not at equilibrium, they are at a steady state.
For example, most people do not change their weight significantly from day to day- their observable properties are constant. But- there is a steady input of food and a steady output of wastes- so the system is not closed. Living systems do not reach equilibrium (instead, they are said to be in "homeostasis" or a "steady state").

Similarly, a burning candle may have a constant flame and a constant rate of reaction. But it is using up the wax and producing carbon dioxide. The reverse reaction will not occur- you will not see carbon dioxide and water recombining to produce wax. A burning candle is a steady state- not equilibrium.



When we discuss equilibrium systems, we must consider two different types of closed systems: homogeneous and heterogeneous.

Recall: a homogeneous catalyst is a catalyst that is in the same phase as the system it catalyzes, while a heterogeneous catalyst is one which is in a different phase than the system.

Similarly, a **homogeneous equilibrium** system is a closed system in which all of the reactants and products are in the same phase. A **heterogeneous system** is a closed system in which all of the reactants and products are not in the same phase.

For example:

1. The equilibrium system: $\mathbf{2\,H_2O\,(l) \leftrightarrow 2\,H_2\,(g) + O_2\,(g)}$ is a heterogeneous system because oxygen and hydrogen are both gases, while water is in the liquid state.

2. The equilibrium system: $\mathbf{2\,NO_2\,(g) \leftrightarrow H_2O_4\,(g)}$ is a homogeneous system because the reactants and products are all in the gas state.

3. The equilibrium system: $\mathbf{NaCl\,(s) \leftrightarrow Na^{1+}\,(aq) + Cl^{1-}\,(aq)}$ is a heterogeneous system because the NaCl is a solid, while the ions are aqueous.

Homework:

1. Read pages 322 to 327 in McGraw-Hill
2. Answer questions 1, 2, 3, and 4 on page 327