Some Examples of Experimental Rate Laws

– General rate law expression:

$$Rate = k[A]^m[B]^n \ldots$$

Examples: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Rate law → $Rate = k[N_2O_5]$

$m = 1$ → **first order in N_2O_5**

$m + n + \ldots = 1$ → **first order overall**

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

Rate law → $Rate = k[NO_2]^2$

$m = 2$ → **second order in NO_2**

$m + n + \ldots = 2$ → **second order overall**

Examples:

$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

Rate law → $Rate = k[CH_3Br][OH^-]$

$m = 1$ → **first order in CH_3Br**

$n = 1$ → **first order in OH^-**

$m + n + \ldots = 2$ → **second order overall**

$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$

Rate law → $Rate = k[(CH_3)_3CBr]$

same as → $Rate = k[(CH_3)_3CBr]^1[H_2O]^0$

$m = 1$ → **first order in $(CH_3)_3CBr$**

$n = 0$ → **zero order in H_2O**

$m + n + \ldots = 1$ → **first order overall**

- The reactions orders are not related to the stoichiometric coefficients of the reactants
- The reaction orders can sometimes be fractional or negative numbers
- The rate law can include concentrations of products

Examples:

$2O_3 \rightarrow 3O_2$

Rate law → $Rate = k[O_3]^2[O_2]^{-1}$

$2SO_2 + O_2 \rightarrow SO_3$

Rate law → $Rate = k[SO_2][SO_3]^{-1/2}$

$2NH_3 \rightarrow N_2 + 3H_2$

Rate law → $Rate = k$ → zero overall order

- The reactions orders can be determined by measuring the changes in the reaction rate upon changing the reactant concentrations

Example:

For the reaction **$2NO + 2H_2 \rightarrow N_2 + 2H_2O$**, the rate increases by a **factor of nine** when the concentration of **NO** is **tripled** while the concentration of **H_2** is kept constant. What is the order of the reaction with respect to **NO**?

Rate law → $Rate = k[NO]^m[H_2]^n$

$9 \times Rate = k(3 \times [NO])^m[H_2]^n = 3^m \times k[NO]^m[H_2]^n$

$9 \times Rate = 3^m \times Rate$

$\Rightarrow 9 = 3^m \rightarrow m = 2 \rightarrow 2^{nd}$ **order in NO**

Experimental Determination of Rate Laws

- Determination of reaction orders and rate constants
  - **The initial rate method** – the initial rate (***Rate***$_o$) of the reaction is measured at various initial concentrations ($[X]_o$) of the reactants

$$aA + bB \rightarrow \textbf{Products} \qquad Rate_o = k[A]_o^m[B]_o^n$$

→ If $[A]_o$ is increased by a factor, f, while $[B]_o$ is kept constant:

$$new\ Rate_o = k(f\times[A]_o)^m[B]_o^n = f^m\times k[A]_o^m[B]_o^n$$

$$new\ Rate_o = f^m\times Rate_o$$

⇒ The initial rate increases by a factor of f^m

Example: Determine the rate law for the reaction $O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$ from the following data:

Exp. #	Initial Conc. $\times10^{-2}$ (mol/L)		Initial Rate $\times10^{-3}$ (mol/L.s)
	O_2	NO	
1	1.1	1.3	3.2
2	2.0	1.3	5.8
3	1.1	3.0	17.0

→ Select experiments with the same concentrations of one of the reactants → (1, 2) and (1, 3)

→ Calculate the relative concentrations and rates by dividing with the smallest number in a column

Exp #	Relative Conc.			Relative Rate	
	O_2		NO		
1	1.1/1.1=1.0	×1.8	1.0	3.2/3.2=1.0	$\times1.8^1$
2	2.0/1.1=1.8		1.0	5.8/3.2=1.8	

Exp #	Relative Conc.			Relative Rate	
	O_2	NO			
1	1.0	1.3/1.3=1.0	×2.3	3.2/3.2=1.0	$\times2.3^2$
3	1.0	3.0/1.3=2.3		17.0/3.2=5.3	

⇒As $[O_2]_o$ increases by a factor of 1.8, the initial rate increases by a factor of $1.8=1.8^1$ → **1st order in O_2**

⇒As $[NO]_o$ increases by a factor of 2.3, the initial rate increases by a factor of $5.3=2.3^2$ → **2nd order in NO**

Alternative method:

Exp.#	Initial Conc. $\times10^{-2}$ (mol/L)		Initial Rate $\times10^{-3}$ (mol/L.s)
	O_2	NO	
1	1.1	1.3	3.2
2	2.0	1.3	5.8
3	1.1	3.0	17.0

→$Rate = k[O_2]^m[NO]^n$

#1 $\quad 3.2\times10^{-3} = k(1.1\times10^{-2})^m(1.3\times10^{-2})^n$

#2 $\quad 5.8\times10^{-3} = k(2.0\times10^{-2})^m(1.3\times10^{-2})^n$

#3 $\quad 17.0\times10^{-3} = k(1.1\times10^{-2})^m(3.0\times10^{-2})^n$

Divide eq.2 by eq.1 and eq.3 by eq.1 :

$$\frac{5.8}{3.2} = \frac{k\times2.0^m\times1.3^n}{k\times1.1^m\times1.3^n} \Rightarrow \frac{5.8}{3.2} = \left(\frac{2.0}{1.1}\right)^m \Rightarrow 1.8 = 1.8^m$$

1

$$\frac{17.0}{3.2} = \frac{k\times1.1^m\times3.0^n}{k\times1.1^m\times1.3^n} \Rightarrow \frac{17.0}{3.2} = \left(\frac{3.0}{1.3}\right)^n \Rightarrow 5.3 = 2.3^m$$

2

$\Rightarrow$ ***Rate*** **=** $\boldsymbol{k[O_2][NO]^2}$

$\rightarrow$The reaction is **3rd-overall order**

$\rightarrow$Determine the rate constant by substituting the initial concentrations and initial rate from one of the experiments and solve the equation for ***k***

$\rightarrow$From Exp. #1:

$$k = \frac{Rate}{[O_2][NO]^2} = \frac{3.2\times10^{-3}\ \text{mol/L}\cdot\text{s}}{1.1\times10^{-2}\,\text{mol/L}\times\left(1.3\times10^{-2}\,\text{mol/L}\right)^2}$$

$$k = 1.7\times10^{3}\ \text{L}^2/\text{mol}^2\cdot\text{s}$$

- Note that the units of ***k*** depend on the overall order of the reaction and are different for different rate laws