some ***randomness*** of distribution. So its entropy in 0K is ***not zero***.

★ GIBBS AND HELMHOLTZ FUNCTIONS

Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities

Gibbs function G is otherwise called **Gibbs free energy** and it is the net work function. Helmholtz Function A is otherwise called **Helmholtz free energy** and it is the maximum work function

The Gibbs free energy - G - Net work function

Definition : $G = H - TS$

Gibb's free energy (also called energy function) G is defined as a thermodynamic property, a decrease in which i.e., $-\Delta G$ gives the net work that can be obtained from a system during a change

$$\text{i.e., } -\Delta G = W - P\Delta V$$

Relationship between Gibb's free energy change and enthalpy change

From definition $G = H - TS$

Since H, T and S are state properties, G is also a state property. For a change at constant temperature, change in G is given as

$$dG = dH - T\,dS$$

dG is an exact differential. Gibbs free energy is useful to study changes at constant pressure and temperature.

For a finite change $\Delta G = \Delta H - T\Delta S$

Relation between helmholtz free energy and Gibbs free energy we know

$$\Delta H = \Delta E + P\Delta V$$

$$\& \quad \Delta G = \Delta E + P\Delta V - T\Delta S$$

$$\text{But } \Delta E - T\Delta S = \Delta A$$

$$\text{So } \Delta G = \Delta A + P\Delta V$$

To show that the decrease in Gibb's free energy gives the net work (work other than work of expansion done by a system)

$$\text{We know } \Delta G = \Delta A + P\Delta V$$

$$\text{But } \Delta A = -W, \ \Delta G = -W + P\Delta V$$

$$\text{or } -\Delta G = W - P\Delta G = W_{net}$$

The Helmholtz free energy - A - Maximum work function

Definition : $A = E - TS$

Helmoholtz free energy (also called work function) A is defined as a thermodynamic property, a decrease in which i.e., ΔA gives the maximum work that can be obtained from a system during a given change.

$$\text{i.e., } -\Delta A = W_{rev}$$

To show $-\Delta A = W_{rev}$:

From definition $A = E - TS$

Since E, T and S are state properties, A is also a state property. The change in A for a change in the system at constant temperature is given below

$$dA = dE - TdS$$

Since A is a state property, dA is an exact differential

For a finite change $A = \Delta E - T\Delta S$

Where ΔA is the change in the function A. ΔE is the corresponding change in internal energy and ΔS is the change in the entropy of the system

For a reversible change at constant T the heat absorbed is Q_{rev}. From definition $Q_{rev}/T = \Delta S$. Substituting this in the above equation we get

$$\Delta A = \Delta E - Q_{rev}$$

But from First law of thermodynamics

$$\Delta E = Q_{rev} - W_{rev}\ ; \ \therefore\ - W_{rev} = \Delta E - Q_{rev}$$

$$\text{i.e.,}\quad \Delta A = -W_{rev} \quad \text{or} \quad -\Delta A = W_{rev}$$

We know in a reversible process the work done is the maximum work. So, the decrease in A, i.e., $-\Delta A$, gives the ***maximum work*** thust can be obtained from a system during a given change. So A, the Helmholts free energy is called a work function. Helmholtz free energy is useful to study change at constant temperature and volume

Differences between Helmholtz free energy and Gibb's free energy

	Helmholtz Free energy	**Gibb's Free energy**
Definition	$A = E - TS$	$G = H - TS$
Indicates	Maximum work content of a system	Useful work that could be obtained (Network
Value	$-\Delta A = W_{rev}$	$-\Delta G = W_{rev} - P\Delta V$

Two show how $T\Delta S$ determines the randomness of a reaction

$$\text{We know } \Delta G = \Delta H - T\Delta S$$

$$\text{or } T\Delta S = \Delta H - \Delta G$$

= Enthalpy – useful work = unavailable energy
(Heat absorbed)

Thus $T\Delta S$ is a measure of unavailable energy ; i.e., the energy which could not be converted into work

$$\text{If } T\Delta S > \Delta H; \quad \text{then} \quad \Delta G = \text{negative}$$

Such a process will be spontaneous. All spontaneous processes lead to an increase in the disorderliness or randomness of the system. So if $T\Delta S$ is > ΔH randomness will increase. Similarly if $T\Delta S < \Delta H$ then randomness will decrease.

Thus $T\Delta S$ determines the randomness of a reaction. $T\Delta S$ also gives us an idea of the unavailable energy.

★ ΔA AND ΔG AS CRITERIA FOR THERMODYNAMIC EQUILIBRIUM AND SPONTANEITY

General condition for equilibrium and spontaneity / Criteria / condition for a reversible and spontaneous process in terms of Helmholts free energy (or) Condition for Equilibrium and spontaneity under Constant termperature and constant volume

$dE - TdS - SdT$

Consider the general conditions for equilibrium and spontaneity

$$-dE - P_{op}\,dV - du + T\,dS \geq 0$$

At Constant volume $P_{OP}dV = 0$

$-P_{op}\,dV - du - TSdT$

$$\therefore -(dE - TdS) - du \geq 0$$

At constant temperature $dA = dE - T\,dS$

$$\text{So} \quad -dA - du \geq 0$$

No work other than work of expansion takes place in the chemical reactions and ordinary physical changes. For these changes du=0 and

$$\therefore -dA \geq 0 ; \quad dA \leq 0$$

Condition for equilibrium : $dA = 0$

Condition for spontaneity : $dA < 0$

Criteria / condition for a reversible and spontaneous process in terms of Gibb's free energy (or) Condition for equilibrium and Spontaneity under constant Temperature and Pressure.

Consider the general condition for equlibrium and spontaneity

$$-dE - P_{op}\,dV - du + T\,dS \geq 0$$

At constant pressure $P = P_{OP}$ Therefore

$$-dE - PdV - du + TdS \geq 0$$

$$-(dE + PdV) - du + TdS \geq 0\ ;\ -dH - du + TdS \geq 0$$

At constant temperature $dH - TdS = dG$; $-dG - du \geq 0$

No work other than work of expansion takes place in chemical reactions and ordinary physical changes, For these changes

$$-dG \geq 0\ ; \quad \therefore \quad dG \leq 0$$

∴ Condition for equilibrium at constant T and P : $dG = 0$

∴ Condition for spontaneity at constant T and P : $dG < 0$

Many chemical reactions are carried out at constant temperature and pressure. In these reactions the Gibbs free energy of the system decreases. When a reaction attains equilibrium, the free energy will not decrease.

Conclusion :

We have seen earlier that first law is unable to tell whether a change of state or a reaction can take place spontaneously or not. That was why we needed a second law. Now let us see how the second law is able to predict the feasibility or the spontaneity of a reaction.

Feasibility of a reaction :

If a reaction can take place spontaneously or on its own accord it is said to be feasible.

Second law gives a method in predict the feasibility of a reaction According to second law, if $\Delta G < 0$ or if $\Delta S > 0$ the reaction will be feasible Normaliy exothermic reactions are spontaneous. We know

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

For exothermic reactions ΔH is negative. So ΔG will be invariably negative provided ΔS is positive. So normally exothermic reactions are spontaneous. However for an exothermic reactions are spontaneous. However for an exothermic reaction where ΔH is negative, if ΔS also is negative, T ΔS will be negative. In such a case,

$$\Delta G = -\Delta H - (-T\Delta S) \quad \Delta G = -\Delta H + T\Delta S\,.$$

Now ΔG will be negative only if $-\Delta H > T\Delta S$. If $T\Delta S > -\Delta H$ then ΔG will be positive. This means that the reaction **cannot take place**. Thus we see that ΔH values alone cannot *determine the* ***feasibility*** *of a reaction*.

For an endothermic reaction ΔH is positive. If ΔS is negative then T ΔS becomes negative

$$\text{i.e.}\quad \Delta G = \Delta H - T\Delta S$$

$$= \text{positive} - [\,\text{negative}\,] = \text{positive} + \text{Positive} = \text{Positive}$$

That means such a reaction **cannot take place**.

For an endothermic process to take place ΔS must be highly positive so that – ΔS is greater than ΔH which is positive

$$\text{i.e.}\quad -T\Delta S > \Delta H$$

then only ΔG will become negative.

Driving forces for natural changes :

We know that the free energy of a system decreases during natural or spontaneous change. A definite change in free energy for a natural change in the system at constant temperature is given by the following expression

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

When ΔG is negative the change is spontaneous or natural. The sign of ΔG depends ΔH and ΔS. If ΔH is negative and ΔS is positive, ΔG is negative. ΔH is related to the energy of the system. For natural changes to take place, the energy of the system, should decrease and entropy should increase. This is observed in exothermic reactions. If enthalpy increases in a certain change then the entropy should increase to larger extent to compensate the increase in enthalpy. This is observed in endothermic reactions. From these we can conclude that the driving forces for natural changes are the *decrease in enthalpy and increase in entropy*.

THEIR (ΔA AND ΔG) ADVANTAGES OVER ENTROPY CHANGE

The movement of physico-chemical system towards equilibrium is controlled by two factors, one involving entropy and the other the energy of the system. We know, spontaneous processes proceed towards equilibrium with increase of entropy. At equilibrium, the value of entropy is maximum. On the other hand the passage of a spontaneous process towards equilibrium is accompanied by a decrease of energy of the system. Hence at equilibrium the energy of the system is minimum. Thus the criteria for a thermochemical equilibrium or spontaneity may be given as follows :

$$\text{(i)}\ (\partial S)_{E,V,T} \geq 0 \quad ; \quad \text{(ii)}\ (\partial E)_{S,V,T} \leq 0$$

But chemical reactions are rarely studied under conditions of constant entropy or constant energy. Usually reactions are carried out at constant pressure (atmospheric pressure) and at constant temperature (in a thermostat). Sometimes they are carried out at constant volume (in bomb calorimeter) and at constant temperature. So it becomes necessary to specify the criteria for equilibrium or spontaneity in terms of ΔA or ΔG. They are given as follows :

$$(\partial A)_{V,T} \leq 0 \ ; \ (\partial G)_{P,T} \leq 0$$

Thus the advantage of ΔA and ΔG over ΔS is that they are more convenient practically, in the study of some concrete problems.

2. The sign of ΔG or ΔA will indicate whether the process will be spontaneous or not, If it is negative the reaction is spontaneous. Thus we can not say with respect to ΔS.

Between ΔG and ΔS. ΔS is more important in deciding the spontaneity of a reaction :

Though we have seen that ΔG is more advantageous than ΔS, ΔS is more important in deciding the spontanity of a reaction as ΔG itself is dependant on ΔS.

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

We see ΔG, depends on ΔH and ΔS. If ΔS is positive and ΔH negative than ΔG will be negative. But if ΔS is negative and sufficiently large so that $T\Delta S > -\Delta H$, than ΔG will become positive. Then the reaction is not feasible. If ΔH is positive (endothermic reactions) then ΔS must be positive and should have large numerical value so that ΔG may be negative. Thus we see that ΔS is more important than ΔG in determining the spontaneity of a reaction.

Thus ΔG and ΔA are more advantageous from a practical point of view where as ΔS is more important from a theoritical point of view.

VARIATION OF G AND A WITH P,V AND T

i) Change in Helmholtz free energy is given by the following fundamental equation.

$$dA = -SdT - PdV \qquad (11)$$

At constant volume PdV = 0

$$\therefore \left(\frac{\partial A}{\partial T}\right)_V = -S$$

Entropy of a system is always positive. Therefore the free energy is inversely related to temperature. Since the entropy of a gas is very high free energy of the gas decreases drastically with an increase in temperature. At constant temperature, equation (II) becomes

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

The free energy decreases with volume.

ii) Gibbs free energy is related to T and P. The following fundamental equation relates Gibb's free energy change with change in T and P.

$$dG = -SdT + VdP \qquad (12)$$

At constant pressure dP = 0

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

At constant temperature dT = 0

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

At constant pressure ΔG is inversely related to temperature. But at constant temperature ΔG is directly related to pressure.

Further $$dG = -SdT + VdP$$

At constant temperature $dT = 0$;

$$\therefore dG = VdP$$

But for an ideal gas $PV = nRT$

and $V = \frac{nRT}{P}$; So $dG = nRT \frac{dP}{P}$

Integrating $$\int_{G1}^{G2} dG = nRT \int_{P1}^{P2} \frac{dP}{P}$$

or $$G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

or $$\Delta G = 2.303\, nRT \log \frac{P_2}{P_1}$$

or $$\Delta G = 2.303\, nRT \log \frac{V_1}{V_2}$$

2.3 BDU Starts

★★ THERMODYNAMIC EQUATIONS OF STATE MAXWELL'S RELATIONS

From the First law of thermodynamics $q = dE + w$

If the process is reversible and the work is restricted to work of expansion alone $W = PdV$; $\therefore q_{rev} = dE + PdV$

Dividing throughtout by T.

$\frac{q_{rev}}{T} = \frac{dE + PdV}{T}$; But $\frac{q_{rev}}{T} = dS$ by definition

So $dS = \frac{dE + PdV}{T}$ or $\frac{dE + PdV}{T} = dS$

or $dE + PdV = TdS$; $\therefore dE = TdS - PdV$ (13)

This equation incorporates first and second law of thermodynamics. It is known as fundamental equation of thermodynamics The definitions of H, A and G are

$H = E + PV$; $A = E - TS$; $G = \overset{H}{E + PV} - TS$

On differentiation : $dH = dE + PdV + VdP$

$dA = dE - TdS - SdT$

$dG = dE + PdT + VdP - TdS - SdT$

After substituting dE from equation (13) these equations become

$$dH = TdS + VdP \qquad (14)$$

$$dA = -SdT - PdV \qquad (11)$$

$$dG = -SdT + VdP \qquad (12)$$

Let us take equation (13) $\quad dE = TdS - PdV$

At const. V $\quad dE = TdS \quad$ or $\left(\dfrac{\partial E}{\partial S}\right)_V = T \qquad (15)$

-pdV

At const. S $\quad dE = -PdV \quad$ dE $\quad$ or $\left(\dfrac{\partial E}{\partial V}\right)_S = -P \qquad (16)$

Differentiating (15) with respect to V at constant S

$$\frac{\partial^2 E}{(\partial S)(\partial V)} = -\left(\frac{\partial T}{\partial V}\right)_S \qquad (17)$$

Differentiating (16) with respect to S at constant V

$$\frac{\partial^2 E}{(\partial V)(\partial S)} = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (18)$$

Comparing (17) and (18) we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (19)$$

Following the same mathematical procedure (20), (21) and (22) can be derived from (14), (11) and (12) respectively.

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad (20)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (21)$$

$$\left(\frac{\partial S}{\partial P}\right) = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (22)$$

Equations (19) to (22) are known as Maxwells relations. S

rom (13) and (14) we can derive

$$\left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \qquad (2$$

From (13) and (11) we can derive

$$\left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T$$

From (14) and (12) we can derive $\quad$ dG = -SdT

dH = TdS

$$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$$

From (11) and (12) we can derive

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right).$$

Equations (23) to (26) are also known as ma

Solved University Proble

1 Calculate the heat requried to convert one

(into its vapour)

(Latent heat of steam at 100^0 C is 540 cals /

Solution : Latent heat of steam at $100^0C = 54$

1 mole = 540 x **Molecular weight of water**

= 540 x 18 = 9720 cals / mole

∴

Answer : Heat required to convert one m

vapour = **9720 cal.**

2 100g of nitrogen initially at 25^0C and

against a constant pressure of 1 atm

the final temperature of the gas (C_p for

Solution Calculation of final volume

and V for an adiabatic change is

$P_1V_1^\gamma =$

$P_1 = 10$ atms (given) $P_2 = 1$ atm

Equations (19) to (22) are known as Maxwells relations. Similarly rom (13) and (14) we can derive

$$\left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \qquad (23)$$

From (13) and (11) we can derive

$$\left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T \qquad (24)$$

From (14) and (12) we can derive

$dG = -SdT + Vdp \rightarrow 12$
$dH = TdS + Vdp \rightarrow 14$

$$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \qquad (25)$$

From (11) and (12) we can derive

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right). \qquad (26)$$

Equations (23) to (26) are also known as ***maxwells relations***.

Solved University Problems

1. Calculate the heat requried to convert one mole of water at 100° C (into its vapour) -**Mar 89.**

(Latent heat of steam at 100° C is 540 cals / gm)

(Latent heat of steam at 100°C = 540 cals / gm

Solution : Latent heat of steam at 100°C = 540 cals / gm Molecular weight of water

1 mole = 540 x Molecular weight of water

= 540 x 18 = 9720 cals / mole

∴ **Answer** : Heat required to convert one mole of water at 100°C into its vapour = **9720 cal.**

2 100g of nitrogen initially at 25°C and 10 atm expands adiabatically against a constant pressure of 1 atm. Calculate the final volume and final temperature of the gas (C_p for the gas is 6.96 cals / deg/mole) **-Nov. 79**

know the relation between P