

[class notes] 2/18

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 fuel's volatility

Reactant concentrations

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

Effect of concentration on rate



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

→ 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

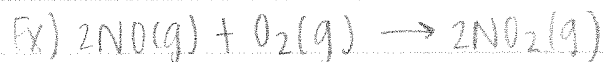
The rate law shows the relationship b/w rate & concentration for all reactants

- the exponents reveal the order of the reaction with respect to each reactant

$$\text{rate} = k [\text{NH}_4^+] [\text{NO}_2^-]$$

→ the order wrt each reactant is 1 (first order in NH_4^+ & NO_2^-)

→ the overall reaction is second order ($1+1=2$)



		$\text{rate} = k [\text{NO}]^m [\text{O}_2]^n$	
$[\text{NO}]$	$[\text{O}_2]$	rate (M/s)	
0.2	0.01	1×10^{-4}	$m = 2$
0.4	0.01	4×10^{-4}	$n = 1$
0.2	0.04	4×10^{-4}	$\text{rate} = k [\text{NO}]^2 [\text{O}_2]^1$
3rd order overall ($m+n$)			

$$k = \frac{\text{rate}}{[\text{NO}]^2 [\text{O}_2]} \rightarrow k = \frac{1 \times 10^{-4}}{(0.2)^2 (0.01)}$$

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



$$\text{rate} = k [\text{CH}_3\text{NC}]$$

(experimentally determined)

- differential rate law expresses how rate depends on concentration

$$\text{rate} = k[\text{CH}_3\text{NC}] = -\frac{\Delta[\text{CH}_3\text{NC}]}{\Delta t} = -\frac{d[\text{CH}_3\text{NC}]}{dt}$$

slope of $[\text{CH}_3\text{NC}]$ vs. time

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

$$\ln[\text{CH}_3\text{NC}]_t = -kt + \ln[\text{CH}_3\text{NC}]_0$$

- plotting $\ln[\text{CH}_3\text{NC}]_t$ vs. time should yield a line w/ slope $-k$ and intercept $\ln[\text{CH}_3\text{NC}]_0$.

★ first order kinetics