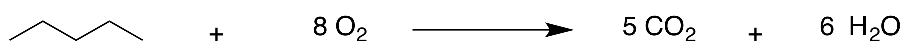
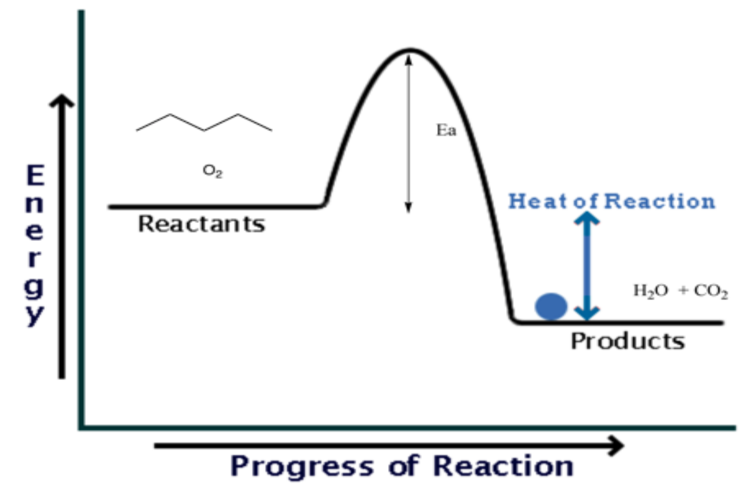
Reactivity/ Reactions

Exothermic Reaction: Negative ΔG

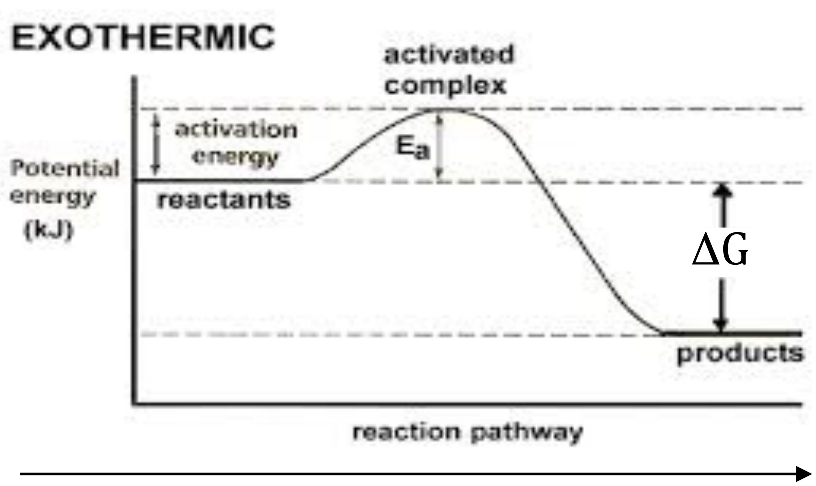
Example: Combustion of Pentane





Progress of reaction is also called **Reaction Coordinate**
S.M. = starting material or reactants (e.g. pentane, oxygen)

Energy diagram for the reaction:



NB: $\Delta E = \Delta G$: Gibbs free energy (total) change for the reaction

Reaction coordinate => progress of reaction

- The above reaction is an exothermic reaction, heat is released during reaction
- ΔG will be negative ($\Delta G < 0$) for an exothermic (heat releasing) reaction, but will be positive ($\Delta G > 0$) for endothermic reaction.

- E_A= Activation energy: minimum amount of energy required to activate molecules or atoms to be able to undergo a chemical reaction.
- Activated complex **or transition state (T.S):** Highest energy point in a reaction pathway in which bonds are being formed and broken simultaneously. A T.S. cannot be observed or isolated. Should not be confused with and an intermediate.

<u>Thermodynamic of a chemical reaction:</u>

Temperature in ^oK
($^oK = {}^oC + 273$)

$\uparrow$

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

$\swarrow \qquad \searrow$

Change in enthalpy = bond energy

Change in entropy = measure of disorder in system

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

R = Gas constant = $0.082 \dfrac{L\cdot atm}{mol\cdot K}$

T = Temperature in ^oK

ΔG = Change in energy of system (determines equilibrium)

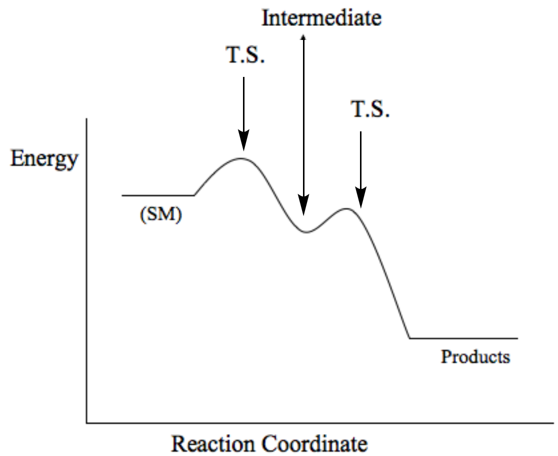
E_a = Activation energy $\rightarrow$ determines rate of reaction

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

ΔG determines product concentrations at equilibrium

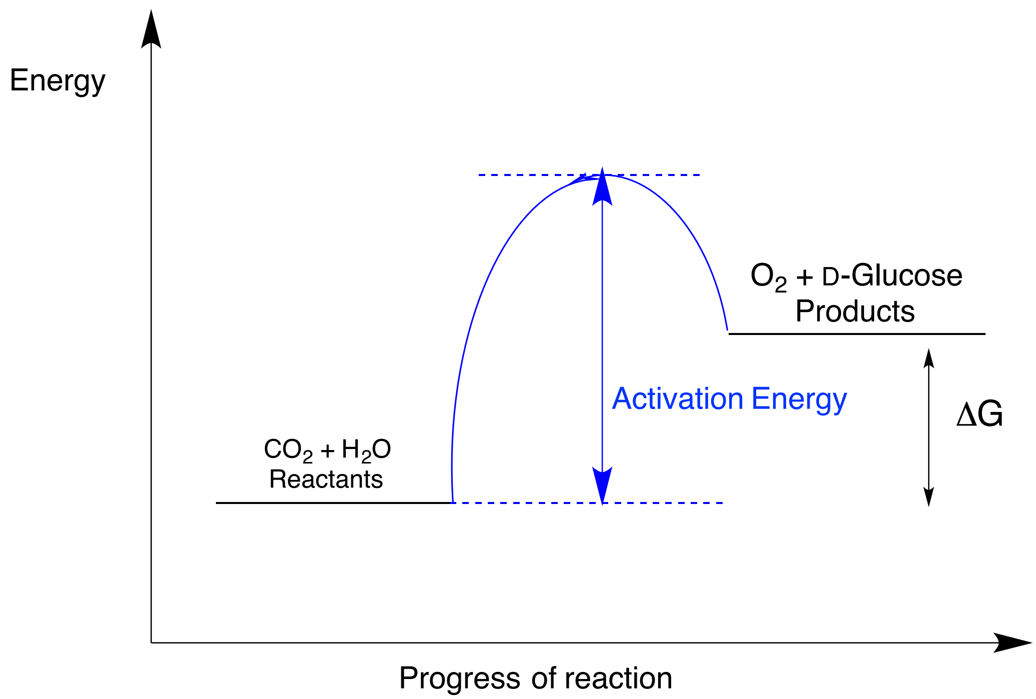
Ea determines rate of reaction

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.

Endothermic Reaction: Positive ΔG



Summary:

$\Delta E = \Delta G$: Gibbs free energy (total) change for the reaction

$$\Delta G = \underbrace{\Delta H}_{\text{Change in enthalpy = bond energy}} - T\overbrace{\Delta S}^{\text{Change in Entropy}} \text{ (2nd law of thermodynamics)}$$

Exothermic reactions have ΔG = Negative

Endothermic reactions have ΔG = Positive

TS = Transition State: Point where bonds are partially broken and partially formed

Intermediate: Short lived species

Bond Energy

Example: Radicals

$$H{-}CH_3 \rightleftharpoons H\bullet + \bullet CH_3$$

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

e.g.) $CH_4 + 2\ O_2 \xrightarrow[\Delta]{} CO_2 + 2\ H_2O$ – 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 = <u>238 kcal/mol</u>
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 = <u>444 kcal/mol</u>
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)