Announcements – Lecture IX – Tuesday, Feb 20th

1. Exam 1: Saturday, February 24th, ISB 155/160 (General Chemistry Labs)

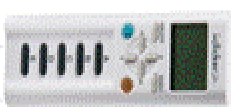
   Session I: 1:00-2:55, Last Name, A-J

   Session II: 3:00-4:55, Last Name, K-Z

   Anyone with extended time accommodation – go to Session I

   Make sure you bring your ID Card and place it on the desk for the duration of the exam.

2. iClicker:  Pick any letter a-e

3. Quiz 3: Place in basket.

14.6 Reaction Mechanisms and Catalysis

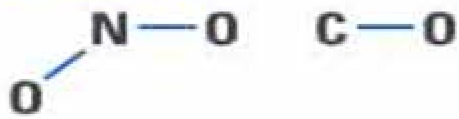
The Components of a Reaction Mechanism

Chemistry Interactive: Mechanism of The Reaction Between NO_2 and CO

Mechanism 1

Step 1. (slow, rate-determining step)

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$



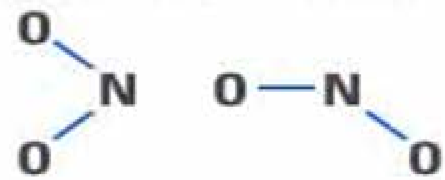
Why is the Rate ≠ $k[NO_2][CO]$?

Because experimentally it is found to be Rate = $k[NO_2]^2$!

Mechanism 2, Step 1

Step 1. (slow, rate-determining step)

$2\,NO_2(g) \longrightarrow NO_3(g) + NO(g)$



Mechanism 2, Step 2

Step 2. (fast)

$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$

14.6 Reaction Mechanisms and Catalysis

The Components of a Reaction Mechanism

Mechanisms:

Series of individual steps the sum of which must equal the overall chemical equation.

The series of steps are considered elementary steps in which the rate equation is that represented by the actual equation.

ELEMENTARY STEP: $2\ NO_2(g) = NO_3(g) + NO(g)$ Initial rate $= k[NO]^2$

THREE MAIN TYPES OF ELEMENTARY STEPS:

i) Unimolecular ... involving one molecule.
ii) Bimolecular ... involving two molecules.
iii) Termolecular ... involving three molecules ... these are rare ... why?

During a mechanism, three chemical events can take place.

- Bond breakage ... costs energy.
- Bond formation ... energy given back.
- Conserted process in which bond breakage and bond formation occur simultaneously.

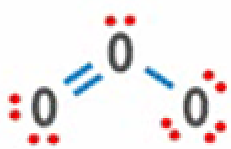
14.6 Reaction Mechanisms and Catalysis

Multistep Mechanisms

$2\ O_3(g) = 3\ O_2(g)$

Chemistry Interactive: Mechanism of Ozone Decomposition

Step 1	Unimolecular	$O_3(g) \longrightarrow O_2(g) + O(g)$
Step 2	Bimolecular	$O_3(g) + O(g) \longrightarrow 2\ O_2(g)$
Overall reaction		$2\ O_3(g) \longrightarrow 3\ O_2(g)$



Step 1:

This is a unimolecular process involving just bond breakage ... this would thus be expected to have a high activation energy.

Step 2:

This is a bimolecular process and is also a conserted process in that we get bond breakage and bond formation at the same time. Thus expect the activation of this step to be smaller than step 1.

Based on Ea, anticipate Step 1 to be the slow step and expect the rate of the reaction to be based on this step.

$$\text{Rate} = k[O_3]$$

14.6 Reaction Mechanisms and Catalysis

Reaction Mechanisms – Rate Law – Catalyst -- Intermediate

$NO_2(g) + CO(g) = NO(g) + CO_2(g)$

There are two proposed mechanisms for this reaction

Mechanism 1

Step 1: $NO_2(g) + CO(g) = NO(g) + CO_2(g)$ *Slow step*

Mechanism 2 ✓

Step 1: $2\,NO_2(g) = NO_3(g) + NO(g)$ *Slow step*

Step 2: $NO_3(g) + CO(g) = NO_2(g) + CO_2(g)$ *Fast step*

Experimentally the rate law = $k[NO_2]^2$

a) Which mechanism best supports the experimentally determined rate law?

b) Intermediate – 1) $NO_2(g)$ 2) $CO(g)$ 3) $NO_3(g)$ 4) $NO(g)$ 5) $CO_2(g)$ 6) None

c) Catalyst – 1) $NO_2(g)$ 2) $CO(g)$ 3) $NO_3(g)$ 4) $NO(g)$ 5) $CO_2(g)$ 6) None

a) Mechanism 2: The sum of the steps = the reaction. Step 1, the slow one, would give a rate = $k[NO_2]^2$ which matches that found experimentally.

b) INTERMEDIATE : Does not appear in the reaction equation. Appears as a product in one step and is then subsequently used up in another step.

c) CATALYST : Does not appear in the reaction equation. Appears as a reactant in one step and is then regenerated in a subsequent step.

14.6 Reaction Mechanisms and Catalysis

Reaction Mechanisms – Rate Law – Catalyst – Intermediate

$$Br_2(g) + H_2(g) = 2\ HBr(g)$$

Mechanism 2

Step 1: $Br_2(g) \Leftrightarrow 2\ Br(g)$ — *Fast in both directions*

Step 2: $Br(g) + H_2(g) = HBr(g) + H(g)$ — *Slow step*

Step 3: $H(g) + Br_2(g) = HBr(g) + Br(g)$ — *Fast step*

a) Intermediate – 1) $Br_2(g)$ 2) $Br(g)$ 3) $H(g)$ ✓ 4) $H_2(g)$ 5) $HBr(g)$ 6) None

b) Catalyst – 1) $Br_2(g)$ 2) $Br(g)$ ✓ 3) $H(g)$ 4) $H_2(g)$ 5) $HBr(g)$ 6) None

The rate is determined by the slow step.

Step 2: Rate = $k[Br][H_2]$

14.6 Reaction Mechanisms and Catalysis

More Complex Mechanisms

$$2\,H_2(g) + 2\,NO(g) = N_2(g) + 2H_2O(g)$$

Mechanism:

Step 1:	$2\,NO(g) \Leftrightarrow N_2O_2(g)$	*Fast in both directions*
Step 2:	$N_2O_2(g) + H_2(g) = N_2O(g) + H_2O(g)$	*Slow step*
Step 3:	$N_2O(g) + H_2(g) = N_2(g) + H_2O(g)$	*Fast step*

What is the rate law for this reaction? Is there an intermediate? Yes Is there a catalyst? No

Slow Step : Step 2

$Rate = k_2[N_2O_2][H_2]$ ↳ Intermediate.

Step 1, the formation of N_2O_2 is a fast equilibrium.

$Rate_f$ = Rate of forward reaction.

$Rate_R$ = Rate of reverse reaction.

@ equilibrium, $Rate_f = Rate_R$

$Rate_f = k_1[NO]^2$

$Rate_R = k_{-1}[N_2O_2]$

@ Eq : $k_{-1}[N_2O_2] = k_1[NO]^2$

$[N_2O_2] = (k_1/k_{-1})[NO]^2$

$Rate = k_2[N_2O_2][H_2]$

$= k_2(k_1/k_{-1})[NO]^2[H_2]$

$Rate = k[NO]^2[H_2]$ where $k = k_2\left(\frac{k_1}{k_{-1}}\right)$