

Gibbs free energy.

* German physicist Hermann Von Helmholtz (1821-1894) was a versatile scientist contribute his research to optics, thermodynamics, acoustics and physiology.

* Let us consider G_1 , H_1 and S_1 represent the thermodynamic function in the initial state. Then the final state was mentioned as G_2 , H_2 and S_2 in the final state. The temperature remains constant. As we know that:

$$G = H - TS \rightarrow (1)$$

∴ for the initial and the final state it is given by

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1) \rightarrow (2)$$

$$\therefore \Delta G = \Delta H - T\Delta S \rightarrow (2)$$

But at constant pressure the relation is mentioned as Internal energy ' U ' therefore

$$\therefore \Delta H = \Delta U + P\Delta V \rightarrow (3)$$

Substitute eq No (3) in eq No (2).

$$\therefore \Delta G = \Delta U + P\Delta V - T\Delta S \rightarrow (4)$$

from the Internal energy relation: $dU = TdS + PdV$

$$\Delta A = \Delta U - T \Delta S$$

$$\Delta U = \Delta A + T \Delta S$$

from eq No ③

$$\Delta G = (\Delta A + T \Delta S) - T \Delta S + P \Delta V$$

$\therefore \Delta G = \Delta A + P \Delta V$ where $c \cdot \Delta A$ is equal to the
work function W_{\max}

$$\Delta G = -W_{\max} + P \Delta V$$

$$-\Delta G = W_{\max} - P \Delta V$$

$P \Delta V$ is the quantity work
done by the gas on expansion
against the constant external
pressure P .

$-\Delta G$ gives the maximum obtained work from the system
other than the system. The work other than the system are
called the Network.

$$\therefore \text{Network} = W - P \Delta V$$

$$= -\Delta G$$

$-\Delta G$ is the Network that can be obtained from the system
at constant temp. and pressure. The quantity G is called
the Gibbs function.

Gibbs Helmholtz equation

Let G_1 represent the free energy of a system in its initial state at a temperature T .

Suppose the temperature arises as then it is mentioned as $T + dT$ where dT is infinitesimally small.

Let the free energy for the new system arise as

$$G_1 + dG_1$$

Now the system is in the final stage then it is mentioned as T_2 and G_2 and by the free energy is mentioned as

$$G_2 + dG_2$$

At the temperature $T + dT$ the pressure remains constant. all along for a closed system

then it is given by

$$\text{Initial state} - dG_1 = -S_1 dT \rightarrow \text{①}$$

$$\text{Final state} - dG_2 = -S_2 dT \rightarrow \text{②}$$

Where S_1 and S_2 are the entropies of the system

Initial and the final, then it is given by the relation

subtracting eq No ② from eq No ①

$$d(G_2 - G_1) = -(S_2 - S_1) dT$$

$$\boxed{\Delta G = -\Delta S dT} \rightarrow \textcircled{3}$$

at the pressure constant therefore

$$\left(\frac{\partial \Delta G}{\partial T} \right)_P = -\Delta S \rightarrow \textcircled{4}$$

also from the relation.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\boxed{-\Delta S = \left(\frac{\Delta G - \Delta H}{T} \right)} \rightarrow \textcircled{5}$$

Combine the equation No ④ and eq No ⑤

$$\boxed{\left(\frac{\Delta G - \Delta H}{T} \right) = \left[\frac{\partial (\Delta G)}{\partial T} \right]_P}$$

This is the final equation of the Gibbs Helmholtz equation

Application:

- * Nernst equation is the precursor for the Gibbs Helmholtz equation
- * Clausius - Clapeyron and Van't Hoff isotherm can be determined
- * EMF of the reversible can be

Calculated

$$\boxed{\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_P}$$

Gibbs free energy for water formation

Consider the reaction for the formation of water



The Gibbs free energy relates the spontaneity of various reactions by looking at the change in enthalpy, temperature and entropy.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

It is an exothermic reaction.

During the reaction the bonds are formed between the hydrogen gas and oxygen gas from water.

Moles of a gas decreased and a liquid is formed so entropy is decreasing well.

Formation of water is a spontaneous reaction, so ΔG° must be negative. Therefore Gibbs free energy is also a state function so looking at

$$\Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}}$$

Both the hydrogen and oxygen gas are in their standard state and have Gibbs free energy Zero.
The Gibbs free energy for the water is:

$$\boxed{-273.13 \text{ kJ mol}^{-1}}$$

$$\Delta G^{\circ}_{\text{reac}} = -273.13 \text{ kJ mol}^{-1} - 0 \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G^{\circ}_{\text{rxn}} = -273.13 \text{ kJ mol}^{-1}}$$