CHEM 206 section 01

LECTURE #12 Wed. Feb.13, 2008

LECTURE TOPICS:

TODAY'S CLASS: **15.6**

NEXT CLASS: **finish Ch.15 (15.5)**

MIDTERM EXAM: **Fri. Feb.29th (all including Ch.15)**
in class

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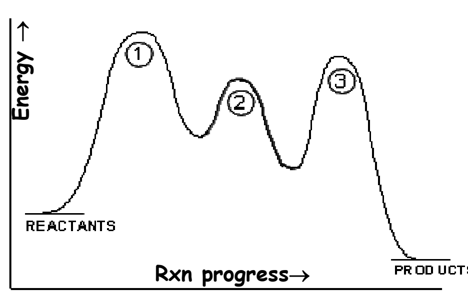
15.6 Reaction Mechanisms *(will do 15.5 last)*

- Kinetics exp'ts aim to find out: **HOW rxn WORKS**
- A chemical equation = summary of overall (NET) process
  → only sometimes matches actual steps involved…

STEP 1:	$2NO \rightarrow N_2O_2$
STEP 2:	$N_2O_2 + H_2 \rightarrow N_2O + H_2O$
STEP 3:	$N_2O + H_2 \rightarrow N_2 + H_2O$
NET:	$2NO + 2H_2 \rightarrow N_2 + 2H_2O$



A Rxn's Mechanism = the series of elementary steps
leading from reactants to products

"Elementary steps" = one-step molecular events

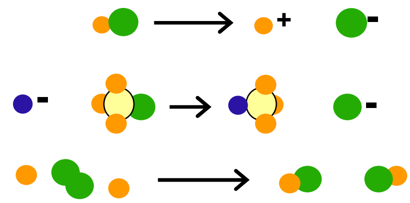
...e.g., all species collide simultaneously & react

Molecularity = # of molecules involved in elementary step

1: Unimolecular — *Decomposition...*

2: Bimolecular — *Probable ⇨ fast*

3: Termolecular — *Improbable ⇨ slow*



1 step (mechanism known) ⇨ rate law matches stoichiometry:

Elementary step	Molecularity	Rate law
A → products	unimolecular	Rate = k [A]
A + B → products	bimolecular	Rate = k [A][B]
2A → products	bimolecular	Rate = k $[A]^2$
2A + B → products	termolecular	Rate = k $[A]^2[B]$

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Mechanistically complex rxns: *MANY STEPS*

A known multi-step rxn: $2\ O_3(g) \rightarrow 3\ O_2(g)$

"decomposition" of ozone
(but not unimolecular...)

EXPERIMENTALLY DETERMINED MECHANISM:

step 1: $O_3 \rightarrow O_2 + O$

step 2: $O + O_3 \rightarrow 2O_2$

NET RXN: $2O_3 \rightarrow 3\ O_2$

- Can write the rate law for each elementary step...but...
- The net process cannot be faster than its SLOWEST STEP

  = **RATE-LIMITING** *OR* **RATE-DETERMINING STEP**

NOTE: in Chem 206, normally you will be told which step is slower
OR you'll be given the experimentally observed rate law
& then asked to deduce which step is slower

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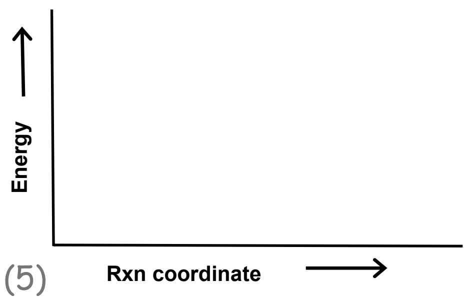
Rate-limiting step determines overall rate law…

- **If FIRST step is SLOWEST:**
  - → does not matter how fast the later steps are…
  - → observed rate law will match 1st step!

step 1: $O_3 \rightarrow O_2 + O$ — SLOWER: stable molecule falling apart

step 2: $O + O_3 \rightarrow 2O_2$ — FASTER: open-shell, reactive O atoms!

NET: $2O_3 \rightarrow 3\,O_2$ — rate = $k_1[O_3]$ because 1st step is RLS



"Intermediate" : O atoms

Species formed in one step but consumed in a subsequent step of the mechanism

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Rate-limiting step determines overall rate law…

- **If a later step is SLOWEST:**
  - → more complicated analysis required
  - → to predict overall rate law:
    - write rate law of RLS
    - will find that [intermediate]'s are involved
    - must figure out how to express these in terms of **original reactant species only**

…because: 1.) **we** do not control [intermediates]
2.) [intermediates] usually unmeasurably small

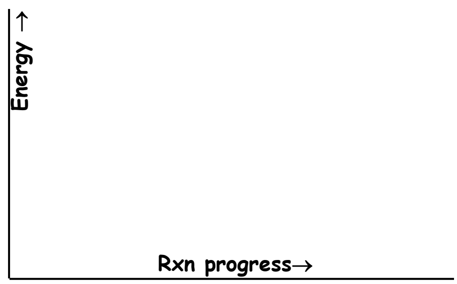
IN GENERAL:

- Steps **after** RLS are "fast" (relatively!)
  - ∴ DO NOT affect overall rate ⇒ not included in analysis…
- Steps **before** RLS must be considered
  - since they'll allow us to express [intermediate]'s in terms of reactant species

Industrial production of hydrazine: three-step mechanism

step 1: $NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$ **FAST**
step 2: $NH_2Cl + NH_3 \rightarrow N_2H_5^+ + Cl^-$ **SLOW**
step 3: $N_2H_5^+ + OH^- \rightarrow N_2H_4 + H_2O$ **FAST**

NET: $2\,NH_3 + OCl^- \rightarrow N_2H_4 + H_2O + Cl^-$



Slowest step = RLS = step 2
⇨ need only consider steps 2 & 1

Write rate law for RLS:

$$\text{Rate}(2) = k_2[NH_2Cl][NH_3]$$

↑ Intermediate, used in step 2
How much is around?

$\text{Rate}(1) = k_1[NH_3][OCl^-]$ ⇦ Rate of NH_2Cl production

$\text{Rate}(-1) = k_{-1}[NH_2Cl][OH^-]$ ⇦ Rate of NH_2Cl reverting back before slow step2 can occur…

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…Step before RLS is a "fast pre-equilibrium"
Intermediates form & unform at same rate ⇨ **[int.] ≈ constant**

To deal with fast pre-eqm:

1) Set form/unform rates equal
2) Solve for [int.]
3) Sub into RLS's rate law
4) Simplify
5) Note effective rate constant

⇨ predicted rate law for rxn

$$k_1[NH_3][OCl^-] = k_{-1}[NH_2Cl][OH^-]$$

$$\Rightarrow [NH_2Cl] = \frac{k_1}{k_{-1}}\frac{[NH_3][OCl^-]}{[OH^-]}$$

$$\Rightarrow \text{Rate}(2) = \frac{k_2 k_1}{k_{-1}}\frac{[NH_3][OCl^-]}{[OH^-]}[NH_3]$$

$$\textbf{Rate} = k_{eff}\frac{[NH_3]^2[OCl^-]}{[OH^-]}$$

If derived from a proposed mechanism:
• compare to exp'tally observed rate law
If matches this proposed rate law:
• mechanism "consistent" with experiment

Implication:
rxn inhibited if solution is basic

Evaluating a proposed reaction mechanism

CRITERIA: 1.) sum of steps = correct stoichiometry
2.) R.L.S. gives observed exp'tal rate law

A redox example: $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$

Proposed mechanism:

Step 1:	$H_2O_2 + I^- \rightarrow$	$H_2O + OI^-$	**SLOW**
Step 2:	$H^+ + OI^- \rightarrow$	HOI	**FAST**
Step 3:	$HOI + H^+ + I^- \rightarrow$	$I_2 + H_2O$	**FAST**

1.) mechanism's overall rxn?
2.) any intermediates?
3.) molecularity of each step?
4.) mechanism's RLS?
5.) mechanism's rate law?
6.) If the rxn is observed to be 1st order in H^+,
is this proposed mechanism reasonable?

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Using kinetics data: evaluating proposed reaction mechanisms

PROPOSING RXN MECHANISMS: (later in your career)

- After determining exptal rate law…
- Use "chemical intuition" to guess at reasonable steps
- Estimate rates of proposed steps (which is RLS?)

EVALUATING RXN MECHANISMS: can do it already!

- A possible proposed mechanism **must** have:
  1.) sum of steps = correct stoichiometric eqn for rxn
  2.) R.L.S. that would give observed exp'tal rate law
- If criteria met: mechanism "consistent" with expt

"PROVING" A MECHANISM: (via lots of experiments!)

→ requires careful expts designed to DISPROVE it!
→ can never *really* prove a mechanism…

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Extra Ex.2: Complex scenario: *K&T* Ch.15 #27-63-82 hybrid

Consider the rxn: $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$
Use the kinetics data to evaluate the proposed mechanisms.

Mechanism #1:
Single step: $NO_2 + CO \rightarrow CO_2 + NO$

Mechanism #2:
Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$
Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$
NET: $NO_2 + CO \rightarrow CO_2 + NO$

Mechanism #3:
Step 1: $NO_2 \rightarrow NO + O$
Step 2: $CO + O \rightarrow CO_2$
NET: $NO_2 + CO \rightarrow CO_2 + NO$

At a certain temperature > 500K:

RUN	INITIAL REACTANT CONC. ($mol{\cdot}L^{-1}$)		INITIAL RATE
	$[CO]_o$	$[NO_2]_o$	$mol{\cdot}L^{-1}h^{-1}$
1	5.0×10^{-4}	0.36×10^{-4}	3.4×10^{-8}
2	5.0×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
3	1.0×10^{-3}	0.36×10^{-4}	6.8×10^{-8}

ANALYSIS: At this T…

$[NO_2] \div 2 \Rightarrow$ rate $\div 2$
$\Rightarrow$ 1st order *wrt* NO_2

$[CO] \times 2 \Rightarrow$ rate $\times 2$
$\Rightarrow$ 1st order *wrt* CO

$\Rightarrow$ rate $= k_{obs}[NO_2][CO]$

$CO + NO_2 \rightarrow CO_2 + NO$ At T>500 K: rate $= k_{obs}[NO_2][CO]$

Mechanism #1:
1 step: $NO_2 + CO \rightarrow CO_2 + NO$
Predict: rate $= k[NO_2][CO]$ ✓

Mechanism #2:
Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$
Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$
Predict:
- If step 1 "slow": rate $= k_1[NO_2]^2$ ✗
- If step 2 "slow": rate $= k_2[NO_3][CO]$

assume rate$_1$ = rate$_{-1}$
$k_1[NO_2]^2 = k_{-1}[NO_3][NO]$

$$[NO_3] = \frac{k_1[NO_2]^2}{k_{-1}[NO]}$$

$$\text{rate} = k_2[CO]\frac{k_1[NO_2]^2}{k_{-1}[NO]} = k_{obs}\frac{[CO][NO_2]^2}{[NO]}$$ ✗

Note: at RT, exp'tally observed rate $= k_{obs}[NO_2]^2$ consistent with mechanism 2

MEANING: Different mechanism at higher temp.!

Mechanism #3:
Step 1: $NO_2 \rightarrow NO + O$
Step 2: $CO + O \rightarrow CO_2$
Predict:
- If step 1 "slow": rate $= k_1[NO_2]$ ✗
- If step 2 "slow": rate $= k_2[CO][O]$

assume rate$_1$ = rate$_{-1}$
$k_1[NO_2] = k_{-1}[NO][O]$

$$[O] = \frac{k_1[NO_2]}{k_{-1}[NO]}$$

$$\text{rate} = k_2[CO]\frac{k_1[NO_2]}{k_{-1}[NO]} = k_{obs}\frac{[CO][NO_2]}{[NO]}$$ ✓

Rxn inhibited by product.

$CO + NO_2 \rightarrow CO_2 + NO$ At T>500 K: rate = $k_{obs}[NO_2][CO]$

Mechanism #1: CONSISTENT

1 step: $NO_2 + CO \rightarrow CO_2 + NO$

Predict: rate = $k[NO_2][CO]$

Mechanism #2: CONSISTENT AT LOW T

Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

Predict:

- If step 1 "slow":
  rate = $k_1[NO_2]^2$

Note: at RT, exp'tally observed rate = $k_{obs}[NO_2]^2$
→ consistent with mechanism 2

MEANING: Different mechanism at higher temp.!

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Mechanism #3: CONSISTENT

Step 1: $NO_2 \rightarrow NO + O$

Step 2: $CO + O \rightarrow CO_2$

Predict:

- If step 2 "slow":
  rate = $k_2[CO][O]$

$$= k_{obs} \frac{[CO][NO_2]}{[NO]}$$

Rxn inhibited by product.

Would have to investigate further to rule out this mechanism.

NOTE: we can never say for sure that our mechanism is "correct", just consistent with experimental data.

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: Ch.15 (all)

+ WORK ON Problems from Ch.15

MIDTERM EXAM: Fri. Feb. 29th
covers: Ch. 6 (all), 9.8, 19.1-6, 13.1-5, 14 (all), 15 (all)
practice general Qs, & midterms on website

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