

Chemistry 12
Reaction Kinetics II

I5-I8
(pg 12-25)

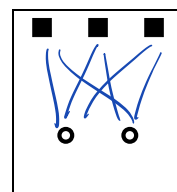
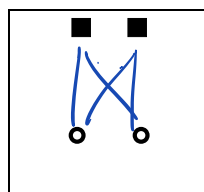
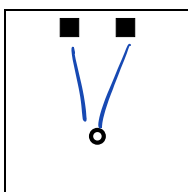
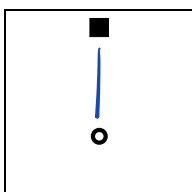
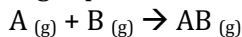
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- 1. Collision Theory
- 2. Activation Energy
- 3. Potential Energy Diagrams

Collision Theory (Kinetic Molecular Theory)

- In order for two molecules to react, they must Collide with each other.
- When they collide they transfer energy among themselves.

Consider a hypothetical reaction between two gas particles, A and B, to form AB according to the reaction:



Total possible collisions:

1

2

4

6

The rate of reaction is directly proportional to the product of the concentrations of the reactants.

- When two variables are directly proportional to one another, there is a constant that relates the two, called a proportionality constant, represented by the letter k.
- Rate Law:

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

- The proportionality constant is called a rate-constant. Each reaction has its own unique rate law and its own unique rate constant.
- **For many reactions, x and y are equal to 1, and are called reactant orders. We will only be dealing with reactions with an order of 1.**

1. Assume a reaction occurs by this rate law: $\text{rate} = k[A]$. How would the rate be affected by each of the following changes in concentration?

a) [A] is doubled.

Rate is also doubled

b) [A] is halved.

Rate is halved

2. Assume a gaseous reaction occurs by this rate law: $\text{rate} = k[A][B]$. How would the rate be affected if the volume of the container were halved?

[A] is doubled

Rate (x4)

[B] is also doubled

3. We also know that **temperature** changes the rate.

a) Considering the rate law, $\text{rate} = k[A]$, how is the rate of a reaction affected by increasing temperature?

rate will ↑

b) What part of the rate law must be affected by changing temperature?

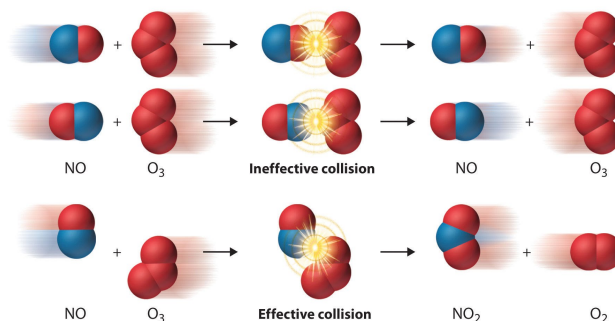
Temperature is in "k" - the proportionality constant
↳ we know this b/c it's not in [A]

Activation Energy (E_a)

Most collisions are not "successful" and do not result in a reaction.

A **successful collision** requires the following:

1. Favourable geometry
2. Sufficient energy to break chemical bonds



Which of the following reaction is fastest?

- a. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
- b. $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$
- c. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- d. $5\text{C}_2\text{O}_4^{2-}(\text{aq}) + 2\text{MnO}_4^{2-}(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow 10\text{CO}_2(\text{g}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$

↑ more energy needed to break original bonds

Activation Energy:

The minimum kinetic energy that the reacting species must have in order to react

• Must overcome:

- Repulsive forces between electron clouds of the reacting molecules
- Weaken or break bonds



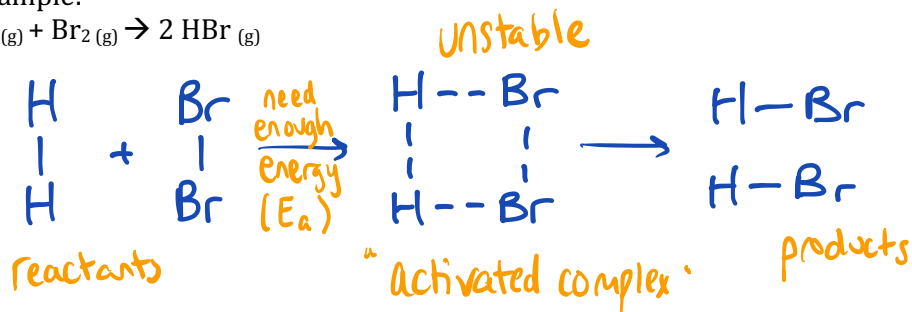
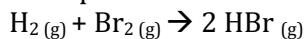
Transition State Theory:

When molecules have enough kinetic energy to react collide, their electron clouds initially repel one another to form an unstable transitory configuration of atoms. "activated complex"

- Because they have sufficient kinetic energy to overcome this, the unstable complex will form the desired products.

Bond breaking requires energy input, while bond forming results in energy release.

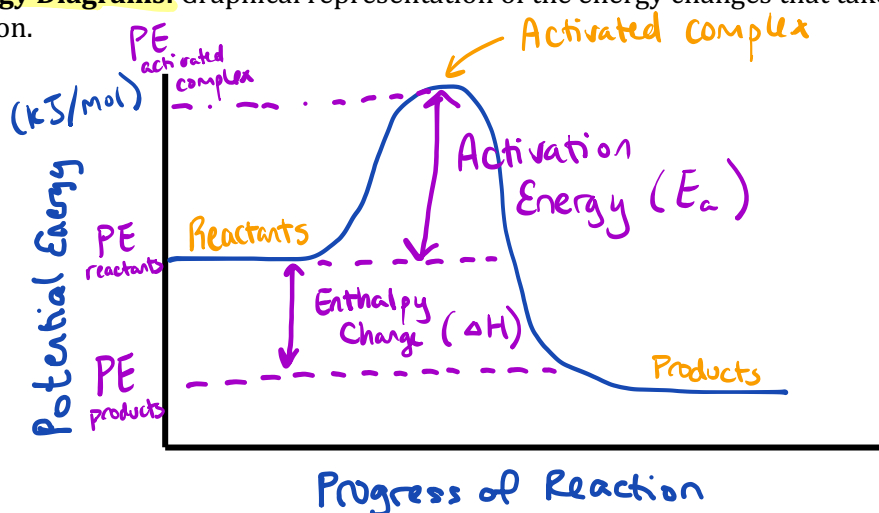
Example:



Potential Energy Diagrams

As bonds are broken/formed, there is energy gained and lost. The total energy in the system depending on the position of the particles is called the potential energy. As bonds are broken and formed, the change in the total energy is represented as a Potential Energy Diagram.

Potential Energy Diagrams: Graphical representation of the energy changes that take place during a chemical reaction.



The activation energy, E_a , is the difference between the potential energy of the activated complex and the potential energy of the reactant molecules.

- It represents the amount of energy the reactant molecules must gain to form an activated complex.

$$E_a = PE_{AC} - PE_R$$

always (+)

The enthalpy change (ΔH) is the difference between the total potential energy of the products and the total potential energy of the reactants.

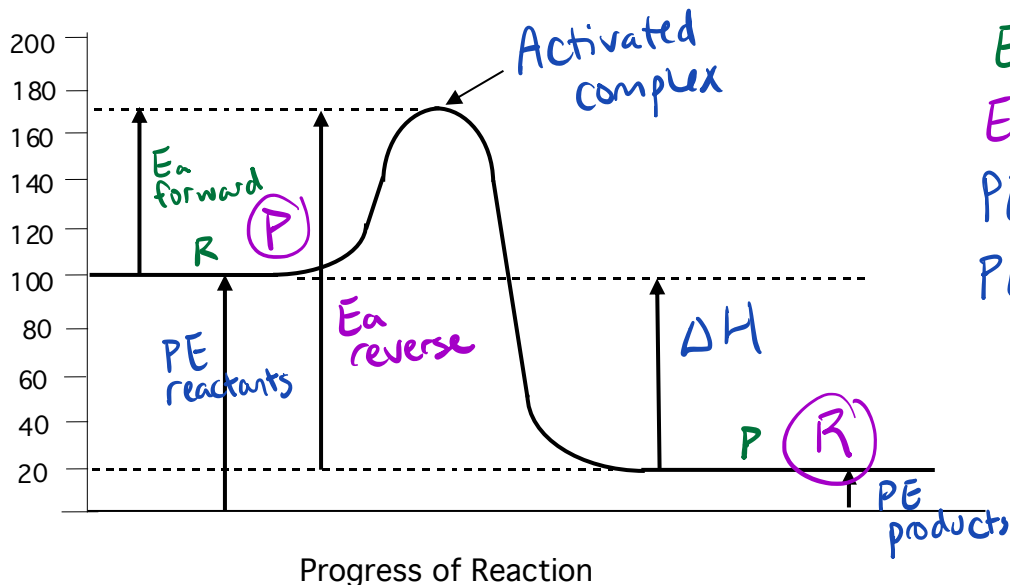
$$\Delta H = PE_P - PE_R$$

(+) endothermic

(-) exothermic

Calorimetry - the science of measuring the change in heat associated with a chemical reaction

1. Label each arrow in the following diagram:



- ΔH
- Activated complex
- E_a forward
- E_a reverse
- PE reactants
- PE products

2. Consider the following graph on the right.

a) What is the potential energy of the activated complex?

45 kJ/mol

b) What is the activation energy of the reaction?

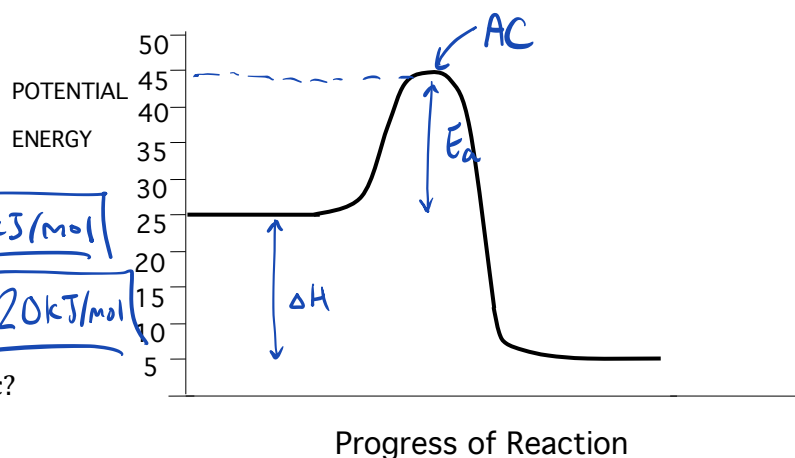
$$E_a = PE_{AC} - PE_R = 45 - 25 = 20 \text{ kJ/mol}$$

c) What is the ΔH for this reaction?

$$\Delta H = PE_P - PE_R = 5 - 25 = -20 \text{ kJ/mol}$$

d) Is the reaction endothermic or exothermic?

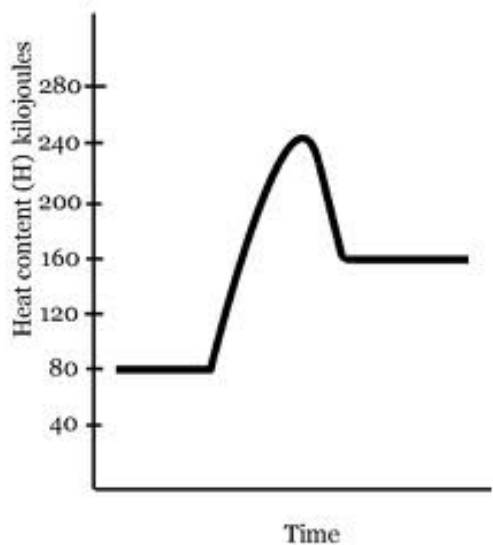
exothermic



Many chemical reactions are **reversible** under certain conditions.

The first potential energy diagram could be read in reverse to give the same measurements provided by the second diagram.

3. Answer the following questions about this potential energy diagram:



a) Give ΔH for the forward reaction. Is this reaction exothermic or endothermic?

$$\Delta H = 160 - 80 = 80 \text{ kJ/mol} \quad \text{endothermic}$$

b) Give ΔH for the reverse reaction. Is this reaction exothermic or endothermic?

$$\Delta H = 80 - 160 = -80 \text{ kJ/mol} \quad \text{exothermic}$$

c) Give E_a for the forward reaction.

$$E_a = 240 - 80 = 160 \text{ kJ/mol}$$

d) Give E_a for the reverse reaction.

$$E_a = 240 - 160 = 80 \text{ kJ/mol}$$

Which requires a lower E_a ?

e) Which is faster, the forward or reverse rate?

reverse

f) Give the potential energy for the activated complex. How does this value compare for the forward and reverse reactions?

$$PE_{AC} = 240 \text{ kJ/mol}$$

This is the same for both the forward & reverse

4. Consider the graph and equation on the right:

a) What species represents the transition state? (Activated complex)



b) Which is faster, the forward or reverse rate?

forward

c) Circle the specie(s) that has the strongest bonds:



OR



d) Explain your answer to the question above.

AB has a higher activation energy
 ↳ requires more energy to break its strong bonds.

