CHEM 20B Week 10

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Measuring Reaction Rates

$$\text{average reaction rate} = \frac{\text{change in concentration of product}}{\text{change in time}}$$

Consider the example:

$$NO_2(g) + CO(g) \to NO(g) + CO_2(g)$$

Average rate $= \frac{\Delta[NO]}{\Delta t} = \frac{[NO]_f - [NO]_i}{t_f - t_i}$
Instantaneous rate $= \lim_{\Delta t \to 0} \frac{[NO]_{t+\Delta t} - [NO]_t}{\Delta t} = \frac{\mathrm{d}[NO]}{\mathrm{d}t}$

$$\text{rate} = \frac{\mathrm{d}[NO]}{\mathrm{d}t} = \frac{\mathrm{d}[CO_2]}{\mathrm{d}t} = -\frac{\mathrm{d}[CO]}{\mathrm{d}t} = -\frac{\mathrm{d}[NO_2]}{\mathrm{d}t}$$

In general, for reaction in form $aA + bB \to cC + dD$,

$$\text{rate} = -\frac{1}{a}\frac{\mathrm{d}[A]}{dt} = -\frac{1}{b}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{c}\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}[D]}{\mathrm{d}t}$$

The **net rate** of a reaction is the forward rate minus the reverse rate.

Order of a Reaction

$$rate = k[A][B]\dots$$

- This relation is called rate law and k is called the **rate constant**.
- k is independent of concentration but depends on **temperature**.

Example:
For a reaction in form $aA \to$ products, then the rate equation is:

$$rate = k[A]^n$$

- The power n in the rate expression has no direct relation to the coefficient of a in the balanced chemical equation.
- This constant is determined experimentally
- Therefore, the reaction order is an experimentally determined property.

Example: Rate of Decomposition of Ethane

$$C_2H_6(g) \to 2CH_3(g)$$
$$rate = k[C_2H_6]^2$$

The power n is the order of the reaction with respect to the reactant.

Determining Order of a Reaction

- Zeroth-order reaction:

$$rate = k$$

- First-order reaction:

$$rate = k[N_2O_5]$$

- Second-order reaction:

$$rate = k[C_2H_6]^2$$

$$rate = k[CH_3CHO]^{3/2}$$

In general, to find the order of a reaction, look at the experimental data and find the relationship between the change in rate and change in concentration. For example,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

At 443°C, the rate of reaction increases with concentration of HI as follows:

[HI] ($\mathrm{mol \cdot L^{-1}}$)	Rate ($\mathrm{mol \cdot L^{-1}s^{-1}}$)
0.0050	7.5×10^{-4}
0.010	3.0×10^{-3}
0.020	1.2×10^{-2}

Looking at the data, when the concentration of [HI] doubled (from 0.0050M to 0.010M), the rate increased by 4 times.
When the concentration of [HI] quadrupled (from 0.0050M to 0.020M), the rate increased by 16 times.
Therefore, the rate with respect to [HI] must be second order.

$$rate = k[HI]^2$$

With the exponent found, k can be determined with some algebra.