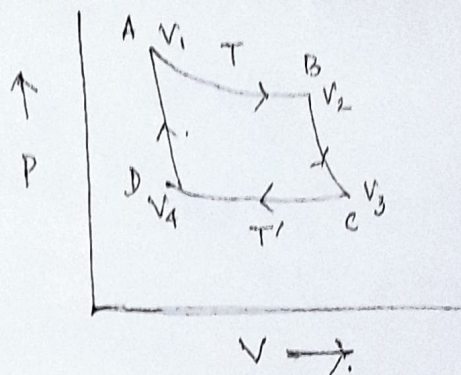


## The Carnot cycle.

Sadi Carnot (1824).



Operation done,

No. 1. Isothermal reversible expansion

The heat absorbed by the gas =  $Q$  (say).

The work done by the gas.  $RT \ln \frac{V_2}{V_1}$

$$Q = RT \ln \frac{V_2}{V_1}$$

Step 2. Adiabatic expansion

→ Cylinder put in sink  $T'$

The work done by the gas =  $C_V (T - T')$

Heat absorbed by the gas = nil

$C_V$  is the heat capacity of the system

Step 3. Isothermal reversible compression

The gas is put in sink (Temperature)  $\rightarrow T'$

The heat given out by the gas ( $Q'$ ).

The work done by the gas =  $RT' \ln \frac{V_4}{V_3}$

Work done on the gas.

Step 4. Adiabatic and reversible compression

Work done by the gas =

$$C_V (T' - T)$$



The net work done by the gas in the complete cycle

$$W = RT \ln \frac{V_2}{V_1} + C_V (T - T') + RT' \ln \frac{V_4}{V_3} + C_V (T' - T).$$

$$= RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_3}{V_4}.$$

$$\text{But } PV_2^{\gamma-1} = T' V_3^{\gamma-1}$$

$$PV_1^{\gamma-1} = T' V_4^{\gamma-1}$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$W = RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_2}{V_1} = R(T - T') \ln \frac{V_2}{V_1}$$

The efficiency of the process is given by the equation

$$\eta = \frac{W}{Q} = \frac{R(T - T') \ln V_2/V_1}{RT \ln V_2/V_1} = \frac{T - T'}{T}$$

$$\text{and } W = Q \frac{T - T'}{T} = Q \cdot \frac{\Delta T}{T}.$$

### Carnot theorem

- (i) A reversible engine is more efficient than irreversible one.
- (ii) All reversible engines are equally efficient working between the same temperature limits



## Third law of thermodynamics.

Entropy at the Absolute Zero: Entropy of any substance at the temperature  $T$  and a given pressure could be expressed by means of the relationship

$$S - S_0 = \int_0^T \frac{C_p}{T} dT = \int_0^T C_p d \ln T$$

$S_0$  is the hypothetical entropy at the absolute zero.

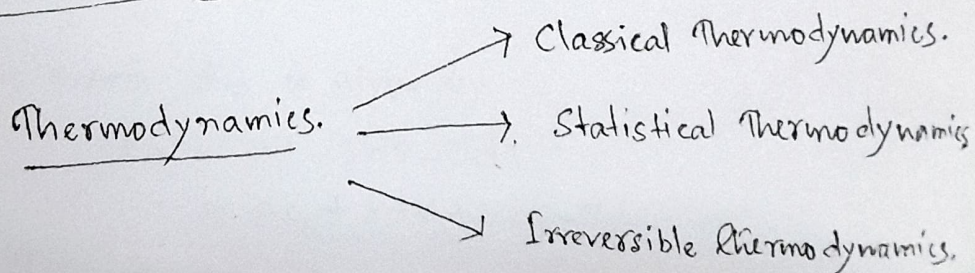
If the value of  $S_0$  were known it would be possible to derive the entropy at any required temperature from heat capacity data.

W. Nernst (1906)

M. Planck (1912) made a new suggestion concerning the value of  $S_0$  which has become known as the third law of thermodynamics.

It may be stated as follows:

"Every substance has a finite positive ~~entropy~~ entropy, but at the absolute zero of temperature the entropy may become zero and does so become in the case of a perfectly crystalline substance."



## Spontaneity of chemical reaction and Gibbs energy.

Helmholtz free energy

$$A = E - TS$$
$$G = H - TS$$

Gibbs free energy



Single valued thermodynamic parameter;  $dA$  and  $dG$  exact differential;  $\oint dA$  and  $\oint dG$  are zero



## Significance of A and G

$$dA = dE - Tds - SdT$$

$$dE = Tds + \delta W_{rev}$$

↓  
maximum magnitude of reversible work done by the and includes both mechanical and non-mechanical work.

$$dA = -SdT + \delta W_{rev}$$

$$(dA)_T = \delta W_{rev}$$

If the process is isothermal  $dT = 0$

$$\cancel{(dA)_T} = \delta$$

$$-(\Delta A)_T = -W_{rev}$$

So A is such a function that a decrease in its value at constant temperature gives the maximum reversible work done by the system.

For Gibbs free energy, dG is given by

$$dG = dH - Tds - SdT$$

$$= dE + PdV + VdP - Tds - SdT \quad (H = E + PV)$$

$$dE = Tds + \delta W_{rev}$$

$$dG = Tds + PdV + VdP - Tds - SdT + \delta W_{rev}$$

$$= PdV + VdP - SdT - PdV + \delta W_{net}$$

$$= VdP - SdT + W_{net}$$

$$\text{At constant } T \text{ and } P \quad dT = dP = 0$$

$$(dG)_{P,T} = \delta W_{net}$$

For a finite change in the state of the system

$$(\Delta G)_{P,T} = -W_{net}$$

So " A decrease in the value of Gibbs free energy function at constant temperature and pressure is a measure of maximum reversible