Rate Laws

Section 6.5

Homework
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Pg. 382 #1-4

Preview

For the reaction **$2\ C_4H_6 \longrightarrow C_8H_{12}$**

The initial rate of reaction depends on the concentration of the reactant.

This is expressed in the *rate law* for the reaction:

rate = $k\ [C_4H_6]^2$

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The exponent 2 describes ***the effect of a change in concentration of C_4H_6, on the rate of reaction.***

Trial	Initial $[C_4H_6]$ (mol/L)	Initial rate (mmol/Ls)
1	0.10	32
2	0.20	128
3	0.30	?

rate $\propto [C_4H_6]^2$

Therefore, if $[C_4H_6]$ is doubled, the rate increases by a factor of $[2]^2$

The Rate Law

The rate, *r*, is **exponentially proportional** to the initial concentrations of the reactants.

Thus, for the theoretical reaction: **a X + b Y → (products)**,

$$r \propto [X]^m\ [Y]^n$$

[X] = initial concentration of X
[Y] = initial concentration of Y
m, n = experimentally-determined exponents

Rate Law Equation aka "rate law" or "rate equation"

$$r = k\ [X]^m\ [Y]^n$$

The "rate constant"
A proportionality constant;
valid only for a specific reaction,
at a specific temperature

The values of k, and all exponents, can only be determined with EXPERIMENTAL DATA

Consider the reaction: **$BrO_3^- + 5\ Br^- + 8\ H^+ \rightarrow 3\ Br_2 + H_2O$**

The experimentally-determined rate law equation is $r = k\ [BrO_3^-]^1\ [Br^-]^1\ [H^+]^2$

If the initial concentration of BrO_3^- is DOUBLED, the rate will also double
- (change by a factor of $[2]^1 = 2$)

If $[BrO_3^-]$ is TRIPLED, multiply rate by 3 (3^1)

DOUBLE $[Br^-]$ → multiply rate by ___

TRIPLE $[Br^-]$ → multiply rate by ___

DOUBLING $[H^+]$ → multiply rate by 4 (2^2)

TRIPLING $[H^+]$ → multiply rate by 9 (3^2)

<u>The Order of Reaction</u> – The exponent value that describes the initial concentration dependence of a particular reactant

$$r = \mathbf{k}\,[BrO_3^-]^1\,[Br^-]^1\,[H^+]^2$$

- the order of reaction with respect to BrO_3^- is **1**
- the order of reaction with respect to Br^- is **1**
- the order of reaction with respect to H^+ is **2**

- the **overall order of reaction** is 4 (**1** + **1** + **2**)

	Order of Reaction			
Concentration change	**0**	**1**	**2**	**3**
x 1	$1^0 = 1$	$1^1 = 1$	$1^2 = 1$	$1^3 = 1$
x 2 (doubling)	$2^0 = 1$	$2^1 = 2$		
x 3 (tripling)	$3^0 = 1$	$3^1 = 3$		

Consider the general reaction **2 X + 2 Y + 3 Z → products**

which has the following rate law equation: $r = \mathbf{k}\,[X]^1\,[Y]^3\,[Z]^0$

What will be the effect on reaction rate, if the initial concentration of…

a) Y is unchanged?

b) X is multiplied by 3?

c) Y is multiplied by 2?

d) Z is multiplied by 2?

Example 1. *<u>Using a Rate Law equation to predict rate</u>*

The decomposition of dinitrogen pentoxide: $\mathbf{N_2O_5 \rightarrow NO_2 + O_2}$

Is first order with respect to N_2O_5. If the initial rate of consumption is 2.1×10^{-4} mol/L·s, when the initial concentration of N_2O_5 is 0.40 mol/L, predict what the rate would be if another experiment were performed in which the initial concentration of N_2O_5 were 0.80 mol/L.

<u>Strategy</u>:
1. Write the rate law equation.
2. Solve!

Example 2. *<u>Finding a rate law equation from experimental data</u>*

$$2\,NO_2 + 2\,H_2 \rightarrow N_2 + 2\,H_2O$$

Run	Initial $[NO_2]$ (mol/L)	Initial $[H_2]$ (mol/L)	Initial rate (mol/L·s)
1	0.400	0.100	1.10×10^{-5}
2	0.400	0.200	2.20×10^{-5}
3	0.800	0.200	8.80×10^{-5}

Part A. **"Determine the rate law equation."** $r = k\,[NO_2]^m\,[H_2]^n$

This means: write the rate law equation with the correct exponents.

$$2\,NO_2 + 2\,H_2 \rightarrow N_2 + 2\,H_2O$$

Run	Initial $[NO_2]$ (mol/L)	Initial $[H_2]$ (mol/L)	Initial rate (mol/L·s)
1	0.400	0.100	1.10×10^{-5}
2	0.400	0.200	2.20×10^{-5}
3	0.800	0.200	8.80×10^{-5}

$[H_2]$ is doubled

$[NO_2]$ is doubled

<u>Strategy</u>: Compare runs in which only ONE of the initial concentrations has changed. Look for the effect on the rate of reaction.

(1) *Compare $rate_2$ to $rate_1$: When $[NO_2]$ is constant*

$$\frac{rate_2}{rate_1} = \frac{2.20 \times 10^{-5}}{1.10 \times 10^{-5}} = 2.00$$

When $[H_2]$ is doubled, the rate is multiplied by 2 (2^1)

The order of reaction with respect to H_2 is ____.

(2) *Compare $rate_3$ to $rate_2$: When $[H_2]$ is constant*

$$\frac{rate_3}{rate_2} = \frac{8.80 \times 10^{-5}}{2.20 \times 10^{-5}} = 4.00$$

When $[NO_2]$ is doubled, the rate is multiplied by 4 (2^2)

The order of reaction with respect to NO_2 is ____.

$$r = k\,[NO_2]^m\,[H_2]^n \rightarrow$$

$2 NO_2 + 2 H_2 \rightarrow N_2 + 2 H_2O$

Run	Initial $[NO_2]$ (mol/L)	Initial $[H_2]$ (mol/L)	Initial rate (mol/L·s)
1	0.400	0.100	1.10×10^{-5}
2	0.400	0.200	2.20×10^{-5}
3	0.800	0.200	8.80×10^{-5}

Strategy:
Plug in the data from any of the runs.

Part B. **"Calculate a value for the rate constant."**
This means: Find the value of k.

$$r = k\,[NO_2]^2\,[H_2]^1$$

$$1.10 \times 10^{-5}\ \text{mol/L·s} = k\,(0.400\ \text{mol/L})^2\,(0.100\ \text{mol/L})^1$$

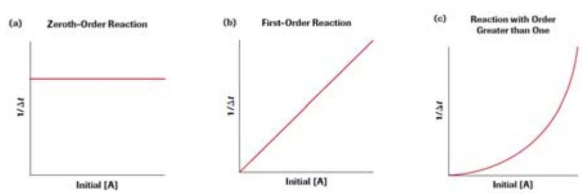
$$0.000688\ \text{L}^2/\text{mol}^2\text{·s} = k$$

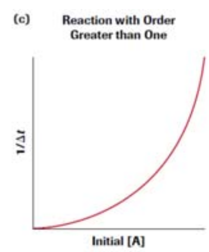
Therefore the rate constant this reaction is $k = 6.88 \times 10^{-4}\ \text{L}^2/\text{mol}^2\text{·s}$

Overall order of reaction	Units of k
1	1/s or s^{-1}
2	L/mol·s
3	L^2/mol^2·s

Relating Reaction Rate to Time

Since $r_{av} \propto \frac{1}{\Delta t}$ and $r_{av} \propto [A]^n$, then $\frac{1}{\Delta t} \propto [A]^n$





For n^{th} order reactions, plot of $\frac{1}{\Delta t}$ vs $[A]^n$ is linear