

Metallurgical Kinetics

Determination of order and rate constant of a reaction



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First Order Reaction

Let us consider a first order reaction



Initially, a 0

At time t , $a - x$ x

Rate equation for first order reaction: $-d[A]/dt = k [A]$

$$-\frac{d[A]}{dt} = -\frac{d(a-x)}{dt} = \frac{dx}{dt}$$

$$\frac{dx}{dt} = k(a-x) \quad \text{or} \quad \frac{dx}{(a-x)} = k dt$$

On integrating

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

The units is measured as $(\text{time})^{-1}$ and can be represented as $(\text{sec})^{-1}$, $(\text{min})^{-1}$, $(\text{hour})^{-1}$



Determination of First Order Rate Constant

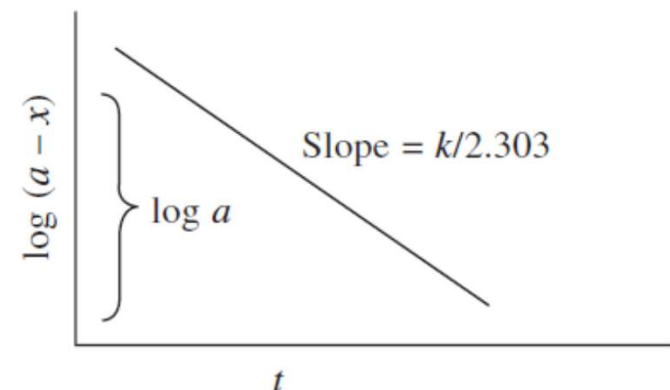
- Substitution Method:

Experimentally determine (a-x) values at different time, t. These values are substituted in equation and an average value of the rate constant is determined.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

- Graphical method:

$$\log (a-x) = -\frac{k}{2.303} t + \log a$$





- Half life method:

The time required for the concentration of reactant to decrease by a fifty percent of the initial concentration

Substituting $t = t_{1/2}$ when $x = a/2$,

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - a/2}$$

$$t_{1/2} = \frac{2.303 \log 2}{k}$$

Independent of initial concentration of reactant



Example:

- 50 min is required to complete 25% of a first order. if the initial concentration of the reactant is $5 \times 10^3 \text{ mol dm}^{-3}$, what will be concentration at the end of another 50 min?



Ans.

- $(a-x) = 5 \times 10^3 - (5 \times 10^3) \cdot 0.25 = 3.75 \times 10^3$
- $k = \frac{2.303}{50} \log \frac{5 \times 10^3}{3.75 \times 10^3} = 5.575 \times 10^{-3} \text{ min}^{-1}$
- Concentration after another 50min. Total time = 100 min
- $(a-x) = ae^{-kt} = 2.81 \times 10^3 \text{ mol/dm}^3$



Example

Decomposition of a reactant at a constant temperature, T

[A], mole/dm ³	Rate, mole dm ⁻³ sec ⁻¹
0.15	0.05
0.6	0.2
1.2	0.4
2.1	0.7

Find the order of reaction.
Calculate rate constant and the rate of decomposition of A, when [A] = 0.45 mol dm⁻³.



Ans.

- $-\frac{d[A]}{dt} \propto [A]$ First order
- $k = \frac{-\frac{d[A]}{dt}}{[A]} = \frac{0.05}{0.15} = 0.33 \text{ sec}^{-1}$
- $-\frac{d[A]}{dt} = k[A] = 0.33 \text{ sec}^{-1} \times 0.45 \text{ mole dm}^{-3}$
 $= 0.1485 \text{ mole dm}^{-3} \text{ sec}^{-1}$



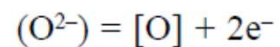
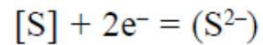
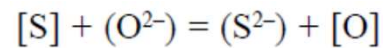
Problem

- Removal of sulfur from hot metal at a constant temperature

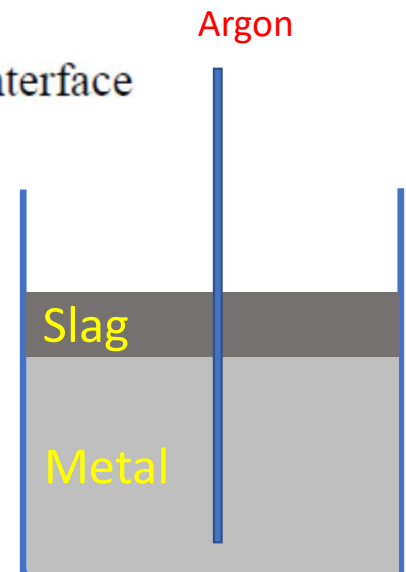
Time, min	[S]
0	1000
4	860
15	825
33	568
63	448
91	208
151	72
234	27

Assuming 1st order reaction kinetics, calculate rate constant

Home Work

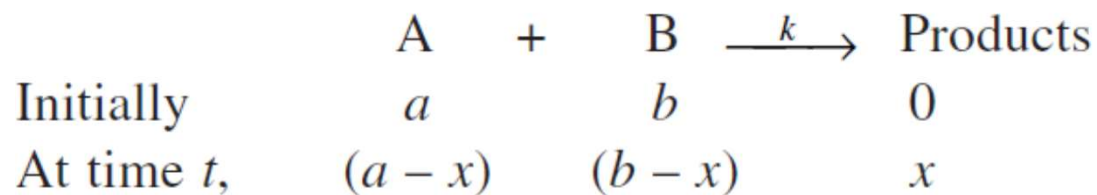


1. Transfer of sulfur from the bulk of the metal phase to the slag-metal interface
2. Transfer of O^{2-} from bulk of the slag phase to the interface
3. Chemical reaction at the interface
4. Transfer of oxygen from the interface to the bulk metal
5. Transfer of S^{2-} from the interface to the slag phase





Second Order Reaction having Different Initial Concentrations



Rate of reaction:

$$\frac{dx}{dt} = k(a - x)(b - x)$$

$$\frac{dx}{(a - x)(b - x)} = k dt$$



Using method of partial fraction:

$$\frac{1}{(a-x)(b-x)} = \frac{p}{(a-x)} + \frac{q}{(b-x)}$$

$$\frac{dx}{(b-a)(a-x)} - \frac{dx}{(b-a)(b-x)} = kdt$$

On integration:

$$\frac{1}{(b-a)} \ln a/(a-x) - \frac{1}{(b-a)} \ln b/(b-x) = kt$$



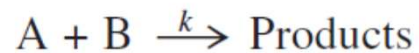
Rearranging

$$k = \frac{1}{(a - b)t} \ln \left\{ \frac{b(a - x)}{a(b - x)} \right\}$$

$$k = \frac{2.303}{(b - a)t} \log \left\{ \frac{(b - x) a}{b(a - x)} \right\}$$



Second Order Reaction



Initial concentration of each reactant A and B is same

$$\frac{dx}{dt} = k(a - x)(a - x) = k(a - x)^2$$

$$\frac{dx}{(a - x)^2} = kdt$$

On integrating and putting $x=0$ at $t=0$,

$$\frac{1}{(a - x)} = kt + \frac{1}{a}$$

$$k = \frac{1}{t} \left[\frac{x}{a(a - x)} \right]$$

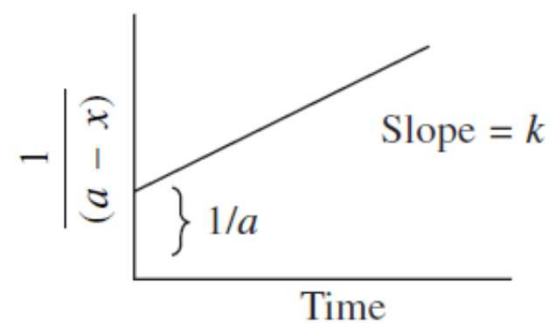


Half life Method

$$k = \frac{1}{t_{1/2}} \cdot \frac{a/2}{a(a - a/2)}$$

$$t_{1/2} = \frac{1}{ka}$$

Graphical Method



The unit of rate constant is (conc.)⁻¹ (time)⁻¹ or mol⁻¹dm³sec⁻¹



Example

- For a second order reaction, both the reactant have same initial concentration of $0.02 \text{ mol. dm}^{-3}$. The rate constant was found to be $5.55 \text{ mol}^{-1}\text{dm}^3\text{min}^{-1}$. Calculate the fraction of the reaction after 30 min and time required for 30% reaction.



Ans.

$$k = \frac{1}{t} \frac{x}{(a - x)}$$

Assume f is the fraction of reaction, so $x=af$

$$f=0.769 \text{ or } 76.9\%$$

For $f=0.3$

$$t = 3.86 \text{ min}$$



Example

- 30% of a second order reaction is completed in 30 min. Calculate the rate constant and final concentration after 60 min of a reaction



Ans.

$$k = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right]$$

Let $a = 100$, $x = 30$ and $a - x = 70$. Putting the values in above, we get

$$k = 1.42 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}.$$

Further

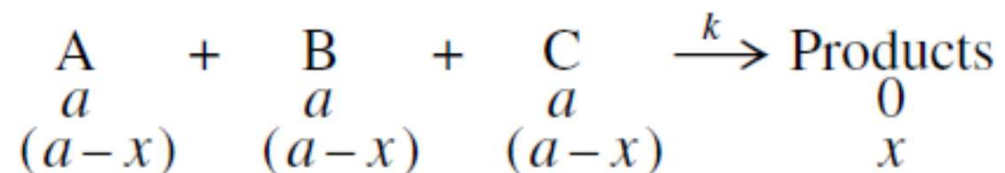
$$k = \frac{1}{60} \left[\frac{1}{a-x} - \frac{1}{100} \right]$$

$$a - x = 1.16\%$$



Third Order Reaction

Consider the reaction: three reactants are involved with same initial concentrations



$$\text{Rate} = \frac{dx}{dt} = k(a-x)^3$$

On rearranging and integrating

$$k = \frac{1}{2t} \left(\frac{1}{(a-x)^2} - \frac{1}{a^2} \right)$$

Units of rate constant is $(\text{conc.})^{-2} (\text{time})^{-1}$
or generally $\text{mol}^{-2} \text{lit}^2 \text{sec}^{-1}$ or
 $\text{mol}^{-2} \text{dm}^6 \text{sec}^{-1}$

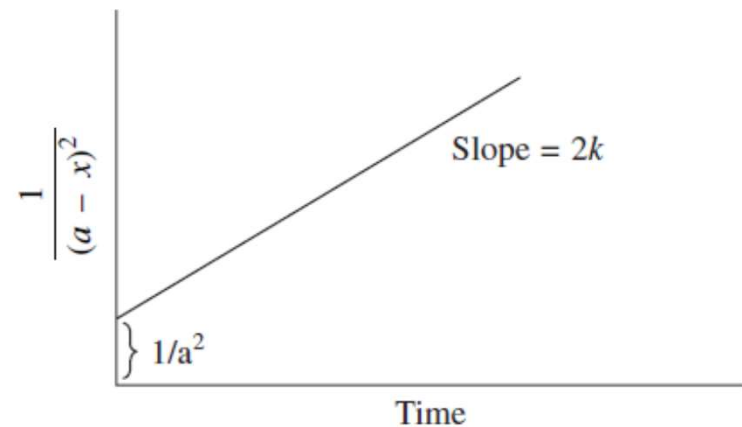


- Half life period: $t = t_{1/2}$ when $x = a/2$

$$t_{1/2} = \frac{3}{2ka^2}$$

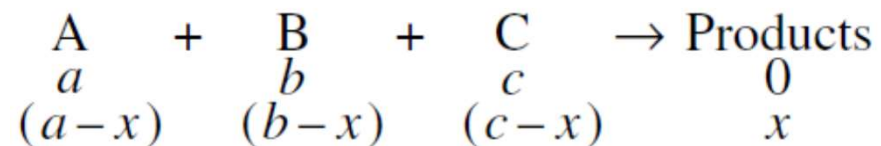
- Graphical method:

$$\frac{1}{(a-x)^2} = 2kt + \frac{1}{a^2}$$





Three reactants with different initial concentrations



$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

Integrated with help of partial

fractions $k = \frac{2.303}{t(a-b)(b-c)(c-a)} \left[(b-c) \ln \frac{a-x}{a} + (c-a) \ln \frac{b-x}{b} + (a-b) \ln \frac{c-x}{c} \right]$



Zero Order Reactions



Rate Equation

$$\frac{dx}{dt} = k$$

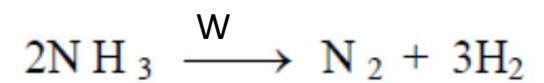
$$x = kt \quad \text{or} \quad k = \frac{x}{t}$$

Unit of rate constant as $\text{mol dm}^{-3} \text{sec}^{-1}$ or conc. (time)^{-1}



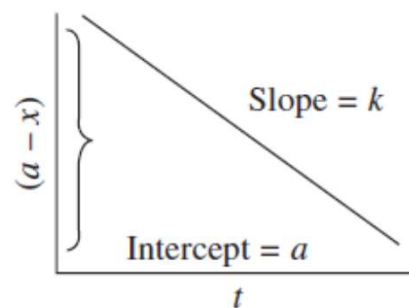
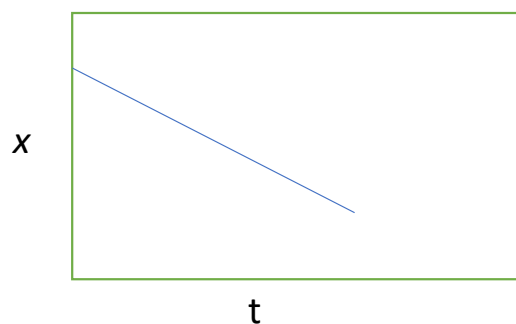
- Half life method:

$$t_{1/2} = \frac{a}{2k}$$



$$\text{rate} = k [\text{NH}_3]^0$$

- Graphical method:





Example

- For a zero order reaction 50% completed in 20min. Calculate the time required to complete 90% reaction



Ans.

Let $a = 100 \text{ mol dm}^{-3}$

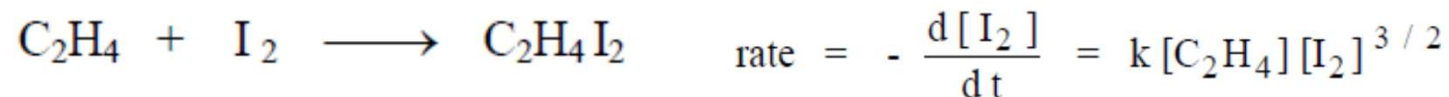
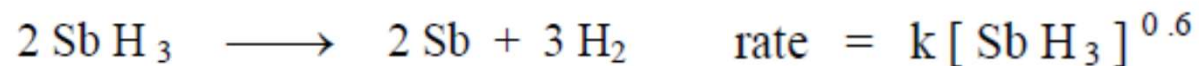
$$k = \frac{50}{20} = \frac{5}{2}$$

For 90% reaction:

$$\frac{5}{2} = \frac{90}{t} \quad t=36 \text{ min}$$

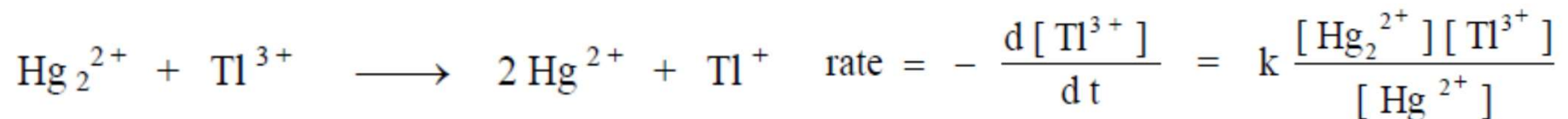
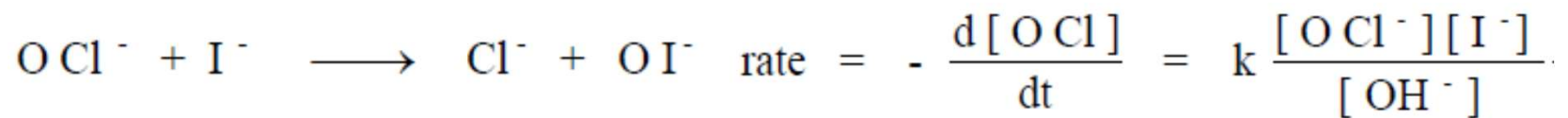
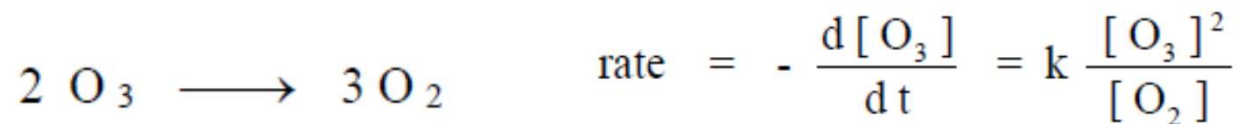


Examples of fractional order





Negative order





Example



S. No	[OCl ⁻]	[I ⁻]	[OH ⁻]	Rate /10 ⁻⁴
1	0.0017	0.0017	1.0	1.75
2	0.0034	0.0017	1.0	3.50
3	0.0017	0.0034	1.0	3.50
4	0.0017	0.0017	0.5	3.50

- Determine order of the reaction



Ans.

$$\text{Rate} = [\text{OCl}^-]^x [\text{I}^-]^y [\text{OH}^-]^z$$

$$1.75 \times 10^{-4} = [0.0017]^x [0.0017]^y [1]^z$$

$$3.5 \times 10^{-4} = [0.0034]^x [0.0017]^y [1]^z$$

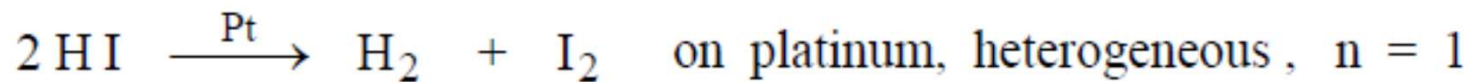
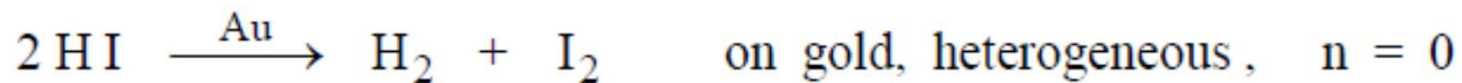
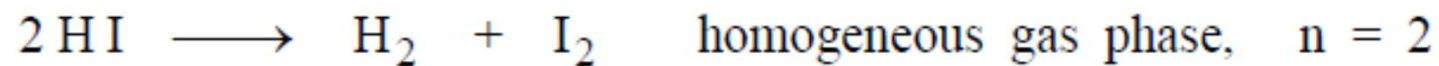
$$3.5 \times 10^{-4} = [0.0017]^x [0.0034]^y [1]^z$$

$$3.5 \times 10^{-4} = [0.0017]^x [0.0017]^y [0.5]^z$$

$$x = 1, y = 1 \text{ and } z = -1$$

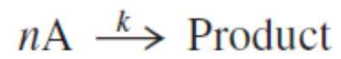


Experimental conditions





General



$$-dc/dt = kc^n$$

$$\int \frac{dc}{c^n} = k \int dt$$

$$dx/dt = k(a - x)^n$$

$$\int dx/(a - x)^n = \int kdt$$



Dimensionless Rate equation

$$\alpha = \frac{C_0 - C}{C_0 - C_\infty}$$

$$C_\infty = 0$$

$$C = C_0(1 - \alpha)$$

Rate equation

$$\frac{d\alpha}{dt} = \frac{k \cdot C_0^n \cdot (1 - \alpha)^n}{C_0} = k' \cdot (1 - \alpha)^n$$

$$n = 0$$

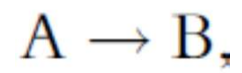
$$\alpha = kt$$

$$n = 1$$

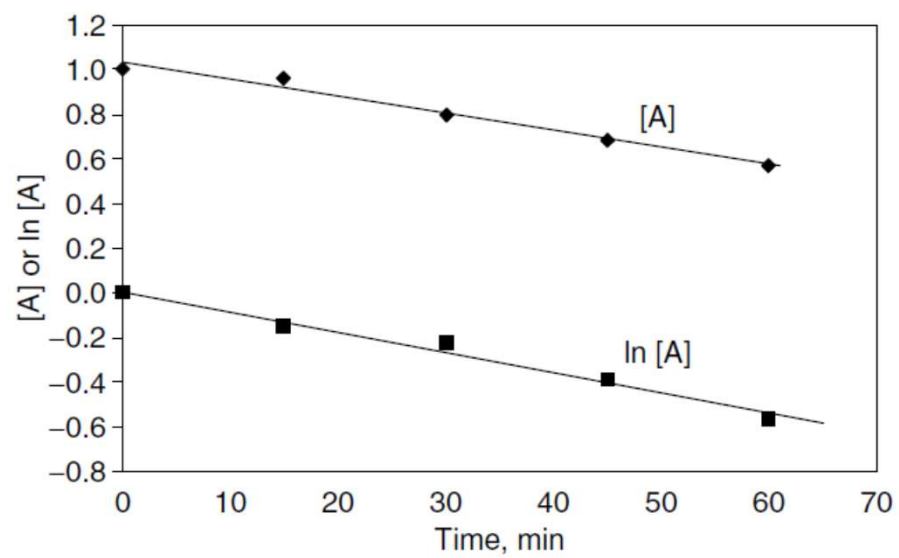
$$-\ln(1 - \alpha) = kt$$

In general, the integral form of the rate equation is written as

$$g(\alpha) = kt$$

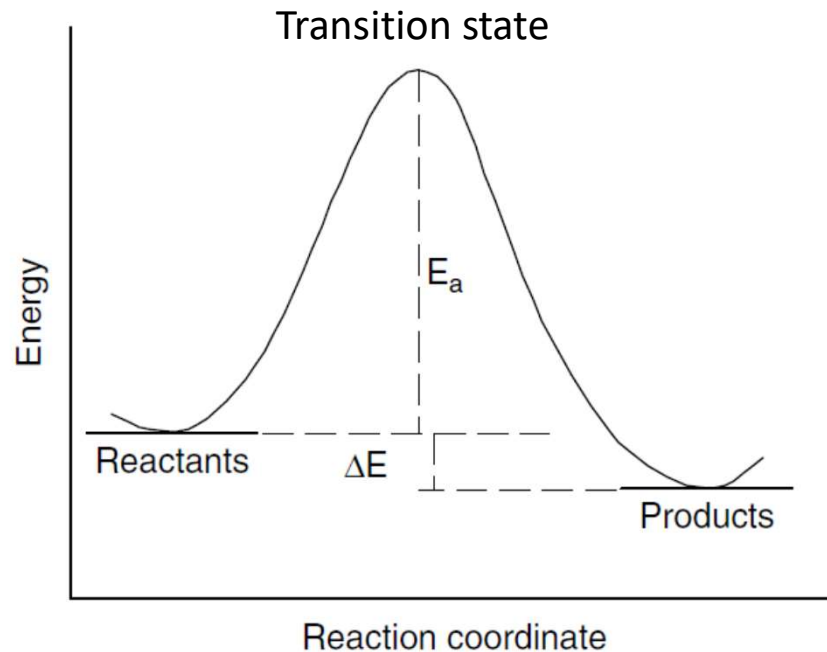


Time,min	[A]
0	1
15	0.86
30	0.8
45	0.68
60	0.57





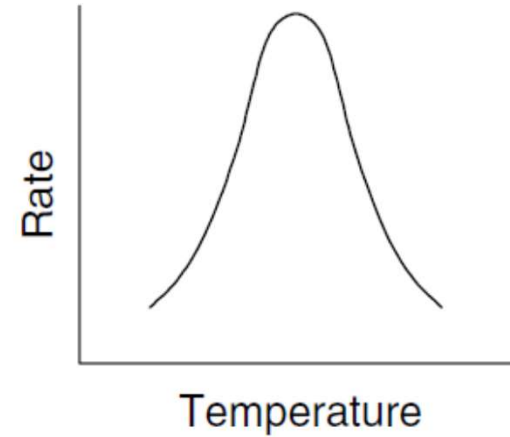
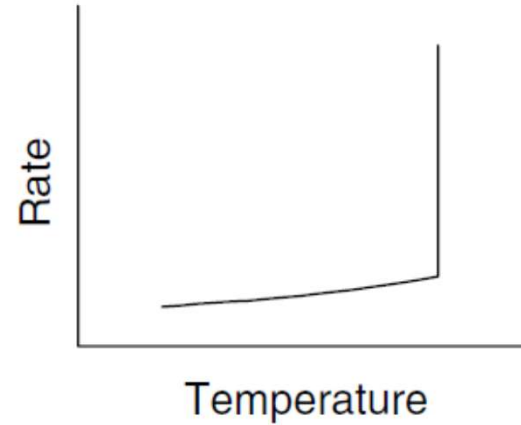
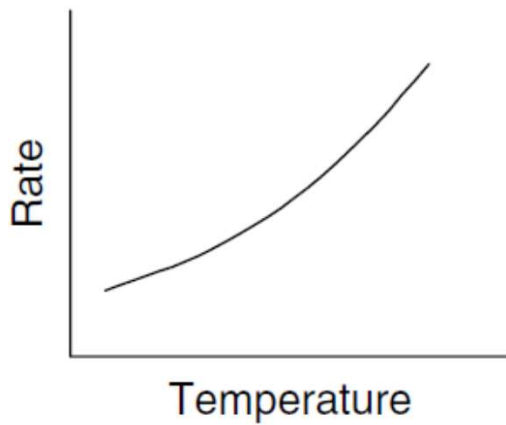
Temperature Effect on Reaction Rate



- The height of the energy barrier over which the reactants must pass on the way to becoming products is known as the activation energy



Reaction rates vary with temperature





Arrhenius Equation

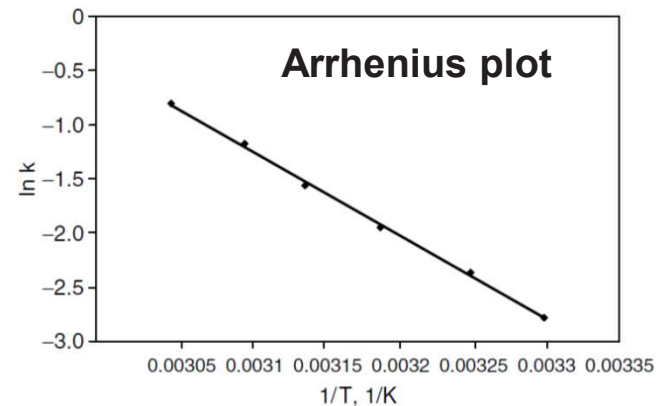
The rates of most reactions vary with temperature

$$k = Ae^{-E_a/RT}$$

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

At 1000K, $1/T = 0.001 \text{ K}^{-1}$
at 1005K, $1/T = 0.00095 \text{ K}^{-1}$

k is the rate constant,
A is the frequency factor (or pre-exponential factor),
R is the molar gas constant,
E_a is the activation energy, and
T is the temperature (K).





$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln k_1 - \ln k_2 = \left(\ln A - \frac{E_a}{RT_1} \right) - \left(\ln A - \frac{E_a}{RT_2} \right)$$

$$\ln \frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{RT_1T_2}$$



Example

The reduction of iron ore-coal composite pellet proceeds with an activation energy of about 56 KJ/mole. How much faster is the reduction reaction at 950°C than 850°C



Different form

$$\begin{aligned}r_i &= f_1(\text{temperature}) \cdot f_2(\text{composition}) \\ &= k \cdot f_2(\text{composition})\end{aligned}$$

- At the same concentration, but at two different temperatures, Arrhenius' law indicates that

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{\mathbf{E}}{\mathbf{R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- Now, the rate is inversely proportional to the reaction time, or rate $\propto 1/\text{time}$ so

$$\ln \frac{r_2}{r_1} = \ln \frac{t_1}{t_2} = \frac{\mathbf{E}}{\mathbf{R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$



Example

- To complete a reaction, 30 min is required when temperature is set at 63°C , but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy?



Answer

$$\ln \frac{30}{0.25} = \frac{\mathbf{E}}{8.314} \left(\frac{1}{336} - \frac{1}{347} \right)$$

$$\mathbf{E} = 422\,000 \text{ J/mol}$$



$$\begin{array}{ll} \text{at 400 K} & -r_A = 2.3 p_A^2 \\ \text{at 500 K} & -r_A = 2.3 p_A^2 \end{array} \quad \text{where} \quad \begin{cases} -r_A = \left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right] \\ p_A = [\text{atm}] \end{cases}$$

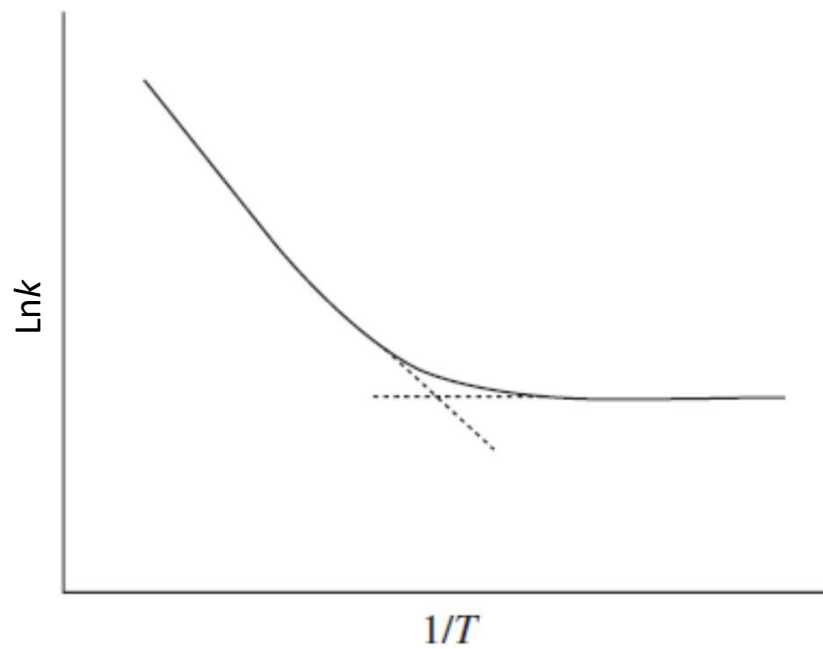
$$\ln \frac{k_2}{k_1} = \ln \frac{2.3}{2.3} = 0$$

$$p_A = \frac{n_A}{V} \mathbf{R}T = C_A \mathbf{R}T$$



Steps to be followed

- The concentration of a reactant or product after various time intervals at a constant temperature
- Fit the data to find the appropriate rate law
- Determine the rate constant at the temperature
- Study the reaction over as wide a range of temperature as possible, repeating steps 1-3
- Fit the rate constants to the Arrhenius equation and determine the activation energy



*A high temperature favors the reaction of higher activation energy,
a low temperature favors the reaction of lower activation energy.*

