



Spontaneous Reactions

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Entropy 'S'

- Entropy is defined as the degree of disorder or randomness of a system
- Today it is also considered as measure of the dispersion of energy in systems or when they under go change

Entropy

$$\Delta S = \frac{\Delta H}{T}$$

Second Law of Thermodynamics

- All changes either directly or indirectly increase the entropy of the universe
- Mathematically $\Delta S_{\text{universe}} > 0$
- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$



Third law of TD

- The entropy of a substance at absolute zero is zero



Factors affecting entropy

- State of matter
- Number of entities
- Temperature



Endothermic reactions and Spontaneity

- Why do endothermic reactions occur spontaneously?
- How will you explain this phenomenon?



What is a spontaneous process?

- **A process which under some conditions may take place by itself or by initiation independent of the rate is called a spontaneous process.**
 - Eg. Melting of ice at room temperature
 - Dissolution of salt in water
 - Flow of water down the hill
 - Evaporation of water at room temperature
 - Dissolution of ammonium chloride in water

Gibbs Free Energy 'G'

- Change in free energy is ΔG
- For spontaneous reactions $\Delta G < 0$
or negative

ΔG Gibbs Free Energy

- $\Delta G = \Delta H - T\Delta S$ at constant T and P

$$\Delta G_{(T,P)} = \Delta H - T\Delta S$$

- This is Gibbs Helmholtz Equation

Conditions for spontaneity

- When $\Delta G < 0$ the reaction is spontaneous
- When $\Delta G = 0$ the reaction is in equilibrium
- When $\Delta G > 0$ the reaction is non-spontaneous

This will explain spontaneity

ΔG	ΔH	$T \Delta S$	$\Delta G = \Delta H - T \Delta S$
Always spontaneous	- ve	+ ve	= -ve
Spontaneous at high temp.	+ ve	+ ve	= -ve at high temperatures
Spontaneous at low temp.	- ve	- ve	= -ve at low temperatures
Non spontaneous	+	- ve	+ ve At all temperatures

Problem

- Calculate the standard free energy change for the reaction
- $4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightarrow 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(l)}$
- Given that the standard free energies of formation for $\text{NH}_{3(g)} = -16.8 \text{ kJ/mol}$, $\text{NO} = 86.7 \text{ kJ/mol}$, $\text{H}_2\text{O} = -237.2 \text{ kJ/mol}$
- Predict the feasibility of the above reaction at the standard state

Solution

- Calculate the change in free energy

$$\Delta G^{\circ}_{reaction} = \sum \Delta G^{\circ}_{f products} - \sum \Delta G^{\circ}_{f reactants}$$

$$\Delta G = -1009.2\text{kJ}$$

Since ΔG is <0 or negative the reaction is spontaneous

Problem

- Using appendix values calculate ΔG for each of the following reactions at 25°C
- $\text{CH}_3\text{OH}_{(L)} + 3/2 \text{O}_{2(G)} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}_{(G)}$
- $\Delta H \text{CH}_3\text{OH}_{(L)} = -238.7\text{kJ/mol}$



Different types of enthalpies

- Enthalpy of formation
- Enthalpy of reaction
- Enthalpy and Phase change
 - Enthalpy of fusion
 - Enthalpy of vaporization
 - Enthalpy of sublimation
- Enthalpy of hydration
- Enthalpy of neutralization
- Enthalpy of dissolution



Bond Energy and Enthalpy

- Bond dissociation energy is the energy required to break one mole of bonds of a particular type between the atoms in the gaseous state
- Bond energy: Average bond dissociation energy required to break bonds in a substance is called bond energy (O-H in water or C-H in methane)

Enthalpy from bond energies

$$\Delta H_{\text{reaction}}^{\circ} = \sum \text{Bond energies of bonds broken} - \sum \text{Bond energies of bonds formed}$$

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Bond breaking and formation

- Breaking a bond is an endothermic reaction
- Forming a bond is exothermic reaction

Calculate enthalpy of formation of HCl

- $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 \rightarrow \text{HCl}$
- Bond energy of $\text{H}_2 = 436 \text{kJ/mol}$
- Bond energy of $\text{Cl}_2 = 243 \text{kJ/mol}$
- Bond energy of $\text{HCl} = 432 \text{kJ/mol}$

Solution

- For the reaction $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 \rightarrow \text{HCl}$
- $\frac{1}{2}$ mole of H_2 reacts with $\frac{1}{2}$ mole of Cl_2 to form one mole of HCl
- $\text{H}_2 \rightarrow 2\text{H}, \Delta\text{H} = + 436\text{kJ/mol}$
- $\text{Cl}_2 \rightarrow 2\text{Cl}, \Delta\text{H} = + 243\text{kJ/mol}$
- $\text{HCl} \rightarrow \text{H} + \text{Cl}, \Delta\text{H} = +432 \text{ kJ/mol}$
- Net energy change
- $(\frac{1}{2} 436 + \frac{1}{2} 243) - (432) \text{kJ/mol} = -92 \text{ kJ/mol}$

Alternatively

- For the reaction $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 \rightarrow \text{HCl}$
- $\frac{1}{2}$ mole of H_2 reacts with $\frac{1}{2}$ mole of Cl_2 to form one mole of HCl
- $\text{H}_2 \rightarrow 2\text{H}, \Delta H = + 436\text{kJ/mol}$
- $\text{Cl}_2 \rightarrow 2\text{Cl}, \Delta H = + 243\text{kJ/mol}$
- $\text{H} + \text{Cl} \rightarrow \text{HCl}, \Delta H = -432 \text{ kJ/mol}$
- Net energy change
- $(\frac{1}{2} 436 + \frac{1}{2} 243) + (-432) \text{kJ/mol}$
 $= -92 \text{ kJ/mol}$