Material Science Research India Vol. **6**(1), 191-195 (2009)

Validity of thermo-dynamic relations and other theoretical formula for thermoelectric power in a conductor and in a thermocouple

S.R. PANDIT, S.B. MAHTO[1], J. P. MAHTO[2], S.K. YADAV[3] and K.K. MANDAL[4]

P.G. Deptt. of Physics, S. K. M. University, Dumka (India).
[1]Department of Physics, K.B.College, Bermo (India).
[2]Department of Physics, Govt. Polytechnic Bhagalpur (India).
[3]Department of Physics, C.N. College, Ramgarh (India).
[4]Research Scholar (India).

(Received: January 06, 2009; Accepted: February 26, 2009)

ABSTRACT

Every conductor belongs to transportentropy function such that when an electric change passes, there is entropy absorbed or evolved between any two points of the conductor. If follows that the peltier heat per unit change developed at the isothermal junction of the two conductors is given by p = T.S where p = Peltier heat, T = Temperature and S= entropy function. Secondly for a single conductor under temperature gradient dT/dx, the Thomson heat is given by s=T.ds/dt, S appears as being the thermoelectric power. The present communication is an attempt to discuss quantitatively the thermodynamic relations of the thermoelectricity. The thermoelectric power of a conductor appears as a transport of the electric charge or, more lossely, of conduction electrons. William Thomsom[13] himself suggested that the Thomson heat might be regarded essentially as a specific heat of electricity in differentmetals, since they appear the quantity of heat absorbed or evolved by the unit current electricity in passing from cold to hot or hot to cold, between localities differing by one degree of temperature in each metal, respectively.

Key words: Quantitatively, phenomenological relations, sophisticated, rigorous

INTRODUCTION

The thermoelectric power of a conductor or a thermocouple obtained on the basis of thermodynamic theory of irreversible processes with the aid of free electron gas theory has been expressed as

$$\frac{d\phi}{dT} = -\frac{\pi^2 K_0^2\, T}{3\mu_o.e} \qquad ...(1)$$

at low temperatures, and

$$\frac{d\phi}{dT} = -\frac{\pi^2 K_0^2\, T}{3\mu_o.e} \qquad ...(2)$$

At high temperature [c.f. Jha and Thakur[5], Wilson[16], Sondheimer[15]]

Where $d\phi/dT$ = Thermoelectric power, K_o= Boltzmann constant, μ_o= Fermi energy of the electron at temperature T=0, e is the electronic charge and

$$\mu_0 = \frac{h^2 T}{2m^*}\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \qquad ...(3)$$

Where h being the Planck's constant, μ* is the effective mass of the electron and n is the number of electrons per unit of the electrons without the aid of phenomenological yielded by thermodynamic theory. Since pressure of the electron is expressed as [Sommerfeld[10]],

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

Where E (energy of the electron) at temp. T. is

$$E = E_0 + \frac{\pi^2 K_0^2\ T}{4\mu_0} \qquad ...(4)$$

where E_o being the zero point energy at T = 0

Now due to the pressure gradient along the element the electrons will diffuse from hotter and to colder end and hence the net amount of work done W_1, by the electron gas in this process may be given by

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

Where J_n the current density of electrons. If df be the potential difference existing across this element and consequently a diffusion thermoelectric current – e J_n may be supposed there. The work done W_2 due to heating on the electrons may be written as

$$W_2 = \frac{d\phi}{dx} dx(-J_n e)$$

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

$$\therefore \quad \frac{d\phi}{dT} = -\frac{2}{3}\ \frac{dE}{dT}\ \frac{1}{e} = -\frac{\pi^2 K_0^2 T}{3\mu_0 . e} \qquad ...(5)$$

Since the electronic specific heat at temp. T is written as

$$C_{ve} = \frac{\pi^2 K_0^2 T}{2\mu_0} \qquad ...(6)$$

And hence eqn. (5) may be written as

$$\frac{d\phi}{dT} = \frac{-2}{3} \cdot \frac{C_{ve}}{e} \qquad ...(7)$$

$$C_{ve} = \frac{-3.e d\phi}{2dT} \qquad ...(8)$$

Eqn (5) is only approximates as Jn is taken as constant which is not necessarily true [Sommerfeld[10], Jha & Thakur[5], Sondheimer[11]] Eqn. (7) or (8) does not involve the thermal conductivity of the metal or the other physical dimensions of the specimen and hence its accuracy in determining the value of dϕ/dT may be expected to be greater than that obtained from the Thomson coefficient from eqn.

$$\frac{d\phi}{dT} = \int_0^T \frac{\sigma\, dT}{T} \qquad ...(9)$$

at temp. T. Recently Roberts[9] and Christian[1] have reported the absolute thermoelectric power of lead. The values were obtained form the calorimetric method i.e, the Thomson coefficient which was calculated from the relation

$$\sigma = \frac{4KAdT}{(T_2 - T_1)IL} \qquad ...(10)$$

Where A is the area of crossection of the wire under test and L is its length, K is the thermal conductivity, dT is the change in temperature from the mid point of T_1 & T_2 I is the electric current.

A more rigorous and sophisticated relation for abosolute thermoelectric power of metal due to electron diffusion has been suggested by sondherimer[11] which is written as

$$\frac{d\phi}{dT} = \frac{-\pi^2 K_e^2 T\ \rho_r + 3\rho_i \{1 - \frac{J_r}{4\pi^2 J_s} + \frac{\mu}{2\pi^2 D}\ (\theta^2)\}}{3e\mu_e\ \rho_r + \rho_i\ \{1 - \frac{J_r}{4\pi^2 J_s} + \frac{3\mu}{2\pi^2 D}\ (\theta^2/T)\}} \qquad ...(10)$$

Where μ_o is the Boltzmann's constant, μ is the Fermi energy at temp. T, r_r,is the residual resistively due to scattering by static lattice defects and an ideal resitivity r_1 due scattering by the lattice vibrations,

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

upto the normal temperatures μ may be replaced by μ_0, n being the number of conduction electrons per atom. For noble and alkali metals n = 1. The value of Jn for n=5 & 7 for different values of T/q, reported by sondheimer[12] are listed in Table - 1.

For noble and alkali metals eqn. (10A) may be reduced to –

$$\frac{d\phi}{dT} = \frac{-\pi^2 K_0^2 T}{3e\mu_o} \cdot \frac{\rho_r + 3\rho i 8 + 4.456x10^{-2}(\Theta/T)^2]}{\rho_r + \rho_i [0.8 + 0.1755\ (\Theta/T)^2]} \quad ...(11)$$

$\mu \approx \mu_o - \frac{\pi^2 K_0^2 T}{2\mu_o}$, C_{ve}

Valid in the temperature zone $T \leq 0.5\ \Theta$. Θ being the Debye temperature, m has been replaced by m as the difference in m and μ_o in this temperature zone is vanishingly small. For pure metals where $\rho_r << \rho_i$ eqn (11) may be reduced to

$$\frac{d\phi}{dT} = \frac{-\pi^2 K_0^2 T}{e\mu_o} \cdot \frac{[0.8 + 4.456x10^{-2}(\Theta/T)}{[0.8 + 0.1755(\Theta/T)^2]} \quad ...(12)$$

Eqn. (10A), in the temperature zone T > 0.5θ, may be reduced to

$$\frac{d\phi}{dT} = \frac{-\pi^2 K_0^2 T}{e\mu_o} \cdot \frac{[(T/\Theta)^2 + 0.0475]}{[(T/\Theta)^2 + 0.15875]} \quad ...(13)$$

For $\rho_r << \rho_i$ which is always satisfied by a pure metal at T. (T>o.5θ). in this temperature zone also we may take [Sommerfeld[10]]. If is replaced by C in eqn. (13) then we have

$$\left(\frac{\partial\phi}{\partial T}\right) = \left(\frac{\partial\phi}{\partial T}\right)_s - \left(\frac{\partial\phi}{\partial T}\right)_e \quad ...(14)$$

Eqn. (14), in terms of electron sp. Heat may be written as

$$\frac{d\phi}{dT} = -2\frac{C_{ve}}{e} \cdot C \quad ...(15)$$

Where $C_{ve} = \frac{-\pi^2 K_0^2 T}{2\mu_o}$, the electron sp. heat at temp. T.

RESULTS AND DISCUSSION

Thus the study of thermoelectric of a metal would given significant information regarding the sp heat of electrons, concentration of conduction electrons, thermal equilibrium of electrons with lattice vibrations etc. and vice versa.

Now we would like to examine the validity of these equations quantitatively. Thermoelectric power of some noble and alkali metals, viz., Au, Ag, Cu, K, Na and Rb has been calculated in normal temperature zone by using eqns. (14) or (15). These values, so obtained, are reported in Table 2. The values of the parameters m_o and q, used in the calculation are taken from the standard texts

Table 1: Value of $J_n = \int_0^{\Theta/T} \frac{z^n dz}{(e^z -)(1 - e^{-z})}$ for, n = 5 and 7, reported by Sondheimeyer[12], where q is the Debye temperature.

T/q	J_5	J_7
0.00	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	0.098845	0.041987

Table 2: Calculated values of df/dT from eqn (14) using m & m_o from eqn. (15) using C_{ve}, for Au,Ag, Cu, K, Na & Rb. m is taken from the literatures [Wilson[16]], m_o has been Calculated from the observed values of the Hall coefficient R_H and df/dT is in microvolts. R_H is from the literature [Londol-Bomstein[7] Table, Vol.II-6, P. 16 (1992), J.M. Goodman[4], Phys. Rev. 171, 641 (1998); cf. Kittle[6] (1997), C_{ve} is from the literatures [Lein & Philipes[8] (1994)]

Metal	TK	- df/dT usingm	- df/dT usingm_o	$\frac{-\mathrm{d}\phi}{\mathrm{dT}} = .\frac{2C_{ve}}{e}$[cf.eqn.(15)
Au	273	3471	2664	3.964
	320	4121	3.163	4.671
	360	4670	3.585	5.294
	400	5217	4004	5.915
	440	5761	4422	6.529
	480	6304	4839	7.145
	520	6846	5254	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	4.112	4.637
	380	4.893	4.358	4.914
Cu	273	2.522	2037	3.470
	300	2.827	2283	3.889
	320	3.051	2464	4.197
	340	3.275	2645	4.504
	360	3.497	2824	4.810
	380	3.719	3.003	5.114
K	100	3.166	3.129	3.021
	140	4.642	4.588	4.430
	180	6.091	6.020	5.812
	220	7.524	7.436	7.179
	260	8.947	8.842	8.537
	273	9.408	9.298	8.977
Na	100	1.830	1.803	1.652
	140	2.286	2.784	2.551
	180	3.807	3.751	3.438
	220	4.774	4.704	4.310
	260	5.728	5.644	5.172
	273	6.037	5.948	5.451
Rb	100	3.930	3.612	3.558
	140	5.600	5.149	5.012
	180	7.256	6.670	6.286
	220	8.903	8.184	8.013
	260	10.545	9.693	9.358
	273	11.078	10.183	10.015

Table 3: Value of the Femi energy μ_o at T = 0 and Dedye's temperature, θ, reported in Standard texts [Wilson[15]]

Metal	m_o (ev)	q (K)
Au	5.5	185
Cu	5.5	220
K	7.0	310
Na	2.1	99
Rb	3.2	160
Li	4.8	430

[Wilson[16], Kittel[6]]. These values have been entered in the Table 3. the absolute thermoelectric power of a metal may determined rapidily from the values of the electronic sp. heat [cf. eqns. (7) & (15)] by using in mind we have calculated the value of df/dT from eqns. (7) & (15) by using the electronic sp. heat reported in the literatures [Lein & Philips[8]]. These values are shown in Table 2.

CONCLUSION

From the above discussions and results it may be concluded that the thermodynamic relations [Thomson[13]] and equations for thermoelectric power suggested by Sondheimer[11] are justified quantitatively to some extent. However, these are unable to decide the sign associated with the thermoelectric power for the metals under test in the said temperature zones. In this context, we would like to mention that recent developments [Vedernikov, Cook[14] et al, cook & Meer[2], Cook & Lanbitz[3]] reveal the that there is no general empirical relation for the thermoelectric properties of metals and it is rather difficult to give the theoretical interpretation of various observed features of thermopower. At this point, the present study differs from the above statements on the ground that eqn (14) in case of K, Na, Rb agree in respect of sing of df/dT and to some extent in magnitude as well. In fact a failure of eqn. (14) or (15) is predicting the sign of df/dT but these are not sufficient to disapprove the validity of thermodynamic relation [Thomson[13]].

REFERENCES

1. Christian, J.W. *et al., Proc. Roy. Soc*., A **245**: 273 (1998).
2. Cook, J.W. & Meer, M.P. *J. Phys. F.Metal Phys*. **3**L: 130 (1993).
3. Cook, J.W. * Lanbitz, N. *Can. J. Phys*. **54**: 928 (1996).
4. Goodman, *J.M. Phy. Rev*. **171**: 641 (2001).
5. Jha, K.M. & Thakur, M.L *Indian Journal of Pure & Applied Phys*. **12**: 751 (1994).
6. Kittel, C. Introduction to Solid State Physics (Wiley Easterm Private Limited New Delhi) 6th Edn. (1997).
7. Landtt Bomstien Landolt-Bometein Tables, **2**(6): 161 (1999).
8. Lein, W.H. & Philips, N.R. Phys. Rev. 133A 1370 (1994).
9. Roberts, R.B., Nature, **265**: 226 (1987).
10. Sommerfield, A., *Z Phys.* **47**: 1 (1978).
11. Sondheimer, E.H., *Proc. Roy. Soc*. A, **203**: 75 (1984).
12. Sondheimer, E.H., *Proc. Comb. Phil. Soc.* **43**: 571 (1978).
13. Thomson, W., *Phil. Trans. Roy. Soc*. (1985).
14. Vedemikov, M.V. *et al., J. Less Common metals* **52**: 221 (1997).
15. Wilson, A.H., The theons of metals, 4th edn. (Cambridge University Press) (1985).
16. Wilson, A.H., The theons of metals Cambridge Univ. Press. (1996).