

## Unit 9: Calculating the Units of the Rate Constant, k & Two Reaction Mechanisms

\*\*Know rate constant units: – (Order – 1) = power on M, power on time is always -1.

Rate =  $k [A]^2[B]^1$  Powers add up to 3, so 3<sup>rd</sup> order rate law.

units of  $k = M^{-(3-1)}\text{min}^{-1} = M^{-2} \text{min}^{-1}$

### Two Reaction Mechanisms:

#### Making a Sandwich

|         |              |            |            |
|---------|--------------|------------|------------|
| Bread   | Mustard      | Turkey     | Lettuce    |
|         | Mayonnaise   | Roast Beef | Pickles    |
|         |              |            | Onions     |
|         |              |            | Tomatoes   |
| 2 Bread | + Mustard    | + Turkey   | + Lettuce  |
|         | + Mayonnaise |            | + Tomatoes |

1)  $B + B \rightarrow I_1$  (intermediate)

2)  $I_1 + \text{Must} + \text{May} \rightarrow I_2$

3)  $I_2 + T \rightarrow I_3$

4)  $I_3 + L + To \rightarrow \text{sandwich}$

slow (need to cut more turkey) \*\*This will slow the line up to this point!

A slow 3<sup>rd</sup> step slows down the two steps behind.

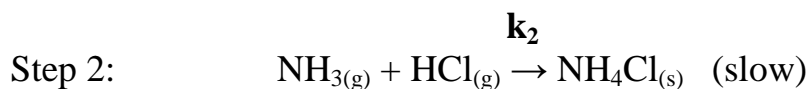
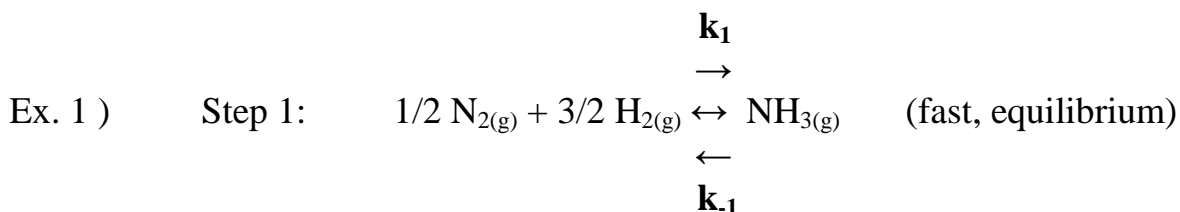
**Rate =  $k [I_2]^1 [T]^1$  3<sup>rd</sup> step, which is slow!**

$I_2$  is equivalent to  $I_1, \text{Must}, \text{and May}$  (from 2<sup>nd</sup> step)

Rate =  $k [I_1]^1 [\text{Must}]^1 [\text{May}]^1 [T]^1$

&  $I_1$  is equivalent to **2B** (from 1<sup>st</sup> step)

**Rate =  $k [B]^2 [\text{Must}]^1 [\text{May}]^1 [T]^1$**  is the overall rate law.



Find the rate law from the slow step #2:

Rate =  $k_2 [\text{NH}_3]^1 [\text{HCl}]^1$ , but in the equilibrium (step #1):

$$\text{forward rate} = \text{reverse rate}$$
$$k_1 [\text{N}_2]^{1/2} [\text{H}_2]^{3/2} = k_{-1} [\text{NH}_3]^1$$

$$\frac{k_1}{k_{-1}} [\text{N}_2]^{1/2} [\text{H}_2]^{3/2} = [\text{NH}_3]^1$$

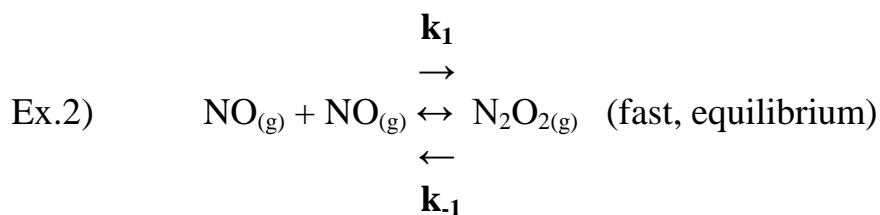
After substituting what  $[\text{NH}_3]$  equals, into the rate law from the slow step #2,

$$\text{Rate} = k_2 [\text{NH}_3]^1 [\text{HCl}]^1$$

$$\text{we get, Rate} = k_2 (k_1/k_{-1}) [\text{N}_2]^{1/2} [\text{H}_2]^{3/2} [\text{HCl}]^1$$

so the experimental rate constant  $k$  will equal  $(k_2 k_1/k_{-1})$

$$\text{so Rate} = k [\text{N}_2]^{1/2} [\text{H}_2]^{3/2} [\text{HCl}]^1$$



What is the expression relating the concentration of  $\text{NO}_{(g)}$  to that of  $\text{N}_2\text{O}_{2(g)}$ ?

forward rate = reverse rate

$$k_1 [\text{NO}]^1 [\text{NO}]^1 = k_{-1} [\text{N}_2\text{O}_2]^1$$
$$k_1 [\text{NO}]^2 = k_{-1} [\text{N}_2\text{O}_2]^1$$

$$[\text{NO}]^2 = (k_{-1}/k_1) [\text{N}_2\text{O}_2]^1$$

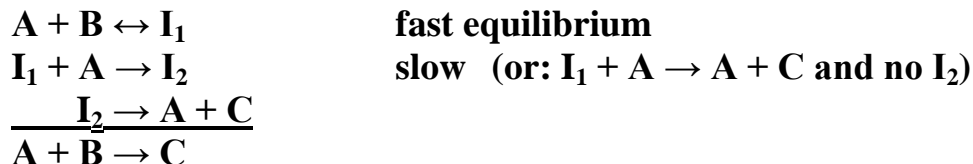
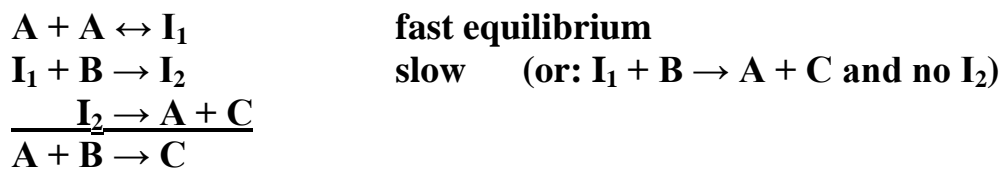
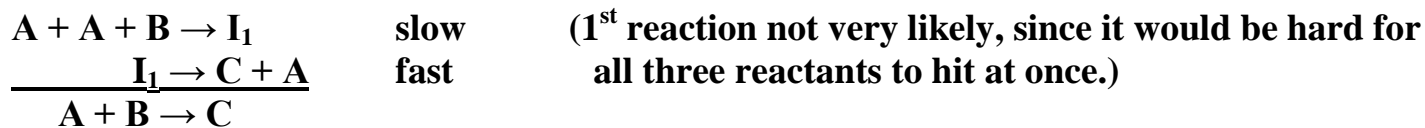
$$\sqrt{\{ [\text{NO}]^2 = (k_{-1}/k_1) [\text{N}_2\text{O}_2]^1 \}} \quad \text{square root both sides}$$

$$[\text{NO}] = ( (k_{-1}/k_1) [\text{N}_2\text{O}_2]^1 )^{1/2}$$

\*\* $k_{-1}/k_1$  would equal  $1/K_{\text{equilibrium}}$

$$(k_1/k_{-1} = \text{products/ reactants} = K_{\text{equilibrium}})$$

Ex. 3) Propose a stepwise mechanism consistent with the rate law of  $\text{Rate} = k [\text{A}]^2 [\text{B}]^1$  and the net reaction (net change) of  $\text{A} + \text{B} \rightarrow \text{C}$ .



### Relationship of Rates Between Different Reactants/Products

The rate of disappearance of different reactants and the rate of appearance of different products will be different values, proportional to the mol ratio of those substances in the reaction.

Ex. 1) What is the rate of disappearance of B in experiment #1, if the rate of disappearance of A in experiment #1 is  $2.2 \times 10^{-4}$ ?  $\text{A} + 2\text{B} \rightarrow 2\text{C}$

1<sup>st</sup> Method: Looking at the reaction, for each A that disappears, 2B must also disappear. So if  $2.2 \times 10^{-4}$  of A is disappearing, then  $4.4 \times 10^{-4}$  of B must be disappearing.

Generally:  $a \text{A} + b \text{B} \rightarrow c \text{C}$

$$\text{rate} = \frac{-1}{a} \frac{\Delta[\text{A}]}{\Delta t} = \frac{-1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{+1}{c} \frac{\Delta[\text{C}]}{\Delta t}$$

$$\text{rate} = \frac{-1}{1} \frac{\Delta[\text{A}]}{\Delta t} = \frac{-1}{2} \frac{\Delta[\text{B}]}{\Delta t} = \frac{+1}{2} \frac{\Delta[\text{C}]}{\Delta t}$$

$$\text{If } \frac{-\Delta[\text{A}]}{\Delta t} = 2.2 \times 10^{-4} \text{ then: } -1 (2.2 \times 10^{-4}) = \frac{-1}{2} \frac{\Delta[\text{B}]}{\Delta t}$$

$$4.4 \times 10^{-4} = \frac{\Delta[\text{B}]}{\Delta t}$$

2<sup>nd</sup> Method: Stoichiometry

$$\frac{2.2 \times 10^{-4} \text{ A disappearing}}{1 \text{ mols A}} \left| \frac{2 \text{ mols B}}{1 \text{ mols A}} \right. = \mathbf{4.4 \times 10^{-4} \text{ B disappearing}}$$

**\*End of Notes\***