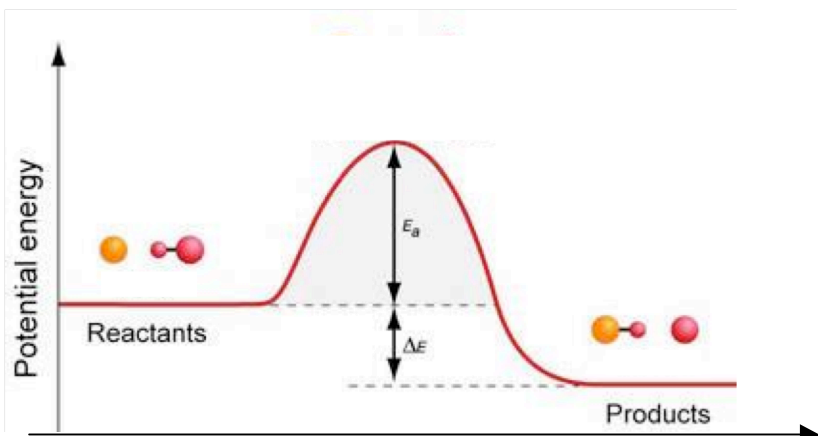
Reactivity:

C_5H_{12} (pentane) + O_2 (excess) $\xrightarrow{\text{heat}}$ 5 CO_2 + 6 H_2O

Energy diagram for the reaction:



Reaction coordinate => progress of reaction

Reactants (starting material): C_5H_{12} and O_2
Products: CO_2 and H_2O

E_a: activation energy
$\Delta E = \Delta G$: Gibbs free energy (enthalpy) change for the reaction
* this reaction is an exothermic reaction, heat is released during reaction

- ΔG = change in energy of system or change in Gibbs free energy.

Temperature in °K
(°K = °C + 273)

↑

$\Delta G = \Delta H - T\Delta S$ (2nd law of thermodynamics)

↙ ↘

Change in enthalpy
= bond energy

Change in entropy
= measure of disorder in system

$\Delta G = -RT\ln K_{eq}$

R = gas constant = $0.082 \frac{L \cdot atm}{mol \cdot K}$

T = temperature in ^oK

ΔG = change in energy of system (determines equilibrium)

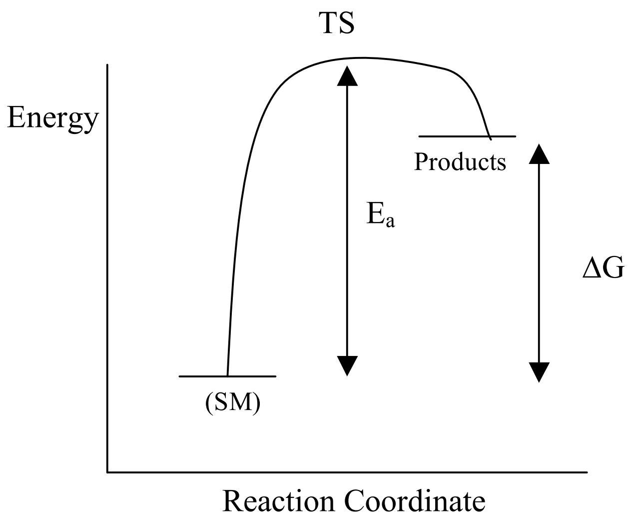
E_a = activation energy → determines rate of reaction

$$A + B \rightleftharpoons C + D$$

K_{eq} = equilibrium constant = $\frac{[C][D]}{[A][B]}$ [C] = concentration of compound C

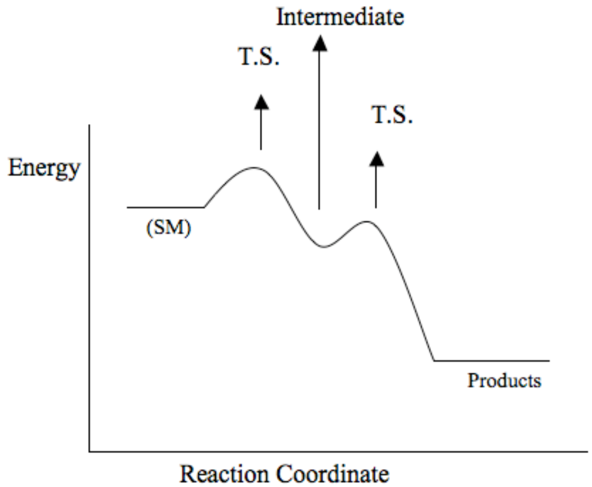
Endothermic Reaction

Transition state (TS) = bonds partially made/broken



- The transition state is the point of highest energy on the diagram.
- The transition state is **not** an intermediate.

Reaction proceeding through an intermediate



NB: The Rate Determining Step is the TS with the larger E_A, which will be the slowest step; that is for the diagram to the left, the first step is the rate determining step.

Review

Change in Entropy

$\Delta G = \Delta H - T\Delta S$ (2nd law of thermodynamics)

Change in enthalpy
= bond energy

Exothermic ΔG = Negative

Endothermic ΔG = Positive

Bond Energy

Bond	Bond Energy (kcal/mol)
H-C	99
H-O	111
C-C	83
C=O	179
O=O	119

Ex) $CH_4 + 2\ O_2 \xrightarrow[\Delta]{} CO_2 + 2\ H_2O$ – Exothermic reaction (releases Energy (E))

$\Delta E_{reaction} = \Delta E_{SM} - \Delta E_{pdt}$

For CH_4:

4 x C-H bonds = 4 x 99 = 396 kcal/mol
2 x O=O = 2 x 119 = 238 kcal/mol
ΔE_{SM} = 634 kcal/mol

ΔE_{SM} = sum of bonds broken (enthalpy)

For products:

2 C=O = 2 x 179 = 358 kcal/mol
4 H-O = 4 x 111 = 444 kcal/mol
ΔE_{pdt} = 802 kcal/mol

ΔE_{pdt} = sum of bonds formed

$\Delta E_{reaction}$ = 634 kcal/mol – 802 kcal/mol = -168 kcal/mol (exothermic reaction, energy released)

Acids – Bases

- **Bronsted – Lowry :**
  - An acid **donates proton (H^+)**
  - A base **accepts a proton (H^+)**

Ex:

$$HCl \longrightarrow H^+ + Cl^-$$

$$NaOH \longrightarrow Na^+ + OH^-$$

$$HCl + NaOH \longrightarrow NaCl + H\text{-}OH$$

- **Lewis Acid/Base:**
  - An **acid accepts a pair of electrons**
  - A **base donates a pair of electrons**

Examples of Lewis acids:

H+ $AlCl_3$ BH_3

Definition

$$H{-}A \rightleftharpoons H^{\oplus} + {:}A^{\ominus}$$

$$K_{eq} = K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a = acidity constant
$pK_a = -\log K_a$

Ex #1) Methane:

$$H\text{-}CH_3 \rightleftharpoons H^+ + CH_3^-$$

$$K_a = \frac{[H^+][CH_3^-]}{[HCH_3]} = 10^{-46}$$

$$pK_a = -\log K_a = 46$$

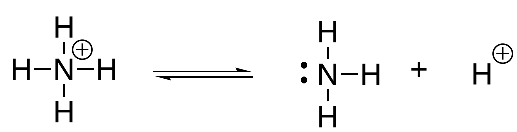
Ex # 2) Ammonia Gas:

$$H\text{-}NH_2 \rightleftharpoons H^{\oplus} + {:}\ddot{N}H_2^{\ominus}$$

$$K_a = \frac{[H^+][^-NH_2]}{[NH_3]} = 10^{-36}$$

$$pK_a = 36$$

“pKa of Ammonia” in biological system



Ammonium Cation

$pK_a = 9.3$

Ex #3) Water:

$$H{-}O{-}H \rightleftharpoons H^{\oplus} + {:}\ddot{O}H^{\ominus}$$

$$K_a = \frac{[H^+][^-OH]}{[HOH]} = 10^{-15.7}$$

$$pK_a = -\log K_a = 15.7$$

Proton Transfer:

Strong Acid + Strong Base $\rightleftharpoons$ Weak Acid + Weak Base

Ex)

$$\underset{\text{Strong Base}}{Li^{+}CH_3^{-}} + \underset{\text{Stronger Acid}}{HOH} \longrightarrow \underset{\text{Weaker Base}}{Li^{+}OH^{-}} + \underset{\text{Weak Acid}}{CH_4}$$

$$\underset{\text{Weak Base}}{Na^{+}\,NH_2^{-}} + \underset{\text{Weak Acid}}{H\text{-}CH_3} \rightleftharpoons \underset{\text{Stronger Base}}{Na^{+}\,{:}CH_3^{-}} + \underset{\text{Stronger Acid}}{H\text{-}NH_2}$$

$$NaOH + H\text{-}CH_3 \longleftarrow Na^{+}\,{:}CH_3^{-} + H_2O$$

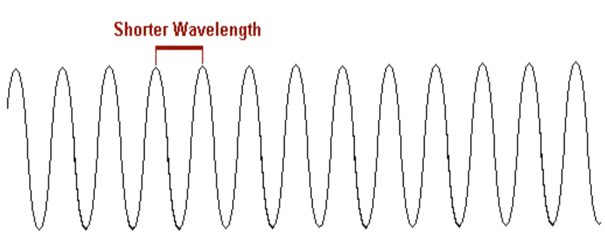
$H\text{-}CH_3$: pKa = 46
Weaker Acid

H_2O: pKa=16
Stronger Acid

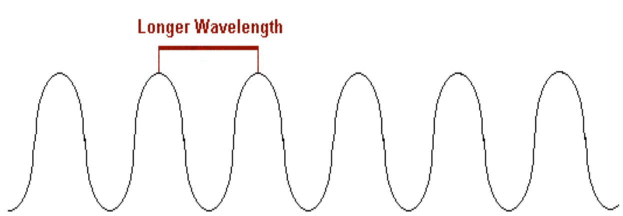
IR = Infrared Spectroscopy

$E = hc/\lambda = h\nu$

E= Energy
h= Planck's Constant= 6.6×10^{-34} joules/sec
ν= Frequency
λ= Wavelength
c=Speed of light = 3.0×10^{10} cm/sec



- Shorter Wavelength
- Higher Energy
- Higher Frequency



- Longer Wavelength
- Low Energy
- Low Frequency