Class 9.1

Introduction to Chemical Kinetics

CHEM 102H

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Chemical Kinetics

- Reaction rates
  - "How fast?"
- Reaction mechanisms
  - "How?"
- Answers to these questions depend on the path taken from reactants to products.

Reaction Rates

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

- Follow progress by measuring any one concentration:

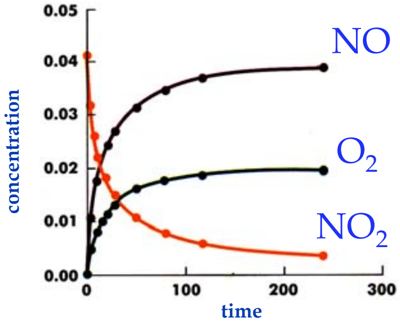
$$-\frac{d[A]}{dt},\ -\frac{d[B]}{dt},\ \frac{d[C]}{dt},\ \frac{d[D]}{dt}$$

Rates of change related by coefficients from balanced equation.

$2\ NO_2 \rightarrow 2\ NO + O_2$

rate =

$$-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$$



Factors That Influence Rates

- Identity & form of reactants, products
  - $H_2 + I_2$ *vs.* $H_2 + Br_2$
  - solution *vs.* gas phase, etc.
- Concentrations of various species
  - usually reactants
  - sometimes products, other species
- Temperature
  - usually, faster at higher T
  - strong dependence
- Catalysts

Concentration Effects: Rate Laws

$$\alpha A + \beta B \rightarrow \text{Products}$$

Empirically, usually find that

$$\text{Rate} = k[A]^n[B]^m$$

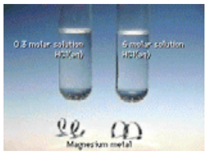
n = "order of reaction with respect to A"

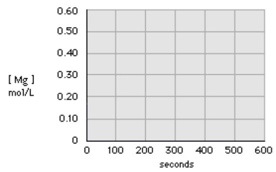
m = "order of reaction with respect to B"

n + m= "overall order of reaction"

k = rate constant = k(T)

Example: rate of a redox reaction





Reaction Orders

- Order of a reaction can NOT be found by looking at a balanced equation!

$$\alpha A + \beta B \rightarrow \text{Products}$$

$$\text{Rate} = k[A]^n[B]^m$$

- In general:
  α & n, β & m are <u>not necessarily equal</u>
- Reaction order can only be discovered in experiments

Examples

$$2\,N_2O_5 \rightarrow 4NO_2 + O_2$$

$$\text{rate} = k[N_2O_5]$$

- BUT

$$2\,NO_2 \rightarrow 2NO + O_2$$

$$\text{rate} = k[NO_2]^2$$

- CAN'T predict these from equations!

More Examples

$$H_2 + I_2 \rightarrow 2HI$$

$$\text{rate} = k[H_2][I_2]$$

- BUT

$$H_2 + Br_2 \rightarrow 2HBr$$

$$\text{rate} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr][Br_2]^{-1}}$$

Finding rate laws, rate constants

- "Method of Initial Rates"
  - combine known amounts of reactants
  - determine rate by measuring change in some concentration over a "short" time
  - repeat with different initial concentrations
  - find experimental rate law

Problem

$$A + 2B \rightarrow \text{products}$$

Expt.	$[A]_0$	$[B]_0$	Initial Rate
1	0.10	0.10	0.0032
2	0.10	0.20	0.0032
3	0.20	0.30	0.0128

- find rate law & rate constant, k
- (concentrations in M, rates in M/min)

Rates & Mechanisms

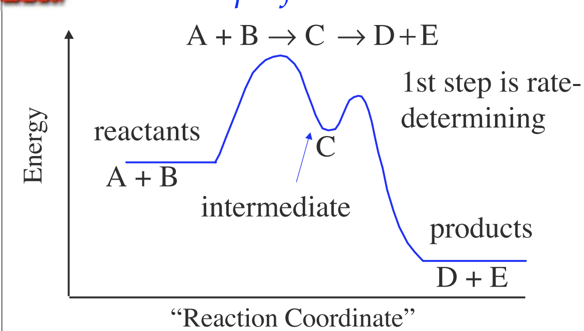
Experiments → Rate Law
Rate Law → Mechanism (?)

- MECHANISM: "The detailed molecular processes by which a chemical reaction proceeds." A series of *"elementary steps"* which combine to give an observed net reaction.

Rate laws & mechanisms

- Start with overall reaction
- Guess some mechanism(s)
- Derive corresponding rate laws
- Compare with experiments
- Repeat as needed
- **We need to relate rates of individual steps to the overall, observable rate laws.**

A reaction profile



Elementary Steps

- ELEMENTARY STEP: A chemical equation or reaction that describes a process as it occurs at the molecular level. A single reaction event which occurs in one simple atomic or molecular collision.
- Most reactions do not occur in a single elementary step.

Reactions vs. Elementary Steps

- Normal chemical eqs. tell us the overall stoichiometry of a reaction.

$$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$$

- Eq. for an elementary step looks just like a "normal" eq., but actually describes a simple molecular event.

$$NO_2 + NO_2 \rightarrow N_2O_4$$

Reactions vs. Elementary Steps

- Not always easy to tell an elementary step from a (slightly) more complicated reaction

$$2\ NO_2 \rightarrow N_2O_4$$
$$2\ NO_2 \rightarrow 2\ NO + O_2$$

- The first one is an elementary step, the second is not. You can't really tell this from the equations.

Types of Elementary Reactions

- Unimolecular decomposition: one molecule falls apart: $A \rightarrow$ Product(s)
- Bimolecular reaction: two reactant molecules collide: $A + B \rightarrow$ Product(s)
- Termolecular reaction: three reactant molecules: $A + B + C \rightarrow$ Product(s)

  (such steps rare in gas-phase and soln. rxns.)

☛ NO examples of more complex elementary reactions are known.

Rates of Elementary Steps

For an elementary step, the rate law can be written from the equation:

- $A \rightarrow$ Product(s) rate = $k[A]$
- $A + B \rightarrow$ Product(s) rate = $k[A][B]$
- $2A \rightarrow$ Product(s) rate = $k[A]^2$
- $A + B + C \rightarrow$ Product(s) rate = $k[A][B][C]$

  (not for gas phase reactions)

☛ Can ONLY write the rate expression for an elementary step!

Rate Determining Steps

- If a single step in a reaction mechanism is much slower than the other steps, then the rate of the slow step is crucial in determining overall rate.
- The rate determining step (RDS) can be thought of as a "bottleneck" in the formation of products. Steps that follow the RDS have negligible effect on the overall rate of reaction.