

FIRST LAW OF THERMODYNAMICS – Energy and Enthalpy. Thermochemistry.

1. a) **DEFINITION:** Change in energy = $\Delta E \equiv q + w$

Change in energy of system = heat absorbed by system + work done on system

b) Energy E is a **state property** (a state function). ΔE is independent of path.

c) Only **changes** in energy (ΔE) can be measured. $\Delta E = E_2 - E_1$.

d) i) **Definition:** Pressure-volume work (work of expansion/compression): $w \equiv -\int PdV$

ii) Pressure-volume work (work of expansion/compression) *at constant P*: $w = -P \Delta V$

iii) *At constant V, if only PV work is possible*, $w = 0$ so $\Delta E = q$. Measure q to find ΔE .

iv) *At constant P, if only PV work is possible*, $q = \Delta E + P \Delta V$.

2. a) **DEFINITION:** Enthalpy $H \equiv E + PV$. Change in enthalpy $\Delta H = \Delta(E + PV)$.

b) Enthalpy H is a **state property** (a state function). ΔH is independent of path.

c) Only **changes** in enthalpy (ΔH) can be measured. $\Delta H = H_2 - H_1 = \Delta E + \Delta(PV)$.

d) *At constant P*, $\Delta H = \Delta E + P \Delta V$.

e) *At constant P, if only PV work is possible*, $\Delta H = q$. Measure q to find ΔH .

f) i) **DEFINITION:** The **standard enthalpy of formation** ΔH_f° of a substance is ΔH° for the reaction that forms *one mole* of the substance (or 1 M concentration of the substance in solution) solely from *elements* in their standard states at $t = 25^\circ\text{C}$ and $P = 1$ atm.

ii) The *standard state* of an element is the most stable form at $t = 25^\circ\text{C}$ and $P = 1$ atm.

SECOND LAW OF THERMODYNAMICS – Entropy and Free Energy. Equilibrium.

3. a) **DEFINITION:** Change in entropy = $\Delta S \equiv \int \frac{dq_{\text{reversible}}}{T}$.

b) Entropy S is a **state property** (a state function). ΔS is independent of path.

c) Changes ΔS for *irreversible* paths $1 \rightarrow 2$ can be determined along *reversible* paths $1 \rightarrow 2$.

4. a) **DEFINITION:** Gibbs free energy $G \equiv H - TS$.

b) Gibbs free energy G is a **state property** (a state function). ΔG is independent of path.

c) Only **changes** in free energy (ΔG) can be measured. $\Delta G = G_2 - G_1 = \Delta H - \Delta(TS)$.

d) *At any constant T and constant P*, $\Delta G = \Delta H - T \Delta S$,

so at the *standard T and standard P*, $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$.

e) i) **At constant T and constant P, the equilibrium state of any system has the minimum total Gibbs free energy G.** In such a system at equilibrium, $dG = 0$ for any change.

ii) $\Delta G_{\text{reaction}} = \sum [\Delta G_f(\text{products formed})] - \sum [\Delta G_f(\text{reactants used up})]$.

Therefore, *at constant T and P*, for a system in which chemical reactions can occur,

if $\Delta G_{\text{reaction}} < 0$, the reaction moves to the right, creating more products;

if $\Delta G_{\text{reaction}} > 0$, the reaction moves to the left, creating more reactants;

if $\Delta G_{\text{reaction}} = 0$, the reaction mixture is at equilibrium, and no net change occurs.

f) i) For reactions *at constant T and constant P*, $\Delta G = \Delta G^\circ + RT \ln Q$

or $\Delta G = \Delta G^\circ + 2.3026 RT \log_{10} Q = \Delta G^\circ + (5.708 \text{ kJ/mole}) \log_{10} Q$ at 25°C .

ii) **At equilibrium at constant T and constant P**, $\Delta G_{\text{reaction}} = 0$, so $\Delta G^\circ = -RT \ln K_{\text{eq}}$

or $\Delta G^\circ = -2.3026 RT \log_{10} K_{\text{eq}} = (-5.708 \text{ kJ/mole}) \log_{10} K_{\text{eq}}$ at 25°C .

g) Electrochemistry: $\Delta G = -n \mathcal{F} \mathcal{E}_{\text{cell}} \Rightarrow$ Nernst equation $\Delta \mathcal{E} = \Delta \mathcal{E}^\circ - (RT/n\mathcal{F}) \ln Q$.

THIRD LAW OF THERMODYNAMICS and Absolute entropy.

5. $S^\circ = 0.0$ for all *perfect crystals* of all pure *elements* and all pure *compounds* at **0 K**.