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Kinetics II

Factors that affect rxn rates

- molecules must collide in order to react
- the more readily the reactants collide, the more rapidly they react

physical state of the reactants

- homogeneous rxns are often faster than heterogeneous
- heterogeneous rxns involving solids are faster if the surface area is increased
- in order for a liquid fuel to burn it must be in the gas phase
- the Reid vapor pressure (RVP) represents a fuels volatility

Reactant concentrations

- increasing reactant concentration generally (but not always) increases rxn rate
- more molecules, more collisions

Effect of concentration on rate

$aA + bB \rightarrow xX$

$\text{rate} = k[A]^m[B]^n$ [the differential rate law]

→ where m and n, the reaction orders, are often whole numbers
→ k is the rate constant

Determining the rate law
- must be experimentally determined
- keep all reactant concentrations constant except for one, which varies in different experiments
- repeat for a different reactant until all reactants have been tested

The rate law shows the relationship btwn rate & concentration for all reactants
- the exponents reveal the order of the reaction with respect to each reactant

$\text{rate} = k[NH_4^+][NO_2^-]$

→ the order wrt each reactant is 1 (first order in NH_4^+ & NO_2^-)
→ the overall reaction is second order (1+1 = 2)

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

$\text{rate} = k[NO]^m[O_2]^n$

[NO]	$[O_2]$	rate (M/s)
0.2	0.01	1×10^{-4}
0.4	0.01	4×10^{-4}
0.2	0.04	4×10^{-4}

$m = 2$
$n = 1$
$\text{rate} = k[NO]^2[O_2]^1$
3rd order overall (m+n)

$k = \frac{\text{rate}}{[NO]^2[O_2]} \rightarrow k = \frac{1 \times 10^{-4}}{(0.2)^2(0.01)}$

Differential vs. Integral rate law

- differential rate law allows calculation of the rate from the reactant concentrations (or k from rate & concentrations)
- we can also predict concentration as a function of time, using the integrated rate laws

Differential rate law: First order

Ex) $CH_3NC \rightarrow CH_3CN$

rate = $k[CH_3NC]$

(experimentally determined)

- differential rate law expresses how rate depends on concentration

$$\text{rate} = k[CH_3NC] = -\frac{\Delta[CH_3NC]}{\Delta t} = -\frac{d[CH_3NC]}{dt}$$

slope of $[CH_3NC]$ vs. time

- we can transform the differential rate law into the integrated rate law by doing calculus

$$\ln[CH_3NC]_t = -kt + \ln[CH_3NC]_0$$

- plotting $\ln[CH_3NC]_t$ vs. time should yield a line w/ slope $-k$ and intercept $\ln[CH_3NC]_0$.

★first order kinetics