

# Asian Resonance

## Quantitative Justification of Theoretical Relations for Thermoelectric Power of Metals

**Shashi Bhushan Mahto**  
 H.O.D.  
 Deptt.of Physics,  
 K. B. College, Bermo,  
 Bokaro, Jharkhand

### Abstract

The theoretical formulae for thermoelectric power of metals suggested by Sondhiemer [4] and Wilson [8] have partial success in explaining the experimental findings in case of Au, Ag, Cu, K, Na, Rb and Pb under test at normal temperatures. The magnitude of thermometric power of metals calculated from the theoretical formulae is much greater than that observed directly. A partial agreement between Sondhiemer's formula and thermodynamic relation [5] is found in meeting the experimental findings in thermocouples. Thermodynamic relation fails to meet the magnitude of thermoelectric power of individual metals, observed directly. The present communication, however, appears to be more competent to meet the experimental findings in respect of magnitude of thermo power of noble metals. The theoretical expression, true for the absolute thermo electric power of metals, is not true for the same in a thermo-couple.

**Keyword:**Quantitative,Thermo Electric Power,Thermocouple,Free Electron, Rigorous, Sophisticated Relation.

#### Introduction

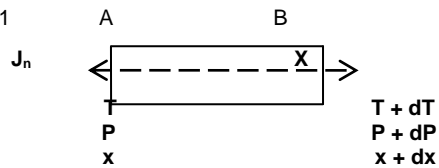
In order to discuss quantitative justification of thermodynamics relations of thermoelectricity [5], we consider the free electron gas theory because the conduction electrons are solely responsible for the phenomena to occur in a conductor or in a thermocouple at least in simple metals. The Kinetic theory, specific heat and pressure of the electrons play a dominating role in these processes.

**Theoretical Approach To Thermoelectric Power:** We consider a homogeneous conductor of unit cross section area having uniform temperature gradient  $dT/dx$  along it.  $T$  and  $T + dT$  are the temperatures of element of length  $dx$  at A and B, respectively, showing in Fig . 1. The pressure of the free electron gas at A is  $P$  and at B is  $(P + dP)$ . Since pressure of the electrons is expressed [2] as

$$P = (2/3) E \cdot n$$

where  $E =$  Energy of electron at  $T$

$$= E_0 + \frac{\pi^2 K_0^2 T^2}{4\mu_0} \dots\dots 1$$



$E_0$  being the zero point energy at  $T = 0$ ,  $K_0$  the Boltzmann's constant,  $n$  being the density of free electrons per unit volume. Now due to the pressure gradient  $dP/dx$  along the element the electrons will diffuse from hotter end to colder end and hence the net amount of work done  $W_1$  by the electron gas in this process may be given by

$$W_1 = \frac{dp}{dx} \cdot J_n \cdot dx = \frac{dp}{dT} \cdot \frac{dT}{dx} \cdot dx \cdot J_n$$

where  $J_n$  is the current density of electrons. If  $d\Phi$  be the potential difference existing across this element and consequently a diffusion thermoelectric current  $-eJ_n$  may be supported there. The work done  $W_2$  due to heating on the electrons may be written as

$$W_2 = \frac{d\Phi}{dx} (-eJ_n)dx$$

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In the equilibrium net balance of work is zero, i.e.,  $W_1 = W_2$

$$\text{or } \frac{dP}{dT} \cdot \frac{dT}{dx} \cdot dx J_n = \frac{d\Phi}{dT} (-eJ_n) \cdot \frac{dT}{dx} \cdot dx$$

$$\text{or } \frac{d\Phi}{dT} = -\frac{dP}{dT} \cdot \frac{1}{e} = -\frac{2}{3} \cdot \frac{dE}{dT} \cdot \frac{1}{e}$$

$$\frac{d\Phi}{dT} = -\frac{1}{3} \frac{\pi^2 K_0^2 T}{\mu_0 e} \quad \dots (2)$$

[cf. eqn. (1)]

Since, the electronic sp. heat at temp. T is written as

$$C_{ve} = \frac{\pi^2 K_0^2 T}{2\mu_0} \quad \dots (3)$$

And eqn. (2) may be written as

$$\frac{d\Phi}{dT} = -\frac{2}{3} \frac{C_{ve}}{e} \quad \dots (4)$$

$$C_{ve} = -\frac{3}{2} e \frac{d\Phi}{dT} \quad \dots (5)$$

Thus, from the measurement of the sp. heat of electrons, the absolute thermoelectric power of a metal may be calculated, provided that the free electron gas theory holds good in the metal under consideration. Eqn. (4) or (5) does not valve the thermal conductivity of the metal or the other physical dimensions of the specimen and hence its accuracy in determining the value of  $d\Phi/dt$  may be expected to be greater than that obtained from the Thomson coefficient from eqn.

$$\frac{d\Phi}{dT} = \int_0^T \frac{\sigma}{T} dT \quad \dots (6)$$

The Thomson coefficient which was calculated from the relation

$$\sigma = \frac{4KA dT}{(T_2 - T_1) I \cdot L} \quad \dots (7)$$

where A is the area of cross section of the wire under test and L is its length, K is the Thermal conductivity,  $dT$  is the change in temperature from the midpoint of  $T_1$  and  $T_2$ . I is the electric current.

A more rigorous and sophisticated relation for absolute thermoelectric power of metal due to electron diffusion has been suggested by Sondheioner [4], which is written as

$$\frac{d\Phi}{dT} = \frac{-\pi^2 K_0^2 T}{3e\mu} \cdot \frac{\rho_r + 3\rho_i \left[1 - \frac{J_7}{4\pi^2 J_5} + \frac{\mu}{2\pi^2 D} (\theta/T)^2\right]}{\rho_r + \rho_i \left[1 - \frac{J_7}{2\pi^2 J_5} + \frac{3\mu}{2\pi^2 D} (\theta/T)^2\right]} \quad \dots (8)$$

where  $K_0$  is the Boltzmann's constant,  $\mu$  is the Fermi energy  $\left[\mu = \mu_0 \left(1 - \frac{\pi^2 K_0^2 T^2}{12\mu^2} + \dots\right)\right]$  at temp.

T,  $\rho_r$  is the residual resistivity due to scattering by state lattice defects and an ideal resistivity  $\rho_i$  due to scattering by the lattice vibrations,

$$J_n = \int_0^{\theta/T} \frac{Z^n dZ}{(e^z - 1)(1 - e^{-z})} dT$$

upto the normal temperature  $\mu$  may be replaced by  $\mu_0$ .

The values of  $J_n$  for  $n = 5$  and  $7$  for different values of  $T/\theta$ , reported by Sondheimer [3] are listed in Table 1.

For noble and alkali metals eqn. (8) may be reduced to

$$\frac{d\Phi}{dT} = \frac{-\pi^2 K_0^2 T}{3e\mu} \cdot \frac{\rho_r + 3\rho_i [0.8 + 4.456 \times 10^{-2} (\theta/T)^2]}{\rho_r + \rho_i [0.8 + 0.1755 (\theta/T)^2]} \quad \dots (9)$$

valid in the pure temperature zone  $T < 0.5\theta$ ;  $\theta$  being Debye temperature  $\mu$  has been replaced by  $\mu_0$  as the difference in  $\mu_0$  and  $\mu$  in this temperature zone is vanishingly small.

For the metal where  $\rho_r \ll \rho_i$  eqn. (9) may be reduced to

$$\frac{d\Phi}{dT} = \frac{-\pi^2 K_0^2 T}{e\mu_0} \cdot \frac{[0.8 + 4.456 \times 10^{-2} (\theta/T)^2]}{[0.8 + 0.1755 (\theta/T)^2]} \quad \dots (10)$$

Eqn. (10), in the temperature zone  $T > 0.5\theta$  may be reduced to

$$\frac{d\Phi}{dT} = \frac{-\pi^2 K_0^2 T}{e\mu_0} \cdot \frac{[(T/\theta)^2 + 0.0475]}{[(T/\theta)^2 + 0.15875]} \quad \dots (11)$$

For  $\rho_r \ll \rho_i$  which is always satisfied by a pure metal at  $T(> 0.5\theta)$ . In this temperature zone always we take  $\mu \sim \mu_0^2$ .

If  $\frac{[(T/\theta)^2 + 0.0475]}{[(T/\theta)^2 + 0.15875]}$  is replaced by C in eqn. (11)

then we have

$$\frac{d\theta}{dT} = \frac{-\pi^2 K_0^2 T}{e\mu_0} C \quad \dots (12)$$

Eqn. (12) in terms of electronic Sp. heat may be written as

$$\frac{d\theta}{dT} = \frac{-2C_{ve}}{e} C \quad \dots (13)$$

where  $C_{ve} = \frac{\pi^2 K_0^2 T}{2\mu_0}$ , electronic Sp. heat at T.

## Results and Discussions

Thermoelectric power,  $d\theta/dT$  of some noble and alkali metals, viz., Au, Ag, Cu, Na, and Rb has been calculated in normal temperature zone by using eqn. (11) or eqn. (12). These values, so obtained are reported in Table 2. The values of the parameters  $\mu_0$  and  $\theta$ , used in the calculation are taken from the standard texts [7-1]. These values have been entered in the Table 3.

With reference to the values of  $d\theta/dT$  reported in Table 2, a tolerable agreement exists among the values of  $(d\theta/dT)$ , from eqns. (12) and (13) with  $\mu_0$  [cf Table 2] values of  $(d\theta/dT)$  Ag, from eqns. (12) and (13) agree satisfactorily [cf Table 2]. The values of  $(d\Phi/dT)_K$  are in close neighbourhood but divergence is appreciable [cf Table 2]. Incase of Na and Rb, values of  $(d\theta/dT)$  from eqns. (12) and (13) and close. In connection with sign associated with thermoelectric power it is to be noted that the formula suggested by Sondheimer has to play double role in deciding the signs of  $d\Phi/dT$  for noble and alkali metals in order to meet the experimental findings.

**Table 1 : Values of  $J_n = \int_0^{\theta/T} \frac{Z^n dZ}{(e^z - 1)(1 - e^{-z})}$  for  $n = 5$  and  $7$ , reported by Sondheimer.  $\theta$  is the Debye's Temperature.**

T/θ	J <sub>5</sub>	J <sub>7</sub>
0	124.43	5082.1
0.05	124.42	5078.2
0.076923	123.14	4809.8
0.1	116.38	3972.1
0.125	101.48	2798.8
0.16667	70.873	1328.9
0.2	50.263	705.56
0.25	29.488	281.75
0.33333	12.771	72.010
0.5	3.2293	8.3763
0.66667	1.1199	1.6538
0.83333	0.47907	0.45534
1.0	0.23662	0.15665
1.25	0.98845	0.041987

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**Table 2 : Calculated values of  $d\Phi/dT$  from eqn. (12) using  $\mu_0$  and  $\mu_0'$  from eqn. (13) using  $C_{ve}$  for Au, Ag, Cu, K, Na and Rb,  $\mu_0$  is taken from literatures [6]  $d\Phi/dT$  is in micro volts.**

Metals	T°K	- $d\Phi/dT$ using $\mu_0$	- $d\Phi/dT$ using $\mu_0'$	(- $d\Phi/dT$ ) = $(2C_{ve}/e).C$ [cf. Eqn. (12)]
Au	273	3.47	2.664	3.934
	320	4.121	3.163	4.671
	360	4.670	3.585	5.294
	400	5.217	4.004	5.915
	440	5.761	4.422	6.529
	480	6.304	4.839	7.145
	520	6.846	5.254	7.760
Ag	273	3.406	3.033	3.420
	300	3.784	3.370	3.801
	320	4.063	3.618	4.080
	340	4.340	3.866	4.361
	360	4.617	4.122	4.637
	380	4.893	4.358	4.914
Cu	273	2.522	2.037	3.470
	300	2.872	2.283	3.889
	320	3.051	2.464	4.197
	340	3.275	2.645	4.504
	360	3.497	2.834	4.810
	380	3.719	3.003	5.114
K	100	3.166	3.129	3.910
	140	4.642	4.588	5.733
	180	6.091	6.020	7.520
	220	7.524	7.436	9.291
	260	8.947	8.842	11.049
	273	9.408	9.298	11.618
Na	100	1.830	1.803	2.285
	140	2.826	2.784	3.528
	180	3.807	3.751	4.754
	220	4.774	4.704	5.958
	260	5.728	5.644	7.150
	273	6.037	5.948	7.535
Rb	100	3.930	3.612	4.817
	140	5.600	5.149	6.876
	180	7.256	6.670	8.897
	220	8.903	8.184	10.917
	260	10.545	9.693	12.931
	273	11.078	10.183	13.585

### Values of the Fermi energy $\mu_0$ at T = 0

Metals	$\mu_0$ (eV)	$\theta$ (K)
Au	5.5	185
Ag	5.5	220
Cu	7.0	310
K	2.1	99
Na	3.2	160
Rb	1.8	59
Li	4.8	430

### Conclusion

The thermodynamic relation for  $d\theta/dT$  is justified in K, Na and Rb and in agrees with Sondheimer's formula [eqn. (13)] based on free electron gas theory, however in the noble metals, it fails. The absolute thermoelectric power of a metal may not be necessarily equal to that derived from thermo e.m.f of a thermo couple. For absolute value of  $d\theta/dT$  eqn. (2) is more competent where as eqn. (13) is for that from Seebeck of a thermocouple.

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