# Equilibrium

# Reversible reactions

- All chemical reactions are reversible.
- This means after the reactants make products, some of the products re-react to create the reactants.
- All reactions are therefore dynamic, meaning both processes are always happening.
- Which reaction is favored is all based on probabilities under the conditions that the reaction is taking place.
- These conditions include the amount of the substances, temperature, and pressure among other things.

# Collision theory

- In order for two reactants to react, two things must happen.
  - First they have to bump into each other at the right angle to initiate the reaction.
  - Second they need to have the energy needed to overcome the activation energy.
- If either of these two things are not right then the reaction will not occur.

# Equilibrium expressions

- A mathematical relationship can be written that represents the likely concentrations of reactants and products.
- The mathematical expression is equal to a constant, or “k” value.
- This k value is different depending on the conditions and either is given or must be determined.
- The k value is also equal to the ratio of the concentrations of the products over the concentration of the reactants.
- [ ] = concentration

# Sample expression

- For the reaction:

$$CH_{4(g)} + 2O_{2(g)} \leftrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

- The equilibrium expression is:

$$k_{eq} = \frac{[CO_2][H_2O]^2}{[CH_4][O_2]^2}$$

- Only gases and aqueous compounds are written in the expression.
- Solids and liquids have no effect on equilibrium and so they are ignored.
- The coefficients in the balanced equation go as exponents in the expression.

# K values

- Since the k value is the ratio of products to reactants, then it tells us what we are likely to see in the container at equilibrium.
  - A k > 1 means that products will be found in higher concentrations than reactants. (Or the foreward reaction is favored.)
  - A k = 1 means products and reactants will be found in equal concentrations. (Or both foreward and reverse reactions have equal probabilities)
  - A k < 1 means that reactants are more likely to be found than products. (Or the reverse reaction is favored.)

# Le Chatelier's Principle

- Le Chatelier stated that if a system is at equilibrium, then if you change anything about the system, it will attempt to undo what you have done.
  - Add a substance, it will try to remove it.
  - Add heat and it will try to use it.
  - Raise the pressure and it will try to lower it.
  - The opposite of each of these is also true.
- When it attempts to undo it we say that the equilibrium shifts in the direction of that reaction.

# Another way to look at it

- If heat is added it will help the endothermic process because now the endothermic process will have the activation energy needed.
- If pressure is added, the reaction will shift in the direction of where there are fewer moles of gas. This will lower the pressure by reducing number of molecules and number of collisions.
- If more of one substance is added, then there will be more collisions with the other substance on that side so the reaction will shift toward the other side.
- The opposite of all of these is also true.

# Examples of shifts (temperature)

- $Mg_{(g)} + 2HCl_{(aq)} \leftrightarrow MgCl_{2\,(aq)} + H_{2\,(g)} + 574kJ$
- If the temperature is dropped what will happen?
- The exothermic process will be favored because it does not need as much activation energy.
- Or the equilibrium will try to release more energy to raise the temperature.
- Therefore the amount of reactants will go down, and the amount of your products will go up.

# Examples of shifts (Pressure)

- $Mg_{(s)} + 2HCl_{(aq)} \leftrightarrow MgCl_{2\,(aq)} + H_{2\,(g)} + 574kJ$
- If the pressure is decreased what will happen?
- The forward reaction will be favored because there are more moles of gas on the product side.
- Or the equilibrium will try to increase pressure.
- Therefore the amount of reactants will go down, and the amount of your products will go up.

# Examples of Shifts (Amounts)

- $Mg_{(s)} + 2HCl_{(aq)} \leftrightarrow MgCl_{2\,(aq)} + H_{2\,(g)} + 574kJ$
- If the amount of HCl is decreased what will happen?
- The reverse reaction will be favored because there less reactant molecules available to collide.
- Or the equilibrium will try to increase the amount of HCl.
- Therefore the amount of reactants will go up, and the amount of your products will go down.