Thermodynamics- Auxiliary Functions

1. The significance of Helmholtz Energy A

Definition of A: $A = U - TS$

Consider a closed system undergoing a change of state from the "State 1" to "State 2"

State 1	State 2
A_1	A_2
U_1, T_1, S_1	U_2, T_2, S_2

$$\Delta A = A_2 - A_1 = (U_2 - U_2) - (T_2 S_2 - T_1 S_1)$$

Suppose that the system can exchange heat (Q) only with a single heat bath (reservoir) which is at the temperature T_B. Often the surroundings or the environment of the system plays the role of the heat reservoir. Moreover the initial temperature (T_1) and the final temperature (T_2) of the system are equal and those are again equal to the temperature of the bath.

$$T_1 = T_2 = T_B = T \text{ (say)}$$

(Note that the temperature at any intermediate state during the change may be different from T. Say at the beginning the temperature of the system was T, then during the change it undergoes a series of temperature changes and at the end in its final state its temperature again becomes T. The temperature of the bath is, however, always T. Such processes are also included in our discussions to follow.)

$$\text{Therefore, } \Delta A = (U_2 - U_2) - T(S_2 - S_1) = \Delta U + T\Delta S$$

$$\text{or, } \Delta A = Q + W - T\Delta S = W + (Q - T\Delta S)$$

$$\text{or, } -W = -\Delta A + (Q - T\Delta S)$$

The Clausius inequality for such a finite change of state can be written as $T\Delta S \geq Q$, Q being the heat exchanged by the system with the surroundings.

Therefore, $(Q - T\Delta S) \leq 0$, and also
                 $-W \leq -\Delta A$.

-W = the total work (both PV work and non-PV work) produced/obtained in the surroundings.
-ΔA = decrease in the Helmholtz energy of the system due the change.
In all the above inequalities the 'greater than' sign applies to an irreversible/ spontaneous change and the 'equality' sign applies to a reversible change.

The last inequality tells that, under the above mentioned conditions, the work obtained in an irreversible change in the surroundings is less than the decrease in Helmholtz energy of the system and is equal to the decrease in the Helmholtz energy when the change occurs reversibly.
The conditions under which the last inequality is valid are again mentioned below.
i) The system is closed ie. no exchange of matter between the system and the surrounding occurs. The total amount of matter present in the system remains constant. But change of the composition of the system due to a chemical reaction or mass transfer taking place within the same system does not invalidate the inequality.
ii) The system exchanges heat only with a single heat bath which is at the temperature T_B.
iii) Initial temperature of the system = its final temperature = temperature of the heat bath. (But this is not necessarily an isothermal process. Because the temperature at the intermediate stages may

vary when the process is going on. If for a particular change $T_1 = T_2 = T_B = T_{intermediate} = T$ (say), then that process will be an isothermal process. This is the case when the system is at thermal equilibrium throughout the change. Also if the change occurs reversibly, then it will be an isothermal change).

If the total work involved $W=0$, then the inequality becomes,

$$\Delta A \leq 0.$$

This is the criterion for the spontaneity and equilibrium for a closed system under the conditions as stated above, where the '<' sign refers to spontaneity and '=' sign implies equilibrium.

In the inequality $-W \leq -\Delta A$ the quantity in the l.h.s is less that the quantity in the r.h.s. Now we make the two sides equal by adding a positive quantity σ to the l.h.s. The significance of the term σ will be made clear later on. Therefore the inequality assumes the following form.

$$-W + \sigma = -\Delta A,$$
$$\text{or, } W = \Delta A + \sigma.$$

Case I – The system does work on the surroundings.

$$W = -|W|$$
$$-|W| = \Delta A + \sigma$$
$$\text{or, } |W| = -\Delta A - \sigma$$
$$\text{or, } |W| \leq -\Delta A$$

Therefore, the amount of the work done by the system ie. the work obtained in the surroundings as output is less than the decrease of Helmholtz energy of the system during the change in an irreversible change and this is equal to the decrease of Helmholtz energy of the system when the same change of state occurs reversibly. This also shows that the work output in a reversible change between a given pair of states under the set of afore mentioned conditions is the maximum. The work output in any irreversible change between the same two states under the same conditions is less than the corresponding reversible work. Remember that, A being a state function, ΔA is same whether the change occurs reversibly or irreversibly provided the initial and final states remain the same.

Case II – The surroundings does work on the system.

$$W = |W|$$
$$|W| = \Delta A + \sigma$$
$$\text{or, } |W| \geq \Delta A$$

Therefore the amount of work that is required to be done on the system is greater than the increase in Helmholtz energy of the system when the change occurs irreversibly. When the system undergoes a reversible change between the same two states, the work that is to be expended to effect the change is equal to the increase in Helmholtz energy of the system. This amount of the reversible work is the minimum as compared to any other irreversible work that is supposed to be expended to bring about the change. This is ascertained by the inequality $|W| \geq \Delta A$, because ΔA is independent of the nature of the change provided the initial and the final states are fixed.

Significance of σ-- The unavailable energy:

$$-W + \sigma = -\Delta A$$
$$-W = -\Delta A + (Q - T\Delta S)$$

Comparing the above two equations, we found that $\sigma = -(Q - T\Delta S)$.

Here $Q = Q_{sys}$ and therefore $Q_{sur} = -Q_{sys} = -Q$. However, the heat exchange of the surroundings can always be considered to be occurring in a reversible manner irrespective of whether the system has actually exchanged heat reversibly or irreversibly. Therefore, $-Q = T\Delta S_{sur}$.

$\qquad\qquad$ σ = -(Q – TΔS) = -(-TΔS$_{sur}$ - TΔS). Here TΔS = TΔS$_{sys}$.

Therefore, $\qquad$ σ = TΔS$_{sur}$ + TΔS$_{sys}$ = TΔS$_{uni}$, where ΔS$_{uni}$ = entropy increase of the universe.

Consider a cyclic change of the system under discussion from state-1 to state-2 irreversibly and then back to state-1 from state-2 reversibly, obeying the conditions as mentioned above. To effect the forward change (1 to 2) W work is done on the system and in the reverse change (2 to 1) the system does W' work.

Forward process(state-1 to state-2): Irreversible, Work $= W = |W|$, Helmholtz energy change = ΔA
Reverse process(state-1 to state-2): Reversible, Work$= W' = -|W'|$, Helmholtz energy change $=$ΔA'=-ΔA
Forward process: $\qquad$ W $= |W| =$ ΔA + σ
Reverse process: $\qquad$ W' $= -|W'| =$ ΔA' = -ΔA (σ = 0 since it is reversible)
Net change in the overall cyclic process: W + W' $= |W| - |W'| =$ σ = TΔS$_{uni}$.

We see that the amount of the work ($|W|$) that has been done on the system to take it from the state-1 to state-2 is more than the amount of the work ($|W'|$) that it yields to the surroundings while returning from the state-2 to state-1 by an amount equal to σ (= TΔS$_{uni}$). The work that is spent to carry out the forward change is not fully recovered in the reverse process. This is because the forward change is irreversible. Had the forward change been reversible too, we would have recovered in the reversible reverse change the whole amount of the work that had been spent to effect the forward change. In an irreversible change some of the energy which is spent to do the necessary work becomes unavailable for any further use. σ measures this amount of unavailable energy. As σ = TΔS$_{uni}$, we find that this amount of energy which is rendered as unavailable in an irreversible change causes the entropy of the universe to increase. Hence, in other words, entropy is a measure of the unavailable energy.

Consider an infinitesimal change of the system at the temperature T = T$_B$.
Clausius inequality: $\qquad\qquad\qquad\qquad$ $đQ \leq TdS$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $đQ = dU - đW$
$\qquad\qquad\qquad$ or, $\qquad$ $dU - đW \leq TdS$
$\qquad\qquad\qquad$ or, $\qquad$ $-đW \leq -dA$, at the constant temperature T=T$_B$.
However, this infinitesimal change is an isothermal change. Here W includes both the PV work and non-PV work. If $đW = 0$, then dA ≤ 0 which states the criterion for spontaneity an equilibrium at constant temperature T = T$_B$.
If the PV work is the only form of work, then $đW = -P_{ex}dV = 0$ implies that V is constant (provided $P_{ex} \neq 0$). Then the criterion for spontaneity and equilibrium becomes dA$_{T,V}$ ≤ 0, where the subscripts T and V indicate that in this infinitesimal change the temperature and the volume remain fixed.
The inequality $-W \leq -\Delta A$ can also be obtained by the integration of the inequality $-đW \leq -dA$ between the initial and final states. Then that would imply that the overall change of state is an isothermal change, because the inequality $-đW \leq -dA$ pertains to an infinitesimal change which is isothermal. But the isothermal condition is not an essential requirement for the integrated form of $-đW \leq -dA$, $\qquad$ ie. -W ≤ -ΔA to be valid.

2. The significance of Gibbs Energy G

Definition of G: $G = H - TS = U + PV - TS$

Consider a closed system undergoing a change of state from the "State 1" to "State 2"

State 1	State 2
A_1	A_2
$G_1, U_1, H_1, T_1, S_1, P_1, V_1$	$G_2, U_2, H_2, T_2, S_2, P_2, V_2$

$$\Delta G = G_2 - G_1 = (H_2 - H_1) - (T_2 S_2 - T_1 S_1) = (U_2 - U_2) + (P_2 V_2 - P_1 V_1) - (T_2 S_2 - T_1 S_1)$$

Suppose that the system can exchange heat (Q) only with a single heat bath (reservoir) which is at the temperature T_B. (Often the surroundings or the environment of the system plays the role of the heat reservoir). Moreover the initial temperature (T_1) and the final temperature (T_2) of the system are equal and those are again equal to the temperature of the bath. Also the initial pressure (P_1) and the final pressure (P_2) of the system are equal and those are again equal to the external pressure, P_{ex}, acting on the system. (Often the external pressure, P_{ex}, is the atmospheric pressure acting on the system).

$$T_1 = T_2 = T_B = T \text{ (say)}$$
$$P_1 = P_2 = P_{ex} = P \text{ (say)}$$

(Note that the temperature at any intermediate state during the change may be different from T. The same is true for its pressure. Suppose at the beginning the temperature of the system was T and its pressure was P. Then during the change it undergoes a series of temperature and pressure changes and at the end, in its final state, its temperature again becomes T and pressure becomes P. The temperature of the bath is, however, always T and the pressure acting on it throughout remains fixed at P. Such processes are also covered by the discussions to follow.)

$$\text{Therefore, } \Delta G = (U_2 - U_2) + P(V_2 - V_1) - T(S_2 - S_1) = \Delta U + P\Delta V - T\Delta S$$

$$\text{or, } \Delta G = Q + W + P\Delta V - T\Delta S = W - W_{PV} + (Q - T\Delta S)$$

$$\text{or, } -W_O = -\Delta G + (Q - T\Delta S), \text{ where } W_O = W - W_{PV}$$

The Clausius inequality for such a finite change of state can be written as $T\Delta S \geq Q$, Q being the heat exchanged by the system with the bath.

Therefore, $(Q - T\Delta S) \leq 0$, and also
      $-W_O \leq -\Delta G$.

-W = the total work (both PV work ($W_{PV} = -P\Delta V$) and non-PV work (W_O)) produced/obtained in the surroundings.
-ΔG = decrease in the Gibbs energy of the system due to the change.
In all the above inequalities the 'greater than' sign applies to an irreversible/ spontaneous change and the 'equality' sign applies to a reversible change.

The last inequality tells that, under the above mentioned conditions, the non-PV work obtained in an irreversible change in the surroundings is less than the decrease in Gibbs energy of the system and is equal to the decrease in the Gibbs energy when the change occurs reversibly.

The conditions under which the last inequality is valid are again mentioned below.

i) The system is closed ie. no exchange of matter between the system and the surroundings occurs. The total amount of matter present in the system remains constant. But change of the composition of the system due to a chemical reaction or mass transfer taking place within the same system does not invalidate the inequality.

ii) The system exchanges heat only with a single heat bath which is at the temperature T_B.

iii) Initial temperature of the system = its final temperature = temperature of the heat bath. (But this is not necessarily an isothermal process. Because the temperature at the intermediate stages may vary when the process is going on. If for a particular change $T_1 = T_2 = T_B = T_{intermediate} = T$ (say), then that process will be an isothermal process. This is the case when the system is at thermal equilibrium throughout the change. Also if the change occurs reversibly, then it will be an isothermal change).

iv) Initial pressure of the system = its final pressure = external pressure on the system. (But this is not necessarily a constant pressure process. Because the pressure of the system in the intermediate stages may vary when the process is going on. If for a particular change $P_1 = P_2 = P_{ex} = P_{intermediate} = P$ (say), then that process will be a constant pressure process. This is the case when the system is at mechanical equilibrium throughout the change. Also if the change occurs reversibly, then it will be an isobaric change).

If no work other than 'PV' work is involved ie $W_O = 0$, then the inequality becomes,
$$\Delta G \leq 0.$$
This is the criterion for the spontaneity and equilibrium for a closed system under the conditions as stated above, where the '<' sign refers to spontaneity and '=' sign implies equilibrium.

In the inequality $-W_O \leq -\Delta G$, the quantity in the l.h.s is less than the quantity in the r.h.s. Now we make the two sides equal by adding a positive quantity σ to the l.h.s. Therefore the inequality assumes the following form.
$$-W_O + \sigma = -\Delta G,$$
$$\text{or, } W_O = \Delta G + \sigma.$$

Case I – The system does work on the surroundings.
$$W_O = -|W_O|$$
$$-|W_O| = \Delta G + \sigma$$
$$\text{or, } |W_O| = -\Delta G - \sigma$$
$$\text{or, } |W_O| \leq -\Delta G$$

Therefore, the amount of the non-PV work done by the system ie. the non-PV work obtained in the surroundings, the non-PV work output, is less than the decrease of Gibbs energy of the system due to the change in an irreversible process and this is equal to the decrease of Gibbs energy of the system when the same change of state occurs reversibly. This also shows that the non-PV work output in a reversible change between a given pair of states under the set of the afore mentioned conditions is the maximum. The non-PV work output in any irreversible change between the same two states under the same conditions is less than the corresponding reversible work. Remember that, G being a state function, ΔG is same whether the change occurs reversibly or irreversibly provided the initial and final states remain the same.

Case II – The surroundings does work on the system.
$$W_O = |W_O|$$
$$|W_O| = \Delta G + \sigma$$
$$\text{or, } |W_O| \geq \Delta G$$

Therefore the amount of non-PV work that is required to be done on the system is greater than the increase in Gibbs energy of the system when the change occurs irreversibly. When the system

undergoes a reversible change between the same two states, the non-PV work that is to be expended to effect the change is equal to the increase in Gibbs energy of the system. This amount of the reversible non-PV work is the minimum as compared to any other irreversible non-PV work that is supposed to be expended to bring about the change. This is ascertained by the inequality $|W_O| \geq \Delta G$, because ΔG is independent of the nature of the change provided the initial and the final states are fixed.

Consider an infinitesimal of the system at the temperature $T = T_B$ at the pressure $P = P_{ex}$

Clausius inequality:
$$đQ \leq TdS$$
$$đQ = dU - đW$$
or, $$dU - đW \leq TdS$$
or, $$dU - đW_{PV} - đW_O \leq TdS$$
or, $$dU + PđV - đW_O \leq TdS$$
or, $$dH - đW_O \leq TdS$$
or, $$-đW_O \leq -(dH - TdS)$$
or, $$-đW \leq -dG, \text{ at the constant temperature T=T}_B \text{ and at}$$
the constant pressure P=P_{ex}.

However, this infinitesimal change is an isothermal isobaric change. If $đW_O$ = 0, then dG ≤ 0 which states the criterion for spontaneity and equilibrium at constant temperature $T = T_B$ and at constant pressure P=P_{ex}.

Then the criterion for spontaneity and equilibrium becomes $dG_{P,V} \leq 0$, where the subscripts P and T indicate that in this infinitesimal change the temperature and the pressure of the system remain fixed.

The inequality $-W_O \leq -\Delta G$ can also be obtained by the integration of the inequality $-đW_O \leq -dG$ between the initial and final states. Then that would imply that the overall change of state is an isothermal isobaric change, because the inequality $-đW \leq -dA$ pertains to an infinitesimal change which is isothermal and isobaric. But the isothermal and the isobaric conditions are not essential requirement $W_O \leq -\Delta G$ to hold.