

Module 2, Lecture 4

Chemical Kinetics

Part 1

$$T(K) = T(^{\circ}C) + 273$$

(given on formula sheet)

Learning Objectives:

- Understand what is meant by the term 'rate of reaction'
- Write a rate expression for a given reaction and understand how the rate is related to the stoichiometry of the reaction
- Write a general rate law for a reaction, give the correct unit for the rate constant, k , and appreciate that the complete rate law can only be obtained experimentally.
- Understand the method of initial rates
- Use experimental data to determine the rate law and rate constant for a reaction

Textbook: Chapter 14

1

1

Thermodynamics and Kinetics

Two important things about a chemical reaction:

- how far it goes (thermodynamics)
- how fast it goes (kinetics)



The two are NOT related!!!

How quickly does a reaction reach equilibrium?

Many reactions with $\Delta G < 0$ do not occur – too slow



2

2

Thermodynamics and Kinetics

There are a very wide range of reaction rates (speeds):



Study of reaction rates important!

e.g. understanding atmospheric processes, designing new drugs, industrial processes.

3

3

Chemical Kinetics: The study of reaction speed

Two parts:

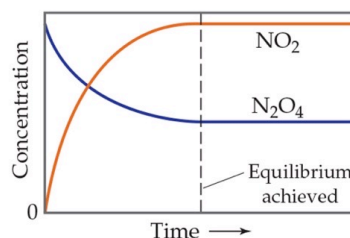
Experimental	Measure reaction rates Study factors influencing rates
Theoretical	Understand rates in molecular terms Use experimental data to probe reaction mechanisms

4

4

Rate and its measurement

Rate is the same as the speed of a reaction – **how does the concentration change with time?**



- At start – only N_2O_4 present
- $[\text{N}_2\text{O}_4]$ falls rapidly at first – slows to no change at equilibrium
- $[\text{NO}_2]$ rises rapidly at first – slows to no change at equilibrium.

5

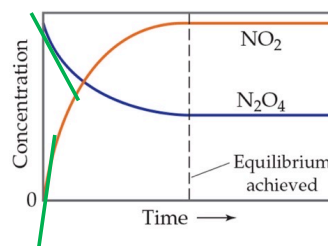
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slope = “rise over run”



- Speed (velocity) found from **gradient** of plot of either $[\text{N}_2\text{O}_4]$ or $[\text{NO}_2]$ with time.

Such a gradient (or slope) is called a **rate**.



- Rate of loss of N_2O_4 is half the rate of formation of NO_2 – **from stoichiometry**.

In symbols:

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_4]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

Use methods of calculus (where Δt becomes very small):

$$\text{rate} = -\frac{d[\text{N}_2\text{O}_4]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

- Cannot have negative rate

So put **–ve sign in front of term for reactants** where concentration **decreases**.


6

6

Rate and its measurement

For a general reaction: $a A + b B \rightarrow c C + d D$

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

- Definition of rate involves stoichiometric coefficients **a, b, c, d**.
- [A], [B] are concentrations of reactants, [C], [D] are concentrations of products.
- Can express rate in terms of **any** reactant or product.
- Units for rate always $= \frac{\text{conc}}{\text{time}}$ i.e. **mol L⁻¹ s⁻¹**  (compare with velocity = distance/time)

7

POP Quiz!!

For the reaction



which of the following defines the rate of reaction?

(A) $-\frac{d[\text{NOBr}]}{dt}$

(B) $-\frac{1}{2} \frac{d[\text{NOBr}]}{dt}$

(C) $\frac{1}{2} \frac{d[\text{NOBr}]}{dt}$

(D) $-2 \frac{d[\text{NOBr}]}{dt}$

8

8

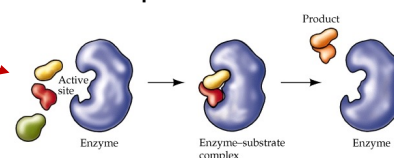
What factors affect reaction rate?

1. Chemical nature of reaction
2. Physical states of reactants and products
3. Concentration of reactants
4. Temperature, T
5. Sometimes substances not involved in the stoichiometric equation:

catalyst – increases rate (e.g. enzyme)

inhibitor – decreases rate

These substances undergo no net change.



9

9

Reaction rate and concentration

Concentration does not affect all reactions in the same way.

- For some reactions, increasing the concentration increases the rate:

e.g. the oxidation of steel wool:



(a) Steel wool heated in air (about 20% O_2) glows red-hot but oxidises to Fe_2O_3 slowly



(b) Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly

10

10

Reaction rate and concentration

- For other reactions, increasing the concentration has no effect on the rate:
e.g. oxidation of ethanol in the liver:



To understand the kinetics of a reaction we need to understand **how the rate depends on concentration.**

11

11

Rate law, rate order and rate constant

The **rate law** describes how rate depends on concentration:



The rate law takes the form:

$$\text{rate} = k [\text{A}]^x [\text{B}]^y$$

x	order with respect to A (x = 0, 1, 2 ...)
y	order with respect to B (y = 0, 1, 2 ...)
x + y	overall order of the reaction
k	rate constant

Rate law **must be determined experimentally, we CANNOT know this from the equation.**

... what about **a, b, c, d** ? **Ignore them!**

(The one time you can ignore stoichiometry!)

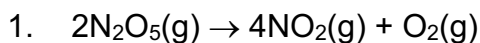


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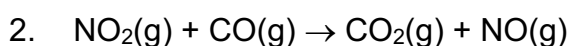
12

Examples

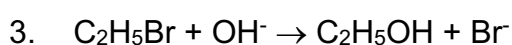
$$\text{rate} = k [\text{A}]^x [\text{B}]^y$$



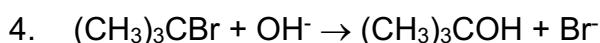
rate = $k [\text{N}_2\text{O}_5]$ **1st order**



rate = $k [\text{NO}_2]^2$ **2nd order**



rate = $k [\text{C}_2\text{H}_5\text{Br}][\text{OH}^-]$ **2nd order**



rate = $k [(\text{CH}_3)_3\text{CBr}]$ **1st order**

Rate laws are all determined experimentally

x and y are usually 0, 1 or 2 but can be negative or fractions.

x and y are NOT related to stoichiometric coefficients a, b, c, d.

13

13

First-order reactions

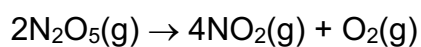
$$\text{rate} = k [\text{A}]^x [\text{B}]^y$$

Processes which are first order overall

1. Only one reactant A

a A → products

1st order in A e.g. example 1

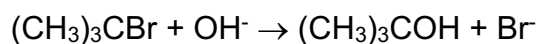


$$\text{rate} = k [\text{N}_2\text{O}_5]$$

2. Two or more reactants

a A + b B + ... → products

1st order in A e.g. example 4
zero order in all other reactants



$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}]$$

14

14

Pseudo first-order reactions

Suppose for some reaction the rate law is

$$\text{rate} = k [A][B]$$

and

$$[B] \gg [A]$$

when $[A]$ changes, $[B]$ may not change much

$\therefore [B]$ is approximately constant

$\therefore \text{rate} = k'[A]$

k' ($= k[B]$) called **pseudo first-order rate constant**

See kinetics lab experiment!

15

15

Rate order affects how rate changes with conc.

Order	Rate law	Effect as $[A]$ doubles
0	$\text{rate} = k$	No change
1	$\text{rate} = k[A]$	Rate doubles
2	$\text{rate} = k[A]^2$ or $\text{rate} = k[A][B]$	Rate increases x 4 if $\text{rate} = k[A]^2$ Rate increases x 2 if $\text{rate} = k[A][B]$

Rate Constant, k

- independent of concentration
- increases with T

Units for k depend on overall order $x + y$

$x + y$	units of k
0	$\text{mol L}^{-1} \text{s}^{-1}$
1	s^{-1}
2	$\text{L mol}^{-1} \text{s}^{-1}$
3	$\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$

16

16

Relationship between rate and time taken

Rate of a reaction and time take are **inversely related**.



e.g. Dunedin and Christchurch are ~400 km apart

- If it takes 4 hours to get there, how fast are we driving?
- How fast are we driving if it takes 8 hours?

If a reaction takes **twice as long** then the rate is **half as fast**.

17

17

Rate constant example

e.g. second order

$$\text{rate} = \frac{\Delta[\]}{\Delta t} = k[A][B] \quad \frac{\text{mol L}^{-1}}{\text{s}}$$

Remember, unit for rate is **always** $\text{mol L}^{-1} \text{s}^{-1}$

What is the unit for k?

$$k = \frac{\text{rate}}{[A][B]} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol}^2 \text{L}^{-2}} = \frac{\text{s}^{-1}}{\text{mol L}^{-1}} = \text{L mol}^{-1} \text{s}^{-1} \quad \text{red flag icon}$$

Careful! Units of k change depending on the order of reaction

18

18

Experimental measurement of reaction rate

Isolation Method

- Based on **initial rates** of reaction
- Vary concentration of one reactant, while all others held constant



$$\text{rate} = k[A]^x [B]^y$$

See kinetics lab experiment!

19

19

Initial rates

$$\text{initial rate} = k[A]_0^x [B]_0^y$$

$[A]_0$ and $[B]_0$ – initial concentrations (i.e. at time = 0)

– these are set by the experimenter and are therefore known

orders **x** and **y** - unknown

To find x – measure initial rates for different values of $[A]_0$
while holding $[B]_0$ constant

To find y – measure initial rates for different values of $[B]_0$
while holding $[A]_0$ constant

20

20

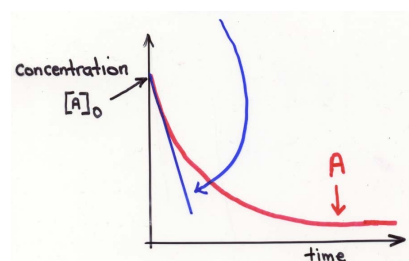
Why measure initial rates?

As reaction proceeds [A] and [B] decrease

∴ rate will decrease.

∴ examine reaction rate over a short time scale, so that [A] and [B] remain close to $[A]_0$ and $[B]_0$

i.e. study **initial rates** for which the change in [A] and [B] with time is linear.
– no tricky calculus!



21

21

Calculating the rate constant, k

$$\text{initial rate} = k[A]_0^x [B]_0^y$$

1. Obtain values of x and y from experiment
2. Calculate k from any set of rate measurements

$$k = \frac{\text{initial rate}}{[A]_0^x [B]_0^y}$$

3. **Remember** to work out the correct units for k !

Careful! Units of k change depending on the order of reaction



22

22

Example

What is the experiment rate law for the reaction?



$$\text{initial rate} = k [\text{S}_2\text{O}_8^{2-}]_0^x [\text{I}^-]_0^y$$

Compare Expts 1 and 2

$[\text{I}^-]_0$ **constant** in both Expts

$[\text{S}_2\text{O}_8^{2-}]_0$ doubled and initial rate doubles

$$\therefore x = 1$$

Compare Expts 1 and 3

$[\text{S}_2\text{O}_8^{2-}]_0$ **constant** in both Expts

$[\text{I}^-]_0$ doubled and initial rate doubles

$$\therefore y = 1$$



Careful! Must remember to state that you are holding one reactant constant

23

23

Rate law

Having determined x and y we can write the **rate law**:

$$\text{rate} = k[\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

Q: What is the overall order of the reaction?

overall order = $x + y = 2$ so 2nd order

Q: What is the rate constant at 298 K ?

(using data from Expt 1)

(can use data from any of the Expts 1, 2 or 3 to calculate k)

$$\begin{aligned} k &= \frac{\text{initial rate}}{[\text{S}_2\text{O}_8^{2-}]_0 [\text{I}^-]_0} \\ &= \frac{1.14 \text{ mol L}^{-1} \text{ s}^{-1}}{(0.15 \text{ mol L}^{-1}) \times (0.21 \text{ mol L}^{-1})} \\ &= 36 \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

24

24

POP Quiz!!

For the gaseous reaction $2\text{ICl(g)} + \text{H}_2\text{(g)} \rightarrow \text{I}_2\text{(g)} + 2\text{HCl(g)}$

the following data were obtained at 500 K:

Expt	$[\text{ICl}]_0 / \text{mol L}^{-1}$	$[\text{H}_2]_0 / \text{mol L}^{-1}$	Initial rate/ $\text{mol L}^{-1} \text{s}^{-1}$
1	1.5×10^{-3}	1.5×10^{-3}	3.7×10^{-3}
2	3.0×10^{-3}	1.5×10^{-3}	7.4×10^{-3}
3	3.0×10^{-3}	4.5×10^{-3}	22×10^{-3}

The rate law is

(A) $\text{rate} = k[\text{ICl}][\text{H}_2]$

(B) $\text{rate} = k[\text{ICl}][\text{H}_2]^2$

(C) $\text{rate} = k[\text{ICl}]$

(D) $\text{rate} = k[\text{H}_2]$

25

25

*** Homework ***

Chemistry – the central science 15th Ed

Brown et al.

Problems 14.7 14.8a 14.12 14.13 14.14

Answers on Blackboard

26

26