

Some Examples of Experimental Rate Laws

– General rate law expression:

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n \dots$$

Examples: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

Rate law $\rightarrow \text{Rate} = k[\text{N}_2\text{O}_5]$

$m = 1 \rightarrow$ first order in N_2O_5

$m + n + \dots = 1 \rightarrow$ first order overall

$2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$

Rate law $\rightarrow \text{Rate} = k[\text{NO}_2]^2$

$m = 2 \rightarrow$ second order in NO_2

$m + n + \dots = 2 \rightarrow$ second order overall

Examples:

$\text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$

Rate law $\rightarrow \text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$

$m = 1 \rightarrow$ first order in CH_3Br

$n = 1 \rightarrow$ first order in OH^-

$m + n + \dots = 2 \rightarrow$ second order overall

$(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HBr}$

Rate law $\rightarrow \text{Rate} = k[(\text{CH}_3)_3\text{CBr}]$

same as $\rightarrow \text{Rate} = k[(\text{CH}_3)_3\text{CBr}]^1[\text{H}_2\text{O}]^0$

$m = 1 \rightarrow$ first order in $(\text{CH}_3)_3\text{CBr}$

$n = 0 \rightarrow$ zero order in H_2O

$m + n + \dots = 1 \rightarrow$ 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:

$2\text{O}_3 \rightarrow 3\text{O}_2$

Rate law $\rightarrow \text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1}$

$2\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$

Rate law $\rightarrow \text{Rate} = k[\text{SO}_2][\text{SO}_3]^{-1/2}$

$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$

Rate law $\rightarrow \text{Rate} = k \rightarrow$ 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 $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, the rate increases by a **factor of nine** when the concentration of **NO** is **tripled** while the concentration of **H₂** is kept constant. What is the order of the reaction with respect to **NO**?

Rate law $\rightarrow \text{Rate} = k[\text{NO}]^m[\text{H}_2]^n$

$9 \times \text{Rate} = k(3 \times [\text{NO}])^m[\text{H}_2]^n = 3^m \times k[\text{NO}]^m[\text{H}_2]^n$

$9 \times \text{Rate} = 3^m \times \text{Rate}$

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

Experimental Determination of Rate Laws

- Determination of reaction orders and rate constants
 - The initial rate method** – the initial rate ($Rate_0$) of the reaction is measured at various initial concentrations ($[X]_0$) of the reactants



→ If $[A]_0$ is increased by a factor, f , while $[B]_0$ is kept constant:

$$\text{new } Rate_0 = k(f \times [A]_0)^m [B]_0^n = f^m \times k[A]_0^m [B]_0^n$$

$$\text{new } Rate_0 = f^m \times Rate_0$$

⇒ 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. $\times 10^{-2}$ (mol/L)		Initial Rate $\times 10^{-3}$ (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	1.0	3.2/3.2=1.0
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	3.2/3.2=1.0
3	1.0	3.0/1.3=2.3	17.0/3.2=5.3

⇒ As $[O_2]_0$ increases by a factor of 1.8, the initial rate increases by a factor of 1.8=1.8¹ → **1st order in O_2**

⇒ As $[NO]_0$ increases by a factor of 2.3, the initial rate increases by a factor of 5.3=2.3² → **2nd order in NO**

$$\Rightarrow Rate = k[O_2][NO]^2$$

→ The reaction is **3rd-overall order**

→ Determine the rate constant by substituting the initial concentrations and initial rate from one of the experiments and solve the equation for k

→ From Exp. #1:

$$k = \frac{Rate}{[O_2][NO]^2} = \frac{3.2 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{1.1 \times 10^{-2} \text{ mol/L} \times (1.3 \times 10^{-2} \text{ mol/L})^2}$$

$$k = 1.7 \times 10^3 \text{ L}^2/\text{mol}^2 \cdot \text{s}$$

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