Free Energy Functions

Entropy is not a convenient criterion of spontaneity. Entropy is the basic concept for discussing the direction of natural change, but to use it as a criterion of spontaneity we have to analyze changes in both the system and its surroundings. It is always not convenient to do so.

The Helmholtz and Gibbs energies:

The Helmholtz free energy or work function (A) and the Gibbs free energy (G) are two such functions which can be used as criteria of spontaneity without explicit reference to the changes of entropy of the surroundings. Because, A and G automatically include entropy changes of the surroundings.

They are defined as

$$A = U - TS$$

$$G = H - TS$$

Like U, H and S, the functions A and G are state functions.

Changes in A and G in isothermal processes

The change in A for an isothermal process is given by,

$$\Delta A = A_2 - A_1$$

$$\Rightarrow \Delta A = (U_2 - TS_2) - (U_1 - TS_1)$$

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

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

The change in G for an isothermal process is given by,

$$\Delta G = G_2 - G_1$$

$$\Rightarrow \Delta G = (H_2 - TS_2) - (H_1 - TS_1)$$

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

$$\Rightarrow \Delta G = \Delta H - T\Delta S$$

When the change is infinitesimal at a constant temperature,

$$dA = dU - TdS$$

$$dG = dH - TdS$$

Significance of A

For a system of fixed composition (closed system), an infinitesimal change in A is given by the total differential of the defining equation $A = U - TS$ as

$$dA = dU - TdS - SdT \dots\dots\dots\dots\dots\dots\dots.(1)$$

The first law gives

$$dU = dq_{rev} + dw_{rev} \dots\dots\dots\dots\dots\dots..(2)$$

From the second law

$$dq_{rev} = TdS$$

Combining this with the first law (2),

$$dU = TdS + dw_{rev} \dots\dots\dots\dots\dots\dots..(3)$$

Putting dU from equations (3) into (1),

$$dA = TdS - TdS - SdT + dw_{rev} = -SdT + dw_{rev}$$

Again, at constant temperature, $dT = 0$, which gives

$$(dA)_T = dw_{rev}$$

A system does maximum work when it is working reversibly. Therefore, the maximum value of $work$ i.e., the maximum energy that can be obtained from the system as work, is given by

$$(dA)_T = dw_{max}$$

Or,

$$(\Delta A)_T = w_{max}$$

The change in the Helmholtz energy (A) at constant temperature gives the maximum work the system can do.

Significance of G

From the definition of enthalpy $H = U + pV$, we get

$$\begin{aligned} dH &= dU + pdV + Vdp && \Big| (neglecting\ dpdV) \\ &= dq + dw + pdV + Vdp && \Big| \because dU = dq + dw \end{aligned}$$

When the change is reversible,

$$dH = dq_{rev} + dw_{rev} + pdV + Vdp$$

From the second law, $dq_{rev} = TdS$,

$$\therefore dH = TdS + dw_{rev} + pdV + Vdp \dots\dots\dots..(1)$$

Now, from definition of Gibbs free energy $G = H - TS$, at constant temperature

$$(dG)_T = dH - TdS \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

Putting dH from (1) into (2)

$$(dG)_T = TdS + dw_{rev} + pdV + Vdp - TdS = dw_{rev} + pdV + Vdp \dots\dots\dots . (3)$$

The reversible work dw_{rev} may include both expansion and non-expansion work,

$$\therefore dw_{rev} = dw_{exp} + dw_{non-exp} = -pdV + dw_{e,rev}$$

Therefore equation (3) becomes

$$(dG)_T = -pdV + dw_{e,rev} + pdV + Vdp = dw_{e,rev} + Vdp$$

At constant pressure, $dp = 0$,

$$(dG)_{T,p} = dw_{e,rev}$$

Because the process is reversible, the work done must be maximum,

$$(dG)_{T,p} = dw_{e,max}$$

For a measurable change

$$(\Delta G)_{T,p} = w_{e,max}$$

The maximum non-expansion work we can obtain from a process at constant pressure and temperature is given by the value of ΔG for the process.

The non-expansion work that ΔG measures may be electrical or chemical work.

Prob: How much non-expansion work can be obtained from the combustion of 1.00 mol of CH_4(g) under standard conditions at 298K? Given, $\Delta S^0 = -140\, JK^{-1}mol^{-1}, \Delta H^0 = -890\, JK^{-1}mol^{-1}$

Variation of G with temperature and pressure

When the system changes its state, G may change because H, T and S change. For infinitesimal changes, taking differential of $G = H - TS$,

$$dG = dH - TdS - SdT \qquad (neglecting\ dTdS) \dots\dots\dots (1)$$

Because $H = U + pV$, we have

$$dH = dU + pdV + Vdp \qquad (neglecting\ dpdV) \dots\dots\dots (2)$$

For a closed system doing no non-expansion work, doing only reversible expansion work

$$dU = TdS - pdV \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

From (1), (2) and (3), we get

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$\Rightarrow dG = TdS - pdV + pdV + Vdp - TdS - SdT$$

$$\Rightarrow dG = Vdp - SdT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

This is a fundamental equation of thermodynamics.

Equation (4) suggests that G may be regarded as a function of p and T. It gives the change of free energy when a system undergoes, reversibly, a change of pressure as well as temperature.

Now, regarding G as a function of p and T,

$$dG = \left(\frac{\delta G}{\delta T}\right)_p dT + \left(\frac{\delta G}{\delta p}\right)_T dp \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

(4) and (5) gives

$$\left(\frac{\delta G}{\delta T}\right)_p = -S$$

$$\left(\frac{\delta G}{\delta p}\right)_T = V$$

Variation of G with temperature at constant pressure

Variation of G with temperature is given by

$$\left(\frac{\delta G}{\delta T}\right)_p = -S \dots\dots\dots\dots..(6)$$

This equation implies that as S is positive, G decreases when the temperature is raised at constant pressure and composition. G decreases most sharply when the entropy of the system is large. Therefore, the Gibbs energy of the gaseous phase of a substance, which has high molar entropy, is more sensitive to temperature than its liquid.

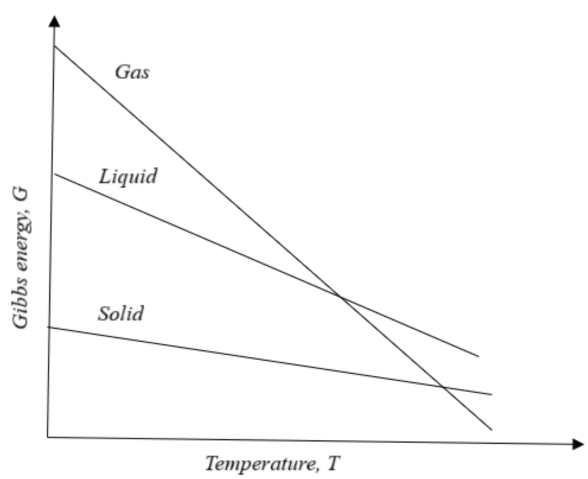

Figure: Variation of G with temperature

From definition,

$$G = H - TS$$

$$\Rightarrow -\mathrm{S} = \frac{G - H}{T}$$

Using equation (6),

$$\left(\frac{\delta \mathrm{G}}{\delta T}\right)_p = \frac{G - H}{T}$$

$$\Rightarrow \left(\frac{\delta \mathrm{G}}{\delta T}\right)_p - \frac{G}{T} = -\frac{H}{T} \dots \dots \dots \dots (7)$$

Now,

$$\left[\frac{\delta}{\delta T}\left(\frac{G}{T}\right)\right]_p = \frac{1}{T}\left(\frac{\delta G}{\delta T}\right)_p + G\left[\frac{\delta}{\delta T}\left(\frac{1}{T}\right)\right]_p$$

$$= \frac{1}{T}\left(\frac{\delta G}{\delta T}\right)_p - \frac{G}{T^2}$$

$$= \frac{1}{T}\left\{\left(\frac{\delta G}{\delta T}\right)_p - \frac{G}{T}\right\}$$

$$\therefore \left(\frac{\delta G}{\delta T}\right)_p - \frac{G}{T} = T\left[\frac{\delta}{\delta T}\left(\frac{G}{T}\right)\right]_p$$

Applying equation (7),

$$-\frac{H}{T} = T\left[\frac{\delta}{\delta T}\left(\frac{G}{T}\right)\right]_p$$

$$\Rightarrow \left[\frac{\delta}{\delta T}\left(\frac{G}{T}\right)\right]_p = -\frac{H}{T^2} \dots \dots \dots \dots \dots (8)$$

Equation (8) is called a **Gibbs-Helmholtz equation**.

LHS of the equation (8) can be written as

$$\left[\frac{\delta}{\delta T}\left(\frac{G}{T}\right)\right]_p = \left[\frac{\delta\left(\frac{G}{T}\right)}{\delta(\frac{1}{T})}\right]_p \left[\frac{\delta(\frac{1}{T})}{\delta T}\right]_p$$

$$= \left[\frac{\delta\left(\frac{G}{T}\right)}{\delta(\frac{1}{T})}\right]_p \times \left(-\frac{1}{T^2}\right)$$

$$\therefore -\frac{H}{T^2} = \left[\frac{\delta\left(\frac{G}{T}\right)}{\delta(\frac{1}{T})}\right]_p \times \left(-\frac{1}{T^2}\right)$$

$$\Rightarrow \left[\frac{\delta\left(\frac{G}{T}\right)}{\delta(\frac{1}{T})}\right]_p = H \;\ldots\ldots\ldots\ldots (9)$$

Equation (9) is another form of **Gibbs-Helmholtz equation**.

Gibbs-Helmholtz equation can also be applied to physical or chemical changes.

If a system of constant composition changes isothermally from an initial state specified by G_1, H_1 and S_1 to another state specified by G_2, H_2 and S_2, the changes in G, H and S are given by

$$\Delta G = G_2 - G_1$$

$$\Delta H = H_2 - H_1$$

$$\Delta S = S_2 - S_1$$

Gibbs-Helmholtz equations for initial and final states are

$$\left[\frac{\delta}{\delta T}\left(\frac{G_1}{T}\right)\right]_p = -\frac{H_1}{T^2} \ldots\ldots\ldots\ldots\ldots\ldots (10a)$$

$$\left[\frac{\delta}{\delta T}\left(\frac{G_2}{T}\right)\right]_p = -\frac{H_2}{T^2} \ldots\ldots\ldots\ldots\ldots\ldots (10b)$$

$(10a) - (10b) \Rightarrow$

$$\left[\frac{\delta}{\delta T}\left(\frac{G_2 - G_1}{T}\right)\right]_p = -\frac{(H_2 - H_1)}{T^2}$$

$$\left[\frac{\delta}{\delta T}\left(\frac{\Delta G}{T}\right)\right]_p = -\frac{\Delta H}{T^2} \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Equation (11) is another form of Gibbs-Helmholtz equation.

Variation of G with pressure at constant temperature (isothermal process)

Variation of G with pressure is given by

$$\left(\frac{\delta G}{\delta p}\right)_T = V \ldots\ldots\ldots\ldots\ldots (12)$$

This equation implies that as V is positive, G always increases when the pressure of the system is increased at constant temperature and composition. Because the molar volume of gases are large, G is more sensitive to changes of pressure for the gaseous phase of a substance than for its liquid and solid phases.

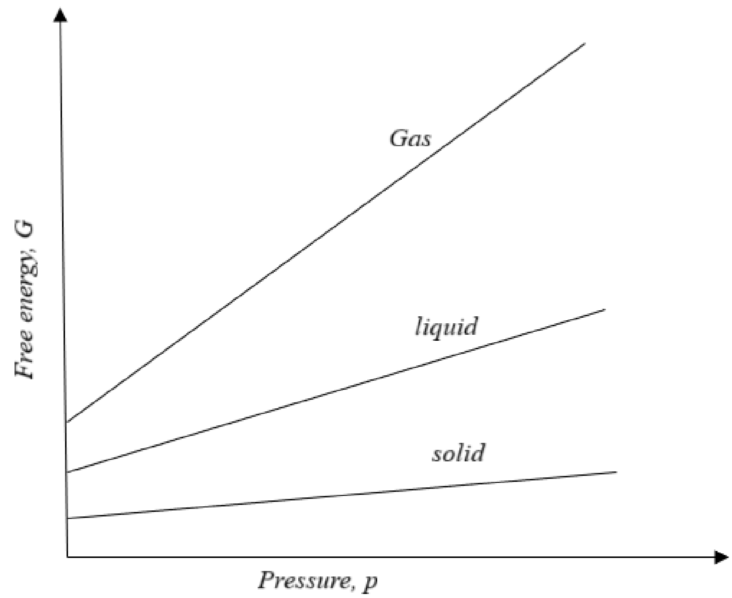

Figure: Variation of G with pressure

Equation (12) implies

$$dG = Vdp$$

Total free energy change for any substance can be obtained by integrating the above equation. When pressure of a gas is increased from p_1 to p_2 at temperature T,

$$\int_{p_1}^{p_2} dG = \int_{p_1}^{p_2} Vdp$$

In case of an ideal gas

$$V = \frac{nRT}{p}$$

Therefore,

$$\int_{p_1}^{p_2} dG = \int_{p_1}^{p_2} \frac{nRT}{p} dp$$

$$\Rightarrow \mathrm{G}(p_2) - \mathrm{G}(p_1) = nRT \int_{p_1}^{p_2} \frac{dp}{p}$$

$$\Rightarrow \Delta G = nRTln\frac{p_2}{p_1} \dots \dots \dots \dots .. (13)$$

To find the Gibbs free energy at one pressure in terms of its value at another pressure, we can use

$$G(p_2) = G(p_1) + nRT \int_{p_1}^{p_2} \frac{dp}{p}$$

In case of condensed phases, e.g., solids or liquids, volume is nearly independent of pressure, so

$$\int_{p_1}^{p_2} dG = \int_{p_1}^{p_2} Vdp$$

gives

$$\Delta G = V(p_2 - p_1)$$

Prob: Calculate the free energy change which occurs when 1 mole of an ideal gas expands reversibly and isothermally at 37°C from an initial volume of 55 dm^3 to 1000 dm^3.

Fundamental equations of thermodynamics for closed system

The four fundamental equations of thermodynamics for closed system are

$$dU = TdS - pdV \dots \dots \dots \dots (1)$$

$$dH = TdS + Vdp \dots \dots \dots \dots (2)$$

$$dA = -SdT - pdV \dots \dots \dots (3)$$

$$dG = -SdT + Vdp \dots \dots \dots (4)$$

Derivations

For an infinitesimally small change in the state of a system. The first law gives

$$dU = dq + dw$$

If the process is reversible and the system does only mechanical work (P-V work) then

$$dw = -pdV$$

The first law becomes

$$dU = dq_{rev} - pdV$$

From the second law,

$$dS = \frac{dq_{rev}}{T}$$

$$\Rightarrow TdS = dq_{rev}$$

Combining these relations

$$dU = TdS - pdV \dots \dots \dots (1)$$

From the definition of enthalpy $H = U + pV$

We obtain

$$dH = dU + pdV + Vdp \quad (neglecting\ dpdV)$$

Substituting the value of dU from equation (1), we get

$$dH = TdS - pdV + pdV + Vdp$$

Or,

$$dH = TdS + Vdp \ldots\ldots\ldots\ldots (2)$$

From the definition of Helmholtz free energy $A = U - TS$

we get

$$dA = dU - TdS - SdT \qquad (neglecting\ dTdS)$$

Using (1)

$$dA = TdS - pdV - TdS - SdT$$

Or,

$$dA = -SdT - pdV \ldots\ldots\ldots\ldots (3)$$

From the definition of Gibbs free energy $G = H - TS$

$$dG = dH - TdS - SdT \qquad (neglecting\ dTdS)$$

Using (2)

$$dG = TdS + Vdp - TdS - SdT$$

Or,

$$dG = -SdT + Vdp \ldots\ldots\ldots\ldots\ldots (4)$$

The Maxwell relations and thermodynamic equation of state

If $f = f(x, y)$ is a state function of the variables x and y, then its exact differential is given by

$$df = \left(\frac{\delta f}{\delta x}\right)_y dx + \left(\frac{\delta f}{\delta y}\right)_x dy$$

Or,

$$df = gdx + hdy$$

where $g = \left(\frac{\delta f}{\delta x}\right)_y$ and $h = \left(\frac{\delta f}{\delta y}\right)_x$

Now, $df = gdx + hdy$ is exact if

$$\left(\frac{\delta g}{\delta y}\right)_x = \left(\frac{\delta h}{\delta x}\right)_y \ldots\ldots\ldots\ldots (5)$$

Since dU is an exact differential, applying (5) to $dU = TdS - pdV$, we get

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta p}{\delta S}\right)_V \ldots\ldots\ldots.(6)$$

Similarly, applying (5) to fundamental equations (2), (3), (4), we get

$$\left(\frac{\delta T}{\delta p}\right)_S = -\left(\frac{\delta V}{\delta S}\right)_p \ldots\ldots\ldots.(7)$$

$$\left(\frac{\delta p}{\delta T}\right)_V = \left(\frac{\delta S}{\delta V}\right)_T \ldots\ldots\ldots..(8)$$

$$\left(\frac{\delta V}{\delta T}\right)_p = -\left(\frac{\delta S}{\delta p}\right)_T \ldots\ldots\ldots..(9)$$

Equations (6), (7), (8) and (9) are called Maxwell relations.

Thermodynamic equation of state

Dividing fundamental equation $dU = TdS - pdV$ by dV and applying constancy of temperature,

$$\left(\frac{\delta U}{\delta V}\right)_T = T\left(\frac{\delta S}{\delta V}\right)_T - p \ldots\ldots(10)$$

Using Maxwell relation

$$\left(\frac{\delta p}{\delta T}\right)_V = \left(\frac{\delta S}{\delta V}\right)_T$$

We get

$$\pi_T = \left(\frac{\delta U}{\delta V}\right)_T = T\left(\frac{\delta p}{\delta T}\right)_V - p \ldots\ldots(11)$$

Here, $\pi_T\ or\ \left(\frac{\delta U}{\delta V}\right)_T$ is called internal pressure and equation (11) is called first Thermodynamic equation of state.

Similarly, dividing fundamental equation $dH = TdS + Vdp$ by dp and applying constancy of temperature,

$$\left(\frac{\delta H}{\delta p}\right)_T = T\left(\frac{\delta S}{\delta p}\right)_T + V \ldots\ldots(12)$$

Using Maxwell relation

$$\left(\frac{\delta V}{\delta T}\right)_p = -\left(\frac{\delta S}{\delta p}\right)_T$$

We get

$$\left(\frac{\delta H}{\delta p}\right)_T = V - T\left(\frac{\delta V}{\delta T}\right)_p \ldots\ldots(13)$$

Equation (13) is called second Thermodynamic equation of state.

Thermodynamic equation of state for an ideal and van der Waals gas

For an ideal gas

$$pV = nRT$$

$$\Rightarrow p = \frac{nRT}{V}$$

$$\Rightarrow \left(\frac{\delta p}{\delta T}\right)_V = \frac{nR}{V}$$

Now,

$$\left(\frac{\delta U}{\delta V}\right)_T = T\left(\frac{\delta p}{\delta T}\right)_V - p$$

$$= T \times \frac{nR}{V} - p$$

$$= p - p$$

$$= 0$$

For a van der Waals gas

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\Rightarrow \mathrm{p} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Since a and b are independent of temperature

$$\left(\frac{\delta p}{\delta T}\right)_V = \frac{nR}{V - nb}$$

Therefore,

$$\left(\frac{\delta U}{\delta V}\right)_T = \frac{nRT}{V - nb} - p$$

$$\Rightarrow \left(\frac{\delta U}{\delta V}\right)_T = \frac{nRT}{V - nb} - \frac{nRT}{V - nb} + \frac{n^2 a}{V^2}$$

$$\Rightarrow \left(\frac{\delta U}{\delta V}\right)_T = \frac{n^2 a}{V^2}$$

$$\Rightarrow \left(\frac{\delta U}{\delta V}\right)_T = \frac{a}{\left(\frac{V}{n}\right)^2}$$

$$\Rightarrow \left(\frac{\delta U}{\delta V}\right)_T = \frac{a}{V_m^2} \dots \dots (14)$$

where V_m is the molar volume.

Equation (1) shows that the internal energy of a van der Waals gas increases when it expands isothermally and this increase is proportional to intermolecular attraction (a) of the gas.

Spontaneous process-enthalpy change, entropy change and free energy change considerations

A process is spontaneous or feasible at a given temperature and pressure, if ΔG for the process is negative. Thus, ΔG is a measure of driving force in any reaction or transformation. Since

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

it implies that a decrease in ΔH and increase in ΔS favour in making ΔG negative. Following cases may be helpful in deciding about the spontaneity of any process/reaction:

(i) When $\Delta H < 0$ and $\Delta S > 0$: For such reactions, ΔG will always be negative and the change will always be spontaneous.

(ii) When $\Delta H < 0$ and $\Delta S < 0$: In such cases, $\Delta G < 0$ only if $|\Delta H| > |T\Delta S|$. The reactions should be strongly exothermic to overcome the entropy decrease. At higher temperatures where $|T\Delta S| > \Delta H$, $\Delta G > 0$ and the change will no longer be spontaneous.

(iii) When $\Delta H > 0$ and $\Delta S > 0$: Under these conditions $\Delta G < 0$ only if $|T\Delta S| > |\Delta H|$. These reactions are nonspontaneous at lower temperatures but spontaneous at higher temperatures.

(iv) When $\Delta H > 0$ and $\Delta S < 0$: The net result in such cases is that ΔG is always positive and the change is always forbidden.