

❖ Free Energy, Enthalpy Functions and Their Significance, Criteria for Spontaneity of a Process

The thermodynamic free energy and enthalpies are extremely useful concepts in the field of chemical thermodynamics. The decrease or increase in free energy is the maximum amount of work that a thermodynamic system can perform in a process at a constant temperature. The sign of thermodynamic free energy simply indicates whether a process is thermodynamically forbidden or feasible. The thermodynamic free energy is a state function, like internal energy and enthalpy. In this section, we will discuss the significance of enthalpy and free energy functions, and the corresponding spontaneity of a process.

➤ *Enthalpy or Heat Content*

As most of the reactions are carried out in open vessels where the atmospheric pressure remains the same, it must be very interesting to study the heat change that occurs during the course of a chemical reaction. The work-done by gas in the piston-fitted chamber against constant pressure (P) with ΔV volume change is

$$w = -P\Delta V \quad (99)$$

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From the first law of thermodynamics, we know that

$$q = \Delta U - w \quad (100)$$

Where q is the heat absorbed and ΔU is the change in the internal energy of the system respectively. After putting the value of work of expansion from equation (99) in equation (100), we get

$$q_p = \Delta U - (-P\Delta V) \quad (101)$$

$$q_p = \Delta U + P\Delta V \quad (102)$$

The symbol q_p is used instead of q because the whole process is carried out at constant pressure. Now suppose that this heat absorbed increases the internal energy from U_1 to U_2 and volume from V_1 to V_2 i.e.

$$\Delta U = U_2 - U_1 \quad (103)$$

$$\Delta V = V_2 - V_1 \quad (104)$$

After putting the values from equation (103) and (104) into equation (102), we get

$$q_p = (U_2 - U_1) + P(V_2 - V_1) \quad (105)$$

or

$$q_p = (U_2 + PV_2) - (U_1 + PV_1) \quad (106)$$

The quantity $U + PV$ is now defined as the enthalpy of the system, and since U , P and V all are state functions, the quantity $U + PV$ must also be a state function. Mathematically, the enthalpy can be shown as

$$H = U + PV \quad (107)$$

Therefore, if the enthalpy changes initial state H_1 to the final state H_2 at constant pressure, we have

$$H_1 = U_1 + PV_1 \quad (108)$$

$$H_2 = U_2 + PV_2 \quad (109)$$

After putting the values from equation (108) and (109) in equation (106), we get

$$q_p = H_2 - H_1 \quad (110)$$

$$q_p = \Delta H \quad (111)$$

Hence, we can conclude that the enthalpy change of a system is simply the amount of heat absorbed at constant pressure. Besides, if we compare equation (102) and equation (111), we have

$$\Delta H = \Delta U + P\Delta V \quad (112)$$

Therefore, the enthalpy change of a reaction may also be defined as the sum of its internal energy change and pressure-volume work done.

The physical significance of enthalpy: There is a certain amount of energy stored in every substance or material called internal energy. This energy comprises of many forms like kinetic, rotational, vibrational or inter-particle interactions. Moreover; like pressure, volume and internal energy; the enthalpy function is also an extensive property. Now recalling the expression of enthalpy again

$$H = U + PV \quad (113)$$

We can say that the enthalpy is nothing but the internal energy that is available for the conversion into heat; which is why the enthalpy is also called as “heat content”. Furthermore, like internal energy, the heat content or enthalpy is also not obtainable absolutely. However, like some other thermodynamic quantities, the parameter that is needed in the various analysis is enthalpy change which can be derived experimentally.

Enthalpy as the criteria for the spontaneity of reaction: The general expression for the enthalpy of a system is given below.

$$H = U + PV \quad (114)$$

After differentiating the equation (114), we get

$$dH = dU + VdP + PdV \quad (115)$$

$$dH - VdP = dU + PdV \quad (116)$$

Also as we know that, for the spontaneity of a process

$$TdS \geq dU + PdV \quad (117)$$

Now after putting the value of $dU + PdV$ from equation (116) in equation (117), we get

$$TdS \geq dH - VdP \quad (118)$$

or

$$dH \leq TdS + VdP \quad (119)$$

For a spontaneous or irreversible process dH must be less than the sum of multiplication of temperature and entropy change, and pressure-volume work.

However, the above relation is reduced to the following if the entropy and pressure of the system are kept constant i.e. $dS = 0$ and $dP = 0$.

$$(dH)_{S,P} \leq 0 \quad (120)$$

Here it is worthy to recall that the sign ‘=’ is for reversible reactions whereas ‘<’ condition is applicable to spontaneity or irreversibility of a reaction.

➤ **Helmholtz Free Energy or Work Function**

The Helmholtz free energy is typically denoted by the symbol ‘ A ’, which is derived from the German word “Arbeit” meaning work. The Helmholtz free energy can be defined mathematically as

$$A = U - TS \quad (121)$$

Where T , S and U are temperature, entropy, and internal energy, respectively. Moreover; like U , T and S ; free energy A is also a state function. Since A is independent of its previous state, we can say that

$$A_1 = U_1 - TS_1 \quad (122)$$

$$A_2 = U_2 - TS_2 \quad (123)$$

Where the subscript 1 and 2 represent the initial and final state. The change in Helmholtz free energy in going from initial to final state can obtain by subtracting equation (122) from equation (123) as

$$A_2 - A_1 = (U_2 - TS_2) - (U_1 - TS_1) \quad (124)$$

$$\Delta A = (U_2 - U_1) - T(S_2 - S_1) \quad (125)$$

$$\Delta A = \Delta U - T\Delta S \quad (126)$$

Where ΔU and ΔS are the change in internal energy and entropy, respectively. Therefore, the Helmholtz free energy change can be described as the difference of internal energy change and the multiplication of entropy change multiplied with the temperature at which the reaction is actually carried out.

The physical significance of Helmholtz free energy: From the definition of entropy change, we know that

$$\Delta S = \frac{q_{rev}}{T} \quad (127)$$

Also, from the first law of thermodynamics, for the work of expansion we have

$$\Delta U = q_{rev} - w_{max} \quad (128)$$

Putting the values of ΔS and ΔU from equation (127) and (128) in equation (126), we get

$$\begin{aligned} \Delta A &= (q_{rev} - w_{max}) - T \left(\frac{q_{rev}}{T} \right) \quad (129) \\ &= q_{rev} - w_{max} - q_{rev} \end{aligned}$$

or

$$-\Delta A = w_{max} \quad (130)$$

Hence, the decrease in Helmholtz free energy at constant temperature is equal to the maximum work done by the system; that is why the Helmholtz free energy is also called as work function.

Helmholtz free energy as the criteria for the spontaneity of reaction: The general expression for the enthalpy of a system is given below.

$$A = U - TS \quad (131)$$

After differentiating the equation (131), we get

$$dA = dU - TdS - SdT \quad (132)$$

$$TdS = dU - SdT - dA \quad (133)$$

Also as we know that, for the spontaneity of a process

$$TdS \geq dU + PdV \quad (134)$$

Now after putting the value of TdS from equation (133) in equation (134), we get

$$dU - SdT - dA \geq dU + PdV \quad (135)$$

or

$$-SdT - dA \geq PdV \quad (136)$$

$$dA \leq -PdV - SdT \quad (137)$$

For a spontaneous or irreversible process, dA must be less than the negative sum of multiplication of pressure and volume change with the multiplication of entropy and temperature change.

However, the above relation is reduced to the following if the volume and temperature of the system are kept constant i.e. $dV = 0$ and $dT = 0$:

$$(dA)_{V,T} \leq 0 \quad (138)$$

Here it is worthy to recall that the sign '=' is for reversible reactions whereas '<' condition is applicable to spontaneity or irreversibility of a reaction.

➤ Gibbs Free Energy or Gibbs Function

The Gibbs free energy is typically denoted by the symbol ' G ', and can be defined mathematically as

$$G = H - TS \quad (139)$$

Where T , S and H are temperature, entropy, and enthalpy, respectively. Moreover; like H , T and S ; the Gibbs free energy G is also a state function. Since G is independent of its previous state, we can say that

$$G_1 = H_1 - TS_1 \quad (140)$$

$$G_2 = H_2 - TS_2 \quad (141)$$

Where the subscript 1 and 2 represent the initial and final state. The change in Gibbs free energy in going from initial to final state can obtain by subtracting equation (141) from equation (140) as

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1) \quad (142)$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1) \quad (143)$$

$$\Delta G = \Delta H - T\Delta S \quad (144)$$

Where ΔH and ΔS are the change in enthalpy and entropy, respectively. Therefore, the Gibbs free energy change can be described as the difference of enthalpy change and the multiplication of entropy change multiplied with the temperature at which the reaction is actually carried out.

The physical significance of Helmholtz free energy: From the definition of entropy change, we know that

$$\Delta S = \frac{q_{rev}}{T} \quad (145)$$

Also, at constant pressure, we have

$$\Delta H = \Delta U + P\Delta V \quad (146)$$

Putting the values of ΔS and ΔH from equation (145) and (146) in equation (144), we get

$$\Delta G = (\Delta U + P\Delta V) - T\left(\frac{q_{rev}}{T}\right) \quad (147)$$

$$= (\Delta U - q_{rev}) + P\Delta V \quad (148)$$

Also, from the first of thermodynamics, for the work of expansion we have

$$\Delta U - q_{rev} = -w_{max} \quad (149)$$

Now, after putting the value of equation (149) in equation (148), we get

$$\Delta G = -w_{max} + P\Delta V \quad (150)$$

$$-\Delta G = w_{max} - P\Delta V \quad (151)$$

Hence, the decrease in Gibbs free energy for the process occurring at constant pressure and constant temperature is equal to the “maximum net work” that can be obtained from the process. The term “maximum net work” refers to maximum work other than the work of expansion.

Gibbs free energy as the criteria for the spontaneity of reaction: The general expression for the enthalpy of a system is given below.

$$G = H - TS \quad (152)$$

Since $H = U + PV$, equation (152) takes the form

$$G = U + PV - TS \quad (153)$$

After differentiating the equation (153), we get

$$dG = dU + PdV + VdP - TdS - SdT \quad (154)$$

$$TdS = dU + PdV + VdP - SdT - dG \quad (155)$$

Also as we know that, for the spontaneity of a process

$$TdS \geq dU + PdV \quad (156)$$

Now after putting the value of TdS from equation (155) in equation (156), we get

$$dU + PdV + VdP - SdT - dG \geq dU + PdV \quad (156)$$

or

$$VdP - SdT - dG \geq 0 \quad (157)$$

$$dG \leq VdP - SdT \quad (158)$$

For a spontaneous or irreversible process, dG must be less than the sum of negative multiplication of volume and pressure change with the multiplication of entropy and temperature change.

However, the above relation is reduced to the following if the pressure and temperature of the system are kept constant i.e. $dP = 0$ and $dT = 0$.

$$(dG)_{P,T} \leq 0 \quad (159)$$

Here it is worthy to recall that the sign ‘=’ is for reversible reactions whereas ‘<’ condition is applicable to spontaneity or irreversibility of a reaction.

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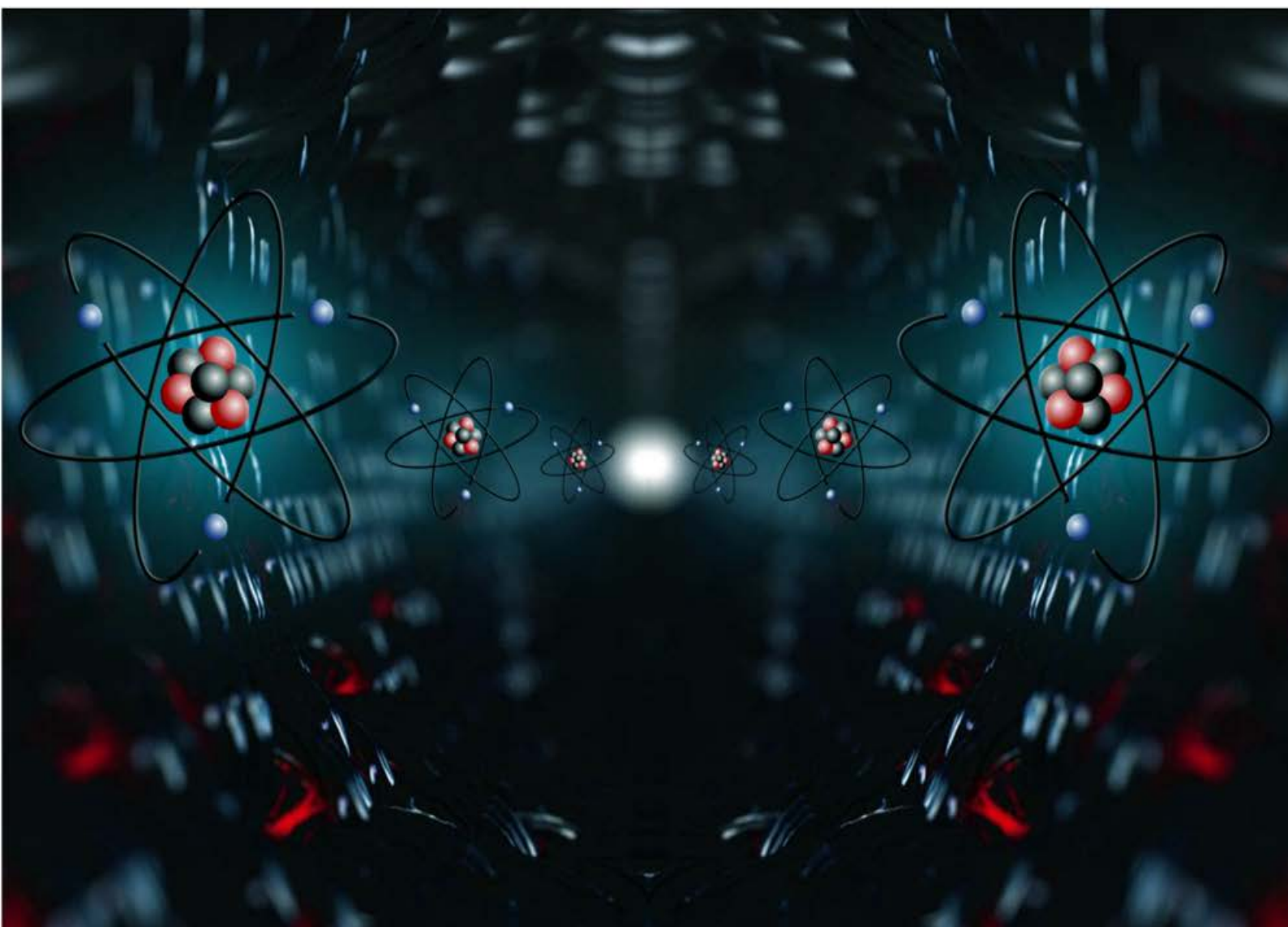
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A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



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