EQUILIBRIUM

Definitions:

Dynamic equilibrium – a reversible reaction where the forward and reverse reaction rates are equal. (Note: This does NOT mean equal reactants and products)

Reversible reaction – a reaction where the products can successfully collide to re-form the reactants. Not all reactions are reversible, combustion, for example, is not.

Conditions Necessary for Equilibrium:

1. **Closed system**
2. **Constant temperature/pressure**
3. **Reversible reaction**
4. **Forward Rate = Reverse Rate**
5. **Constant macroscopic properties (like pH, colour, mass, volume, etc.)**

<u>How Equilibrium is Established</u>:

Take a chemical reaction A $\leftrightarrow$ B

Initially, since A is the reactant, [A] is high and [B] is 0. At the start, the forward reaction is fast and the reverse reaction is non-existent because not enough B has built up to collide back into A. As the A gets used up, the [B] increases, and the reverse reaction speeds up.

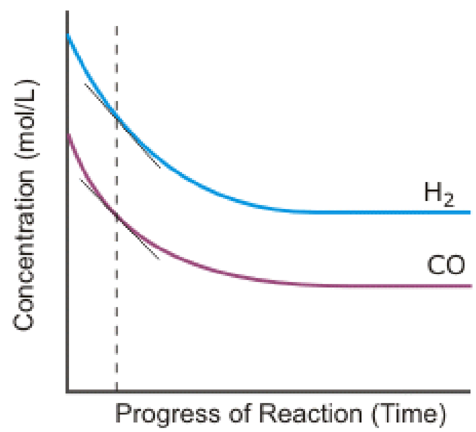
When the forward rate equals the reverse rate EQUILIBRIUM is reached. Please remember this balance is the rates, not concentrations of products and reactants. Depending on the reaction, one is normally favoured.

<u>Graphs and Achieving Dynamic Equilibrium</u>

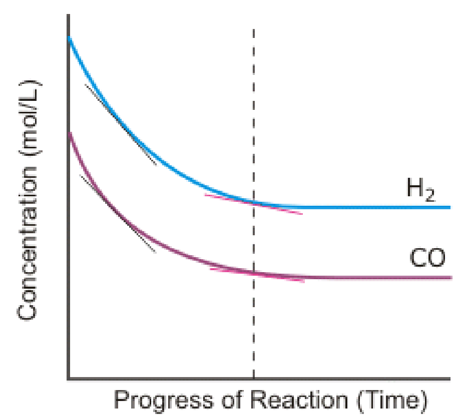
Consider this equation for a dynamic equilibrium involving carbon monoxide, hydrogen, and methanol:

$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$

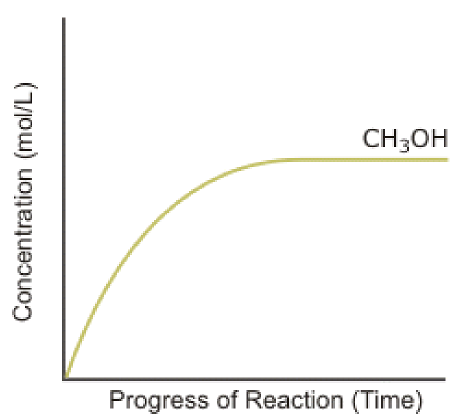
CO and H_2 are put into a sealed flask. At time zero, the concentrations are at their maximum, so initial reaction will be fast. We can see this by looking at the slope of the tangent on the graph.



As the forward reaction proceeds, their concentrations will decrease, and due to fewer collisions, their reaction rate will decrease over time. You can see this by looking at tangents further along on the curve.

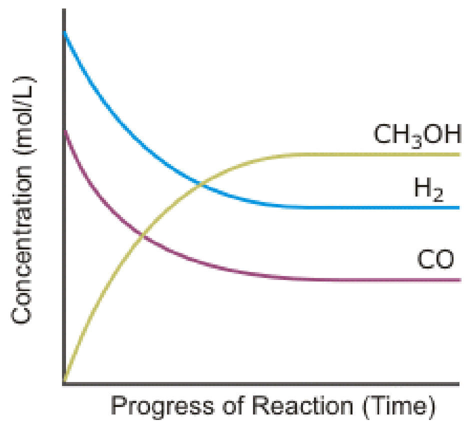


At zero time there isn't any CH_3OH. Its concentration increases as the forward reaction continues.



Its rate of formation will also eventually decrease because the reverse reaction will proceed and it will decompose back into H_2 and CO.

Eventually the rates will both equalize and the amounts for all three will become stable. **There are no further changes in their amounts but the reactions are still occurring. This is dynamic equilibrium**



NOTE THAT THE CONCENTRATIONS ARE NOT EQUAL, BUT THEY REMAIN CONSTANT. ONLY THE RATES OF REACTION ARE EQUAL.

Disturbing (Perturbing) Equilibrium

A French chemist by the name of Henri LeChatelier studied equilibrium extensively. He developed a series of laws that explained what would happen when equilibrium was disturbed.

He said when it is disturbed, the equilibrium will shift to try and compensate for the change. This will cause the concentrations of reactants and products to change until a new equilibrium forms. Either the forward reaction rate will increase, which decreases the concentrations of the reactants and increases the concentrations of the products, or the reverse reaction rate will increase, causing an increase in the reactant concentrations and a decrease of the product concentrations.

Let's examine how equilibrium shifts when the following changes are made to the reaction:

A. Concentration

*Changes in concentrations affect gaseous or aqueous systems the most.

GENERAL RULE: INCREASE THE CONCENTRATION OF A SPECIES AND EQUILIBRIUM SHIFTS AWAY FROM THE INCREASE (NATURE TRIES TO USE IT UP)

Fe^{3+} (aq) + SCN^- (aq) $\leftrightarrow$ $FeSCN^{2+}$
(orange) (colourless) (red-orange)

If we add more Fe^{3+} ions, they will react with the SCN^- ions, decreasing $[SCN^-]$. This will cause an increase in the forward reaction rate and $[FeSCN^{2+}]$ will increase. This would be seen as the mixture turning red-orange.

GENERAL RULE: DECREASE THE CONCENTRATION OF A SPECIES AND EQUILIBRIUM SHIFTS TOWARDS THE DECREASE (NATURE TRIES TO PUT IT BACK)

Fe^{3+} (aq) + SCN^- (aq) $\leftrightarrow$ $FeSCN^{2+}$
(orange) (colourless) (red-orange)

If we remove Fe^{3+} ions, there will be fewer collisions with the SCN^-, and the forward rate will slow. There will be more reverse reaction instead to put back the Fe^{3+}, so the concentrations of both the SCN^- and the Fe^{3+} will increase and the $[FeSCN^{2+}]$ will decrease.

B. Temperature

How temperature affects the position of equilibrium depends on whether the reaction is exothermic or endothermic.

GENERAL RULE: **INCREASING TEMPERATURE** WILL SPEED UP COLLISIONS ON BOTH SIDES BUT WILL ULTIMATELY **SHIFT AWAY FROM THE ENERGY TERM**

$2SO_2$ (g) + O_2 (g) → $2SO_3$ (g) + energy

Since this is an exothermic reaction, an increase in temperature would cause a shift away from the side with the energy term. Equilibrium will shift towards the reactant side, which will increase the [SO_2] and [O_2]. And decrease the [SO_3]. Think of it as nature trying to get rid of the excess energy.

GENERAL RULE: **DECREASING TEMPERATURE** WILL SPEED UP COLLISIONS ON BOTH SIDES BUT WILL ULTIMATELY **SHIFT TOWARDS THE ENERGY TERM**

$2SO_2$ (g) + O_2 (g) → $2SO_3$ (g) + energy

Since this is an exothermic reaction, a decrease in temperature would cause a shift towards the side with the energy term. Equilibrium will shift towards the product side, which will decrease the [SO_2] and [O_2] and increase the [SO_3]. Think of it as nature put energy back.

C. Change in Pressure (this is for GASES ONLY)

If you increase the pressure, it pushes molecules closer together, so the side of the equation with the most gaseous moles (add the coefficients) will react more, thereby shifting to the side of the least gaseous moles.

3 H_2 (g) + N_2 (g) → 2 NH_3 (g)

4 moles of gas 2 moles of gas

Increase pressure will shift to the product side (least number of gaseous moles), increasing the [NH_3]

Decreasing the pressure will have the opposite effect. It shifts equilibrium to the side with the greatest number of gaseous moles. This will increase the concentrations of both the hydrogen and the nitrogen.

GENERAL RULE: INCREASING PRESSURE SHIFTS EQUILIBRIUM TO SIDE WITH LEAST NUMBER OF GASEOUS MOLES

GENERAL RULE: DECREASING PRESSURE SHIFTS EQUILIBRIUM TO THE SIDE WITH THE GREATEST NUMBER OF MOLES.

D. Change in Volume (this is for GASES ONLY)

Since volume has an inverse relationship with pressure, the following shifts will happen:

GENERAL RULE: INCREASING THE VOLUME (DECREASING THE PRESSURE) WILL CAUSE A SHIFT TO THE SIDE WITH THE GREATEST NUMBER OF GASEOUS MOLES.

DECREASING THE VOLUME (INCREASING THE PRESSURE) WILL CAUSE A SHIFT TO THE SIDE WITH THE LEAST NUMBER OF GASEOUS MOLES.

E. Adding a catalyst

Adding a catalyst will speed up the reactions on BOTH sides, forward and reverse, therefore **equilibrium will not shift to favour either side.**

F. Changing the Surface Area

Like adding a catalyst, changing the surface area will **not affect** the position of equilibrium.