

$$\text{or, } \frac{\pi T + T d\pi - \pi T - \pi dT}{T(T+dT)} + \frac{(\sigma_{Cu} - \sigma_{Fe})dT}{T} = 0 \quad 130$$

$$\text{or, } \frac{T d\pi}{T^2} - \frac{\pi dT}{T^2} + \frac{(\sigma_{Cu} - \sigma_{Fe})dT}{T} = 0 [T(T+dT) = T^2]$$

$$\therefore d\pi - \frac{\pi dT}{T} + (\sigma_{Cu} - \sigma_{Fe})dT = 0$$

$$\text{or, } d\pi + (\sigma_{Cu} - \sigma_{Fe})dT = \pi \frac{dT}{T} \quad \text{--- (2)}$$

For a thermocouple, say, Cu-Fe, we have

$$dE = d\pi + (\sigma_{Cu} - \sigma_{Fe})dT \quad \text{--- (3)}$$

Substituting (2) in (3) we get

$$dE = \pi \cdot \frac{dT}{T}$$

$$\therefore \frac{\pi}{T} = \frac{dE}{dT}$$

$$\text{or, } \pi = T \cdot \frac{dE}{dT} \quad \text{--- (4)}$$

Thus the Peltier Co-efficient at any ~~junction~~ temperature for any two metals forming a thermocouple is equal to the product of the absolute temperature of the junction and the thermoelectric power at the temperature.

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Ques :- Applying Thermodynamics to a thermo-  
 - couple, show that  $\pi = T \frac{dE}{dT}$ . Symbols  
 have their usual meaning. 129

Peltier and Thomson effects are reversible. If we neglect the Joule heating effect, a thermo-electric circuit may be compared to a reversible heat engine. The second Law of thermodynamics may be applied to an ideal thermocouple.

Let the two junctions of a thermo-couple, say, Cu-Fe be at temperatures  $T+dT$  and  $T$ , and let the amount of energy absorbed and that given out due to Peltier effect be  $\pi+d\pi$  and  $\pi$  respectively. Hence the corresponding heat absorbed and given out =  $\frac{\pi+d\pi}{J}$  and  $\frac{\pi}{J}$ , where  $J$  is Joule's mechanical equivalent.

Amount of heat absorbed due to Thomson effect

$$= - \frac{(\sigma_{Cu} - \sigma_{Fe}) dT}{J}$$

Hence by the Second Law of Thermodynamics we have

$$\frac{\pi + d\pi}{T + dT} - \frac{\pi}{T} + \frac{(\sigma_{Cu} - \sigma_{Fe}) dT}{T} = 0$$

## Lagrange's equation (6)

The second integral of (5) can be solved by integration by parts.

$$\begin{aligned} \int_{t_1}^{t_2} \frac{dL}{dq} \delta q dt &= \int_{t_1}^{t_2} \frac{dL}{dq} \frac{d}{dt} (\delta q) dt \\ &= \left[ \frac{dL}{dq} \delta q \right]_{t_1}^{t_2} - \int_{t_1}^{t_2} \frac{d}{dt} \left( \frac{dL}{dq} \right) \delta q dt \\ &= - \int_{t_1}^{t_2} \frac{d}{dt} \left( \frac{dL}{dq} \right) \delta q dt \quad \dots (7) \end{aligned}$$

because,

$$\frac{dL}{dq} \delta q \Big|_{t_1}^{t_2} = 0$$

Substituting (7) in (5) we get

$$\delta S = \int_{t_1}^{t_2} \left[ \frac{dL}{dq} - \frac{d}{dt} \left( \frac{dL}{dq} \right) \right] \delta q dt = 0 \quad \dots (8)$$

This will be zero only when the integrand will be zero. Thus we have

$$\frac{dL}{dq} - \frac{d}{dt} \left( \frac{dL}{dq} \right) = 0 \quad \dots (9)$$

If the system have  $S$  degree of freedom then we have the equations of the form

$$\frac{dL}{dq_i} - \frac{d}{dt} \left( \frac{dL}{dq_i} \right) = 0 \quad (i=1,2,3 \dots S)$$

This is the second order differential

direct

equation and called Lagrange's equation in mechanics.

(7)

\* Lagrange's equation in cartesian coordinates

Let us consider a particle of mass  $m$  in cartesian coordinates  $x, y, z$ . The Lagrangian  $L$  of the particle is

$$L = T - U \\ = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) - U(x, y, z) \quad (1)$$

The Lagrange equations in this case are

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{x}} \right) - \frac{\partial L}{\partial x} = 0 \quad (2)$$

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{y}} \right) - \frac{\partial L}{\partial y} = 0 \quad (3)$$

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{z}} \right) - \frac{\partial L}{\partial z} = 0 \quad (4)$$

Substituting (1) in Eqns

(2)-(4) we get,

$$\frac{d}{dt} (m\dot{x}) = - \frac{\partial U}{\partial x} \quad (5)$$

$$\frac{d}{dt} (m\dot{y}) = - \frac{\partial U}{\partial y} \quad (6)$$

$$\frac{d}{dt} (m\dot{z}) = - \frac{\partial U}{\partial z} \quad (7)$$

The negative gradient of potential is a force

So equations (5)-(7) can be written as

$$\frac{d}{dt} (m\dot{x}) = F_x \quad (8)$$

$$\frac{d}{dt} (m\dot{y}) = F_y \quad (9)$$

$$\frac{d}{dt} (m\dot{z}) = F_z \quad (10)$$

Thus the rate of change of momentum is a force which are Newton's second law of motion along  $x, y$ , and  $z$  axis.

of particles among the energy levels, which is the condition of equilibrium distribution. Hence,

$$S(S/R) = 0 \quad \text{--- (13)}$$

Substituting (12) in (13) we get,

$$\sum_i \left[ S n_i \log g_i - S n_i \log n_i - n_i \frac{S n_i}{n_i} + S n_i \right] = 0$$

$$\text{or, } \sum_i S n_i \log (g_i/n_i) = 0 \quad \text{--- (14)}$$

Multiplying (6) by  $\alpha$  and (7) by  $\beta$  and subtracting from (14) we get,

$$\sum_i S n_i [\log (g_i/n_i) - \alpha - \beta E_i] = 0 \quad \text{--- (15)}$$

This is possible only when each term in the sum is separately zero. Thus  $\log (g_i/n_i) - \alpha - \beta E_i = 0$ .

$$\text{or, } \log (g_i/n_i) = \alpha + \beta E_i$$

$$\text{or, } n_i = g_i / e^{\alpha + \beta E_i} \quad \text{--- (16)}$$

This is known as Maxwell Boltzmann distribution or statistics where  $\alpha$  and  $\beta$  are constants. They are related with  $T$  and  $\mu$  by,

$$\beta = 1/RT$$

$$\alpha = \mu/RT$$

where  $\mu$  is the chemical potential. Finally we have,

$$n_i = g_i e^{(\mu - E_i)/RT} \quad \text{--- (17)}$$

— x —

To calculate the statistical weight  $\Delta \Gamma_i$  of the  $i$ th cell it is sufficient to find the number of distinct ways in which  $n_i$  particles can occupy the  $g_i$  states (levels).

In Boltzmann gas the particles are distinguishable. In the  $i$ th cell there are  $g_i$  levels. Each of the  $n_i$  particles can occupy these levels in  $g_i$  ways. Hence  $n_i$  particles can occupy  $g_i$  levels in  $g_i^{n_i}$  ways. Since the particles are identical so among these distribution which differ only by permutation of the particles, are identical. The number of permutation of  $n_i$  particles is  $n_i!$ . Hence the statistical weight of the distribution of  $n_i$  particles in  $g_i$  levels is

$$\Delta \Gamma_i = \frac{g_i^{n_i}}{n_i!} \quad \text{--- (9)}$$

$$\text{and } \Delta \Gamma = \prod_i \frac{g_i^{n_i}}{n_i!} \quad \text{--- (10)}$$

The entropy  $S$  of the system is

$$S = k \log \Delta \Gamma = k \sum_i \log \Delta \Gamma_i$$

$$= k \sum_i [n_i \log g_i - \log n_i!] \quad \text{--- (11)}$$

Using Stirling's formula,

$$\log N! = N \log N - N$$

we can write,

$$S/k = \sum_i [n_i \log g_i - n_i \log n_i + n_i] \quad \text{--- (12)}$$

Let us calculate the statistics for most probable distributions