Kinetics 15.1

Reaction Rates

The Order of Reactions

Rate Laws

Kinetics

The study of reaction rates

The rate of a reaction can be viewed 3 ways:

1) The rate of disappearance of a reactant.
2) The rate of appearance of a product.
3) The rate at which the overall reaction proceeds.

All reaction rates are found by looking at the change in concentration over a period of time.

Kinetics

$$A + B \rightarrow D + E$$

1) Rate of disappearance of a single reactant

$$\text{Rate}_A = \frac{-\Delta[A]}{\Delta t}$$

The negative sign is needed, as rates are always positive values.

2) Rate of appearance of a single product

$$\text{Rate}_D = \frac{\Delta[D]}{\Delta t}$$

Kinetics

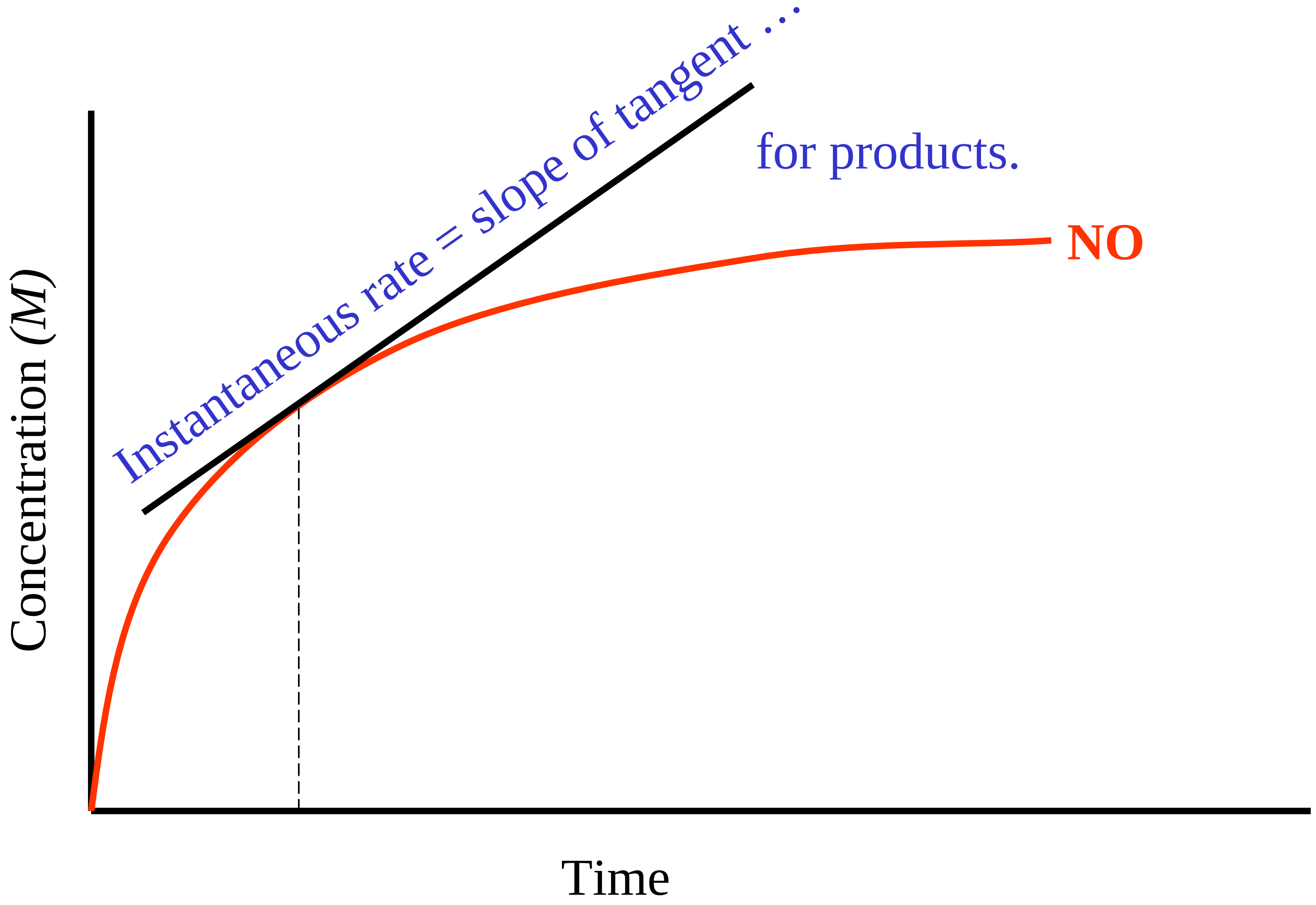
The rate at which one species appears or disappears can be used to find other rates.

$$aA + bB \rightarrow dD + eE$$

$$\frac{1}{a} \times \frac{-\Delta[A]}{\Delta t} = \frac{1}{b} \times \frac{-\Delta[B]}{\Delta t} = \frac{1}{d} \times \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \times \frac{\Delta[E]}{\Delta t}$$

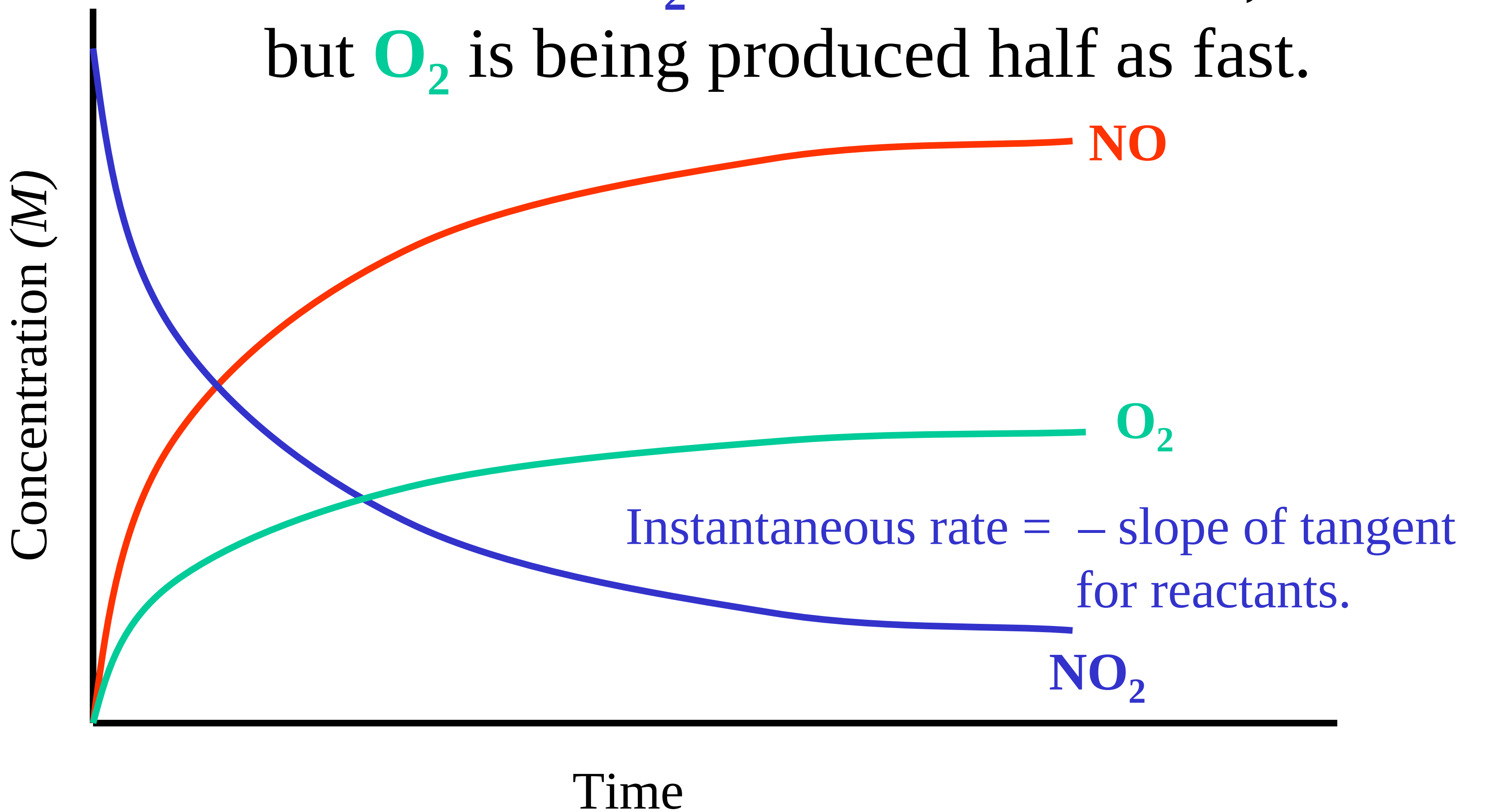
$Rate_A$ $Rate_B$ $Rate_D$ $Rate_E$

$$2\ NO_{2(g)} \rightarrow 2\ NO_{(g)} + O_{2(g)}$$

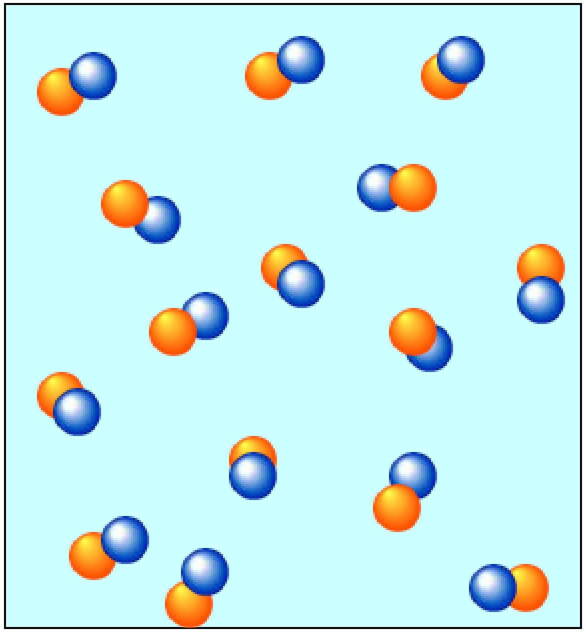


$$2\,NO_{2(g)} \rightarrow 2\,NO_{(g)} + O_{2(g)}$$

NO and **NO_2** share the same rate, but **O_2** is being produced half as fast.



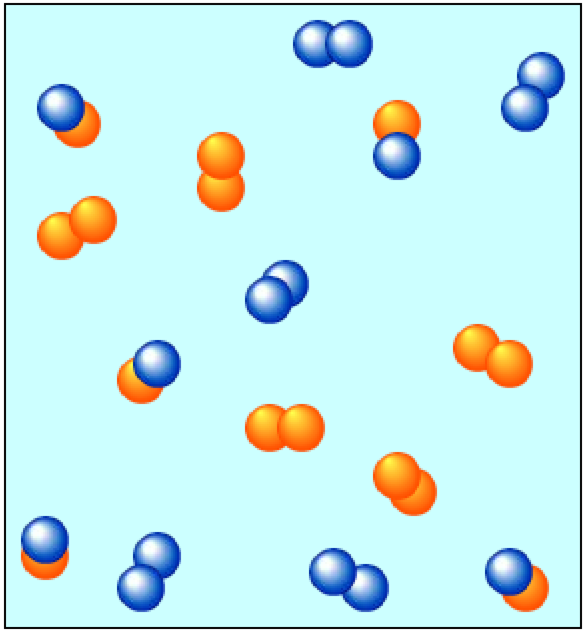
$$2\,AB \rightarrow A_2 + B_2$$



t = 0.00 s

[AB] = 15.00 M,

[A_2] = 0 M, [B_2] = 0 M



t = 60.00 s

[AB] = 5.00 M,

[A_2] = 5.00 M, [B_2] = 5.00 M

$$2\,AB \rightarrow A_2 + B_2$$

Rate of disappearance of AB

$$\text{Rate}_{AB} = \frac{-\Delta[AB]}{\Delta t} = \frac{-(5.00M - 15.00M)}{60.00\text{ s}} = \frac{-(-10.00M)}{60.00\text{ s}}$$

$$\text{Rate}_{AB} = 0.1667\ M/\text{s}$$

Rate of appearance of A_2

$$\text{Rate}_{A_2} = \frac{\Delta[A_2]}{\Delta t} = \frac{(5.00M - 0.00M)}{60.00\text{ s}} = \frac{(5.00M)}{60.00\text{ s}}$$

$$\text{Rate}_{A_2} = 0.0833\ M/\text{s}$$

or -

$$\text{Rate}_{A_2} = \frac{1}{2} \times \text{Rate}_{AB} = \frac{1}{2} \times 0.1667\ M/\text{s} = 0.08335\ M/\text{s}$$

Rate Law

3) The rate of the overall reaction.

$$A + B \rightarrow C + D$$

$$\mathbf{Rate} = \boldsymbol{k}\,\mathbf{[A]}^{\boldsymbol{m}} \bullet \mathbf{[B]}^{\boldsymbol{n}}$$

Rate = rate of disappearance of reactants (*M*/time)

k = rate constant, specific to a certain reaction at a certain temperature.

m = reaction order in terms of A

n = reaction order in terms of B

Reaction Orders (*m* and *n*)

Reaction orders cannot be predicted from the balanced equation.

They are only found through experimental data.

Reaction orders may be:

- **Zero Order**
- **First Order**
- **Second Order**

Meaning that ***m*** or ***n*** may be 0, 1, or 2.

Reaction Orders (*m* and *n*)

Zero Order Reactions

- Doubling the concentration of that species, has no affect on the reaction rate.

$$\text{Rate} = k\,[A]^0$$

$$\text{Rate} = k$$

Doubling [A] gives the same rate

$$\text{Rate} = k\,(2[A])^0$$

$$\text{Rate} = k$$

Reaction Orders (*m* and *n*)

First Order Reactions

- Doubling the concentration of that species, doubles the reaction rate.

$$\text{Rate} = k\,[\text{A}]^1$$

$$\text{Rate} = k\,(x)^1$$

$$\text{Rate} = k\cdot x$$

Doubling [A] doubles the rate

$$\text{Rate} = k\,(2x)^1$$

$$\text{Rate} = 2(k\cdot x)$$

Reaction Orders (*m* and *n*)

Second Order Reactions

- Doubling the concentration of that species, quadruples the reaction rate.

$$\text{Rate} = k\,[\text{A}]^2$$

$$\text{Rate} = k\,(x)^2$$

$$\text{Rate} = k \cdot x^2$$

Doubling [A] quadruples the rate

$$\text{Rate} = k\,(2x)^2$$

$$\text{Rate} = 4(k \cdot x^2)$$

Overall Order for a Reaction

- To find the overall order of a reaction you simply add the exponents in the rate law.

$$\mathbf{Rate} = \boldsymbol{k}\ \mathbf{[A]}^{\boldsymbol{m}} \bullet \mathbf{[B]}^{\boldsymbol{n}}$$

Overall Order of the Reaction = $m + n$

Units for *k* – The Rate Constant

Order of Reaction	Basic Formula	Units for *k*
0	Rate = k	$M\mathrm{s}^{-1}$
1	Rate = k [A]	s^{-1}
2	Rate = k [A]^2	$M^{-1}\mathrm{s}^{-1}$
3	Rate = k [A]^3	$M^{-2}\mathrm{s}^{-1}$

Ex1) Rate Law

Ex1) Three experiments were conducted at a specific temperature for the following reaction.

$$2\ NO_{(g)} + 2\ H_{2(g)} \rightarrow N_{2(g)} + 2\ H_2O_{(g)}$$

Experiment	$[NO]_{initial}$	$[H_2]_{initial}$	$Rate_{initial}$
1	0.20 *M*	0.30 *M*	0.0900 *M*/s
2	0.10 *M*	0.30 *M*	0.0225 *M*/s
3	0.10 *M*	0.20 *M*	0.0150 *M*/s

Find: a) The rate law.

b) The rate constant at this temperature.

c) The order for the overall reaction.

Ex1) a) Find the Rate Law

Experiment 2 to Experiment 1

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{NO}]_1^{\,n}\,[\text{H}_2]_1^{\,m}}{k[\text{NO}]_2^{\,n}\,[\text{H}_2]_2^{\,m}}$$

$$\frac{0.0900\ M/\text{s}}{0.0225\ M/\text{s}} = \frac{k(0.2)^n(0.3)^m}{k(0.1)^n(0.3)^m}$$

$$4 = \frac{(0.2)^n}{(0.1)^n} = 2^n$$

***n* = 2 (second order)**

[NO] doubled and $[H_2]$ stayed the same

- **–The rate quadruples**
- **–2^{nd} order for NO**

Ex1) a) Find the Rate Law (cont.)

Experiment 3 to Experiment 2

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{k[\text{NO}]_3{}^n\,[\text{H}_2]_3{}^m}{k[\text{NO}]_2{}^n\,[\text{H}_2]_2{}^m}$$

$$\frac{0.0150\ M/\text{s}}{0.0225\ M/\text{s}} = \frac{k(0.1)^n(0.2)^m}{k(0.1)^n(0.3)^m}$$

$$0.67 = \frac{(0.2)^m}{(0.3)^m} = 0.67^m$$

***m* = 1 (first order)**

$[H_2]$ goes up by ½ and [NO] stays the same

- **The rate goes up by a factor of ½**
- **1st order for H_2**

Ex1) a) Find the Rate Law (cont.)

Second Order for NO

First Order for H_2

$$\textbf{Rate} = k\,[\mathbf{NO}]^2[\mathbf{H_2}]$$

Ex1) b) Find the Rate Constant

Ex1) b) Find the Rate Constant

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

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{H}_2]} =$$

Ex1) b) Find the Rate Constant

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

Use data from any experiment

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{0.0900 M/\text{s}}{(0.20M)^2(0.30M)}$$

$$k = 7.5\ M^{-2}\text{s}^{-1}$$

Ex1) b) Find the Rate Constant

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

Use data from any experiment

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{0.0900 M/\text{s}}{(0.20M)^2(0.30M)}$$

$$k = 7.5\ M^{-2}\text{s}^{-1}$$

The overall reaction is 3rd order, as *m* + *n* = 3

Ex2) Rate Law

Ex2) Three experiments were conducted at a specific temperature for the following reaction.

$$2\ ICl + H_2 \rightarrow I_2 + HCl$$

Experiment	$[ICl]_{initial}$	$[H_2]_{initial}$	$Rate_{initial}$
1	0.20 *M*	0.20 *M*	0.0060 *M*/s
2	0.40 *M*	0.20 *M*	0.012 *M*/s
3	0.20 *M*	0.60 *M*	0.018 *M*/s

Find: a) The rate law.

b) The rate constant at this temperature.

c) The order for the overall reaction.

Ex2) a) Find the Rate Law

Ex2) a) Find the Rate Law

Experiment 1 to Experiment 2

Ex2) a) Find the Rate Law

Experiment 1 to Experiment 2

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{ICl}]_2^{\,n}\,[\text{H}_2]_2^{\,m}}{k[\text{ICl}]_1^{\,n}\,[\text{H}_2]_1^{\,m}}$$

Ex2) a) Find the Rate Law

Experiment 1 to Experiment 2

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{ICl}]_2^{\,n}\,[\text{H}_2]_2^{\,m}}{k[\text{ICl}]_1^{\,n}\,[\text{H}_2]_1^{\,m}}$$

$$\frac{0.012\ M/\text{s}}{0.0060\ M/\text{s}} = \frac{k(0.4)^n(0.2)^m}{k(0.2)^n(0.2)^m}$$

Ex2) a) Find the Rate Law

Experiment 1 to Experiment 2

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{ICl}]_2^{\,n}\,[\text{H}_2]_2^{\,m}}{k[\text{ICl}]_1^{\,n}\,[\text{H}_2]_1^{\,m}}$$

$$\frac{0.012\ M/\text{s}}{0.0060\ M/\text{s}} = \frac{k(0.4)^n(0.2)^m}{k(0.2)^n(0.2)^m}$$

$$2 = \frac{(0.4)^n}{(0.2)^n} = 2^n$$

***n* = 1 (first order)**

[ICl] doubled and $[H_2]$ stayed the same

- **The rate doubled**
- **1^{st} order for ICl**

Ex2) a) Find the Rate Law (cont.)

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Experiment 1 to Experiment 3

Ex2) a) Find the Rate Law (cont.)

Experiment 1 to Experiment 3

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{k[\text{ICl}]_3^{\,n}\,[\text{H}_2]_3^{\,m}}{k[\text{ICl}]_1^{\,n}\,[\text{H}_2]_1^{\,m}}$$

Ex2) a) Find the Rate Law (cont.)

Experiment 1 to Experiment 3

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{k[\text{ICl}]_3{}^n [\text{H}_2]_3{}^m}{k[\text{ICl}]_1{}^n [\text{H}_2]_1{}^m}$$

$$\frac{0.018\ M/\text{s}}{0.0060\ M/\text{s}} = \frac{k(0.2)^n(0.6)^m}{k(0.2)^n(0.2)^m}$$

Ex2) a) Find the Rate Law (cont.)

Experiment 1 to Experiment 3

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{k[\text{ICl}]_3^{\,n}\,[\text{H}_2]_3^{\,m}}{k[\text{ICl}]_1^{\,n}\,[\text{H}_2]_1^{\,m}}$$

$$\frac{0.018\ M/\text{s}}{0.0060\ M/\text{s}} = \frac{k(0.2)^n(0.6)^m}{k(0.2)^n(0.2)^m}$$

$$3 = \frac{(0.6)^m}{(0.2)^m} = 3^m$$

***m* = 1 (first order)**

$[H_2]$ goes up by a factor of 3 and [ICl] stays the same

- **The rate goes up by a factor of 3**
- **1^{st} order for H_2**

Ex2) a) Find the Rate Law (cont.)

Ex2) a) Find the Rate Law (cont.)

First Order for NO

First Order for H_2

$$\textbf{Rate} = k\,[\mathbf{ICl}][\mathbf{H_2}]$$

Ex2) b) Find the Rate Constant

Ex2) b) Find the Rate Constant

$$\text{Rate} = k[\text{ICl}][\text{H}_2]$$

$$k = \frac{\text{Rate}}{[\text{ICl}][\text{H}_2]}$$

Ex2) b) Find the Rate Constant

$$\text{Rate} = k[\text{ICl}][\text{H}_2]$$ **Use data from any experiment**

$$k = \frac{\text{Rate}}{[\text{ICl}][\text{H}_2]} = \frac{0.018M/\text{s}}{(0.20M)(0.60M)}$$

$$k = 0.15\ M^{-1}\text{s}^{-1}$$

Ex2) b) Find the Rate Constant

$$\text{Rate} = k[\text{ICl}][\text{H}_2]$$ **Use data from any experiment**

$$k = \frac{\text{Rate}}{[\text{ICl}][\text{H}_2]} = \frac{0.018M/\text{s}}{(0.20M)(0.60M)}$$

$$k = 0.15\ M^{-1}\text{s}^{-1}$$

The overall reaction is 2$^{\text{nd}}$ order, as *m* + *n* = 2