Chapter 14

CHEMICAL KINETICS

(Part I)

14.1

Chemical Kinetics

- **Kinetics**: the study of how fast reactions take place.
  - Some reactions are fast (combustion, photosynthesis).
  - Some reactions are slow (conversion of diamond to graphite, corrosion).
- Importance of studying chemical rates:
  - Speed up desirable reactions.
  - Minimize damage and products by undesirable reactions.
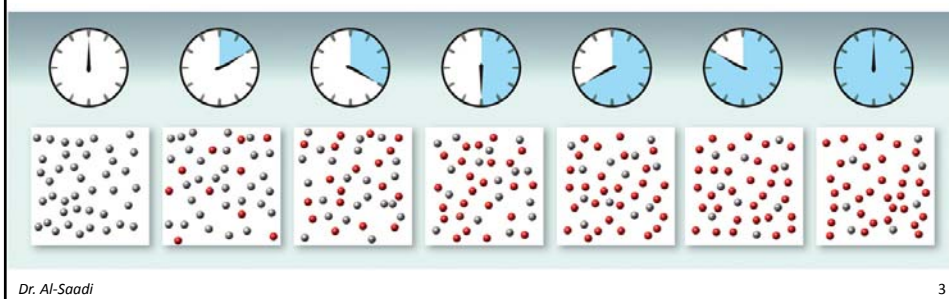 - Useful in drug design, pollution control, and food processing.

Rate of Reaction

- For the reaction A → B

   As time progresses, there are more B molecules and less A molecules.

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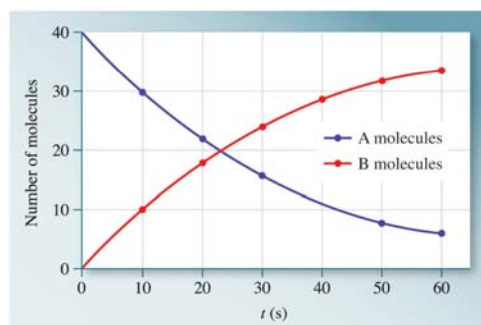

Rate of Reaction

- For the reaction A → B
- Expressed as either:
   o Rate of disappearance of reactants (decrease or negative)

   or

   o Rate of appearance of products (increase or positive)

The rate of growth or decay in a chemical reaction is not linear but exponential.

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14.1

Average Reaction Rate

- For the reaction A $\rightarrow$ B

- Average rate $= \dfrac{-\Delta[A]}{\Delta t} = \dfrac{\Delta[B]}{\Delta t}$

  The quantity $\Delta[A]$ is negative ($[A]_f$ - $[A]_i$ = -ve), because concentration of A is decreasing.
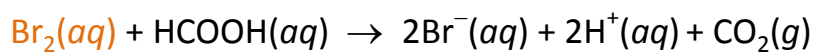
  The quantity $\Delta[B]$ is positive ($[B]_f$ - $[B]_i$ = +ve), because concentration of B is increasing.

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14.1

Average Reaction Rate

$Br_2(aq)$ + HCOOH(aq) $\rightarrow$ 2Br$^-$(aq) + 2H$^+$(aq) + CO$_2$(g)

Formic acid

Br_2 disappears over time

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14.1

Average Reaction Rate

$$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$
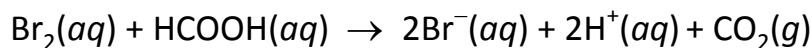
The change in Br₂ concentration over time

Time (s)			[Br₂] (M)
0.0	t_i	$[Br_2]_i$	0.0120
50.0	t_f	$[Br_2]_f$	0.0101
100.0			0.00846
150.0			0.00710
200.0			0.00596
250.0			0.00500
300.0			0.00420
350.0			0.00353
400.0			0.00296

What is the average rate over the first 50 seconds time interval?

$$\text{Average rate} = \frac{-\Delta[Br_2]}{\Delta t}$$

$$= \frac{-(0.0101 - 0.0120)\ M}{50.0\ s}$$

$$= 3.80 \times 10^{-5}\ M/s$$

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7

14.1

Average Reaction Rate

$$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$
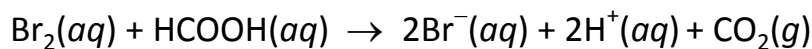
The change in Br₂ concentration over time

Time (s)			[Br₂] (M)
0.0	t_i	$[Br_2]_i$	0.0120
50.0			0.0101
100.0	t_f	$[Br_2]_f$	0.00846
150.0			0.00710
200.0			0.00596
250.0			0.00500
300.0			0.00420
350.0			0.00353
400.0			0.00296

What is the average rate over the first 100 seconds time interval?

$$\text{Average rate} = \frac{-\Delta[Br_2]}{\Delta t}$$

$$= \frac{-(0.00846 - 0.0120)\ M}{100.0\ s}$$
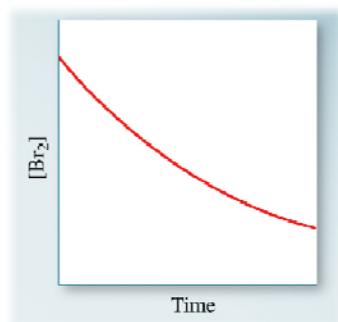
$$= 3.54 \times 10^{-5}\ M/s$$

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8

Average Reaction Rate

- The average reaction rate depends on the time interval.
- The average reaction rate changes over time.

Plot of $[Br_2]$ vs time is a curve

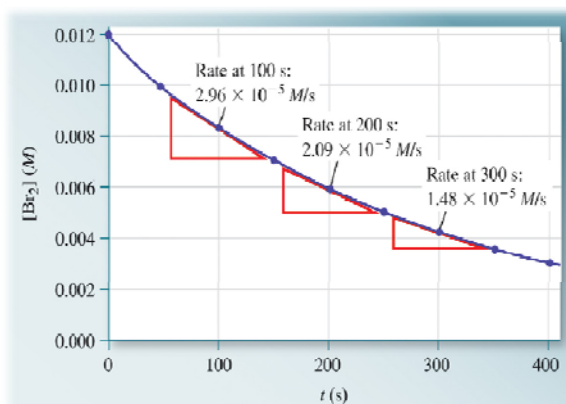*Dr. Al-Saadi*   9

Instantaneous Rate

- When we make Δt shorter and shorter, *instantaneous rates* could be obtained.

- *instantaneous rate* is the rate at a specific instance of time (slope of a tangent to the curve)

Rate at 100 s: 2.96×10^{-5} M/s

Rate at 200 s: 2.09×10^{-5} M/s

Rate at 300 s: 1.48×10^{-5} M/s

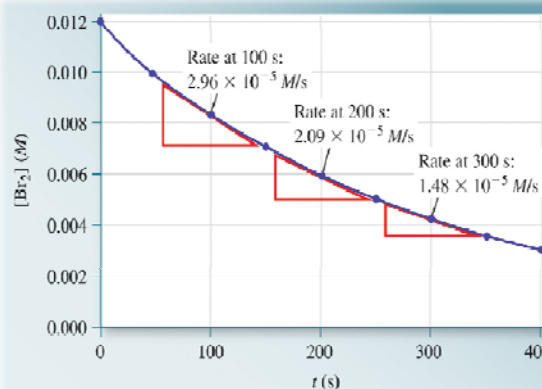*Dr. Al-Saadi*   10

14.1

Instantaneous Rate

- Instantaneous rate is a more useful quantity than the average rate.

- For example,

  at 100 s:

  $[Br_2]$ = 0.0085 M

  Rate = 2.96×10^{-5} M/s

Rate at 100 s:
2.96 × 10^{-5} M/s

Rate at 200 s:
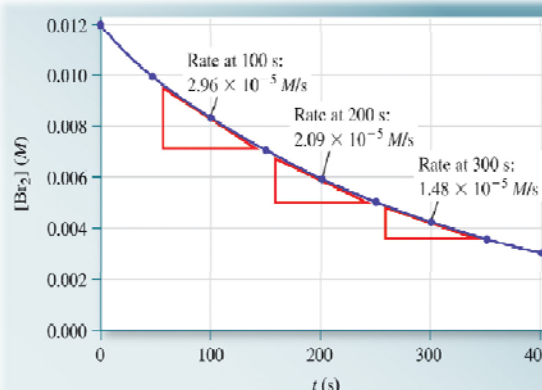2.09 × 10^{-5} M/s

Rate at 300 s:
1.48 × 10^{-5} M/s

11

14.1

Instantaneous Rate

- Instantaneous rate is more useful quantity than the average rate.

- For example,

  at 200 s:

  $[Br_2]$ = 0.0060 M

  Rate = 2.09×10^{-5} M/s

Rate at 100 s:
2.96 × 10^{-5} M/s

Rate at 200 s:
2.09 × 10^{-5} M/s

Rate at 300 s:
1.48 × 10^{-5} M/s

12

Instantaneous Rate

TABLE 14.1	Rates of the Reaction of Molecular Bromine and Formic Acid at 25°C	
Time (s)	$[Br_2]$ (M)	Rate (M/s)
0.0	0.0120	4.20×10^{-5}
50.0	0.0101	3.52×10^{-5}
100.0	0.00846	2.96×10^{-5}
150.0	0.00710	2.49×10^{-5}
200.0	0.00596	2.09×10^{-5}
250.0	0.00500	1.75×10^{-5}
300.0	0.00420	1.48×10^{-5}
350.0	0.00353	1.23×10^{-5}
400.0	0.00296	1.04×10^{-5}

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Instantaneous Rate

14.1

TABLE 14.1	Rates of the Reaction of Molecular Bromine and Formic Acid at 25°C	
Time (s)	$[Br_2]$ (M)	Rate (M/s)
50.0	0.0101	3.52×10^{-5}
250.0	0.00500	1.75×10^{-5}

- What can you conclude?

  When the $[Br_2]$ is halved; the rate is halved.

  Rate is directly proportional to $[Br_2]$, and the relationship is linear.   rate α $[Br_2]$

                  rate = k $[Br_2]$
                           ↑
              Rate constant

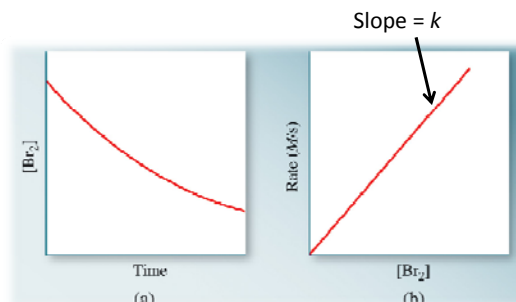*Dr. Al-Saadi*   14

14.1

Rate Constant

Slope = k

rate = k [Br$_2$]

k is a proportionality constant and is constant as long as the temperature remains constant.

Time
(a)

[Br$_2$]
(b)

- Calculate the value of the rate constant (k) for this reaction.

  You can use the data for any given time to get the answer.

14.1

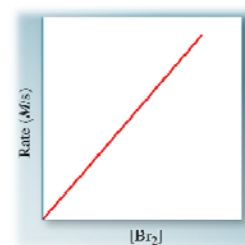# Rate Constant

[Br$_2$]

rate = k [Br$_2$]

- Calculate the value of the rate constant (k) for this reaction.

at t = 50.0 s

$$k = \frac{3.52 \times 10^{-5} M / s}{0.0101 \ M} = 3.49 \times 10^{-3} s^{-1}$$

at t = 300.0 s

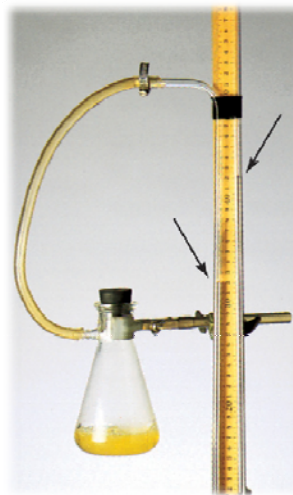$$k = \frac{1.48 \times 10^{-5} M / s}{0.00420 \ M} = 3.52 \times 10^{-3} s^{-1}$$

Rate Constant

- Rate constant can be calculated for reactions involving gaseous reactants and/or products by monitoring their pressures.

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

The rate of appearance of the O_2 gas can be determined by monitoring its pressure.

14.1

Rate Constant

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

$$P_{O_2}V = n_{O_2}RT$$

$$P_{O_2} = (n_{O_2}/V)\,RT$$

$$= [O_2]\,RT$$

$$[O_2] = (1/RT)\,P_{O_2}$$

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT}\frac{\Delta P_{O_2}}{\Delta t}$$
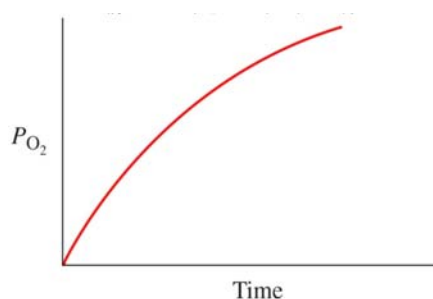
Rate Constant

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The rate of appearance of O_2 gas can be related to the change in P_{O_2}.

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT}\frac{\Delta P_{O_2}}{\Delta t}$$

Instantaneous rate can be determined at any point on the P_{O_2} curve.

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14.1

Stoichiometry and Reaction Rate

- Recall that for the reaction A $\rightarrow$ B

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

- What do you think the rate would be for the reaction:

$$A \rightarrow 2B \quad ?$$

Note that B appears at *twice* the rate that A disappears.

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} \quad \text{and} \quad 2 \times \text{rate} = \frac{\Delta[B]}{\Delta t}$$
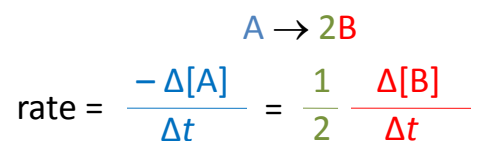
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10

14.1

Stoichiometry and Reaction Rate

- For the reaction:

$$A \rightarrow 2B$$

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{1}{2}\frac{\Delta[B]}{\Delta t}$$

- When stoichiometric ratios are not 1:1

$$a\,A \;+\; b\,B \;\rightarrow\; c\,C \;+\; d\,D$$
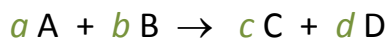
$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

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21

14.1

Stoichiometry and Reaction Rate

- Exercise:

  Write the rate expression for the following reaction:

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

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22

Stoichiometry and Reaction Rate

- Exercise:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

If molecular hydrogen is formed at a rate of 0.168 M/s, at what rate is P_4 being produced?

The rate expression for the reaction is:

$$\text{rate} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = \frac{1}{1}\frac{\Delta[P_4]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$

$$\frac{1}{6}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{6}(0.168\ M/s) = 0.028\ M/s$$

$$\frac{1}{1}\frac{\Delta[P_4]}{\Delta t} = \boxed{0.028\ M/s}$$

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Stoichiometry and Reaction Rate

- Exercise:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

At what rate is PH_3 being consumed if the rate of formation of H_2 is 0.168?

The rate expression for the reaction is:

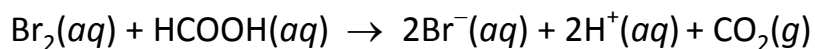$$\text{rate} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = \frac{1}{1}\frac{\Delta[P_4]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$
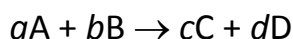
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The Rate Law

$$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

$$rate = k\,[Br_2]$$

- The equation that relates the rate of the reaction to the concentration of the reactants is the **rate law**.
- In general, for the chemical raction:

$$aA + bB \rightarrow cC + dD$$

$$rate = k\,[A]^x\,[B]^y$$

- k : proportionality constant known as the rate constant.
- x and y : the **order of the reaction** with respect to each reactant. The values of x and y are determined experimentally.

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The Rate Law

$$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$
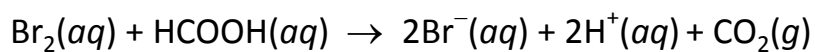
- Applying the general rate law equation to the reaction gives:

$$rate = k\,[Br_2]^x\,[HCOOH]^y$$

- $x = 1$ and $y = 0$.
- The reaction is **first order** with respect to Br_2 .
- The reaction is **zeroth order** with respect to HCOOH.
- The **overall order** of the reaction (**reaction order**) is equal to 1.

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# Reaction Order

- The order of the reaction can only be determined from experimental data, and it is <u>not</u> related to the stoichiometric coefficients.
  - o **First order** - rate directly proportional to concentration.
  - o **Second order** - exponential relationship.
  - o **Zeroth order** - no relationship, and the reaction rate is independent of the reactant concentration.
  - o The sum of exponents (orders) indicates the **overall reaction order**.
- The order of the reaction is always defined in terms of reactant (and <u>not</u> product) concentrations.

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How is a Reaction Order Determined?

$$F_2 \ (g) + 2ClO_2 \ (g) \rightarrow 2FClO_2 \ (g)$$
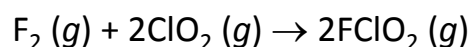
- *Initial rate* is the instantaneous rate at the beginning of the reaction (*time* = 0 s).

  The initial rate of the reaction changes by varying the initial concentrations of the reactants.

TABLE 14.2	Initial Rate Data for the Reaction Between F_2 and ClO_2		
Experiment	$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M/s*)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

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How is a Reaction Order Determined?

TABLE 14.2	Initial Rate Data for the Reaction Between F_2 and ClO_2		
Experiment	**$[F_2]$ (M)**	**$[ClO_2]$ (M)**	**Initial Rate (M/s)**
➡ 1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
➡ 3	0.20	0.010	2.4×10^{-3}

$$\text{rate} = k\,[F_2]^x\,[ClO_2]^y$$

- The reaction order with respect to F_2 can be determined by holding $[ClO_2]$ constant.

How is a Reaction Order Determined?

TABLE 14.2	Initial Rate Data for the Reaction Between F_2 and ClO_2		
Experiment	**$[F_2]$ (M)**	**$[ClO_2]$ (M)**	**Initial Rate (M/s)**
➡ 1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
➡ 3	0.20	0.010	2.4×10^{-3}

$$\text{rate} = k\,[F_2]^1\,[ClO_2]^y$$

- The rate doubles as $[F_2]$ doubles. Thus, the rate is linearly proportional to $[F_2]$.

  The reaction is 1st order with respect to F_2 .

  $x = 1$

14.2

How is a Reaction Order Determined?

TABLE 14.2	Initial Rate Data for the Reaction Between F_2 and ClO_2			
Experiment		[F_2] (M)	[ClO_2] (M)	Initial Rate (M/s)
1		0.10	0.010	1.2×10^{-3}
2		0.10	0.040	4.8×10^{-3}
3		0.20	0.010	2.4×10^{-3}

rate = k [F_2]^1 [ClO_2]^y

- The reaction order with respect to ClO_2 can be determined by holding [F_2] constant.

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14.2

How is a Reaction Order Determined?

TABLE 14.2	Initial Rate Data for the Reaction Between F_2 and ClO_2			
Experiment		[F_2] (M)	[ClO_2] (M)	Initial Rate (M/s)
1		0.10	0.010	1.2×10^{-3}
2		0.10	0.040	4.8×10^{-3}
3		0.20	0.010	2.4×10^{-3}

rate = k [F_2]^1 [ClO_2]^1

- The rate quadruples as [F_2] quadruples. Thus, the rate is also linearly proportional to [ClO_2].

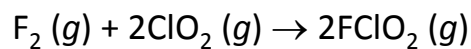 The reaction is 1st order with respect to ClO_2 .

  y = 1

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16

How is a Reaction Order Determined?

$$F_2 \ (g) + 2ClO_2 \ (g) \rightarrow 2FClO_2 \ (g)$$

▪ The rate law of the reaction is:

$$\text{rate} = k \ [F_2][ClO_2]$$

Notice that a reaction order is not related to the reaction stoichiometric coefficients.

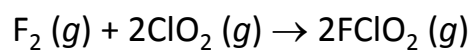▪ The reaction is :

○ first order with respect to F_2

○ first order with respect to ClO_2

○ second order overall.

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How is a Reaction Order Determined?

$$F_2 \ (g) + 2ClO_2 \ (g) \rightarrow 2FClO_2 \ (g)$$

▪ The rate law of the reaction is:

$$\text{rate} = k \ [F_2][ClO_2]$$

▪ Rate constant can be calculated (Consider Expt. 1)

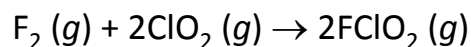| Experiment	$[F_2]$ (M)	$[ClO_2]$ (M)	Initial Rate (M/s)
1	0.10	0.010	1.2×10^{-3}

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How is a Reaction Order Determined?

$$F_2\ (g) + 2ClO_2\ (g) \rightarrow 2FClO_2\ (g)$$

- The rate law of the reaction is:

$$\text{rate} = k\ [F_2][ClO_2]$$

- Rate constant can be also calculated from another set of date (Now consider Expt. 2)

Experiment	[F$_2$] (M)	[ClO$_2$] (M)	Initial Rate (M/s)
2	0.10	0.040	4.8×10^{-3}

Reaction Order

- Exercise:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) +\ 2H_2O\ (g)$$
The following experiments were run at 1280°C.

Expt.	[NO] (M)	[H$_2$] (M)	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	1.0×10^{-2}	2.0×10^{-3}	5.0×10^{-5}
3	1.0×10^{-2}	4.0×10^{-3}	1.0×10^{-4}

(a) Write down the correct rate law.

(b) Determine the rate constant.

(c) What is the rate of the reaction when [NO] is 4.8×10^{-3} M and [H$_2$] is 6.2×10^{-3} M?

Units of Rate Constant

Overall Reaction Order	Sample Rate Law	Units of k
0	rate = k	$M \cdot s^{-1}$
1	rate = $k[A]$ or rate = $k[B]$	s^{-1}
2	rate = $k[A]^2$, rate = $k[B]^2$, or rate = $k[A][B]$	$M^{-1} \cdot s^{-1}$
3*	rate = $k[A]^2[B]$ or rate = $k[A][B]^2$	$M^{-2} \cdot s^{-1}$

TABLE 14.4 Units of the Rate Constant k for Reactions of Various Overall Orders

*Another possibility for a third-order reaction is rate = $k[A][B][C]$, although such reactions are very rare.

- The units of the rate constant (k) depend on the overall reaction order.

Integrated Rate Law
1st order reactions

- Consider the following first-order reaction:

$$A \rightarrow \text{products}$$

The reaction rate can be expressed either as:

$$\text{rate} = k[A] \qquad \text{(Rate law)}$$

or:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \qquad \text{(Average rate)}$$

Then,

$$-\frac{\Delta[A]}{\Delta t} = k[A]$$

Integrated Rate Law

1st order reactions

- Consider the following first-order reaction:

$$A \rightarrow products$$

  integrating both sides from $t = 0$ to t gives:

$$\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt$$ *Integrated rate law*

  which can be rearranged as:

$$\ln[A]_t = -kt + \ln[A]_0 \qquad \longleftarrow \text{linear equation}$$

$$y \quad = \quad m \ x + \quad b$$

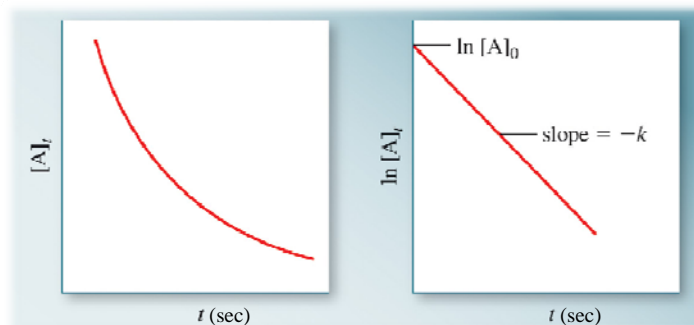*Dr. Al-Saadi*   39

14.3

Integrated Rate Law

1st order reactions

- For a 1st order reaction, a plot of ln[A] vs. time yields a straight line with slope = $-k$ (the rate constant).

$$\ln[A]_t = -kt + \ln[A]_0$$

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Integrated Rate Law
1st order reactions

- Exercise:

$$2A \rightarrow B$$

The above reaction is 1st order in A, and its rate constant is 7.5×10^{-3} s^{-1} at 110°C. How many minutes will it take for [A] to decrease from 1.25 *M* to 0.71 *M*?

$$\ln \left(\frac{[A]_t}{[A]_0}\right) = - kt$$

Half Life
1st order reactions

- **Half-life ($t_{1/2}$)** is the time that it takes for the reactant concentration to drop to half of its original value.
- For 1st order reactions:

$$\ln \left(\frac{[A]_t}{[A]_0}\right) = - kt$$

when $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$. Then,

$$t_{1/2} = \frac{1}{k} \, \ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right)$$

ln2 = 0.693

For 1st order reaction, $\quad t_{1/2} = \dfrac{0.693}{k}$

Half Life

1st order reactions

- For 1st order reactions, the $t_{1/2}$ is independent of the initial concentration of the reactant.

  For a 1st order reaction, it takes the same time for a reactant conc. to decrease from 1.0 *M* to 0.5 *M* as it does for the conc. to decrease from 0.5 *M* to 0.25 *M*.

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Half Life and Rate Constant

For 1st order reaction, $t_{1/2} = \dfrac{0.693}{k}$

- The half life is inversely proportional to the rate constant of the reaction. A short half-life corresponds to a larger rate constant (faster reactions).
- Measurement of the half-life is one way to determine the rate constant.

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2nd Order Reactions

- The integrated rate law and half-life for 2nd order reactions can be also derived.

  o Integrated rate law

  $$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

  o Half-life

  The half-life of second-order reaction is NOT constant, and it depends on the initial conc. of the reactant.

  $$t_{1/2} = \frac{1}{k[A]_0}$$

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Integrated Rate Law & Half Life

TABLE 14.5	Summary of the Kinetics of Zeroth-Order, First-Order, and Second-Order Reactions		
Order	**Rate Law**	**Integrated Rate Law**	**Half-Life**
0	rate = k	$[A]_t = -kt + [A]_0$	$\dfrac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln \dfrac{[A]_t}{[A]_0} = -kt$	$\dfrac{0.693}{k}$
2	rate = $k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\dfrac{1}{k[A]_0}$

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14.4

Collision Theory

- Particles must collide with each other in order to react.
- **Collision Theory**: The greater the frequency of collisions, the higher the reaction rate.

$$\text{rate} \propto \frac{\text{number of collisions}}{1 \text{ second}}$$

Does every collision result with a chemical reaction?
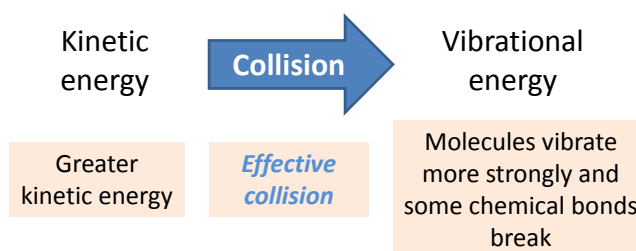
Is every collision an **effective collision**?

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47

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Collision Theory

- In order to have an **effective collision** which causes a reaction to proceed, some factors must be met:
  - Proper orientation of the reactant molecules.
  - Sufficient kinetic energy (faster motion) of the reactant molecules.

Kinetic energy → **Collision** → Vibrational energy

| Greater kinetic energy | *Effective collision* | Molecules vibrate more strongly and some chemical bonds break |

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48

24

Collision Theory

14.4

$$Cl + NOCl \rightarrow Cl_2 + NO$$

Before collision   Collision   After collision

Proper orientation & sufficient kinetic energy
The reaction is more likely to take place

Effective collision

Before collision   Collision   After collision

Improper orientation and/or insufficient kinetic energy
The molecules bounce off of each other and the
reaction doesn't take place

Ineffective collision

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Activation Energy

14.4

▪ ***Activation energy*** (E_a) is the minimum amount of energy required to initiate a chemical reaction.

Potential energy

E_a

Cl + NOCl

Cl_2 + NO

Reaction pathway

An ***activated complex*** or ***transition state*** is a temporary species that forms upon effective collisions.

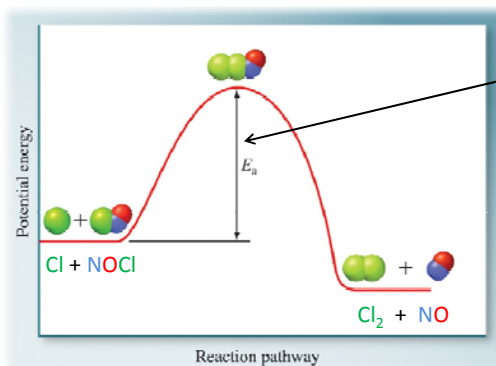Potential energy profile for the reaction:
$$Cl + NOCl \rightarrow Cl_2 + NO$$

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Activation Energy

- *Activation energy* (E_a) is the minimum amount of energy required to initiate a chemical reaction.

E_a is an energy barrier that prevents less energetic molecules from proceeding to the product side.

Potential energy profile for the reaction:
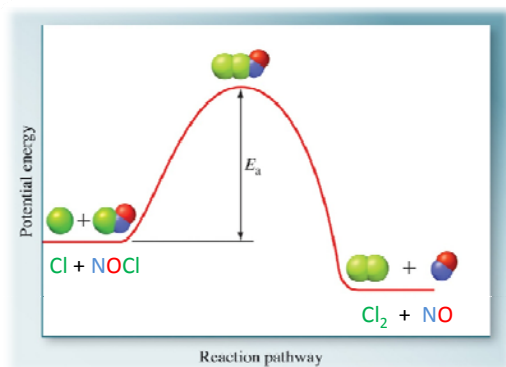Cl + NOCl → Cl$_2$ + NO

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51

Do Reactions Depend on Temperature?

- Cocking food at 200°C and at 20°C. Which one would be faster?

- Hard-boiling eggs in boiling water or just in warm water. Which process would be faster?

- Keeping fruits on the shelf, keeping food inside the refrigerator, or keeping food in the freezer. Where would the fruit spoil more slowly?

- Making tea in Dhahran or in Sodah. Where would it be faster?

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52

14.4

Temperature Effect on Reaction Rate

Potential energy profile for the reaction:
$Cl + NOCl \rightarrow Cl_2 + NO$

According to kinetic molecular theory (CHEM 101),

$$KE_{ave} \propto \text{absolute } T$$

When the temperature is raised, more molecules will have sufficient KE to exceed the activation energy barrier. As a result, the reaction rate increases.

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53

14.4

The Arrhenius Equation

- The dependence of the rate constant of a reaction on temperature can be expressed by ***the Arrhenius equation:***

$$k = Ae^{\frac{-E_a}{RT}}$$

Rate constant decreases with the increase of activation energy, with the increase of collision frequency, and with the decrease in temperature

E_a : activation energy.

R : universal gas constant (8.314 J/K·mol).

A : frequency factor (collision frequency).

T : Kelvin temperature.

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54

14.4

The Arrhenius Equation

$$k = Ae^{\frac{-E_a}{RT}}$$

▪ Arrhenius equation can be expressed in other useful forms.

Taking the natural logarithm of both sides:

$$\ln k = \ln Ae^{\frac{-E_a}{RT}}$$

Then:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Rearrangement gives a linear equation as:

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

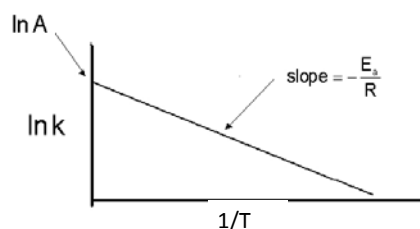*y*   *slope*   *x*   *intercept*

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14.4

Plot of Arrhenius Equation

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

▪ The straight line resulting from plotting the Arrhenius equation has a slope that is equal to $-E_a/R$.

Thus, the value of the activation energy (E_a) can be determined from knowing the rate constant (k) at a specific temperature.

slope $= -\dfrac{E_a}{R}$

ln k

1/T

Note that the slope is –ve. As a result, the value of E_a will be +ve.

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Another Form of Arrhenius Equation

- Simple mathematical treatment of Arrhenius equation gives:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

   o If we know the rate constants at two temperatures, then the activation energy can be calculated.
   o If we know the activation energy and the rate constant at a given temperature, the value of the rate constant at any other temperature can be calculated.
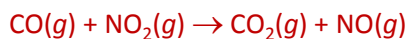
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Using Arrhenius Equation

- Exercise:

   Find the activation energy for the following reaction:

   $$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$$

   The rate constants were found to be 0.028 $M^{-1}s^{-1}$ at 327°C and 23 $M^{-1}s^{-1}$ at 527°C.

   k_1 = 0.028 $M^{-1}s^{-1}$
   @ T_1 = 327 + 273 = 600 K

   k_2 = 23 $M^{-1}s^{-1}$
   @ T_2 = 527 + 273 = 800 K

   What is the total
   order of this reaction?

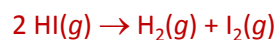 $= 133800 \text{ J/mol} = 130 \text{ kJ/mol}$

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14.4

Using Arrhenius Equation

▪ Exercise:

Consider the reaction:

2 HI(g) → H$_2$(g) + I$_2$(g)

The data shown in the table were measured at different temperatures.

Find the activation energy.

k (M^{-1}s^{-1})	T (°C)
3.52×10^{-7}	283
3.02×10^{-5}	356
2.19×10^{-4}	393
1.16×10^{-3}	427
3.95×10^{-2}	508

To answer the question, we need to find:
- ln k
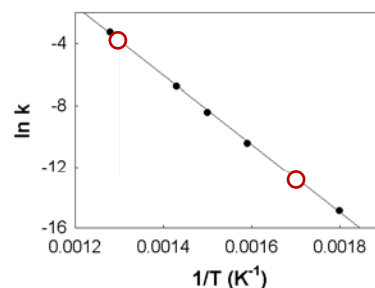- 1/T ; where T in K
- and then plot ln k vs. 1/T.
  The slope of the line will lead us to the activation energy.

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14.4

k	ln k	T (°C)	T (K)	1/T (K^{-1})
3.52×10^{-7}	−14.860	283	556	1.80×10^{-3}
3.02×10^{-5}	−10.408	356	629	1.59×10^{-3}
2.19×10^{-4}	−8.426	393	666	1.50×10^{-3}
1.16×10^{-3}	−6.759	427	700	1.43×10^{-3}
3.95×10^{-2}	−3.231	508	781	1.28×10^{-3}

We select any two points from the straight line.

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{[(-3.8) - (-12.8)]}{[0.00130 - 0.00170]} = -23000$$

$$\text{slope} = -\frac{E_a}{R}$$

so

$$E_a = -\text{slope} \times R = -(-23000) \times (8.314) = 190000 \text{ J/mol} = 190 \text{ kJ/mol}$$

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