April 29, 2002

✓**Labs**

ALL LABS DUE NO LATER THAN:

MIDNIGHT, MAY 1st

✓**Final Exam**

- **Friday, May 10th - 8:30 am start time**
- ***Alternate day/time:*** I'll be in email contact with details
- **Review Session:** Wed., May 8th, noon (?), room TBA
- **Exam Info Page:** online by Wednesday

1

Reaction Mechanisms

- **3-Step Process**
  1. **Propose a Mechanism**
     - Sequence of *elementary reactions* which sum to the total reaction
  2. **Determine Rate Law from Mechanism**
     - Rate Law for any *elementary reaction*:

       $aA + bB \rightarrow$ products Rate = $k[A]^a[B]^b$
  3. **Compare Rate Law with Experiment**
     - Assess *plausibility* of the mechanism

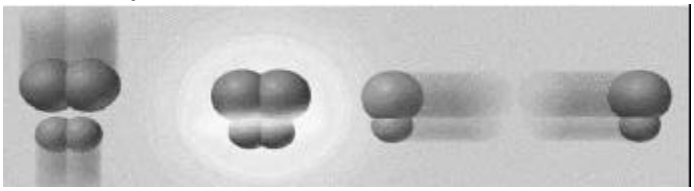
2

An Example

$$H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$$

Proposed Mechanism: *Single-Step*

✓Reaction proceeds as written: **bimolecular**



✓Rate = $k[H_2][I_2]$

✓Rate Law agrees with experiment

3

Another Mechanism

- A 2-Step Mechanism:

1. Iodine Dissociates (unimolecular process)

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2I \quad \textit{rapid, equilibrium}$$

Reactive Intermediate

2. Iodine atoms combine with H_2 (termolecular)

$$2I + H_2 \xrightarrow{k_2} 2HI \quad \textit{slow}$$

4

Rate Law from Mechanism

- *Slow Step* determines the rate:

$$\text{Rate} = k_2[H_2][I]^2$$

From Step 1: *Fwd Rate = Rev Rate* (equilibrium)

$$k_1[I_2] = k_{-1}[I]^2$$

Solve for $[I]^2$: $[I]^2 = (k_1/k_{-1})[I_2]$

Substitute: $$\text{Rate} = \frac{k_2 k_1}{k_{-1}}[H_2][I_2]$$

Finally: **Rate = k[H_2][I_2]** agrees with expt.

5

YAM (yet another mechanism)

- A 3-Step Mechanism:

1. Iodine Dissociates (unimolecular process)

$$I_2 \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} 2I \quad \textit{rapid, equilibrium}$$

2. Displacement

$$I + H_2 \xrightarrow{k_2} HI + H \quad \textit{slow}$$

3. Combine Remaining Atoms

$$H + I \xrightarrow{k_3} HI \quad \textit{fast}$$

6

On to the Rate Law

- From the *slow* displacement step:

$$\text{Rate} = k_2[I][H_2]$$

From Step 1: (equilibrium) *Fwd Rate = Rev Rate*

$$k_1[I_2] = k_{-1}[I]^2$$

Does NOT agree with experiment! MECHANISM 3 is not plausible.

Solve for [I]: $[I] = \{(k_1/k_{-1})[I_2]\}^{1/2}$

Substitute: $\text{Rate} = k_2(k_1/k_{-1})^{1/2}[I_2]^{1/2}[H_2]$

Finally: **$\text{Rate} = k[H_2][I_2]^{1/2}$**

7

Which Mechanism is Correct?

- Mechanisms I and II are both *plausible*
  (rate laws are consistent with experiment)
  - ✓Do additional experiments:
    look for the *reactive intermediate*
    (evidence for the existence of **I**?)
  - ✓**Results?**
    - ⇨Evidence favors ***Mechanism II***

8

Nuclear Chemistry

Chem 36

Spring 2002

Nuclear Review

- Some chemical reactions can involve changes in *nuclear* structure
- Nuclear Properties
  - ✓**Small Size:** radius ≈ 10^{-13} cm
  - ✓**High Density:** 1.6 x 10^{14} g/cm^3
  - ✓**HUGE Energies:** 10^{11} J/mol

10 million times smaller than atomic radius

2.5 billion ton golf ball

10