Introduction to Chemical Kinetics

CHEM 102

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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:

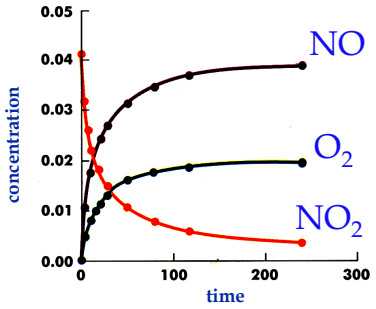
$$-\frac{1}{\alpha}\frac{\Delta[A]}{\Delta t}, \; -\frac{1}{\beta}\frac{\Delta[B]}{\Delta t}, \; \frac{1}{\gamma}\frac{\Delta[C]}{\Delta t}, \; \frac{1}{\delta}\frac{\Delta[D]}{\Delta t}$$

- Rates of change related by coefficients from balanced equation.

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

rate =

$$-\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$



Factors Which 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

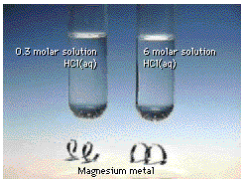
Concentration Effects: Rate Laws

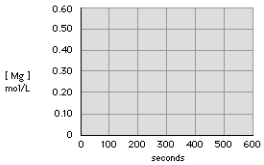
$$\alpha A + \beta B \rightarrow \text{Products}$$

- 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 not necessarily equal
  – because this isn't an elementary step
- Reaction order can only be found by 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

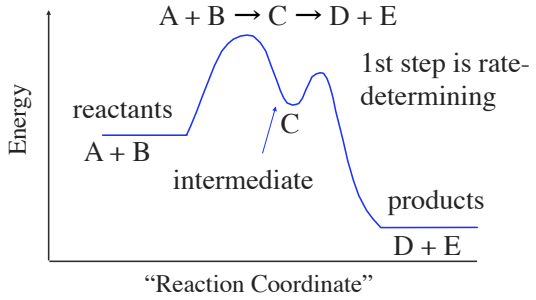
Experiments → Rate Law
Rate Law → Mechanism (?)

- 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 example



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 → Product(s)
- Bimolecular reaction: two reactant molecules collide: A + B → Product(s)
- Termolecular reaction: three reactant molecules: A + B + C → 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 → Product(s) rate = k[A]
- A + B → Product(s) rate = k[A][B]
- 2A → Product(s) rate = k[A]^2
- A + B + C → Product(s) rate = k[A][B][C]

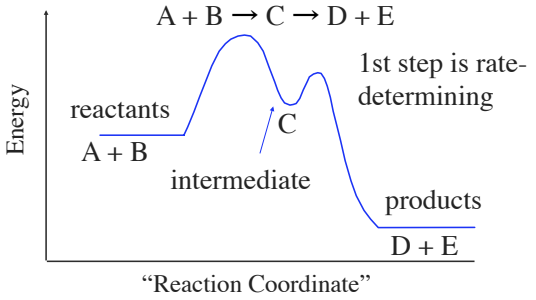
(not for gas phase reactions)

☛Can ONLY do this 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.

A reaction profile example



Example: rates & mechanisms

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

- Consider 2 mechanisms for this:
- $NO_2 \rightarrow NO + O$ (slow)
  $O + NO_2 \rightarrow O_2 + NO$ (fast)
- $2\,NO_2 \rightarrow NO_3 + NO$ (slow)
  $NO_3 \rightarrow NO + O_2$ (fast)

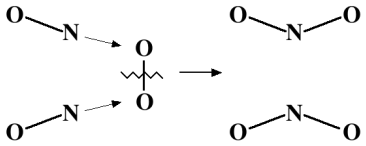
Example: rates & mechanisms

- experimental rate law is: rate = k[NO_2]^2
- $NO_2 \rightarrow NO + O$ (slow)
  $O + NO_2 \rightarrow O_2 + NO$ (fast)
  rate = ?
- $2\,NO_2 \rightarrow NO_3 + NO$ (slow)
  $NO_3 \rightarrow NO + O_2$ (fast)
  rate = ?

Rate Laws Can Prove a Mechanism is Wrong but Can't Prove one Right!

$2\ NO + O_2 \rightarrow 2NO_2$ rate = $k[NO]^2[O_2]$

A single step mechanism?



Rate Law is consistent.

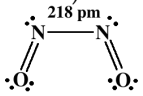
Rate Laws ... Proof?

$2\ NO + O_2 \rightarrow 2NO_2$ rate = $k[NO_2]^2[O_2]$

Two-step mechanism?

(1) $NO + NO \rightleftharpoons N_2O_2$ (fast equilibrium)

(2) $N_2O_2 + O_2 \rightarrow 2NO_2$ (slow)



Rate Law for this mechanism?

Mechanism & Rate

(1) $NO + NO \rightleftharpoons N_2O_2$ (fast equilibrium)

(2) $N_2O_2 + O_2 \rightarrow 2NO_2$ (slow)

- rate = rate of slow step = $k_2[N_2O_2][O_2]$
- N_2O_2 is a *reactive intermediate*, NOT a reactant or a product. We should eliminate it from the rate law.

Reversible Step: $2\ NO \rightleftharpoons N_2O_2$

$2\ NO \rightleftharpoons N_2O_2$ (fast)

- Rates of forward and backward reactions will quickly become equal.
- Set: rate forward = rate backward

  $k_f[NO]^2 = k_r[N_2O_2]$
- From this:

  $[N_2O_2] = (k_f / k_r)\,[NO]^2$

$2\ NO_2 + O_2 \rightarrow 2\ NO_2$, cont...

$2\ NO \rightleftharpoons N_2O_2$ (fast)

$N_2O_2 + O_2 \rightarrow 2NO_2$ (slow)

- rate = rate of slow step = $k_2[N_2O_2][H_2]$
- $[N_2O_2] = (k_f / k_r)\,[NO]^2$
- So:

  rate = $k_2\,[N_2O_2][O_2] = k_2\,(k_f / k_r)[NO]^2[O_2]$

  $= k_{observed}\,[NO]^2[O_2]$

Equilibrium: $2\ NO \rightleftharpoons N_2O_2$

The interconversion of products and reactants are an example of equilibrium

Set: rate forward = rate backward

$k_f[NO]^2 = k_r[N_2O_2]$

The Equilibrium Constant, K_{eq}, is defined as:

$$\frac{k_f}{k_r} = \frac{[N_2O_2]}{[NO]^2} = \textbf{constant} = K_{eq}$$

Reversible Step: $2\ NO \rightleftharpoons N_2O_2$

$$2\ NO \rightleftharpoons N_2O_2 \text{ (fast)}$$

- Rates of forward and backward reactions will quickly become equal.
- Set: rate forward = rate backward

  $k_f[NO]^2 = k_r[N_2O_2]$
- From this:

  $[N_2O_2] = (k_f / k_r)\,[NO]^2$

$2\ NO_2 + O_2 \rightleftharpoons 2\ NO_2$, ***cont...***

$$2\ NO \rightleftharpoons N_2O_2 \quad \text{(fast)}$$
$$N_2O_2 + O_2 \rightarrow 2NO_2 \quad \text{(slow)}$$

- rate = rate of slow step = $k_2[N_2O_2][O_2]$
- $[N_2O_2] = (k_f / k_r)[NO]^2$
- So:

  rate = $k_2\,[N_2O_2][O_2] = k_2 (k_f / k_r)[NO]^2[O_2]$

  $= k_{\text{observed}}\,[NO]^2[O_2] = k_2\,K_{eq}[NO]^2[O_2]$