Something to Note:

Many reactions never go to completion

Once some product is formed, reactants begin to reform

These are called ***reversible reactions***

Let's start by saying:

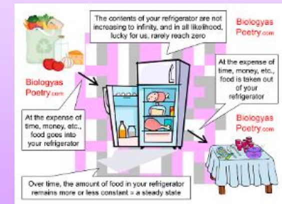
There are ***3 types of systems***

Steady-State System

- Exhibits ***constancy*** of properties
- Exhibits ***no evidence of reversibility***

Ex: stream/water

burner/molecules



Open System

- Exhibits no constancy of properties
- Can exchange mass and heat energy
- May exhibit some evidence of reversibility

Ex: evaporation

Closed System

- Exhibits constancy of properties
- Matter cannot be exchanged
- Heat can be exchanged
- Exhibits reversibility
- Equilibrium systems are this type!

Ex: closed jar of liquid/vapor

$$\text{Ex:}\quad \left.\begin{array}{l} 2\,HgO \rightarrow 2\,Hg + O_2 \\ 2\,HgO \leftarrow 2\,Hg + O_2 \end{array}\right\} \; 2\,HgO \leftrightarrows 2\,Hg + O_2$$

Initially, only the forward reaction occurs

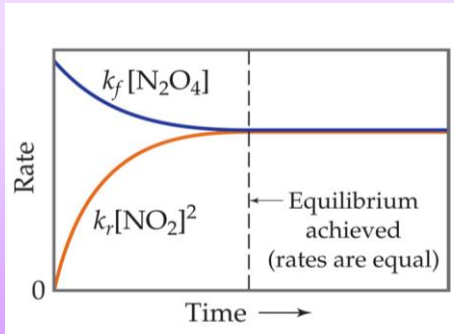
Then, the reverse reaction begins and increases in rate

As time continues, the forward reaction decreases in rate

Eventually, the forward rate equals reverse rate

Equilibrium

$R_f = R_r$



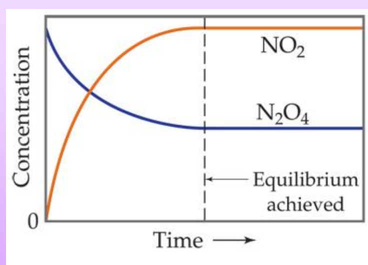
Chemical Equilibrium

The point at which concentrations of reactants and products in a closed system remain constant

Occurs when opposing reactions proceed at equal rates

$R_f = R_r$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$



Once equilibrium is reached,

it appears that the reaction has stopped because concentrations don't change.

However…

The reactions (collisions) do not cease!

So it's really **"Dynamic Equilibrium"**

Equilibrium Expression

A quantitative expression of the equilibrium position

A ratio of products to reactants at equilibrium

The rate of a reaction is proportional to the concentration of the reactants

Ex: $A \leftrightarrows B$

$R_f = k_f[A]$ $R_r = k_r[B]$

At equilibrium … $R_f = R_r$

So….. $k_f[A] = k_r[B]$

And therefore … $\frac{k_f}{k_r} = \frac{[B]}{[A]} = K_{eq}$

Equilibrium Constant, K_{eq}

The magnitude of K_{eq} is a measure of the extent to which the reaction has taken place at equilibrium

$K_{eq} = 1$ conc. of reactant and product are equal

$K_{eq} > 1$ concentration of products greater (favors the products, lies to the right)

$K_{eq} < 1$ concentration of reactants greater (favors the reactants, lies to the left)

When writing the equilibrium expression and calculating the equilibrium constant, the coefficients from the balanced equation become exponents on their corresponding concentrations.

Ex: $aA + bB \leftrightarrows cC + dD$

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Ex: Write the equilibrium expression for:

$H_2(g) + I_2(g) \leftrightarrows 2\,HI(g)$ at 100°C

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

There are two kinds of K_{eq}:

- K_c is the K_{eq} using molar concentrations, M
- K_p is the K_{eq} using partial pressures

pressure caused by a substance in the gas phase in units of atmospheres, atm

Ex: Write the equilibrium expressions for:

$H_2(g) + I_2(g) \leftrightarrows 2\,HI(g)$ at 100°C

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad K_p = \frac{P_{HI}^2}{P_{H_2}P_{I_2}}$$

You can convert between K_c and K_p

$K_p = K_c(RT)^{\Delta n}$

change in # of moles of gas

Kelvin temp

0.0821 (Gas Law Constant)

Ex: Calculate K_c for the following reaction at 100°C.

$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$

Equilibrium concentrations: $[H_2] = 0.31$ $[I_2] = 0.065$ $[HI] = 0.092$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.092)^2}{(0.31)(0.065)} = 0.42$$

Ex: Calculate K_p for the above K_c.

$K_p = K_c(RT)^{\Delta n}$

$= 0.42(0.0821 \times 373)^0$

$= 0.42$

NOTE: Keq's don't have units on them

Ex: An equilibrium mixture of H_2, I_2 and HI gases at 425°C consists of 4.6×10^{-3}M H_2, 0.74×10^{-3} M I_2, and 13.5×10^{-3}M HI. What is the equilibrium constant for the system at this temp?

<u>Homogeneous Equilibrium</u>

Reactions in which all species are in the same phase

Ex: $N_2O_4(g) \rightleftarrows 2NO_2(g)$

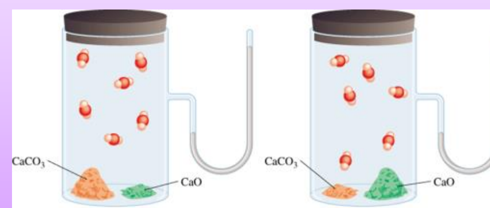
<u>Heterogeneous Equilibrium</u>

Reactions with substances in more than one phase

Ex: $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$

NOTE: Concentrations of **solids and liquids** are **not** included in the equilibrium expression

At a constant temperature, the concentration of a liquid or solid is constant and therefore, are incorporated into the K_{eq}



$CaCO_3(s) \rightleftarrows CO_2(g) + CaO(s)$

As long as some $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.

Ex: $BaCO_3(s) \rightleftarrows BaO(s) + CO_2(g)$

$$Keq = [CO_2]$$

Ex: $BaO(s) + CO_2(g) \rightleftarrows BaCO_3(s)$

$$Keq = \frac{1}{[CO_2]}$$

Reaction Quotient, Q

- The constant calculated using concentrations that aren't necessarily equilibrium concentrations
- If Q = Keq, the reaction is at equilibrium
- If Q < Keq, it is too far left (reactants favored)
  forward reaction is spontaneous
- If Q > Keq, it is too far right (products favored)
  reverse reaction is spontaneous

Ex: A ⇆ B   Keq = 4.4×10^{2}

$[A] = 2.3 \times 10^{-4}$, $[B] = 5.8 \times 10^{-3}$

Is the system at equilibrium?

$$Q = \frac{[B]}{[A]} = \frac{5.8 \times 10^{-3}}{2.3 \times 10^{-4}} = 2.5 \times 10^{1}$$

This system is not at equilibrium.

Too much reactant

Needs to move in the forward direction to reach equilibrium