

Thermodynamic Potentials

(Thermodynamics)

e-content for B.Sc Physics (Honours)

B.Sc Part-I

Paper-II

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Thermodynamic Potentials

A number of thermodynamic quantities have been defined—useful under differing conditions of fixed pressure, volume, temperature, particle number, etc. These are the enthalpy, the Helmholtz free energy, and the Gibbs free energy. Together with the internal energy, these are referred to as *thermodynamic potentials*.

a. Enthalpy

The total energy required to create a system of particles at sea level air pressure would include the expansive work done in displacing the air.

We define the *enthalpy* to be $H \equiv U + PV$. The enthalpy is useful when a change takes place in a system while pressure is constant.

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V = Q + W + P\Delta V = Q + (-P\Delta V) + W_{other} + P\Delta V \\ \Delta H &= Q + W_{other}\end{aligned}$$

Now, if no *other* work is done, then $\Delta H = Q$ exactly. In practice, tables of measured enthalpies for various processes, usually chemical reactions or phase transitions are compiled. The text mentions the enthalpy of formation for liquid water. Evidently, when oxygen and hydrogen gases are combined to form a mole of liquid water, the change in enthalpy is -286 kJ. In other words, burning hydrogen at constant pressure releases this much energy.

[Efficiency of a steam engine: $e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{H_4 - H_1}{H_3 - H_2}$. Now, $H_2 \approx H_1$ since the water is not compressed as it is pumped, and only a little energy is added to the water (it's not accelerated).

COP of refrigerators:

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{H_1 - H_4}{H_2 - H_3 - (H_1 - H_4)} = \frac{H_1 - H_4}{H_2 - H_3 - H_1 + H_4} = \frac{H_1 - H_3}{H_2 - H_1} \quad \boxed{Q_{4 \rightarrow 3} = 0}$$

b. Helmholtz

Let's say the system is in contact with a heat bath, so that the temperature is constant. The pressure may not be constant. To create the system, some of its total energy can be taken from the environment in the form of heat. So the total work required to create the system is not all of U , but less than U . Define the *Helmholtz Free Energy* of the system as $F \equiv U - TS$.

Any change in a system at constant temperature will entail a change in F .

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S,$$

Where W is all the work done on the system.

c. Gibbs

Now, if the system is at constant pressure as well as constant temperature, then the extra work needed to create the system is the *Gibbs Free Energy*,

$$G \equiv U - TS + PV.$$

If pressure is constant, we use the Gibbs free energy:

$$\Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V$$

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

Again, W is the total work done on the system.

d. Identities

If we envision infinitesimal changes in thermodynamic variables, we can derive thermodynamic identities for the thermodynamic potentials. We have already, the thermodynamic identity for internal energy

$$dU = TdS - PdV + \mu dN.$$

Now, consider the enthalpy, H .

$$H = U + PV$$

$$dH = dU + PdV + VdP = TdS - PdV + \mu dN + PdV + VdP$$

$$dH = TdS + VdP + \mu dN$$

For instance, if $dP = 0$ and $dN = 0$, then we could write $T = \left(\frac{\partial H}{\partial S} \right)_{P,N}$, which is

equivalent to the $T = \left(\frac{\partial U}{\partial S} \right)_{V,N}$ that we obtained earlier.

We can do the same for F and for G .

$$F = U - TS$$

$$dF = dU - TdS - SdT = TdS - PdV + \mu dN - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN$$

From this equation we can derive relationships like $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$.

$$G = U - TS + PV$$

$$dG = dU - TdS - SdT + PdV + VdP = TdS - PdV + \mu dN - TdS - SdT + PdV + VdP$$

$$dG = -SdT + VdP + \mu dN$$