CHAPTER 10.3: FACTORS AFFECTING REACTION RATE

Objectives:

- Explain the following effects on the reaction rate
  - Temperature change
    - Maxwell-Boltzman distribution curve
  - Catalyst
    - Using energy profile diagram
  - Concentration or pressure change
  - Particle size
- Arrhenius Equation

Factor Affecting Reaction Rate

- ***CONCENTRATIONS OF REACTANTS*:**

  Reaction rates generally **increase** as the **concentrations** of the reactants **are increased**.

- ***TEMPERATURE*:**

  Reaction rates generally **increase** rapidly as the **temperature** is **increased**.

- ***CATALYSTS*:**

  Catalysts **speed up** reactions.

- ***PARTICLE SIZE*:**

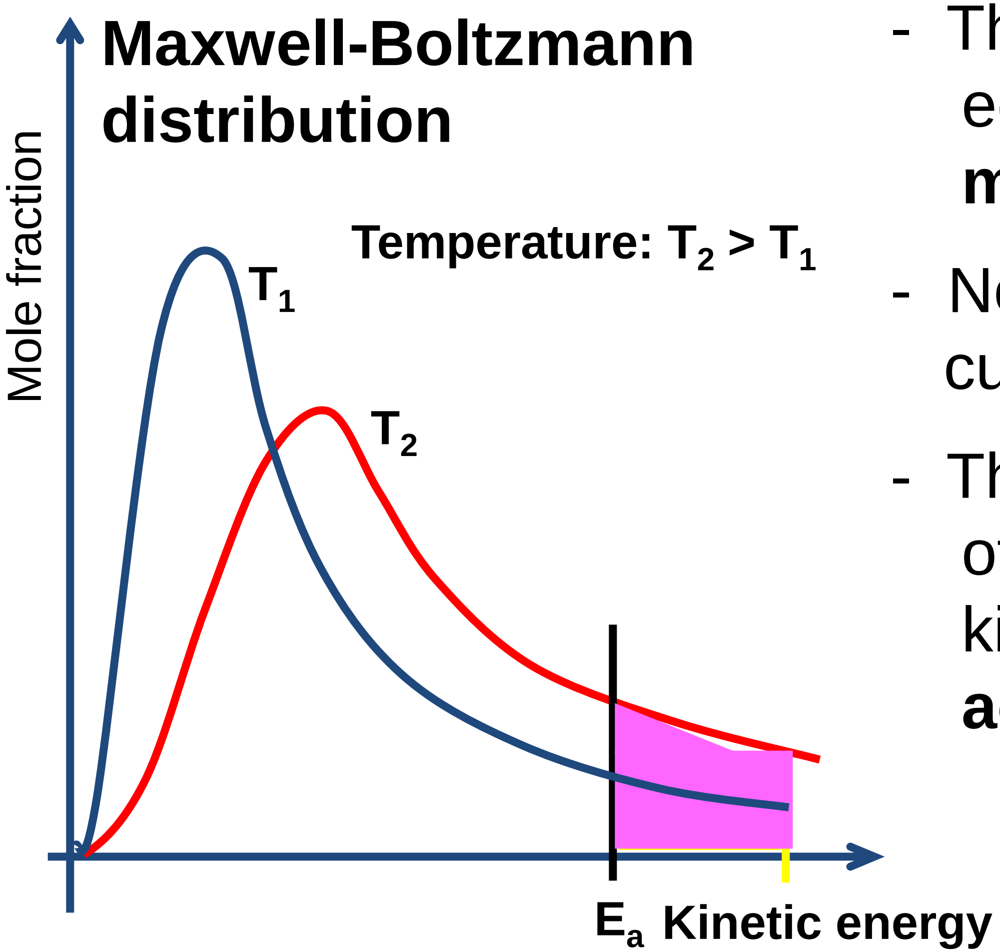
  The **rate increases** as **the smaller the size** of reacting particles.

Effect of Temperature

- As **temperature** increases, **kinetic energy** of molecules increases
- More **collisions** occur in a given time
- **Effective collisions** will increase
- More molecules will have energy greater than **activation energy, E_a**
- Thus, the **rate of reaction** increases

Temperature ↑
Kinetic energy ↑
Frequency of collision ↑
Effective collision ↑
Rate of reaction ↑

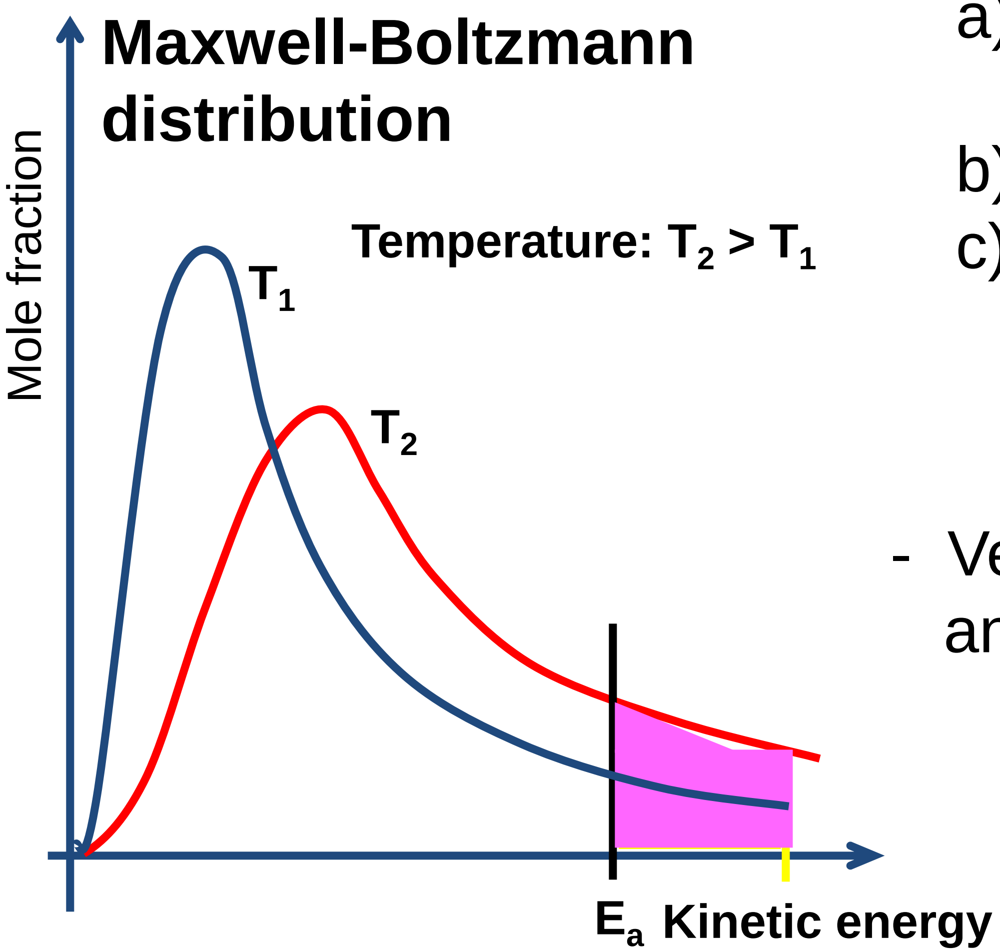
Effect of Temperature



Features:

- The area under the curve equal to the **total number of molecules**
- No of molecules below **both** curve are the **same**
- The shaded area represent no of molecules possessing kinetic energy, **KE ≥ activation energy, Ea**

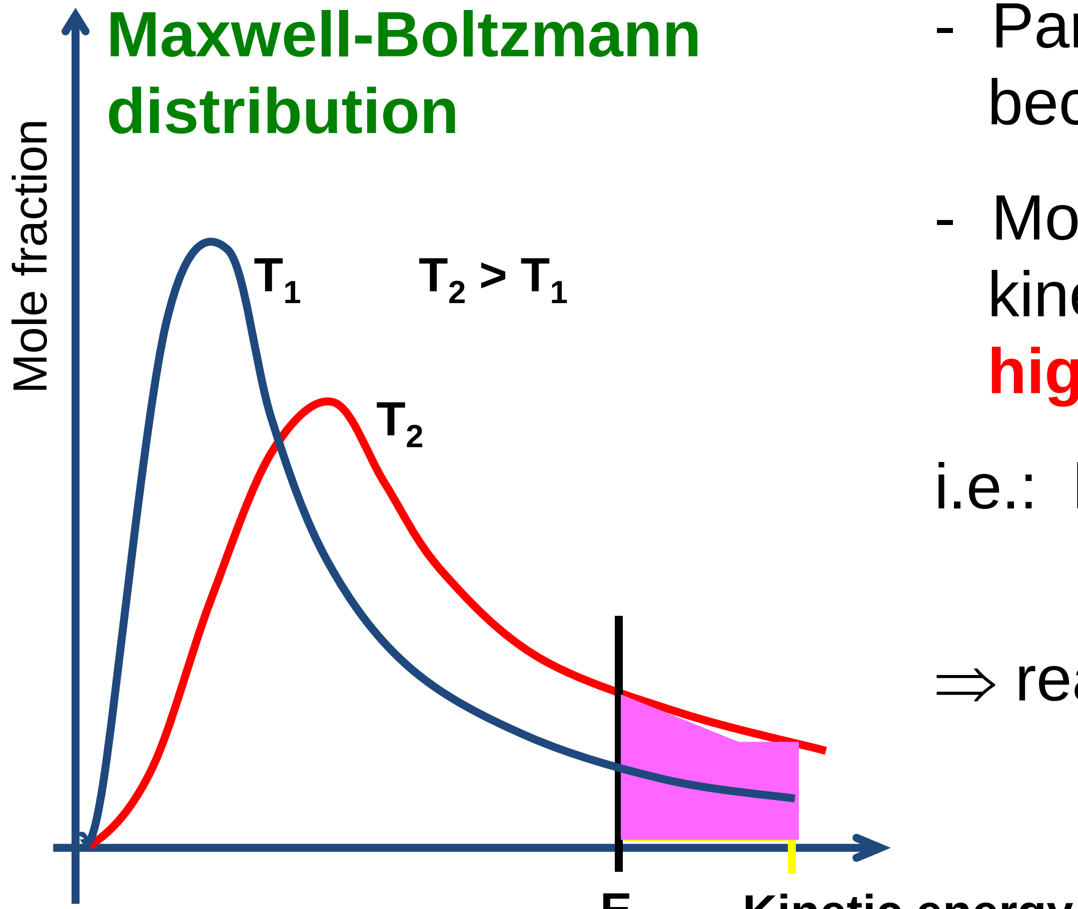
Effect of Temperature



Features:

- At higher temperature (T_2),
  a) the peak of the curve **moves** to the right
  b) the curves **flattens**
  c) more molecules with **higher kinetic energy, KE** (larger pink shaded area)
- Very **few molecules** have low and high KE

Effect of Temperature



At **higher temperature (T_2)**

- Particles absorb energy and become **more energetic**

- More molecules posses kinetic energy **equal to or higher** than E_a

i.e.: higher frequency of effective collision

$\Rightarrow$ reaction rate at T_2 **increases**

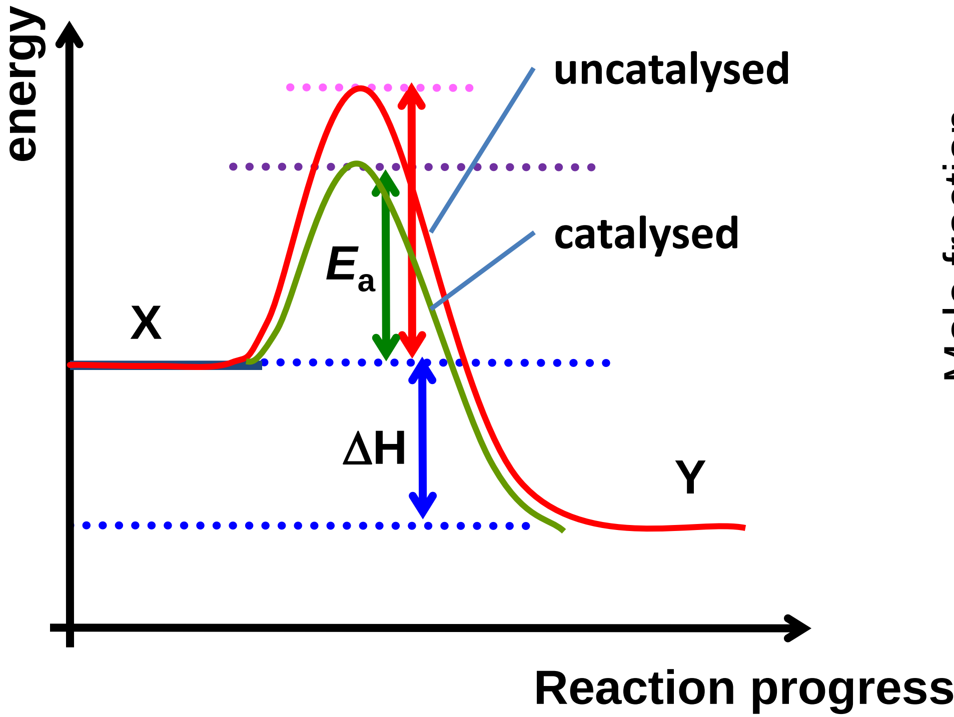
E_a: activation energy – minimum energy needed to initiate a chemical reaction

Effect of Catalyst

- A ***catalyst*** is **a substance that increases the rate of a chemical reaction without itself being consumed.**
- Addition of a catalyst increases the reaction rate by **increasing the frequency of effective collision**. That is by
  - **Decreasing the E_a**, and
  - **Correct orientation**

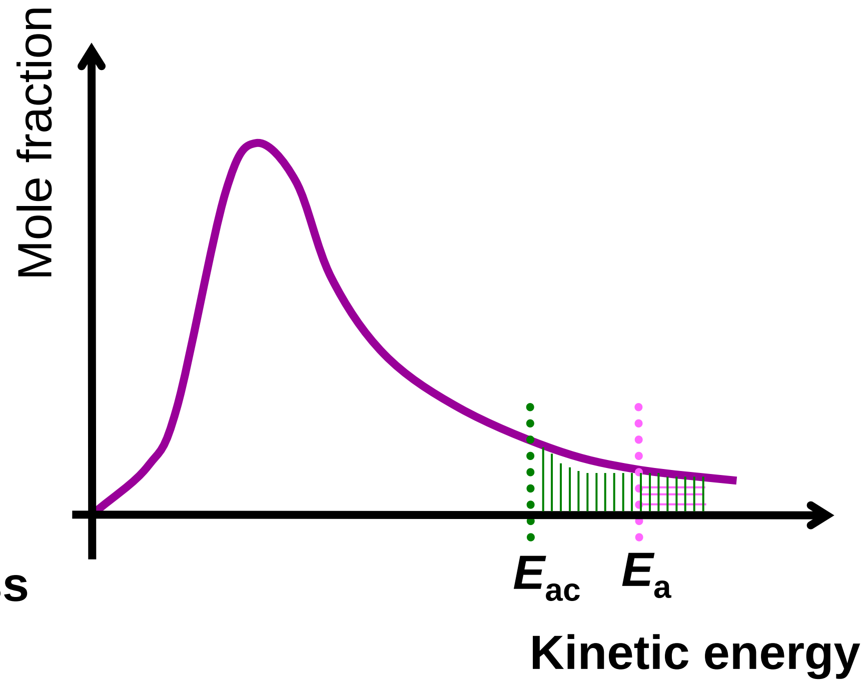
Effect of Catalyst

Exothermic reaction



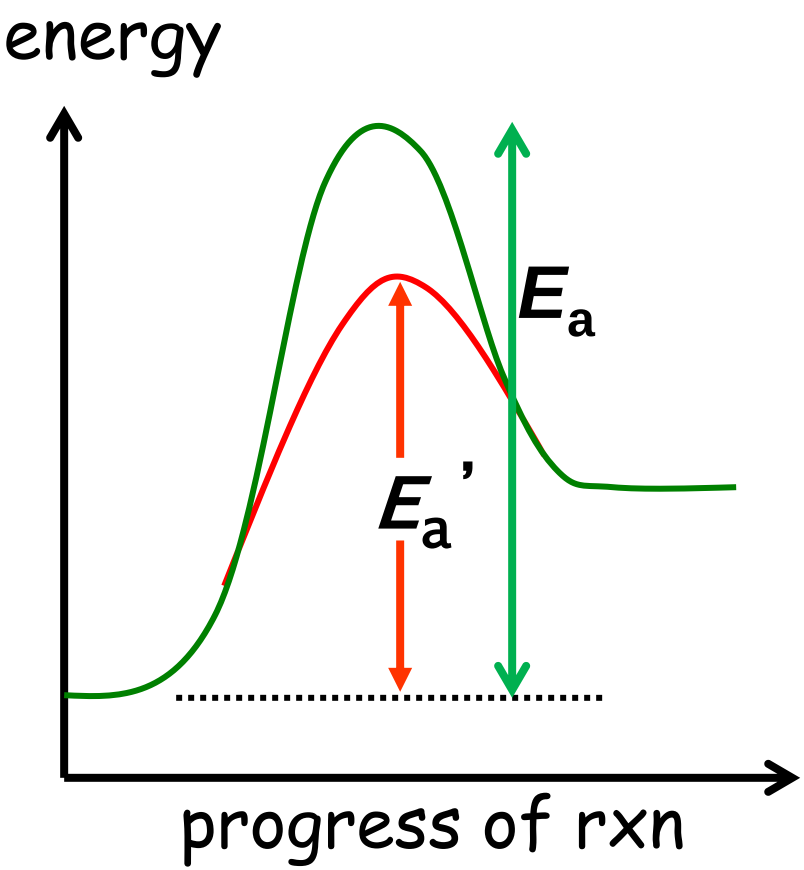
When $E_a \downarrow$

$\Rightarrow$ **more** molecules with **high KE**



Effect of Catalyst

Endothermic reaction



In the presence of catalyst, E_a is lower

- **More** molecules have KE equal to or higher than E_a
- the probability of effective collisions also **increases**
- thus, reaction rate **increases**.

Effect of Catalyst

Characteristics **of Catalyst:**

- They catalyze a **specific reaction**
- Catalysts **lower by the same amount** the activation energies of the forward and backward reactions of a reversible reaction.
- A catalyst neither **alters the position** of equilibrium nor **increases the yield of products**.
- Catalysts **do not** change the value of **ΔH** (enthalpy change) and ***K*** (equilibrium constant) but **change** the ***K*** (rate constant) – rate law @ arrhenius eq
- The catalyst may be **changed physically** but the **mass** of catalyst is **unchanged** at the end of the reaction.
- It won’t be **denaturalised** at high temperature.

Effect of Catalyst

Catalyst added
Activation energy, Ea ↓
Molecules posses kinetic energy
equal to or higher than E_a ↑
Frequency of collision ↑
Effective collision ↑
Rate of reaction ↑

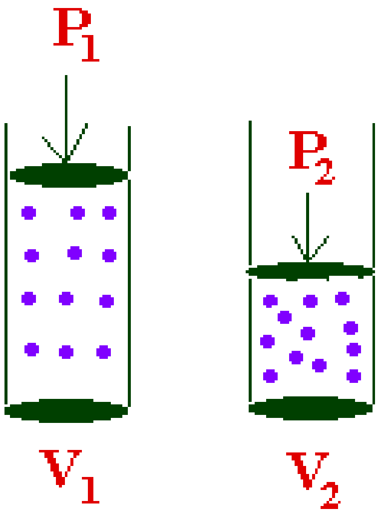
Effect of Concentration / Pressure

Reactant concentration / Pressure of gases

$$p\,V = n\,R\,T$$

$$p = (n/V)\,RT \quad \Rightarrow \quad p = c\,R\,T$$

$$\Rightarrow \quad \textbf{pressure, } \boldsymbol{p} \;\propto\; \textbf{concentration, } \boldsymbol{c}$$



Explanation:

p **or** ***c*** ↑,
- particles are **closer** to each other
- More likely to collide (higher collision frequency)
- Probability of **Effective collision increases**
- More molecules with kinetic energy equal to or greater than $\boldsymbol{E_a}$
- Reaction rate **increases**

Effect of Concentration / Pressure

However:,

Concentration change has

No effect on zero-order

reaction

Example: $\boldsymbol{R} \longrightarrow$ **product**

Rate law: $r = \mathrm{k}\,[\boldsymbol{R}]^{\circ}$

Rate is independent of [*R*]

Effect of Concentration / Pressure

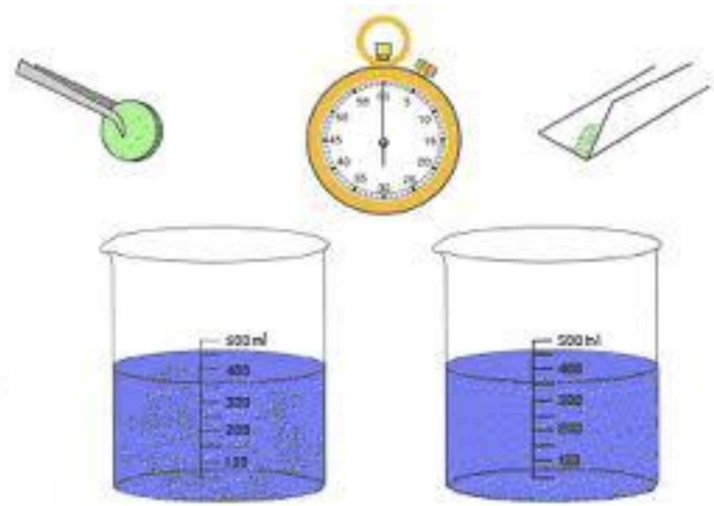
No of collision of molecule per unit volume ↑

Frequency of collision ↑

Effective collision ↑

Rate of reaction ↑

Effect of Particle Size



- The **smaller** the size of reacting particles, the **<u>larger</u>** the **contact surface area** (*solid reactant*).
- thus frequency of collision increases
- probability of **<u>effective collision</u>** also **<u>increases</u>**
- thus the reaction rate **<u>increases</u>**.

Effect of Particle Size

Size particle ↓

Total surface area ↑

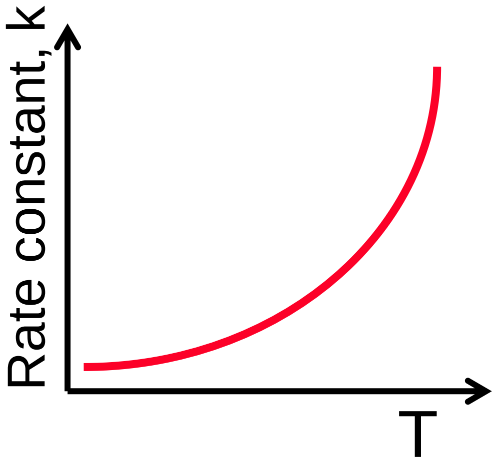
Frequency of collision ↑

Effective collision ↑

Rate of reaction ↑

Arrhenius Equation

$$k = A\, e^{-E_a/RT}$$



T↑ k↑ rate↑

Where…

k = rate constant

A = collision frequency factor
(is a measure of the probability of a favorable collision)

e = natural log exponent

E_a = activation energy for the reaction (**kJ/mol**)

R = universal gas constant (8.314 J mol^{-1} K^{-1})

T = absolute temperature (T in **Kelvin**)

Arrhenius Equation

$$\text{rate constant, } k = A\, e^{-E_a/RT}$$

T ↑, $\mathbf{E_a}$ ↓

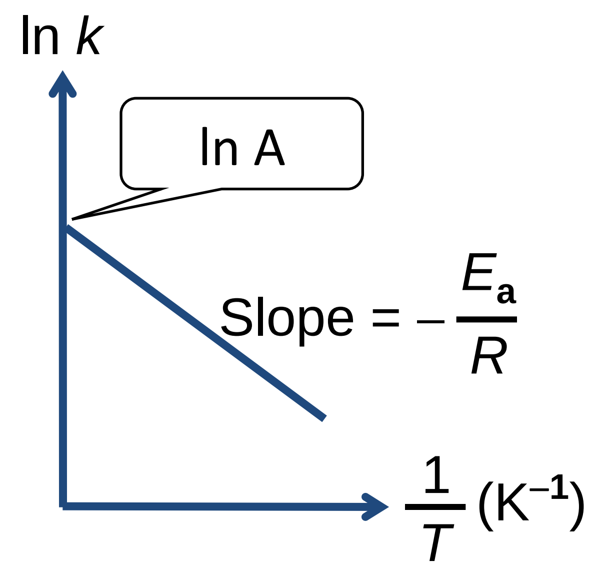
Rate constant, k increases

Reaction rate increases

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

y = c + m x

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$



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

A and E_a are specific to a given reaction

Points to Remember

- Values of k are determined by **temperature** and **catalyst**
- Unit A = unit k
- Unit T = Kelvin, K
- Unit E_a = J mol^{-1}
- R = 8.314 J mol^{-1} K^{-1}
- $\boldsymbol{r \propto k}$

$\Rightarrow$

$$\frac{k_1}{k_2} = \frac{r_1}{r_2}$$

Example 1:

The table below gives the rate constants, k for the reaction between potassium hydroxide and bromoethane at different temperatures.

k(M^{-1} s^{-1})	T (K)
0.63	322
2.50	331
10.0	347
22.6	353

a) Using a graphical method, calculate the activation energy ($kJmol^{-1}$) for this reaction.

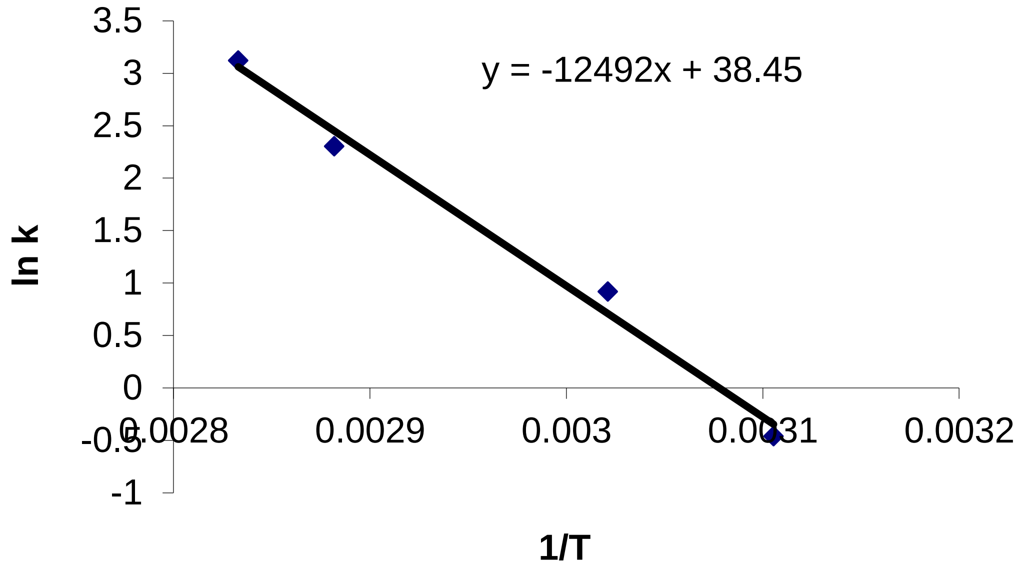
b) What is the overall order of reaction? Explain

c) Calculate the initial rate of reaction at 330 K when the concentrations for both KOH and CH_3CH_2Br are 0.1M

Solution:

Plot ln k vs 1/T

1/T	0.0031	0.0030	0.0029	0.0028
ln k	-0.46	0.92	2.30	3.12



a) Slope = E_a/R

$= 12492$

$E_a = 12492 \times 8.314$

$= 1.04 \times 10^5$ J mol^{-1}

$= 104$ kJ mol^{-1}

b) Second order,

unit of k = $M^{-1}\,s^{-1}$

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

$$\ln k = -12492\left(\frac{1}{330}\right) + 38.45$$

$\boldsymbol{k} = 1.81\ M^{-1}\,s^{-1}$

Rate = $\boldsymbol{k}$ $[KOH][CH_3CH_2Br]$

$= 1.81 \times 0.1 \times 0.1$

$= 1.81 \times 10^{-2}\ M\,s^{-1}$

Example 2:

The decomposition of hydrogen iodide,

$$2\,HI\,(g) \rightarrow H_2(g) + I_2(g)$$

has rate constants of 9.51×10^{-9} L mol^{-1} s^{-1} at 500 K and 1.10×10^{-5} L mol^{-1} s^{-1} at 600 K. Find E_a.

DATA: $k_1 = 9.51 \times 10^{-9}$ L mol^{-1} s^{-1} $T_1 = 500$ K

$k_2 = 1.10 \times 10^{-5}$ L mol^{-1} s^{-1} $T_2 = 600$ K

SOLUTION:

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

$$\ln\frac{9.51\text{x}10^{-9}}{1.10\text{x}10^{-5}} = \frac{E_a}{8.314}\left(\frac{1}{600} - \frac{1}{500}\right)$$

$E_a = 1.76 \times 10^5$ J mol^{-1}

$= 176$ kJ mol^{-1}

Check Point

1. For the reaction $NO_2Cl + NO \longrightarrow NO_2 + NOCl$, the frequency factor is 8.3×10^8 $dm^3\ mol^{-1}\ s^{-1}$ and E_a is 28.9 kJ mol^{-1}. At 25°C the reaction is first-order with respect to NO_2Cl and first-order with respect to NO, what is the rate constant for the reaction.
   <$7.13\times10^3 dm^3 mol^{-1} s^{-1}$>

2. The rate constant for the reaction $C_4H_8(g) \longrightarrow 2C_2H_4(g)$ is 3.2×10^{-2} s^{-1} at 527°C. Calculate the rate constant at 577°C if the activation energy for the reaction is 260 kJ mol^{-1}.

   <$3.2 \times 10^{-1}\ s^{-1}$>

Check Point

3. In the presence of platinum as a catalyst, hydrogen iodide decomposes to form hydrogen and iodine. The activation energy for this reaction is 58 kJ mol^{-1}. Calculate the ratio of the rate constant at 30°C and 20°C.

$$\frac{k_1}{k_2} = 0.46$$

4. Hydrogen iodide decomposes on heating according to the equation ; $2HI(g) \longrightarrow H_2(g) + I_2(g)$

At 227°C, the rate constant of the reaction is 5.71×10^{-7} dm^3 mol^{-1} min^{-1}. At 327°C, the rate constant is 6.6×10^{-4} dm^3 mol^{-1} min^{-1}.

a) Calculate the activation energy tor this reaction <176 kJ/mol>

b) The activation energy of a certain reaction is 148 kJ mol^{-1}. How many times does the rate of reaction increases when the temperature changes from 37°C to 47°C? <6X>

Check Point

5. The results of the decomposition of N_2O_5 at two different temperature were recorded as;

Temperature(K)	rate constant, k (s-1)
298	1.74×10^{-5}
308	6.61×10^{-5}

a) Base on the unit of the rate constant, k, determine the order of the reaction. **<1st>**

b) Find the value of E_a and A for the reaction <102 kJ mol^{-1}>

c) What would happen to the reaction if a catalyst were added?

<rate increases>

d) How does a catalyst work?

e) By using the Maxwell-Boltzmann distribution curves, explain the effect of a catalyst on a particular reaction?

SUMMARY

- To speed up a chemical reaction, one should
  - increase the concentrations/partial pressures of reactant
  - increase the temperature
  - add catalyst