Kinetics Day 1: *Zoom!*

Chemical Kinetics: area of chemistry concerned with the rate of chemical reactions.

→ Simply because a reaction is considered spontaneous, implies NOTHING about the speed. *Spontaneous does not mean fast.*

→ Thermodynamics says "if." Kinetics says "how" and "how fast."

The Rate of a Chemical Reaction: a measure of how fast the reaction occurs.

→ The reaction rate of a chemical reaction is defined as the change in concentration of a reactant or product per unit time.

$$Rate = \frac{-\Delta[Reactant]}{\Delta time} \; OR \; \frac{\Delta[Product]}{\Delta time}$$

$$\text{Rate Unit: } \frac{\text{M}}{\text{time}}, \text{M time}^{-1}, \frac{\text{mol}}{\text{L time}}, \text{mol L}^{-1}\text{time}^{-1}$$

(Hint: all of these units are all the same thing!!)

For reactants, a – sign is placed in front of the definition. Because reactant concentrations decrease as a reaction proceeds, the change in the concentration in the reactants is negative. The negative sign thus makes the overall rate positive.

Reaction Rate Changes Over Time

- As time goes on, the rate of a reaction generally slows down because the concentration of the reactants decreases.
- At some point in time the reaction stops, either because the reactants run out or because the system has reached equilibrium.

Reaction Rate and Stoichiometry: For reactions in which the coefficients of the balanced equation are not all the same, the change in the number of molecules of one substance is a multiple of the change in the number of molecules of another.

To be consistent, the change in the concentration of each substance is multiplied by 1/coefficient.

Given the reaction: A + 3 B → 2 C

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$$

For example: given the following equation:

$$2NO_2(g) \rightarrow O_2(g) + 2NO(g)$$

If we know, through experimentation, that the rate of production of NO is 8.57×10^{-6} M/s, what is:

1. What is the rate of NO_2 consumption? same stoich coeff. ⇒ same rate!

   8.57×10^{-6} M/s

2. What is the rate of O_2 production? $1\ O_2 : 2\ NO \Rightarrow \frac{1}{2}$ the rate!

   $\frac{8.57}{2} \times 10^{-6} = 4.29 \times 10^{-6}$ M/s

Four Factors Affecting Reaction Rate: MEMORIZE THESE!!!!

1. Increasing the Surface area of a solid reactant can increase the rate by increasing the number of collisions between the reactant particles.
2. Catalysts increase the rate by lowering the activation energy of a reaction.
3. Increasing the temperature results in a faster reaction: heat 'em up, Speed 'em up!
   - ➔ The rate constant is temperature dependent and a rise in temperature will increase the rate constant!
4. Increasing concentration of reactants increases the number of reactants colliding with each other, thus yielding more product.

The Rate Law: the mathematical relationship between the rate of the reaction and the concentrations of the reactants and homogeneous catalysts as well.

➔ The rate law ***must*** be determined experimentally!

For the reaction $aA + bB \rightarrow \text{products}$

The rate law would have the form $\text{Rate} = k[A]^n[B]^m$

1. The exponent on each reactant, *n* and *m*, are called the order with respect to that reactant.
2. *k* is called the rate constant: a larger k means a faster reaction!
3. *n* and *m* are NOT necessarily the stoichiometric coefficients of A and B.
4. *n* + *m* = p, the overall **rate order** (*or* the order of the reaction).

Note: The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.

Example

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

the experimentally determined rate law is

$$\text{Rate} = k[NO]^2[O_2].$$

The reaction is said to be:

2nd order with respect to NO,

1st order with respect to O_2,

3rd order overall.

For example: given the following equation: $NO_2 + F_2 \rightarrow NO_2F + F$

If we know, through experimentation, rate law = $k[NO_2][F_2]^3$,

1. What the order of the reaction relative to NO_2? 1st order w/ respect to NO_2
2. What the order of the reaction relative to F_2? 3rd order w/ respect to F_2
3. What is the order of the reaction overall? 4th order overall (1+3=4 ☺)