Equilibrium Law

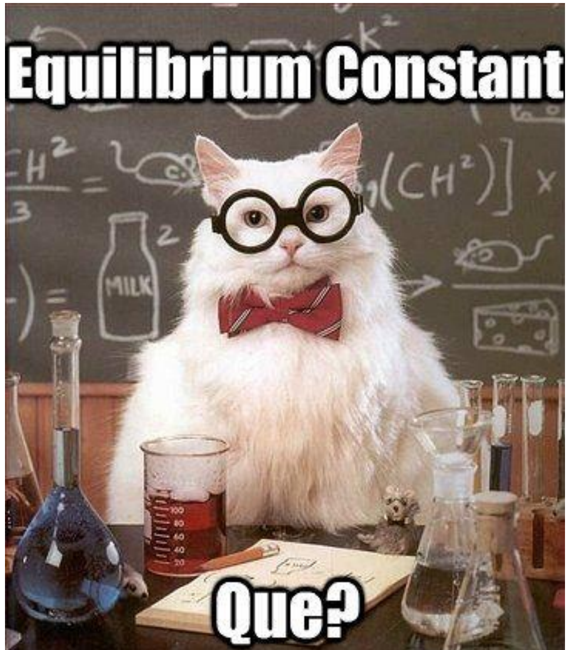
Outcome:

Write equilibrium law expressions from balanced reactions for heterogeneous and homogeneous systems.

Equilibrium Law…

Cato Guldberg and Peter Waage (1864):

- Proposed the **LAW OF MASS ACTION** or the **EQULIBRIUM LAW**.
- They studied many systems at equilibrium and found there was a **RELATIONSHIP** between the **CONCENTRATION** of **REACTANTS** and **PRODUCTS** at **EQUILIBRIUM**.
- They suggested the equilibrium law be a **RATIO** of **PRODUCT** concentrations to **REACTANT** concentrations.
- The value of this ratio is called the **EQUILIBRIUM CONSTANT**



Equilibrium Law…

They proposed that, for the reaction:

$$aA + bB \leftrightarrow cC + dD$$

The forward and reverse processes were elementary reactions. This means that:

$$Rate_{forward} = K_f[A]^a[B]^b$$

And

$$Rate_{reverse} = K_r[C]^c[D]^d$$

At equilibrium,

$$Rate_{forward} = Rate_{reverse}$$

So,

$$K_f[A]^a[B]^b = K_r[C]^c[D]^d$$

Equilibrium Law…

By rearranging the expression to solve for rate constants, we get:

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

The ratio of rate constants was condensed to one constant ***k_{eq}***, The **EQUILIBRIUM CONSTANT.**

The **LAW OF MASS ACTION** (Equilibrium Law) then states:

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

OR

$$k_{eq} = \frac{[products]}{[\mathrm{Re}\,acts]}$$

Homogeneous Equilibria:

Those where the reactants and products are all in the **SAME PHASE**. (solid, liquid, gas)

Example:

Write the equilibrium law for the following reaction:

$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

Heterogeneous Equilibria:

- Those where the reactants and products are in **DIFFERENT PHASES**.
- When writing **MASS-ACTION EXPRESSIONS**, substances which are **SOLIDS** or **LIQUIDS** are **OMITTED**.
- **SOLIDS** & **LIQUIDS** rarely change in **CONCENTRATION**, therefore are **NOT INCLUDED**.

Ex. The **CONCENTRATION** of **LIQUID WATER** will not **CHANGE** significantly over the course of a reaction.

Example:

Write the equilibrium law for the following reaction:

$$C_{(s)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2(g)}$$

Factors That Affect K_{eq}:

- **TEMPERATURE** is the **ONLY** factor that will affect the value of K_{eq}.
  - Consider the following **ENDOTHERMIC** reaction:

$$A + B + heat \rightleftarrows C$$

  - The ***Keq*** expression for this is:

- Now, let's say that we **INCREASE** ***the*** **TEMPERATURE** of this system.

- Adding **HEAT** to an **ENDOTHERMIC** reaction will make it **SHIFT** ***to the*** **RIGHT*:***

Shift to the Right

$$A + B + heat \rightleftarrows C$$

Factors That Affect K_{eq}:

- Because it **SHIFTS** ***to the*** **RIGHT*,*** a **NEW** equilibrium is established which has a ***higher [C]*** and a ***lower [A] and [B]*.**

- Therefore the ***Keq*** will have a **LARGER NUMERATOR** and a **SMALLER DENOMINATOR**:

$$Keq = \frac{[C]}{[A][B]}$$

This will make the value of ***Keq larger*** than it was before.

Therefore:

- When **TEMPERATURE** is increased in an **ENDOTHERMIC** reaction, K_{eq} **INCREASES**, if **DECREASED**, K_{eq} **DECREASES**.
- The **OPPOSITE** is true for **EXOTHERMIC** reactions.

NOTE:

- Changes in **CONCENTRATION**, **VOLUME**, or **PRESSURE** will **NOT** change the value of K_{eq}. The reaction may **SHIFT** one way or the other, but the **RATIO** of **PRODS**/**REACTS** will **NOT CHANGE**.