

THERMODYNAMICS

The study of **energy** (heat) changes involved in physical and chemical processes.

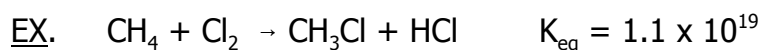
Equilibrium Constant, K_{eq}

Reactants, R's \rightleftharpoons Products, P's

$$K_{eq} = \frac{[P's]}{[R's]}$$

When $K_{eq} \gg 1$; **P's** are favored & equilibrium lies to the **right**

When $K_{eq} \ll 1$; **R's** are favored & equilibrium lies to the **left**



Free Energy, ΔG°

$$\Delta G = \Sigma G (P's) - \Sigma G (R's)$$

When $\Delta G < 0$ (negative value) ; process (reaction) is **favorable**

When $\Delta G > 0$ (positive value) ; process (reaction) is **unfavorable**

$$\Delta G^\circ \text{ is related to } K_{eq} : \Delta G^\circ = -RT \ln K_{eq} \text{ or } K_{eq} = e^{-\Delta G/RT}$$

So, a favorable reaction has $-\Delta G$ and $K_{eq} \gg 1$ & an unfavorable reaction has $+\Delta G$ & $K_{eq} \ll 1$



The value ΔG° is dependent on two other thermodynamic properties: Enthalpy & Entropy:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Enthalpy, ΔH°

The **heat** transferred (at constant pressure) in a chemical or physical process.

$$\Delta H = \Sigma H (P's) - \Sigma H (R's)$$

Exothermic Reaction, $-\Delta H^\circ$

- heat is **evolved** (released)

- **weaker** bonds are **broken**, **stronger** bonds are **formed**

Endothermic Reaction, $+\Delta H^\circ$

- heat is **consumed** (absorbed)
- **stronger** bonds are **broken**, **weaker** bonds are **formed**

Entropy, ΔS°

The **disorder** or freedom of motion involved in a chemical or physical process.

$$\Delta S = \sum S (\text{P's}) - \sum S (\text{R's})$$

When $\Delta S > 0$ (positive value) ; process (reaction) **favors P's**

When $\Delta S < 0$ (negative value) ; process (reaction) **favors R's**

A favorable reaction ($-\Delta G$ and $K_{\text{eq}} \gg 1$) would then be promoted by a **$-\Delta H^\circ$** & a **$+\Delta S^\circ$**

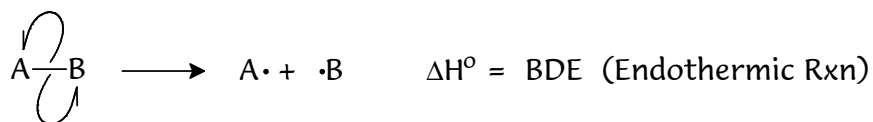
Since the $T\Delta S^\circ$ term is usually small and negligible, ΔH° is the more important factor in determining the value of ΔG° , K_{eq} and whether or not a reaction is favorable.

Therefore, assuming that $\Delta G^\circ \approx \Delta H^\circ$, a more exothermic reaction (stronger bonds formed) is a more favorable reaction with a larger K_{eq} .

Bond Dissociation Energy, BDE

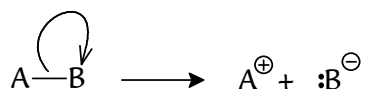
The energy required to break a bond homolytically.

Homolytic Bond Cleavage



Note – For bond **formation** the BDE has a **negative** value (Exothermic process).

Heterolytic Bond Cleavage



BDE's (for homolytic bond cleavage) can be used to approximate ΔH° values for reactions:

$$\Delta H^\circ = \sum \text{BDE (R's)} - \sum \text{BDE (P's)}$$

endothermic *exothermic*
(positive) (negative)

KINETICS

The study of reaction **rates** (or how fast a reactant disappears or a product appears).

Rate Law

An equation which relates rate to concentration (experimentally obtained).

For the reaction: $A + B \rightarrow P$'s

$$\text{Rate} = k[A]^a[B]^b$$

where: k = rate constant
[] = concentration
 a, b = rate order

Activation Energy, E_A

The minimum kinetic energy required for molecules to have successful collisions and react.

E_A is related to k by the Arrhenius Equation:

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

where: A = frequency factor
 R = gas constant
 T = temperature

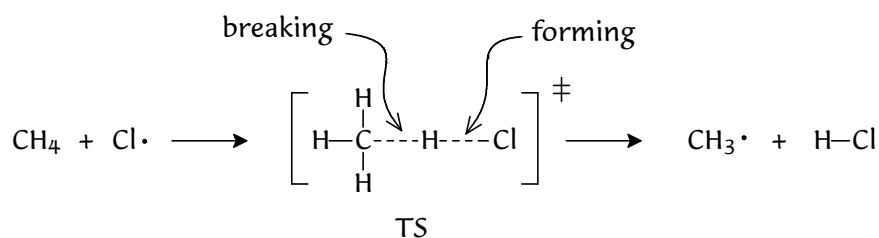
\therefore as $E_A \downarrow$ $k \uparrow$ **Rate** \uparrow (also as $T \uparrow$ $k \uparrow$ **Rate** \uparrow)

Transition State, TS

The energy maximum between R's & P's in any collision that leads to a reaction.

- the difference in energy between the R's & the TS is the E_A
- the TS is **not** an intermediate – its bonds cannot vibrate
- the TS is symbolized with **partial** bonds

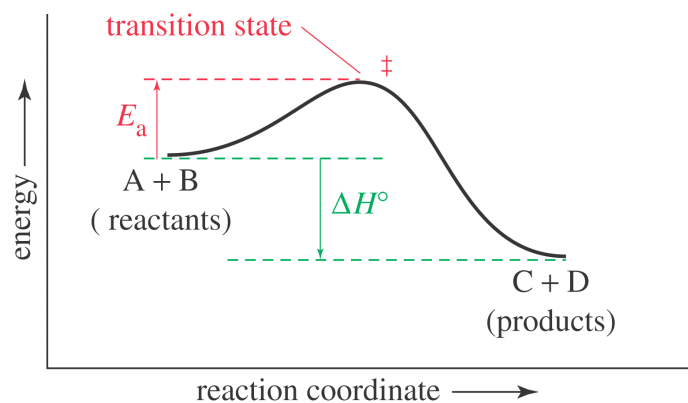
EX.



Reaction Energy Profile, REP

A graphical account of the energy change vs. structural change during the course of a reaction.

For the reaction: $A + B \rightarrow C + D$ Exothermic, $-\Delta H^\circ$



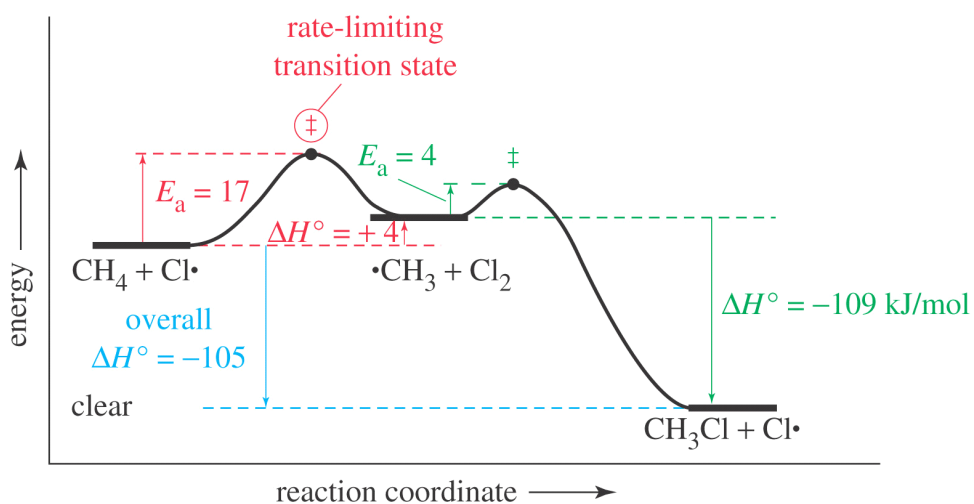
Note – the reverse rxn would be **endothermic** ($+\Delta H^\circ$), & would have a **larger** E_a .

Multistep Reaction Rates

Many reactions have several steps & intermediates.

The REP 's for these reactions will have several energy minima & maxima.

Maxima (peaks) = transition states Minima (valleys) = reactive intermediates

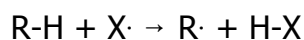


Rate-Determining Step, RDS

The **slowest step** (or bottleneck) in a multistep reaction.

- the RDS determines the **overall rate** of the rxn (or overall reactivity)
- the RDS has the largest E_A (highest energy TS) in the REP

EX. RDS in Alkane Halogenation = Propagation Step **2a**



| X | E_A , kcal | Rate @300K | Rate @500K | Comments on Overall Reactivity |
|----|--------------|-----------------------|----------------------|--|
| F | 1.2 | 1.4×10^5 | 3.0×10^5 | F reacts too fast – explodes |
| Cl | 4.0 | 1.3×10^3 | 1.8×10^4 | Cl reacts at room temperature (with light) |
| Br | 18 | 9.0×10^{-8} | 1.5×10^{-2} | Br requires heat |
| I | 34 | 2.0×10^{-19} | 2.0×10^{-9} | I reacts too slow – no reaction (NR) |

Note – these values are for R = CH₃

Conclusion: as E_A for RDS↑ Overall **Rate**↓ **Reactivity**↓