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 3rd order rate law.

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

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 → I_1 (intermediate)
2) I_1 + Must + May → I_2
3) I_2 + T → I_3 slow (need to cut more turkey) **This will slow the line up to this point!
4) I_3 + L + To → sandwich

A slow 3rd step slows down the two steps behind.

Rate = k $[I_2]^1\ [T]^1$ 3rd step, which is slow!
I_2 is equivalent to I_1, Must, and May (from 2nd step)

Rate = k $[I_1]^1$ $[Must]^1$ $[May]^1$ $[T]^1$
& I_1 is equivalent to 2B (from 1st step)

Rate = k $[B]^2$ $[Must]^1$ $[May]^1$ $[T]^1$ is the overall rate law.

Ex. 1) Step 1: $\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NH_{3(g)}$ (fast, equilibrium)

Step 2: $NH_{3(g)} + HCl_{(g)} \xrightarrow{k_2} NH_4Cl_{(s)}$ (slow)

Find the rate law from the slow step #2:

Rate = $k_2\,[NH_3]^1\,[HCl]^1$, but in the equilibrium (step #1):

forward rate = reverse rate

$$k_1\,[N_2]^{1/2}\,[H_2]^{3/2} = k_{-1}\,[NH_3]^1$$

$$\frac{k_1}{k_{-1}}\,[N_2]^{1/2}\,[H_2]^{3/2} = \mathbf{[NH_3]^1}$$

After substituting what $[NH_3]$ equals, into the rate law from the slow step #2,

$$\text{Rate} = k_2\,\mathbf{[NH_3]^1}\,[HCl]^1$$

we get, $\text{Rate} = k_2\,\mathbf{(k_1/k_{-1})\,[N_2]^{1/2}\,[H_2]^{3/2}}\,[HCl]^1$

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

so $\mathbf{Rate = k}\,[N_2]^{1/2}\,[H_2]^{3/2}\,[HCl]^1$

Ex.2) $NO_{(g)} + NO_{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_{2(g)}$ (fast, equilibrium)

What is the expression relating the concentration of $NO_{(g)}$ to that of $N_2O_{2(g)}$?

forward rate = reverse rate

$$k_1\,[NO]^1\,[NO]^1 = k_{-1}\,[N_2O_2]^1$$

$$k_1\,[NO]^2 = k_{-1}\,[N_2O_2]^1$$

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

$\sqrt{\{\,[NO]^2 = (k_{-1}/k_1)\,[N_2O_2]^1\,\}}$ square root both sides

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

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

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

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

$A + A + B \rightarrow I_1$ **slow** **(1^{st} reaction not very likely, since it would be hard for all three reactants to hit at once.)**
$\underline{I_1 \rightarrow C + A}$ **fast**
$A + B \rightarrow C$

$A + A \leftrightarrow I_1$ **fast equilibrium**
$I_1 + B \rightarrow I_2$ **slow (or: $I_1 + B \rightarrow A + C$ and no I_2)**
$\underline{I_2 \rightarrow A + C}$
$A + B \rightarrow C$

$A + B \leftrightarrow I_1$ **fast equilibrium**
$I_1 + A \rightarrow I_2$ **slow (or: $I_1 + A \rightarrow A + C$ and no I_2)**
$\underline{I_2 \rightarrow A + C}$
$A + B \rightarrow C$

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 $X10^{-4}$? $A + 2B \rightarrow 2C$

1^{st} Method: Looking at the reaction, for each A that disappears, 2B must also disappear. So if 2.2 $X10^{-4}$ of A is disappearing, then **4.4 $X10^{-4}$** of B must be disappearing.

Generally: $a\,A + b\,B \rightarrow c\,C$

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

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

If $-\frac{\Delta[A]}{\Delta t} = 2.2\ X10^{-4}$ then: $-1\,(2.2\ X10^{-4}) = \frac{-1}{2}\ \frac{\Delta[B]}{\Delta t}$

$$\mathbf{4.4\ X10^{-4} = \frac{\Delta[B]}{\Delta t}}$$

2^{nd} Method: Stoichiometry

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

<u>*End of Notes*</u>