

CHEM 20B Week 10

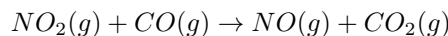
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Measuring Reaction Rates

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

Consider the example:



$$\text{Average rate} = \frac{\Delta[\text{NO}]}{\Delta t} = \frac{[\text{NO}]_f - [\text{NO}]_i}{t_f - t_i}$$

$$\text{Instantaneous rate} = \lim_{\Delta t \rightarrow 0} \frac{[\text{NO}]_{t+\Delta t} - [\text{NO}]_t}{\Delta t} = \frac{d[\text{NO}]}{dt}$$

$$\text{rate} = \frac{d[\text{NO}]}{dt} = \frac{d[\text{CO}_2]}{dt} = -\frac{d[\text{CO}]}{dt} = -\frac{d[\text{NO}_2]}{dt}$$

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

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

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

Order of a Reaction

$$\text{rate} = k[A][B] \dots$$

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

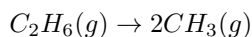
Example:

For a reaction in form $aA \rightarrow \text{products}$, then the rate equation is:

$$\text{rate} = k[A]^n$$

- 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



$$\text{rate} = k[\text{C}_2\text{H}_6]^2$$

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:

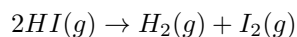
$$rate = k[N_2O_5]$$

- 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,



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

[HI] (mol · L ⁻¹)	Rate (mol · 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.