Diploma in Industrial Fermentation & Alcohol Technology - II

THERMODYNAMICS

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THERMODYNAMICS – I

Important Thermodynamical Terms:

1. **SYSTEM:** A system is defined as any specified portion of matter under study which is separated from rest of universe. The surface may consist of one or more substance.
2. **SURROUNDING:** The rest of the universe which might be in a position to exchange energy and matter with the system is called surrounding.
3. **Type of system:**
   (a) **Open System:** A system which can exchange energy as well as matter with its surrounding is called ***Open system***.
   (b) **Closed System:** A system which can exchange energy but not the matter with its surrounding is called ***Closed system***.
   (c) **Isolated System:** A system which can exchange neither energy nor matter with its surrounding is called ***Isolated system***.

4. **Processes and their types:** The operation by which a system changes from one state to another state is called processes. In the processes there is change in energy.
   (a) **Isothermal Process:** A process is called isothermal if the temperature of the system remains constant throughout the process.
   (b) **Adiabatic Process:** A process is said to adiabatic if no heat enters or leaves the system during any stage of process.
   (c) **Isobaric Process:** A process is said to be isobaric if the pressure of the system remains constant during each step of the process.
   (d) **Reversible Processes**. A process carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force1 is called a reversible process.
   (e) **Irreversible Processes** Any process ‘which does not take place in the above manner, i.e., a process which does not take place infinitesimally slowly, is said to be an irreversible process.A reversible process cannot be realised in practice because it would require infinite time for its completion.

5. **Extensive and Intensive properties:** An extensive property of a system is that which depends upon the amount of the substance or substance present in the system viz. mass, volume, energy etc.

   An intensive property of a system is that which does not depends upon the amount of the substance present in the system. The examples are temperature, pressure, density, concentration, viscosity, refractive index, surface tension and specific heat.

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics states that 'Energy can neither be created nor be destroyed, although its form can be transformed from one form to other'. This is also known as law of conservation of energy.

This may be formulated in terms of thermodynamical quantity. Let E_1 be the energy of system in initial state and let heat q be given to it. The heat absorbed by the system may be used to increase its internal energy or perform work or both. If the energy of the system in the final state is E_2, then $(E_2 - E_1) = \Delta E$ is the increase in the internal energy.

Heat absorbed = Increase in + Work done by Energy the system.

i.e. $$q = \Delta E + (-w)$$
$$= \Delta E - w$$

The minus sign appears because the work done by the system is taken as $(-w)$ since it will decrease the internal energy of the system.

(i) If no work is done, $w = 0$ and

$$q = \Delta E = E_2 - E_1$$
= increase in the energy.
$$E_2 = q + E_1$$

(ii) If there is no change in the energy then $E_1 - E_2$ and $\Delta E = 0$. Hence

$$q = (-w)$$
= work done by the system.

For infinitesimal change the Law may be stated as

$$dq = dE + (-dw)$$

Or $$dq = dE - dw$$

If only mechanical work is considered then $dw = -PdV$ and we have.

$$dE = dq - PdV$$

This is the mathematical expression for 1st Law of thermodynamics.

State Function and its Differentials:

The thermodynamic functions are state function. These are independent of how the change brought about. They depend only upon initial and final of the system. Internal energy, Enthalpy Entropy, Free Energy, P, V, T etc.

State functions give exact differentials. These exact differentials can be integrated between limits, without considering actual change that occur as the system moves from position to other. This can be better explained by taken example of volume of definite amount of substance.

Mathematically we can write volume as a function of temp and pressure.

$$V = f(T, P)$$

If T and P are given some fix value then volume is fixed. If T and P are changed the value of V will accordingly change. Therefore T and P are called independent variables and V is called dependent variables.

The change in V can be calculated if derivatives of the function V w.r.t. T and P are known. i.e.

$(\partial V / \partial P)_P =$ rate of change of vol. with temp. at constant pressure

$(\partial V / \partial P)_T =$ rate of change of vol. with pressure at const. temp.

It temp. is changed by infinitesimal amount (dT) the change in vol. is given by.

$$dV = (\partial V / \partial T)_P \, dT$$

Similarly for pressure

$$dV = (\partial V / \partial P)_T \, dP$$

If both are changed the dV is given by

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

This is called the total differential at the function (V). This eqn. was obtained by assuming that whether we first change temp then pressure or first change the pressure then temp.; the final total change in vol. is the same. This is true because V is a state for and dV is exact differentials.

INTERNAL ENERGY :

All matter process energy. This energy is either the kinetic or potential or both associated with each unit (atom, mol, ion etc) of the substance. In the case of molecular system the various energy contribution to the total energy of the mol. are translational K.E. (E_t), rotational energy (E_r), vibrational energy (E_v), bond energy (E_b) intermolecular intraction energy (V_T), electronic energy (E_e) and the relativistic energy $(E = mc^2)$. The energy of the mol is thus given by :

$$E = E_t + E_r + E_v + E_b + V_T + E_e$$

The total energy contained in an assembly of mol. is called the intrinsic or enternal energy. The internal energy of a substance or a system is a definite quantity and it is a function only of the state (i.e. chemical nature, composition, temp., pressure and vol.)

ENTHALPY:

In general chemical and physical process occurs at constant pressure rather then const. vol. because the reaction vessels are generally open. [In other word most of reaction are carried out in an open system instead of close system]. Thermal changes at constant pressure are expressed in terms of a new thermodynamically function denoted by H and called as the 'Enthalpy' or 'Heat content' of the system. This is given by :

$$H = E + PV \qquad \text{... (1)}$$

At constant pressure the total heat supplied to the system will increase the internal energy of the system and part of it will be utilized for work to be done.

ENTHALPY AS STATA FUNCTION:

According to the first Law of thermodynamics.

$$(q)_p = \Delta E + P\Delta V \qquad \text{... (2)}$$

$$= (E_2 - E_1) + P(V_2 - V_1)$$

$$= (E_2 + PV_2) + (E_1 + PV_1) \qquad \text{... (3)}$$

Since E, P and V are state of the system $\therefore$, therefore we can say the quantity H $(= E + PV)$ is also a state function. If H_1 and H_2 are the initial and final enthalpies of the system then eqn. (3) can be written as :

$$(q)_p = H_2 - H_1$$

$$= \Delta H \qquad \text{... (4)}$$

Substituting the value $(q)_p$ in eqn. (2) we get

$$\Delta H = \Delta E + P\Delta V \qquad \text{... (5)}$$

For enfinitismally small change, we can write

$$dH = dE + PdV$$

And $$(q)_p = \Delta H \, . \qquad \text{... (6)}$$

The magnitude of change in enthalpy ΔH, like internal energy, also depends only on the enthalpies of the initial and final state of the system. Thus

$$\boxed{\Delta H = H_{Final} - H_{Initial}}$$

HEAT CAPACITY OF A SYSTEM:

Heat capacity of a system between any two temp., is defined as the quantity of heat required to raise the temperature of the system from lower to the higher temp. divided by the temp. difference.

If the mass of the system is 1 mole, then the heat capacity is termed as molar heat capacity. Thus the molar heat capacity of a a system between temp. T_1 and T_2 is given by

$$C_{(T_1,T_2)} = \frac{q}{T_2 - T_1}$$

As the heat capacity varies with temp, hence the true molar heat capacity is given by differential eqn.

$$C = \frac{dq}{dT}$$

Heat Capacities at Constant Volume:

The molar heat capacity of a gaseous system is determined at constant vol. In this case, no external work is done by the system or on the system (i.e. w = 0) since there is no change in vol. Hence from first law of thermodynamics $\left[\Delta E = q + w\right]$

$$q = \Delta E$$

$$C_{V(T_2-T_1)} = \left[\frac{q}{T_2 - T_1}\right]_V = \left[\frac{\Delta E}{T_2 - T_1}\right]_V$$

$$\boxed{C_{V(T_2-T_1)} = \left[\frac{\partial E}{\partial T}\right]_V}$$

Heat Capacities at Constant Pressure:

For a thermodynamic system it is easer to work at constant pressure instead at constant volume. Because there is change in volume while doing an experiment. Let there is increase in volume by ΔV and the work done is w. Then,

$$(q)_p = \Delta E - w$$

$$C_{P(T_2-T_1)} = \left[\frac{q}{T_2 - T_1}\right]_P$$

Increase in volume means, work is done by the system i.e. $w = -P\Delta V$ Hence,

$$(q)_p = \Delta E - (-P\Delta V)$$

$$(q)_p = \Delta E + P\Delta V$$

$$C_{P(T_2-T_1)} = \left[\frac{\Delta E + P\Delta V}{T_2 - T_1}\right]_P$$

$$C_{P(T_2-T_1)} = \left[\frac{\Delta H}{T_2 - T_1}\right]_P$$

$$\boxed{c_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

Relation Between C$_p$ and C$_v$:

As we know Internal energy is state fn. it can be regarded as a function of too independent variables V and T i.e.

$$E = f(V, T)$$

The increase in internal energy dE can be ex pressed as

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \qquad .....(1)$$

Dividing the above equation by dT, and keeping pressure constant. We get

$$\left(\frac{dE}{dT}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{dV}{dT}\right) \qquad .....(2)$$

The heat capacity at constant pressure of a system is defined as the rate of change of enthalpy with temperature pressure

$$\mathrm{Cp} = \left(\frac{\mathrm{dH}}{\mathrm{dT}}\right)_{\mathrm{p}}.$$

But we know that H=E+PV.

$$\therefore\ Cp = \left[\frac{d}{dT}(E+PV)\right]_p$$

$$= \left(\frac{dE}{dT}\right)_p + P\left(\frac{dV}{dT}\right)_p \qquad \text{.....(3)}$$

Substituting the value of $\left(\frac{\mathrm{dE}}{\mathrm{dT}}\right)_{\mathrm{p}}$ from eq ^{n} (2) in the eq ^{n} (3), We will get

$$c_p = \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{dV}{dT}\right) + P\left(\frac{dV}{dT}\right)_p.$$

$$= \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{dV}{dT}\right)\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

But we know that the rate of change internal energy with temperature is the heat capacity at constant volume. Therefore,

$$c_p = c_v + \left(\frac{\partial V}{\partial T}\right)\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

But for an ideal gas, we know.

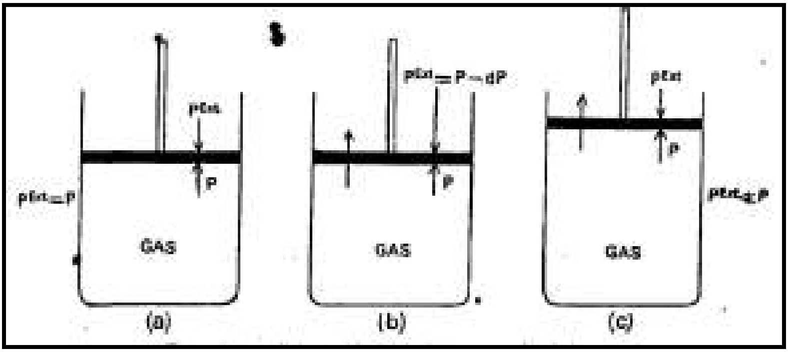
$$\left(\frac{\partial E}{\partial V}\right) = O \text{ and } P\left(\frac{dV}{dT}\right)_P = R.$$

Therefore eq^n become as

$$\boxed{\begin{array}{l} c_P = c_V + R \\ c_P - c_V = R \end{array}}$$

Work Done in Isothermal Reversible Expansion :

Consider a gas in a isothermal condition is enclosed in a cylinder fitted with a weightless and frictionless piston. The cylinder is not isolated.



Initially the ext. pressure P on the piston is equal to the pressure of the gas within the cylinder. As shown (Fig. a) If the ext. pressure is lowed by infinitesimal amount dP i.e. it falls from P to d–dP (Fig. b), the gas will expand by an infinitesimal vol. dV, i.e. the volume changes from V to V+dV. As a result pressure will fall to P–dP i.e., it become again equal to the ext. pressure. It this process is continued such that the external pressure is low— by successive small amounts and as a result the gas undergoes a series of small successive increment of vol. dV at a time.

As the system is in thermal equilibrium with surrounding, the infinitesimally small cooling produced as a result of infinitesimal small expansion of the gas at each steps, is offset or makeup by the heat observed from the surrounding and the temperature remains constant throughout the operation.

The work done by the gas in infinitesimal expansion is thus given by

$$dw = -\left(P - dP\right)dV$$

$$= -PdV$$

Ignoring the product dPdV.

The total work done w by the gas in expansion i.e. from initial vol. V_1 to final vol. V_2 will be given by:

$$w = -\int_{V_1}^{V_2} PdV$$

$$= -nRT\int_{V_1}^{V_2} \frac{dV}{V} \qquad [PV = nRT]$$

$$= -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Since for ideal gas $P_1V_1 = P_2V_2$ at constant temperature.

$$w = -nRT \ln\left(\frac{P_1}{P_2}\right)$$

$$\boxed{w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -nRT \ln\left(\frac{P_1}{P_2}\right)}$$

(a) Heat Absorbed by Gas :

As the process is isothermal i.e. during the process the temperature. Of the system is maintained constant. i.e. …. Therefore according to first law of thermodynamics i.e.

$$q = \Delta E + (-w)$$

$$q = -w$$

$$\boxed{q = -w = -nRT \ln\left(\frac{V_2}{V_1}\right)}$$

(b) Change in Internal Energy :

In an isothermal process, the temperature of the system remains constant throughout the process of expansion. For an ideal gas the E depends only on temperature, therefore, it follows that at constant temperature, the internal energy of the system (gas) remains constant.

$$\boxed{\Delta E = 0}$$

(c) Change in Enthalpy :

From first law of thermodynamics we can derive :

$$H = E + PV$$

$$\Delta H = \Delta(E + PV)$$

$$= \Delta(E + nRT)$$

Since for isothermal process … and …. Both are equal to zero.

$$\boxed{\Delta H = 0}$$

Work Done in Adiabatic Expansion :

In adiabatic expansion, no heat is allowed to enter or leave the system. Hence.

$$q = 0$$

According to 1st law of thermodynamics, since q = 0 therefore:

$$q = \Delta E + \left(-w\right)$$

$$0 = \Delta E - w$$

$$w = -\Delta E$$

In expansion work is done by the system on the surrounding, hence w is negative. Accordingly ΔE is (–)ve i.e. there is decrease in the internal energy of the system and an increase in temperature. Work is done at the expense of the internal energy of the gas.

(a) Change in Internal Energy (..) :

The motor heat capacity at instant vol. of an ideal gas is given by

$$c_V = \left(\frac{dE}{dT}\right)_V$$

$$dE = c_V dT$$

For finite change $\boxed{\Delta E = c_V dT}$

(b) change in Enthalpy ΔH :

$$H = E + PV$$

We know

$$\Delta H = \Delta E + \Delta(PV)$$

$$= \Delta E + \Delta(RT)$$

$$= \Delta E + R\Delta T$$

Substituting the value of ΔE

$$\Delta H = c_V dT + RdT$$

$$= (c_V + R)dT$$

$$\boxed{\Delta H = c_P dT}$$

(c) Calculation of w:

Since in an adiabatic process q = 0 hence according to the 1st Law of Thermodynamics equation. The work done in this case is given by the expression.

$$\boxed{w = \Delta E = c_V \Delta T}$$

THERMODYNAMICS – II

NEED FOR SECOND LAW OF THERMODYNAMICS
(Limitation of 1st law of thermodynamics)

The first law of thermodynamics was very exact but has some limitations which due to which second law was given, they are given as under.

1. The first law gives definite relationship between the heat absorbed and the work performed by a system in a process but it puts no restriction on the direction of the law of heat.

2. According to the first law the energy of an isolated system remains constant during a change of state. But it does not tell whether a specified change or a process including a chemical reaction can occur spontaneously.

3. The first law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work.

ENTROPY:

The concept of entropy is vital for thermodynamics. It is a Greek word meaning ‘change’, the suffix ‘en’ is written to identify it with energy. It is denoted by S. Entropy is a measure of randomness or disorder ness in a molecular system More is randomness large is the value of entropy. Entropy is also a measure of unavailable energy. As entropy is a measure of randomness of a molecular system, this statement is also in line with the observation at boiling it of a fluid. Under ordinary normal condition when liquid is heated its temperature increases, at the B.P the temperature remains constant till whole of the liquid is transformed into vapour state with the continuous supply of heat. This can be explained by considering the molecular arrangement in the liquid and vapour state at a given temperature. The molecular arrangement in the liquid is a bit more regular than the vapour state of the some substance. To disturb the regularly in the liquid stale some work must be done. This work done on the system increases the disorderness of the system, but not the temperature at the boiling point. There is more disorder ness in the vapour phase than the liquid. We can say the entropy of the vapour is greater than that of the liquid state of the same substance. In general for any substance

$$\boxed{S_{gas} > S_{liquid} > S_{solid}}$$

ENTROPY AS A FUNCTION OF V & T:

The concept of entropy can be given mathematical foundation for this we shall start from 1st law let us consider an ideal gas that is under going a reversible change from an initial state T_1, V_1 to find state T_2, V_2 the 1st law can be given by.

$$dq_{rev} = dE + (-dw) \qquad \text{……….(1)}$$

If only mechanical work is considered then

$$-dw = PdV$$

$$\therefore\ dq_{rev} = dE + PdV$$

For an ideal gas $dE = C_v dT \text{ and } P = \frac{nRT}{V}$ hence

$$dq_{rev} = C_v dT + \frac{nRT}{V} dV \qquad \text{……….(2)}$$

Dividing equation (2) by T we will get

$$\frac{dq_{rev}}{T} = C_v \frac{dT}{T} + nR\frac{dV}{V} \qquad \text{……….(3)}$$

To know the total heat change we must integrate this eq^n between the initial and final limits.

$$\int_1^2 \frac{dq_{rev}}{T} = C_v \int_{T_1}^{T_2} \frac{dT}{T} + nR\int_{V_1}^{V_1} \frac{dV}{V}$$

$$\boxed{\int_1^2 \frac{dq_{rev}}{T} = C_v \ln\left(\frac{T_1}{T_2}\right) + nR\ln\left(\frac{V_2}{V_1}\right)} \text{……….(4)}$$

Since is an exact differential therefore the function whose change is given by must also be a state function let this state function by 'S' and hence.

$$\boxed{\frac{dq_{rev}}{T} = S} \qquad \text{……….(5)}$$

We know entropy dS is a exact function and S is a state function.

$$\boxed{\int_1^2 \frac{dq_{rev}}{T} = C_v \ln\left(\frac{T_1}{T_2}\right) + nR\ln\left(\frac{V_2}{V_1}\right)}$$

The R.H.S of the eq^n depends only on the state variable T_1, V_1 and T_2, V_2 therefore the quantity on L.H.S. should also be a function only of state variables.

$$\int_1^2 \frac{dq_{rev}}{T} = \int_1^2 dS$$

$$= S_2(T_2, V_2) - S_1(T_1, V_1)$$

$$= \Delta S$$

$$\boxed{\int_1^2 \frac{dq_{rev}}{T} = \Delta S}$$

ENTROPY AS A FUNCTION P & T:

It P_1 is the pressure of the gas in the initial state and P_2 in the final state, then

$P_1V_1 = RT_1$ for one mole of gas in initial state

$P_2V_2 = RT_2$ for one mole of gas in final state

$$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2V_1} = \frac{T_2/T_1}{P_2/P_1}$$

substituting this in equation (4)

$$\Delta S = C_v \ln\left(\frac{T_1}{T_2}\right) + R\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$$

$$= [C_v + R]\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$$

$$\boxed{\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)}$$

FREE ENERGY:

Free energy is the thermodynamic function of state and is defined as a property of the system at the expense of which the system doses work. We know that energy can be converted into work. The portion of energy which can be converter into useful work is termed available energy while the remaining portion of energy which cannot be converted into useful work is termed as unavailable energy.

$$\boxed{Total\ Energy = (Isothermally\ avalable\ energy) + (Isothermally\ unavalable\ energy)}$$

When entropy is multiplied by absolute temperature the product 'TS' is equal to the amount of heat not free to be used for useful work, because entropy in considered to be measure of unavailable energy. Therefore, out of total heat absorbed by the system, an amount less then by 'TS' should be the available heat which is used for doing useful work and is called 'FREE ENERGY'. If 'X' be the tree energy then by definition

$$\mathbf{X = q - TS}$$

Since heat is absorbed at either constant volume or at constant pressure, therefore the term 'q' may either be replaced by 'E' or 'H'. Therefore, we may have two solutions.

i. $X = E - TS$ (at constant volume)
ii. $X = H - TS$ (at constant pressure)

(i) The first type of free energy is known as ***Helmoltz's free energy*** denoted by 'F' or 'A'. This isothermally available internal energy is written as

$$\mathbf{F = E - TS}$$

(ii) The first type of free energy is known as ***Gibb's free energy*** denoted by 'G' and represent isothermally available enthalpy which is used for doing work by system.

$$\mathbf{G = H - TS}$$

1. HELMOLTZ'S FREE ENERGY

The system will do maximum work when it goes from initial to final state and if the process is reversible, hence

$$\Delta E = q_{rev} + w_{\max}$$

$$w_{\max} = \Delta E - q_{rev} \qquad \ldots\ldots\ldots\ (1)$$

From second law for an isothermal process $q_{rev} = T\Delta S$. Therefore equation (1) can be written as

$$w_{\max} = \Delta E - T\Delta S \qquad \ldots\ldots\ldots\ (2)$$

where Δ S is change in entropy of the system when it goes from initial to final state. But this maximum work is done on the expense of free energy of the system defined as

$$A = E - TS$$

Since E, T and S are state function of the system, therefore A is also the state function of the system and we can write

$$\Delta A = \Delta E - T\Delta S \qquad \ldots\ldots.(3)$$

Under isothermal condition comparing equation (2) and (3)

$$\Delta A = w_{\max} \qquad \ldots\ldots\ldots.(4)$$

which means, maximum work done by the system in an isothermal proce3ss is at the expanse of Helmoltz free energy.

2. GIBB'S FREE ENERGY

The Helmoltz free energy describe the process taking place at constant volume, therefore, it is not very useful, since in chemistry or biology most of the process occurs at constant pressure due to this reason another thermodynamic function of state known as Gibb's free energy was introduced. This describes the process taking place at constant pressure and at this stage dose maximum work at the expense of Helmoltz free energy 'A'. All the work done may not be useful or net work done by the system. The Gibb's free energy 'G' is defined as that energy which is available for doing the useful work or net work. The useful work done in a process is at the expense of Gibb's free energy.

In solid and liquid all work except the PV work done is considered to be useful work

$$w_{useful} = w_{\max} - w_{PV} = \Delta G$$

If the process is isothermal and pressure is kept constant then

$$w_{PV} = P\Delta G$$

$$\text{and} \quad w_{\max} = \Delta A$$

$$w_{useful} = \Delta A + P\Delta V \qquad \ldots\ldots.(1)$$

or in general

$$G = A + PV \qquad \ldots\ldots(2)$$

In the process involving ideal gas and under isothermal condition when the volume of gas is kept constant then

$$\Delta G = \Delta F = w_{\max}$$

The Gibb's free energy can best defined by equation (2) i.e.

$$G = A + PV$$

but it is known that

$$A = E + PV$$

$$G = E - TS + PV$$

And it is also known that

$$E + PV = H$$

Hence

$$\boxed{G = H + TS} \qquad \text{.....(3)}$$