CHM 101: GENERAL CHEMISTRY I

- Elementary Thermochemistry
- Rates of reaction

CREDIT: 2 UNITS

TARGETED STUDENTS

Undergraduate students of:

- Engineering, Sciences, Science Education and Agriculture Programmes

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What is Thermochemistry?

Thermochemistry is an aspect of chemistry that deals with the amount of heat exchange (i.e., absorbed or released) during a chemical reaction

A thermochemical equation is a chemical equation with the ΔH for the reaction included

Rules of Thermochemistry

1. The magnitude of ΔH is directly proportional to the amount of reactant or product

2. ΔH for the reaction is equal in magnitude but opposite in sign for ΔH for the reverse of the reaction

3. The value of ΔH is the same whether the reaction occurs in one step or as a series of steps. This rule is a direct consequence of the fact that ΔH is a state variable. This rule is a statement of Hess's Law.

Reaction Energy

a. The study of energy in chemical reactions is called *thermodynamics*, which literally means "**changes in heat**."

b. The standard conditions for thermodynamics:

(i) Standard temperature = 25 °C (298 K)

(ii) Standard Pressure = 1 atm

c. All chemical reactions either release or require (absorb) energy when they occur.

d. Heat energy is referred to in this course as enthalpy (H).

i. Enthalpy is the heat absorbed or released by a system at constant pressure.

ii. It is impossible to measure enthalpy directly. Only changes in enthalpy are measured: $\Delta H = H_{final} - H_{initial}$

Reaction Energy cont'd

iii. **System**: the chemical reaction under study

iv. Surroundings: every place in the universe except the system,

v. Universe: the system and the surroundings

v. **Exothermic reactions:** An exothermic reaction is a reaction in which heat is released by the system to the surroundings. ΔH is –ve. It is a **favourable** condition. E.g., as water freezes, it must get rid of (release, give off) heat.

vi. **Endothermic reactions:** An endothermic reaction is a reaction in which heat is absorbed by the system from the surroundings. E.g., as ice melts, it has to absorb heat.

Types of Heat (Enthalpy) of Reaction

Heat of formation is defined as the change in enthalpy that takes place when 1 mole of the compound is formed from its element. It is denoted by

- Change in heat of formation = ΔH_f.
- The enthalpy of formation of an element in its standard state at 25 °C is "0" for its ΔH^θ_f.

Question: Find the standard change in enthalpy for the evaporation of water, and state whether the reaction is exothermic or endothermic.

(Water vapour, H^θ_f = -241.82 kJ/mol; liquid water, H^θ_f = - 285.82 kJ/mol).

Answer: $H_2O_{(l)} \longrightarrow H_2O_{(g)}$

$$\Delta H^\theta_{rxn} = \Delta H^\theta_{f(products)} - \Delta H^\theta_{f(reactants)}$$

$$\Delta H^\theta_{rxn} = -241.82 - (-285.82)$$

ΔH^θ_{rxn} = 44 kJ/Kmol. Thus, the reaction is endothermic

ENTROPY

- The randomness or disorder of a system is the entropy (S) of that system. The change in entropy denotes "ΔS".
- Units of ΔS is **J/(K.mol)**

Highlights:

- When a reaction has a +ve ΔS, that is a **favourable** condition. Entropy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which increase entropy are more likely to occur than ones in which the entropy decreases, all things being equal.
- When a reaction has a –ve ΔS, that is an **unfavourable** condition. Reactions which decrease entropy are less likely to occur than ones in which the entropy increases, all things being equal.

Gibbs free energy and Reaction spontaneity

- ➢ The spontaneity of a chemical reaction is the possibility of the reaction occurring or not without the aid of outside energy.
- ➢ Gibbs free energy, ΔG: The energy that is "free" to do work

$$\Delta G\ (kJ/mol) = \Delta H - T\Delta S$$

Highlights:

- ❖ If a reaction occurs without a net input of energy, it is called "spontaneous." This type of reaction actually releases energy.
- ❖ If a reaction requires energy in order to occur, it is called "nonspontaneous." This type of reaction "takes in" energy.

End Result	Sign of ΔH	Sign of ΔS	Sign of ΔG
Spontaneous	-ve (favourable)	+ve (favourable)	–
Depends on T	-ve (favourable)	-ve (unfavourable)	?
Depends on T	+ve (unfavourable)	+ve (favourable)	?
Nonspontaneou	+ve	-ve (unfavourable)	+

LATTICE ENERGY

The positive and negative ion in an ionic crystal are held together by electrostatic forces. The bond energy is expressed in terms of the lattice energy which may be defined as **the change in enthalpy (heat change) that occurs when one mole of a solid crystalline substance is formed from its gaseous ions.**

HESS's LAW APPLICATION IN THE DETERMINATION OF LATTICE ENERGY

Hess's Law: Hess law state that if a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat changes is same, no matter by which method the change is brought about.

The lattice energy of an ionic crystal can be found by applying Hess law.

Hess Law Application in the Determination of Lattice Energy cont'd

Consider an enthalpy change for the direct formation of NaCl

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow NaCl_{(s)}, \qquad \Delta H_f^{\theta} = -411\ KJmol^{-1}$$

Step 1: conversion of sodium metal to gaseous atom

$$Na_{(s)} \longrightarrow Na_{(g)}, \qquad \Delta H_1^{\theta} = +108\ KJmol^{-1}$$

Step 2: Dissociation of chlorine molecules to chlorine atoms

$$\frac{1}{2}Cl_2 \longrightarrow Cl_{(g)}, \qquad \Delta H_2^{\theta} = +121\ KJmol^{-1}$$

Step 3: Enthalpy of ionization; conversion of gaseous sodium to sodium ion by loss of an electron

$$Na_{(g)} \longrightarrow Na^+_{(g)} + e^-, \qquad \Delta H_3^{\theta} = +495\ KJmol^{-1}$$

Step 4: Chlorine atom gains an electron to form chlorine ion. The energy of electron affinity of chlorine

$$Cl + e^- \longrightarrow Cl^-_{(g)}, \qquad \Delta H_4^{\theta} = -348\ KJmol^{-1}$$

Step 5: Sodium and chloride ions get together and form the crystal lattice

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl, \qquad \boldsymbol{\Delta H_5^{\theta} = -(\text{lattice energy})}$$

$$\Delta H_f^{\theta} = \Delta H_1^{\theta} + \Delta H_2^{\theta} + \Delta H_3^{\theta} + \Delta H_4^{\theta} + \boldsymbol{\Delta H_5^{\theta}}$$

$$-411 = 108 + 121 + 495 + (-348) + (-\text{lattice energy})$$

CHEMICAL KINETICS: RATES OF REACTION

Chemical kinetics is the study of the rate of reaction in chemistry

Chemical kinetics covers the following.

1. The rate of reactions and rate laws;
2. The factors as temperature, pressure, concentration and catalyst that influences the rate of reaction;
3. The mechanism or the sequence of steps by which a reaction occurs.

Types of Reaction and Rate of Reactions

Kinetically, ***reactions*** can be distinguished into two types:

i. **Homogeneous**: Reaction takes place entirely in one phase

ii. **Heterogeneous Reactions**: Reaction takes place in two or more phases. *e.g., gaseous reaction taking place on the surface of a solid*

Rates of Reaction

- The rate of reaction is defined as the change in concentration of any reactant or products per unit time
- Rate of a reaction tells us to what speed the reaction occurs

consider a simple reaction: **A** $\rightarrow$ **B**

- concentration of the reactant **A** decreases and that of B increases as time passes.
- The rate of reaction = rate of disappearance of **A** = rate of appearance of **B**:

$$Rate = -d[A]/dt = d[B]/dt$$

- Where, [] = concentration in **mol/L**
- whereas 'd' = infinitesimally small change in concentration
- The **-ve sign** shows the concentration of the reactant **A decreases**
- The **+ve sign** indicates **increase** in concentration of the product **B**.

RATE OF REACTION

Question

Using the data provided below

Time (s)	(Br_2) (M)	Rate(M/s)	k = rxn rate(s^{-1})/[Br_2]
0	0.012	4.2×10^{-5}	3.50×10^{-3}
50	0.0101	3.52×10^{-5}	3.49×10^{-3}
100	0.00846	2.96×10^{-5}	3.50×10^{-3}
150	0.00710	2.49×10^{-5}	3.51×10^{-3}
250	0.00500	1.75×10^{-5}	3.50×10^{-3}

Question: Calculate the average rate over the first 50secs.

Answer

(1). Rate = -(0.0101 – 0.012)/(50 – 0)

Rate = (1.9 x 10-3)/50

Rate = 3.8×10^{-5}

THE RATE OF REACTION AND RATE LAW

At a fixed temperature the rate of a given reaction depends on concentration of reactants. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations.

- The **rate of a reaction** is directly proportional to the reactant concentrations, each concentration being raised to some power. **Case 1.** Substance **A** undergoing reaction: **A** ⟶ **product(s)**

rate α $[A]^m$;

$$\textbf{Rate} = k[A]^m$$

Case 1. a reaction: **2A +B → Products**

The reaction rate with respect to **A** and **B** is determined by varying the concentration of one reactant, keeping that of the other constant.

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

The Rate Law or rate equation

- An expression which shows how rate is related to concentrations is called **the rate law or rate equation**.

example: **2A +B → Products**

Reaction rate =k[A]^m[B]^n

- The power(exponent) of concentration m or n in the rate law is usually a small whole number integer(1,2,3) or fractional.
- The proportionality constant **k** is called the **rate constant** for the reaction.

Order of reaction

- The order of a reaction is defined as the sum of the powers of the concentrations in the rate law.

Let us consider the example of a reaction which has the rate law:

$$rate = k[A]^m[B]^n$$

Order of the reaction = "**m+n**"

- With respect to reactant "A", order of the reaction is **m**
- With respect to reactant "B", order of the reaction is **n**

Overall order of a reaction may range from 1 to 3.

Molecularity of a reaction is defined as the number of reactant molecules involved In a reaction.

Differences between Order and Molecularity of a Reaction

S/N	Order of a reaction	Molecularity of a reaction
1	It is the sum of powers of the concentration terms in the rate law expression	It is number of reacting species undergoing simultaneous collision in the elementary or simple reaction
2	It is an experimentally determined value	It is a theoretical concept
3	It can have fractional value	It is always whole number
4	It can assume zero value	It cannot have zero value
5	Order of a reaction can change with the conditions	Molecularity is invariant for a chemical equation.

DETERMINATION OF THE ORDER OF REACTION AND ITS RATE CONSTANT

By the Inspection method

For a reaction: $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$

$[N_2O_5]$ (mol/L)	Rate (mol/L/h)
0.1	0.016
0.2	0.032
0.4	0.064

- The data indicate that **the rate is doubled as the concentration is doubled**. Thus, **rate ∝ $[N_2O_5]^1$**.
- The reaction is therefore first-order and the rate equation is:

$$\textbf{rate} = k[N_2O_5]^1$$

- The **rate constant, "k"** for the reaction is obtained by substitution of any pair of values from the table into the rate reaction:

k = rate/$[N_2O_5]$

$k = 0.016/0.1$ $k = 0.16\ h^{-1}$

Integrated Rate Laws: *Time dependence of concentration*

(i). Zero order reaction

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus, $[A]^0 = 1$

Thus, rate = k

A zero order reaction is one whose rate is independent of concentration. For example, the rate law for the reaction

$NO_2 + CO \rightarrow NO + CO_2$ at 200°C is ***rate =k[NO$_2$]^2***

Here the rate does not depend on [CO], so this is not included in the rate law and the power of [CO] is understood to be zero. The reaction is zeroth order with respect to CO. The reaction is second order with respect to $[NO_2]$. The overall reaction order is 2+0 = 2

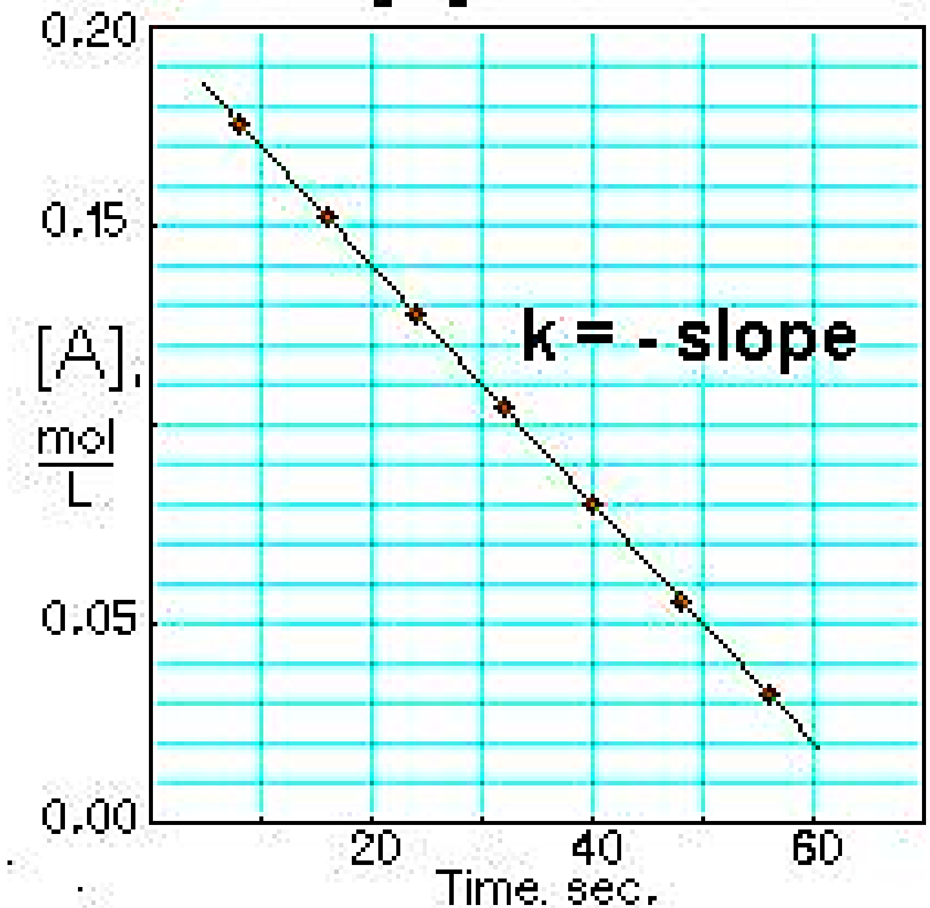
Integrated Rate Laws: *Time-dependence of concentration*

For a zero order reaction, as shown in the following figure, the plot of **[A] versus time** is a straight line with **k = -ve slope** of the l

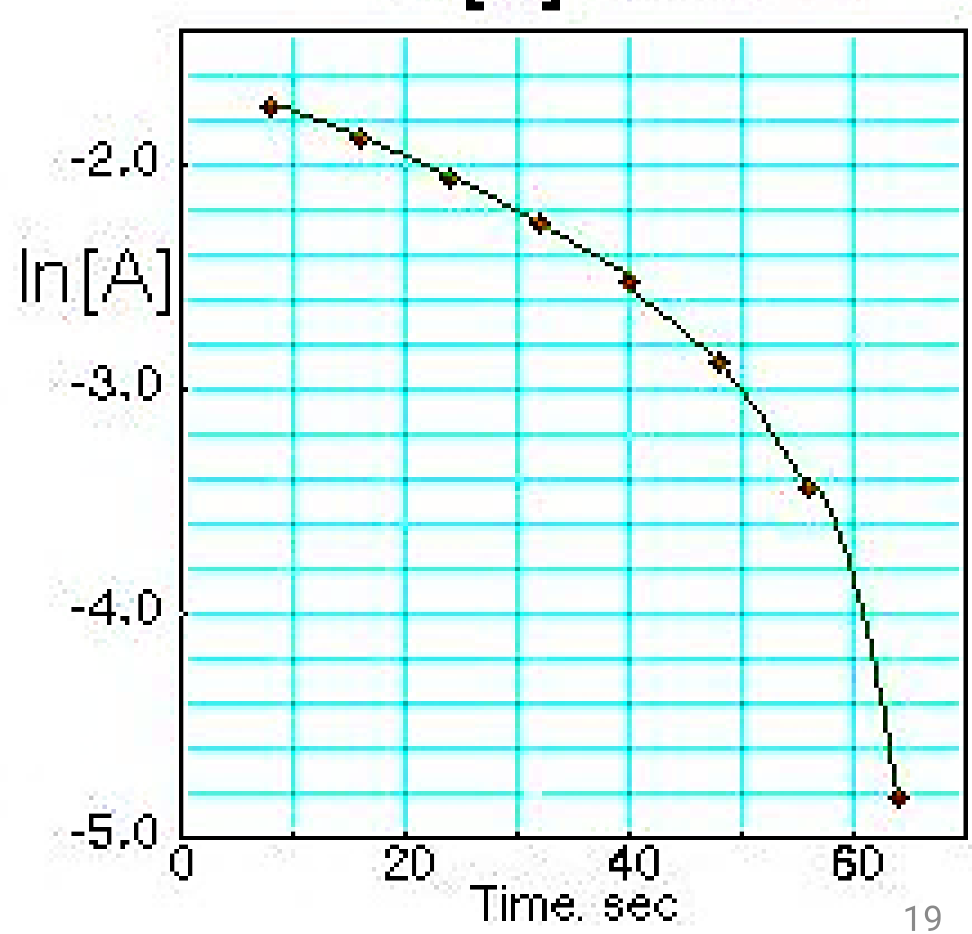
$[A]_t = -kt + [A]_0$

Other graphs are curved for a zero order reaction

[A] vs time



ln[A] vs time



Integrated Rate Laws: *Time-dependence of concentration*

(ii). **<u>First order rxn</u>**, the rate law can be written: **A → products**

$$\boxed{\text{Rate}(\text{Ms}^{-1}) = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]}$$

This is the "***average rate***"

If one considers the infinitesimal changes in concentration and time the rate law equation becomes:

$$\text{Rate}(\text{Ms}^{-1}) = -\frac{d[\text{A}]}{dt} = k[\text{A}]$$

→ This is the "***instantaneous rate***"

Integrating, where [A] = $[A]_0$ at time t = 0, and [A] = [A] at time t = t:

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -k\int_0^t dt$$

Transformed to →

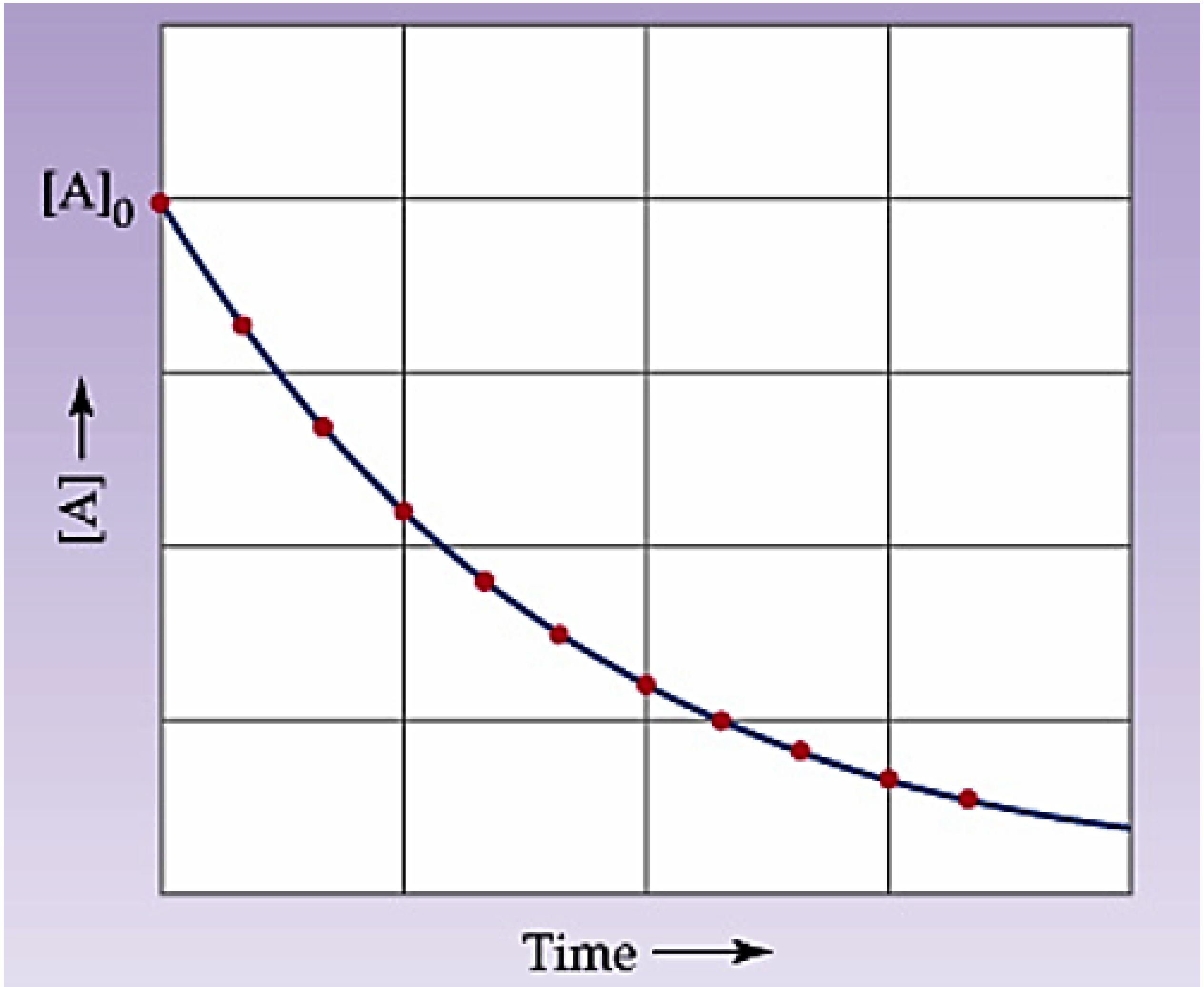
$$\ln\left(\frac{[A]}{[A]_o}\right) = -kt$$

i.e., $$[A] = [A]_o e^{-kt}$$

Integrated Rate Laws: *Time-dependence of concentration*

(ii). First order rxn

$$[A] = [A]_o e^{-kt}$$



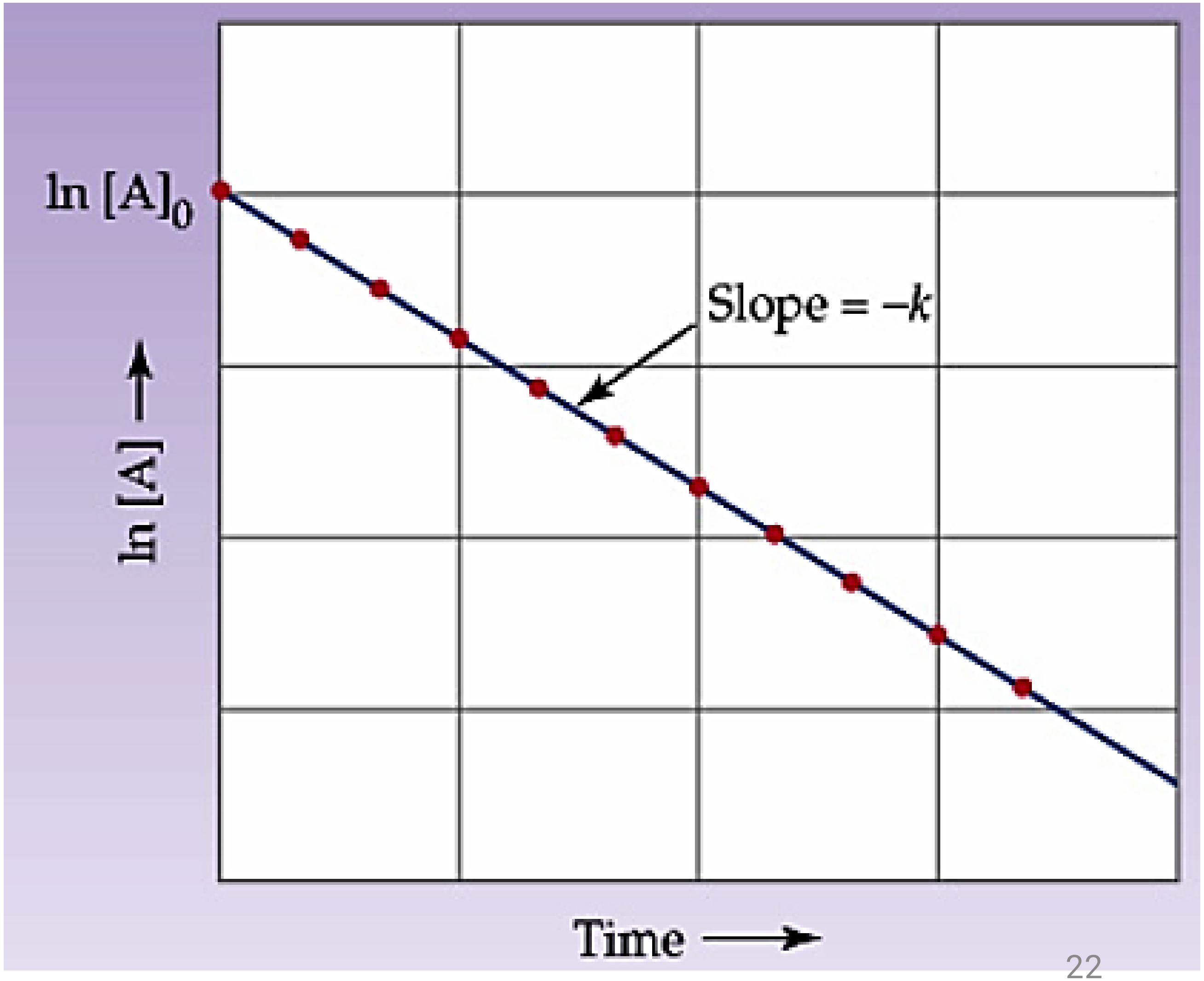
The concentration of a reactant governed by first order kinetics falls off from an initial concentration exponentially with time

Integrated Rate Laws: *Time dependence of concentration*

(ii). First order rxn: To obtain a straight line graph:

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

A plot of ln[A] versus time (t) is a straight line with slope $-k$ and intercept as $\ln[A]_0$



Integrated Rate Laws: *Time-dependence of concentration*

Question:

The conversion of cyclopropane to propene in the gas phase is a first order reaction with a rate constant of $6.7 \times 10^{-4}\ s^{-1}$ at 500 ºC

i. If the initial concentration of cyclopropane was 0.25 M, what is the concentration after 8.8 min?
ii. How long (in minutes) will it take the concentration of cyclopropane to decrease from 0.25 to 0.15 M
iii. How long (in mins) will it take to convert 74% of the starting material

Answer

(a) The reaction is a first order and concentration-time dependent.

Thus, $\ln([A]_t / [A]_o) = -kt$ applies

$[A]_t = ?$

$[A]_o = 0.25$

$k = 6.7 \times 10^{-4}\ s^{-1}$

t = 8.8 min (i.e., 528 s)

$\ln(x/0.25) = -(6.7 \times 10^{-4} \times 528)$

$(x/0.25) = e^{-0.3538}$

$x = 0.176$ M

(b) $\ln([A]_t / [A]_o) = -kt$

i.e., $\ln[A]_t - \ln[A]_o = -kt$

$\ln 0.15 - \ln 0.25 = -(6.7 \times 10^{-4})t$

$-0.5108 = -(6.7 \times 10^{-4})t$

t = 762.4 s (or 12.7 min)

(c) If at time *t*, 74% of the starting material is converted, then what remains as $[A]_t$ is:

26% of 0.25 M = 0.065 M

Hence, $[A]_t = 0.065$ M

$\ln[A]_t - \ln[A]_o = -kt$

$\ln 0.065 - \ln 0.25 = -(6.7 \times 10^{-4})t$

$-1.347 = -(6.7 \times 10^{-4})t$

t = 33.5 min.

Integrated Rate Laws: *Time-dependence of concentration*

(iii). Second order reaction: A → Products

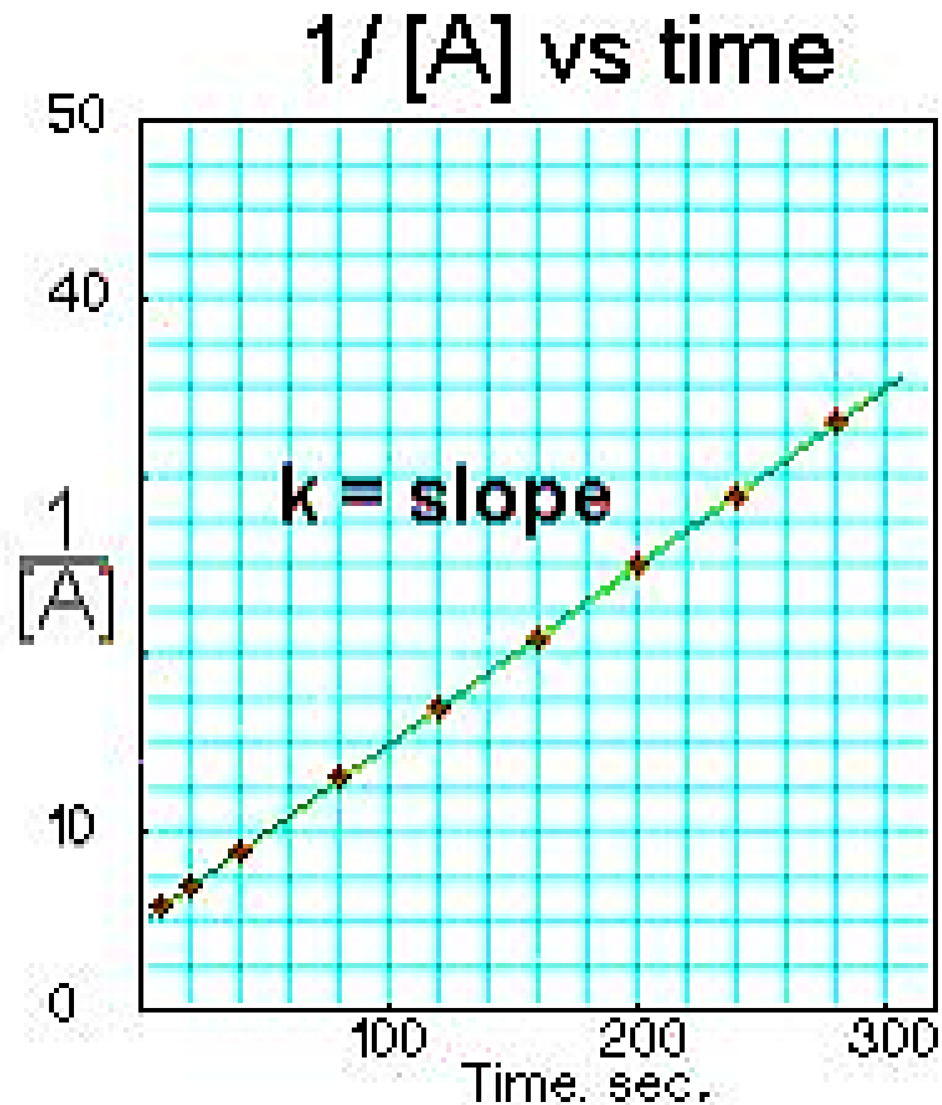
Rate = $k[A]^2$

$$\text{Rate}(\text{Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]^2$$

Integrating as before we find

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

A plot of 1/[A] versus time (t) is a straight line with slope *k* and intercept $1/[A]_0$

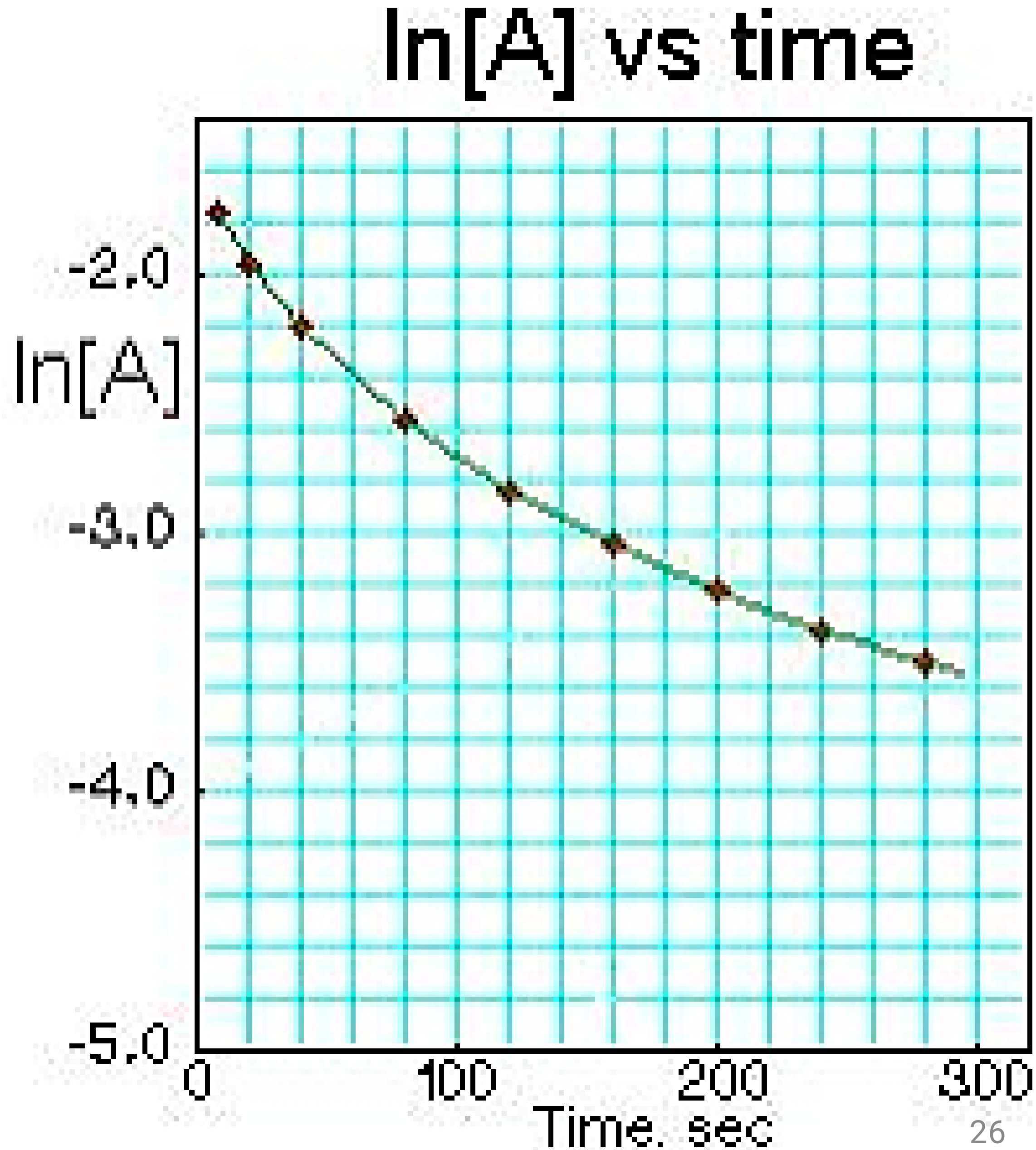


For a second order reaction, a plot of ln[A] vs. *t* is not linear

Integrated Rate Laws: *Time dependence of concentration*

(iii). Second order reaction: A → Products

Non-linearity indicates that the reaction is not first order



Rate law and order of reaction

Question: The reaction of nitric oxide (NO)with hydrogen at 1280^{o}C

$$2NO + 2H_2 \longrightarrow N_2(g) + 2H_2O$$

From the following data collected at this temperature, determine

Experiment	[NO] (M)	[H_2] (M)	Initial rate (M/s)
1	5×10^{-3}	2×10^{-3}	1.3×10^{-5}
2	10×10^{-3}	2×10^{-3}	5×10^{-5}
3	10×10^{-3}	4×10^{-3}	10×10^{-5}

(i) the rate law
(ii) the rate constant
(iii) the rate of the reaction when the concentration of NO = 12×10^{-3} M and concentration of H_2 = 6×10^{-3} M

Answer:

The rate law for the reaction is:

In Exp 1, $r = 1.3 \times 10^{-5}$, then

$$1.3\times10^{-5} = k(5\times10^{-3})^x(2\times10^{-3})^y \;.....(1)$$

In Exp 2, $r = 5 \times 10^{-5}$

$$5\times10^{-5} = k(10\times10^{-3})^x(2\times10^{-3})^y \;......(2)$$

In Exp 3, $r = 10 \times 10^{-5}$

$$10\times10^{-5} = k(10\times10^{-3})^x(4\times10^{-3})^y \;....(3)$$

Equation 2÷1 results:

$$\frac{5\times10^{-5}}{1.3\times10^{-5}} = \frac{k(10\times10^{-3})^x(2\times10^{-3})^y}{k(5\times10^{-3})^x(2\times10^{-3})^y}$$

$$3.85 = \frac{10^x}{5^x}$$

$$2^2 = 2^x$$

$$x = 2$$

Equation 3÷2 results:

$$\frac{10\times10^{-5}}{5\times10^{-5}} = \frac{k\times(10\times10^{-3})^x\times(4\times10^{-3})^y}{k\times(10\times10^{-3})^x\times(2\times10^{-3})^y}$$

$$2 = 2^y$$

$$y = 1$$

the rate law is: **$r = k[NO]^2[H_2]$**

(ii) from equation 1,

$$1.3\times10^{-5} = k(5\times10^{-3})^2(2\times10^{-3})$$

$$k = \frac{1.3\times10^{-5}}{(5\times10^{-3})^2\times(2\times10^{-3})} = 260\ M^{-2}\ s^{-1}.$$

(iii) from the rate law, $r = k[NO]^2[H_2]$,

When $[NO] = 12\times10^{-3}$ M & $[H_2] = 6\times10^{-3}$ M

Then,

$$r = 260\,(12\times10^{-3})^2(6\times10^{-3})$$

$r = 2.25\times10^{-4}\ M\ s^{-1}$.

Summary of Kinetics of Zero order, first order and second order reactions

Order	Rate law	Conc.-time equation	Half-life ($t_{½}$)
0	rate = k	$[A]_t = -kt + [A]_0$	$t_{½} = [A]_0/2k$
1	rate = k[A]	$\ln([A]_t / [A]_0) = -kt$	$t_{½} = 0.693/k$
2	rate = $k[A]^2$	$(1/[A]_t) = kt + (1/[A]_0)$	$t_{½} = 1/k[A]_0$

ACTIVATION ENERGY AND TEMPERATURE DEPENDENCE OF RATE CONSTANTS

The Collision Theory of Chemical Kinetics

A reaction between two particles can occur only if they collide (usually in a gas or liquid phase). Therefore, a reaction rate is proportional to the rate of collision or the number of collisions per second.

Important Facts about Collision

- Rate is not the same as the collision rate but is often directly proportional to it.
- Chemical reactions occur when the energy of collision is enough to break reactant bands and form product bonds.
- If there is not enough kinetic energy in colliding species, reactant bonds will not break and new, product bonds will not form.

Important Facts about Collision cont'd

- Kinetic energy of a gas ∝ temperature. As temperature is increased, more and more molecules will acquire necessary energy greater than *Ea* to cause productive collisions. This increases the rate of reaction
- The kinetic energy of the colliding particles must equal or exceed a certain minimum value in order for a reaction to proceed. ***This minimum energy is called the Activation Energy, Ea***.
- If a collision has enough energy to break some reactant bonds, an ***Activated Complex*** may form
- The products that form may be lower in energy than the reactants (***exergonic or exothermic reaction***) or may be higher in energy than the reactants (***endergonic or endothermic reaction***)

The Arrhenius Equation

The Arrhenius Equation relates the rate constant ***k*** to the ***Ea*** (activation energy, J/mol or kJ/mol), ***R*** (the gas law constant, 8.314 J mol^{-1} K^{-1}) and ***T*** (the absolute temperature, K):

$k = Ae^{-Ea/RT}$, *A* is a dimensionless constant (**Arrhenius constant**) called **the collision frequency** or frequency factor.

To adapt the equation to graphing, take the natural log of both sides. The equation becomes:

$$ln\, k = ln\, A - Ea/RT$$ **or**

$$ln\, k = (-Ea/R)(1/T) + ln\, A$$

compare with: $y = mx + c$

- **A graph of *ln k* against 1/T is linear; where m (the slope, –ve) = Ea/R and *ln* A = intercept of the graph.**

Calculations involving use of Arrhenius Equation

Question: The rate constant for a first-order reaction is $4.5 \times 10^{-4}\ s^{-1}$ at 25 °C. What is its rate constant at 50 °C if the activation energy is 35.6 kJ/mol?

Answer:

$T_1 = (25 + 273.2)$ K = 298.2 K, and $T_2 = (50 + 273.2)$ K = 323.2 K.

Ea = 35.6 kJ/mol = 35600 J mol^{-1}, since **R** is 8.314 J mol^{-1} K^{-1}

Note: collision frequency A (Arrhenius constant), being the same, has cancelled out of the equation

Recall: $ln\ k = ln\ A - Ea/RT$

Using $ln\ k_1 - ln\ k_2 = -Ea/RT_1 + Ea/RT_2$

$$\boxed{ln\ k_2 = ln\ k_1 + Ea/R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$ln\ k_1 + Ea/RT_1 - Ea/RT_2 = ln\ k_2$;

$ln\ k_2 = -7.71\ s^{-1} + 4281.93\ K\ (2.597 \times 10^{-4}\ K^{-1})$

$ln\ k_2 = -6.60$, $k_2 = 1.36\ 10^{-3}\ s^{-1}$.

THANK YOU FOR LISTENING