THERMODYNAMICS

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

Equilibrium Constant, K_{eq}

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

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

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

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

<u>EX</u>. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ $K_{eq} = 1.1 \times 10^{19}$

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**

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

So, a favorable reaction has -ΔG and K_{_{eq}} >> 1 & an unfavorable reaction has +ΔG & K_{_{eq}} << 1

<u>EX</u>. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ $\Delta G^\circ = -25.9 \text{ kcal/mol}$

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, -ΔH°

- 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.

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

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 (- ΔG and $K_{eq} >> 1$) would then be promoted by a - ΔH° & a + ΔS°

Since the T Δ S° term is usually small and negligible, Δ H° is the more important factor in determining the value of Δ G°, 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

$$A \xrightarrow{\frown} B \longrightarrow A \cdot + \cdot B \qquad \Delta H^{\circ} = BDE \text{ (Endothermic Rxn)}$$

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

Heterolytic Bond Cleavage

$$A \xrightarrow{\bigcirc} B \longrightarrow A^{\oplus} + :B^{\ominus}$$

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

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\Delta H^{\circ} = \Sigma BDE (R's) - \Sigma BDE (P's)
endothermic exothermic
(positive) (negative)
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Table 4-2, p. 136, lists the BDE values for bonds found in some simple organic molecules.

<u>EX</u>. Using BDE's, approximate the value of ΔH° for the chlorination of methane:

 $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Bonds Broken	BDE (kcal/mol)	Bonds Formed	<u>BDE</u> (kcal/mol)	
C-H CI-CI	104 58	C-Cl H-Cl	84 103	
Total	162	Total	187	
$\Delta H^{\circ} = 162 - 187 \text{ kcal/mol}$				
	$\Delta H^{\circ} = \frac{-25 \text{ kcal/mol}}{-25 \text{ kcal/mol}}$			

BDE's can also be used to approximate ΔH° values for elementary steps. Since propagation steps 2a & 2b provide all the energy necessary to sustain the free radical chain reaction, the sum of the values of ΔH° for the propagation steps (2a & 2b) gives the same value of ΔH° as for the overall reaction determined above.

Propagation Steps:

2a) $CH_4 + CI \rightarrow CH_3 + HCI$ BDE = 104 -103 kcal/mol $\Delta H^{\circ}_{2a} = +1 \text{ kcal/mol}$ 2b) $CH_3 + CI_2 \rightarrow CH_3CI + CI + CI + S8$ -84 kcal/mol $\Delta H^{\circ}_{2b} = -26 \text{ kcal/mol}$ $\Delta H^{\circ}_{2b} = -25 \text{ kcal/mol}$

KINETICS

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

Rate Law

For

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

the reaction:	$A + B \rightarrow P 's$
	Rate = $k[A]^{a}[B]^{b}$
where:	<pre>k = rate constant [] = concentration a,b = rate order</pre>

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			
∴ as E _A ↓	<i>k</i> ↑ Rate↑	(also as T↑	<i>k</i> ↑	Rate↑)

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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 $E_{\!\scriptscriptstyle A}$

- the TS is **not** an intermediate - its bonds cannot vibrate

- the TS is symbolized with **partial** bonds

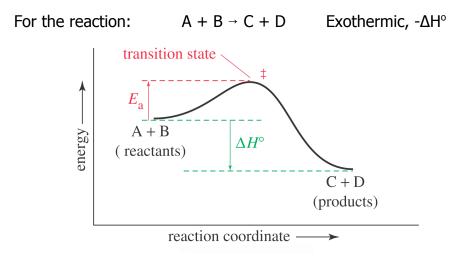


breaking forming

$$CH_4 + Cl \cdot \longrightarrow \begin{bmatrix} H \\ H \\ -C \\ H \end{bmatrix}^{\ddagger} CH_3 \cdot + H - Cl$$

Reaction Energy Profile, REP

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



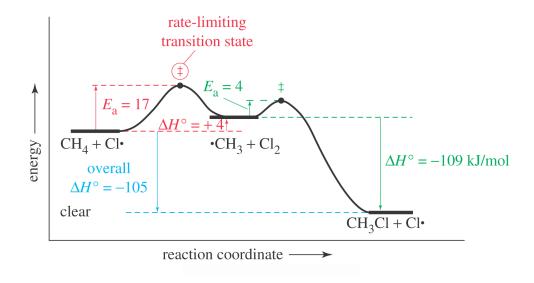
Note – the reverse rxn would be **endo**thermic ($+\Delta H^{\circ}$), & would have a **larger** E_A.

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

 $R\text{-}H + X \cdot \rightarrow R \cdot + H\text{-}X$

x	E _A , kcal	Rate @300K	Rate @500K	Comments on Overall Reactivity
F	1.2	1.4 x 10⁵	3.0 x 10 ⁵	F reacts too fast – explodes
Cl	4.0	1.3 x 10 ³	1.8×10^4	Cl reacts at room temperature (with light)
Br	18	9.0 x 10 ⁻⁸	1.5 x 10 ⁻²	Br requires heat
Ι	34	2.0 x 10 ⁻¹⁹	2.0 x 10 ⁻⁹	I reacts too slow – no reaction (NR)

Note – these values are for $R = CH_3$

Conclusion: as E_A for RDS[↑] Overall Rate[↓] Reactity[↓]