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ENTHALPY CONTRIBUTION TO HEAT OF TRANSPORT

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ABSTRACT

The heat of transport Q^* was measured for carbon in Fe-32.5wt% Ni alloy for different carbon concentrations in regular solutions. The heat of solution of carbon in the iron-nickel-carbon system studied was determined from thermodynamic principles and graphical methods using literature data of the carbon solubility limit in the Fe-Ni-C system, and the activity formulation for the system as suggested by Natesan and Kassner. Our results suggest that the sign of Q^* does not depend on whether or not an ideal solution is assumed. But the absolute value of the Q^* does seem to depend on whether such results are obtained from the plot of In activity vs 1/T or In c vs 1/T for regular solutions. The difference from such absolute values strongly suggest the use of In activity vs the reciprocal of temperature plots for more reliable results. Barring the margin of error in the results of this and our previous work, the Q^* values measured on the assumption of ideality conditions seem to contain contributions from the solute enthalpy.

KEYWORDS: The heat of transport Q^*, Fe-Ni-C system.

INTRODUCTION

Most austenitic stainless steels for high temperature applications contain various amounts of chromium and nickel concentrations as alloying elements. Such high temperature uses include as steam generators, turbines, piping in electric power generating plants, and as fuel cladding materials for the liquid sodium-cooled fast breeder nuclear reactors. In most of these

service conditions, the steel of interest is subjected to a severe temperature gradient sometimes of up to a few hundreds of degrees.

In consequence to the temperature variations in the service metal, microstructural and composition changes particularly in the nonmetallic elements such as carbon, nitrogen and boron also occur after long- term service-at high temperatures.[1] A number of investigators[2,3,4,5] have studied the relationship between the composition, microstructure and mechanical properties of these alloys. The problem of interstitial migration in these materials has interested a few investigators[6-9] too.

Unfortunately most of the migration studies[6-9] reported in the literature except for a couple[10] have been carried out using single phase alloys where ideality conditions are assumed. The purpose of this work, some of which has been published elsewhere,[10] is to report more results on two-phase mass transport and to attempt an explanation of these results using thermodynamic principles and graphical solutions.

Our choice of the experimental alloy has been dictated by our continuing interest in the Fe-Ni-C system which shows minimum, amount of swelling upon neutron irradiation and because some thermodynamic relationships have been developed[1] for these alloys.

BASIC CONCEPTS

When a piece of metal or an initially homogeneous alloy is subjected to a temperature gradient, a concentration gradient is frequently established. This phenomenon is called "thermomigration, thermo-transport or thermal migration". The basic macroscopic equations governing thermomigration in such systems are obtained from irreversible thermodynamics and have been discussed by several others.[11-15] The steady state solute concentration gradient is related to the impressed temperature gradient through the well-known equation

$$\frac{d \ln c_i}{dT} = \frac{Q_i}{RT^2} \tag{1}$$

which reverts to

$$\ln c_i \frac{Q_i^*}{RT} + \text{constant} \tag{2}$$

after integration.

In this equation, c_i _is_ the solute concentration, R is the gas constant, T the absolute temperature and $Q_i^{\ddagger}$ is called the "heat of transport."

The quantity $Q_i^{\ddagger}$, characterises the phenomenon of thermotransport and its sign and magnitude determine the direction and magnitude of solute movement. From the concepts of irreversible thermodynamics $Q_i^{\ddagger}$ is defined as the flux of heat J_H, accompanying unit (1 mol) flux of matter J_i in an isothermal system, i.e.

$$Q_i^{\ddagger} = \left(\frac{J_H}{J_i}\right) \nabla T = 0 \qquad (3)$$

By using the thermodynamic identity $\mu = \bar{H} - T\bar{S}$ where $\bar{H}$ and $\bar{S}$ are the partial molar enthalpy and entropy of the solute respectively and by defining the heat of transport $Q_i^{\ddagger}$ by $Q_i^{\ddagger} = Q - \bar{H}$ (Ref.[13,14]), it can easily be shown[15] that at steady stale, i.e. $J = 0$

$$- Q_i^{\ddagger} = T\left\{\frac{dU}{dT}\right\} + T\bar{S} \qquad (4)$$

Measurements of $Q_i^{\ddagger}$, in principle provide information on the energy transfer processes associated with elementary diffusive atomic jumps.

Equation (2) has been used extensively[17,18,22] for calculating the heat of transport. But all the work reported using the said equation (2) have been done for dilute solutions. For dilute solutions, the equation of the chemical potential can be written as

$$U = U_0 + RT \ln c \qquad (5)$$

where c is the steady-state solute concentration and Uo the chemical potential of the pure solute.

For a regular solution however, Raleigh and Sommer[15] suggest that equation (5) be re-written as

$$U = U_0 + RT \ln a \qquad (6)$$

where a is the activity of the solute with pure solute as the standard state. By differentiating equation (6) at constant pressure we obtain

$$dU = \left\{\frac{\partial U}{\partial a}\right\}_T da \left\{\frac{\partial U}{\partial T}\right\}_a dT \qquad (7)$$

where

$$\left\{\frac{\partial U}{\partial T}\right\}_a = -S_0 + R \ln a \ \text{and} \ S_0$$

is the molar entropy of the pure solute. By taking the partial molar enthalpy and entropy of the solute in solution as ΔH and ΔS we can write[16]

$$R \ln a = \left\{\frac{U - U^0}{T}\right\} = \left\{\frac{\Delta \bar{H} - T\Delta \bar{S}}{T}\right\} \tag{8}$$

But

$$\left\{\frac{\partial U}{\partial T}\right\}_a = \left\{\frac{\Delta \bar{H}}{T}\right\} - \bar{S} \tag{9}$$

and

$$\left\{\frac{\partial U}{\partial a}\right\}_T = \frac{RT}{a} \tag{10}$$

from equation (6),

By substituting equations (9) and (10) into equation (7) and differentiating U (i.e. dU) with respect to temperature (dT) one obtains

$$\frac{dU}{dT} = \frac{(\Delta \bar{H})}{T} - \bar{S} + RT \frac{(d \ln a)}{dT} \tag{11}$$

By combining equations (11) and (4) one obtains

$$\frac{(d \ln a)}{dT} \qquad \frac{(Q^* + \Delta \bar{H})}{RT^2} \tag{12}$$

where ΔH is the partial molar heat of solution and Q^* is the thermal gradient effect.

EXPERIMENTAL

(A) *Materials and specimen preparation with analysis*

The iron used in this work was obtained from a science equipment shop at presidentail road, Enugu Nigeria in the form of electrolytic platelets and had a reported purity of 99.95%. Glidden Corporation of America in the form of electrolytic platelets and had a reported purity of 99.95%. Analysis of the iron showed it to contain 0.002 wt%C, 0.001 Al, 0.05 H, 0.001 Mn, 0.001 Ni, 0.002 N, 0.013 O, 0.002 P, 0.003 S, and 0.003 Si. The nickel used in the alloy was obtained from Head bridge market Onitsha, Nigeria in the form of rods and was reported to be 99.99% pure. The major impurities were found to be 0.0004 wt% C, 0.001 Mn, 0.0008

O, and 0.0001 H from chemical analysis. Carbon in the form of spectrographite grade graphite was used in making up the Iron-Nickel-Carbon alloys used in this study.

A master alloy of Fe-32.5 wt% Ni-0.002 wt% C was prepared by arc-melting in an argon atmosphere. The carbon concentration of 0.002 wt% in the master alloy was there as an impurity contained in the 99.95% iron platelets. The master alloy was remelted in an electron beam furnace at a pressure of 10^{-7} torr to remove volatile impurities. Spectrographite grade graphite was then arc melted into portions of the master alloy to produce specimens containing nominal carbon concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.8 wt% C. All the alloys were homogenized in a tantalum resistance furnace at 1370 K for 24 h under a vacuum of 10^{-6} torr. A portion of each of the alloys containing 0.5, 0.6 and 0.8 wt% carbon was then swaged to 0.64cm diameter for use in solid solubility studies. The remaining portion was swaged to a diameter of 0.25 cm for use in the thermotransport studies used to investigate the enthalpy contribution to the heat of transport. The specimens were then electropolished in a 6% perchloric acid in methanol bath at 203 K and a current density of 0.2 A/cm^2.

(B) *Solid solubility and metallographic studies*

The 0.64 cm diameter specimens were cut into 0.60cm long discs and equilibrated at 1123, 1223, 1323 and 1370 K for 120, 96, 72 and 30 h respectively, under a vacuum of 10^{-4} torr, and then quenched in oil. The quenched samples were then polished and etched. With the aid of a quantitative metallographic technique[19] the photomicrographs were used to determine the solvus boundary.

(C) *Thermotransport studies*

The thermotransport experiments were performed in a stainless steel chamber in vacuum of 10^{-7} torr for lower temperature runs, and in purified argon atmosphere for higher temperature experiments. The chamber was equipped with two water-cooled OFHC copper electrodes which supported the experimental sample, and a viewing port through which the temperature distribution on the specimen was monitored and measured, using a disappearing filament-type optical pyrometer. Each thermotransport specimen measuring 3cm was cut from the swaged 0.25cm diameter wire, heat-treated to remove cold work, and supported between the electrodes. The water-cooling produced a symmetrical and parabolic temperature distribution [Fig. l(a)]. The specimen was resistively heated by a current- and voltage-stabilized a.c. power source, and the measured temperature was corrected for sight glass and emissivity.
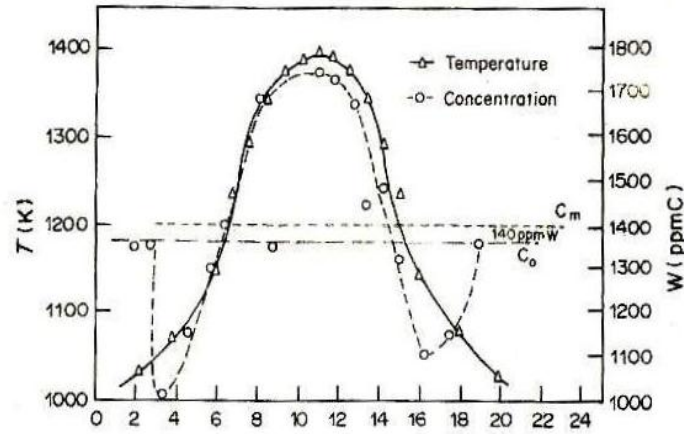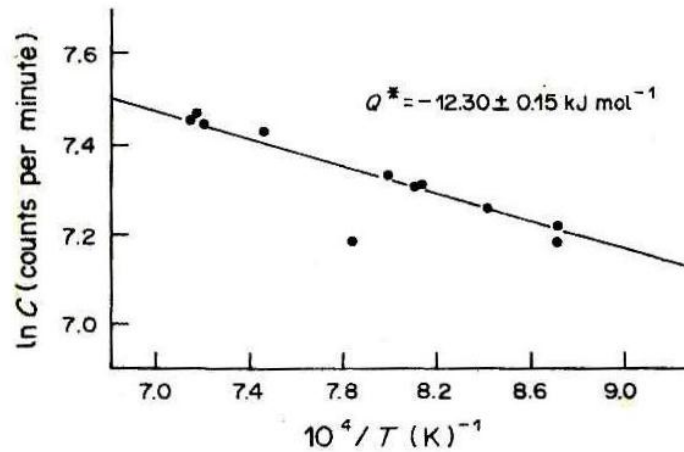
Distance (mm)

Fig. 1: (a) Temperature and Carbon concentration profiles for Fe-32.5 Ni-0.14C alloy after heating for 102 h (10). (b) Plot of In C vs *I/T* for thermotransport of carbon in 0.14C alloy (10).

In a thermal migration experiment of this nature with a temperature gradient, the difference between the initial and final concentrations decrease approximately as exp (- t/0) [20,21]) where *"t"* is the run time, *"θ"* is a. time constant defined as "θ" = $a^2/\Box^2D$, where "a" is the specimen half length along the gradient, and "D", the solute diffusivity at the mean run temperature. To achieve 99.3% of the steady state, a time of "50" is therefore required. Each specimen was run for a period of about l00h which corresponds to about 90% of steady state.

Table 1: Summary of thermotransport results.[10]

| Initial condition	c.wt%	Time of run (hours)	Atmosphere	Temperature range (K)	Method of analysis	Mass balance (%)	$Q^* + a$ (%) (KJmol⁻¹)
Single phase	0.14	102	Vacuum	1025-1400	Combustion	97	-12.30 ± 0.15
Single phase	0.22	96	Argon.	1330-1490	tracer	98	-11.70 ± 0.63
Single phase	0.22	96	Argon	1325-1500	tracer	98	-11.90 ± 0.19
Two phases	0.37	72	Argon	1210-1440	tracer	73	-11.90 ± 0.24
Two phases	0.50	103	Vacuum	1150-1400	Combustion	99	-13.27 ± 0.02
Two phases	0.62	96	Argon	1200-1450	Combustion	98	-11.97 ± 0.26
Two phases	0.62	55	Vacuum	1210-1440	Combustion	85	-12.60 ± 0.56
Two phases	0.78	82	Vacuum	1125-1430	Combustion	>99	-12.30 ± 0.20
Two phases	0.78	103	Vacuum	1250-1425	Combustion	95	-12.30 ± 1.10

C_Q — initial analysed composition
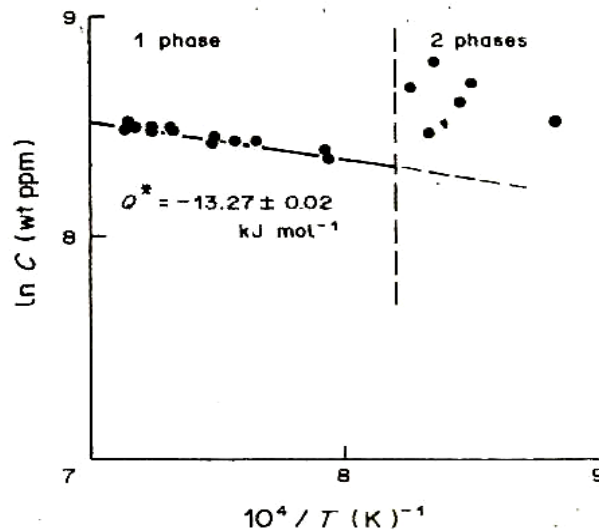
Fig. 2: Plot in In C vs *l/T for* 0.50% C alloy showing linear fit in 1-phase region of system.[10]

EXPERIMENTAL RESULTS AND DISCUSSION

Portions of the results of this study have been published elsewhere.[10] Such results include those of the solid solubility studies, thermotransport in single phase alloys and mass transport

in two-phase alloys. A summary of the thermotransport results are shown in Table 1 and will serve as a reference data bank in the discussions that follow.

(A) *Discussion on the enthalpy contribution*

In Figs l(b) and *2* the plots of in *c* vs 1/T for thermotransport of carbon in 0.14 C single phase and 0.5 C two phase alloys are shown. Both plots contain the Q_i^* values obtained for carbon in the alloys as calculated from the data in the single phase portions of the specimen when subjected to a temperature gradient, using equation (2). The vertical broken line in Fig. 2 corresponds to the temperature composition point lying on the solvus boundary.[10,22] The experimental data points beyond this boundary belong to the two-phase domain of the alloy where the solubility limit of carbon in Fe-32.5 Ni-C system has been exceeded.

(B) *Heat of transport in the two-phase region*

Calculations of heat of transport are usually obtained from plots of In *c* vs 1/T as deduced from equation (2). The equation is derived on the assumption of an ideal solution. In this study, alloys of high concentrations from 2000 up to 7800 ppm. C initial compositions were used. Natesan and Kassner [1] have shown that these are not ideal solutions. A plot of In *a* vs *l/T* would therefore be more appropriate for such regular solutions[15] in determining the "true" heat of transport Q_i^* *thermal* due to thermal gradient.

(C) *Heat of solution: the enthalpy* $(\overline{\overline{\Delta H}})$

To determine the heat of transport *Q** in a regular solution, the heat of solution (ΔH) must be known, or determined independently. The free energy of formation of the solution is

$$(\overline{\overline{\Delta G}}) \quad = \quad RT \ In \ a_c \qquad (13)$$

Taking the partial derivative of Δ*G/T with* respect to composition at constant pressure and temperature we obtain,

$$\left\{ \frac{d\overline{\overline{\Delta G}}/T}{dX_c} \right\} P, T = \frac{\partial \overline{\overline{\Delta G}}/T}{\partial X_c} \frac{dX_c}{dX_c} + \left\{ \frac{\partial \overline{\overline{\Delta G}}/T}{\partial I/T} \right\} \frac{dI/T}{dX_c} \qquad (14)$$

where X_c = mole fraction, *P* = pressure, *T* = temperature and $\partial \Delta G/T/(\partial \ I/T)$ is the heat of solution ΔH.

At constant temperature

$$\left\{\frac{\partial \overline{\Delta G}/T}{\partial X_c}\right\}_{P,\,T} = \frac{I}{T}\left\{\frac{\partial \overline{\Delta G}}{dX_c}\right\}_{P,\,T}$$

$$\left\{\frac{\partial \overline{\Delta G_c}}{\partial X_c}\right\}_{P,\,T} = RT\,\frac{\partial\,\ln a_c}{\partial X_c}$$

$$\left\{\frac{\partial \overline{\Delta G}/T}{\partial X_c}\right\}_{P,\,T} = R\left\{\frac{\partial\,\ln a_c}{\partial X_c}\right\}_{P.T} \qquad (15)$$

The first term on the left of equation (14) is obtained from the slope of a plot of $\overline{\Delta G}/T$ vs X_c. The mean value of the slope taken from the temperatures of interest, 1073 and 1273 K gives a value of -49.31 cal.mol -K. (-206.31 J/mol-K) for $d\overline{\Delta G}/T/dX_c$. The $\overline{\Delta G}/T$ vs X_c plot was made for the literature data[23,24] of carbon solubility in the Fe- Ni- *C* system.

(D) *Deducing* $\overline{\overline{\Delta H}}$ *from the activity of carbon in Fe –Ni -C system*

According to-Natessan and Kassner[1] the activity of carbon in Fe- Ni-C alloy can be deduced from

$$\ln a_c{}^{(Fe\text{-}Ni\text{-}C)} = \ln \frac{X_c}{(I-X_c)} + \left(11.92 - \frac{6330}{T}\right)\frac{X_c}{(I-X_c)}$$
$$- 1.845 + \frac{5100}{T} - \left(2.2 - \frac{7600}{T}\right)X_{Ni} \qquad (16)$$

Where X_c and X_{Ni} are mole fractions of carbon and nickel respectively. By differentiating equation (16) with respect to X_c, a value is obtained for equation (15).

Theoretically ΔH is independent of temperature. But from the carbon solubility curve of Okafor *et al.*[10] reproduced as Fig. 3, the carbon composition and hence X_c, change with temperature. Therefore the mean value 258.86 J/mol-K (61.87cal/mol-K) of the partial derivative of In a as a function of X_c taken at two different temperatures was used. From equation (14) we obtain

$$\frac{(\partial \Delta G/T)}{\partial 1/T}\,\frac{d1/T}{dX_c} = \overline{\overline{\Delta H}}\,\frac{d1/T}{dX_c}$$

$$= \left(\left\{\frac{d\overline{\Delta G}/T}{dX_c}\right\} - \frac{\partial \Delta G/T}{\partial X_c}\right) \qquad (17)$$

$$\overline{\overline{\Delta H}} = \left(\left\{\frac{d\overline{\Delta G}/T}{dX_c}\right\}_{P,\,T} - \frac{\partial \Delta G/T}{\partial X_c}\right)\cdot\frac{dX_c}{dI/T} \qquad (18)$$

A plot of X_c (carbon mole fraction) as a function of I/T gives a slope which is equal to $dX_c/(dI/T)$ needed in equation (18). To ensure reliability, the slope was taken as the mean of four values obtained from four points spanned over the entire curve, where such points include the two temperatures used in deducing the "In a" in equation (15). A mean value of — 112.12 was obtained for the slope, $dX_c/dI/T$, from such a plot.

By using the numerical values obtained from the plots of $\Delta G/T$ vs X_c and X_c vs I/T and from the calculation using equation (15) in equation (18) we obtain

$$\overline{\Delta H} = (-49.31 \ -61.87)\text{cal/mol-K} \ (- 112.I2)K$$
$$= 12.465 \ \text{Kcal/mol}$$
$$\overline{\Delta H} = (52.1 \ 5 \ \text{KJ/mol}). \hspace{2cm} (19)$$

A plot of In a_c *vs I/T* for the 0.22 wt% C alloy is shown in Fig. 4. The slope of that curve gives

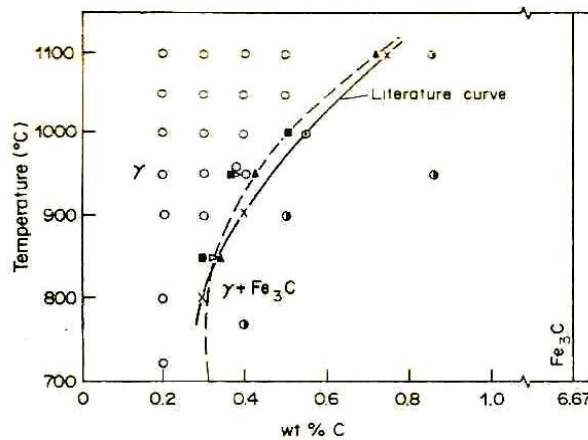$$Q^*_{thermal} + \overline{\Delta H} = 40.753 \ \text{KJ/mol}$$

Fig. 3: Carbon solubility limit in Fe-32.5 wt% Ni.[10]

▷■▲ Quantitative metallography data

▷Q4 wt % C alloy

■0.5 wt % C alloy

▲0.86 wt % alloy

○ One phase

◑ Two phase

◎ From Chipmaris data (24)
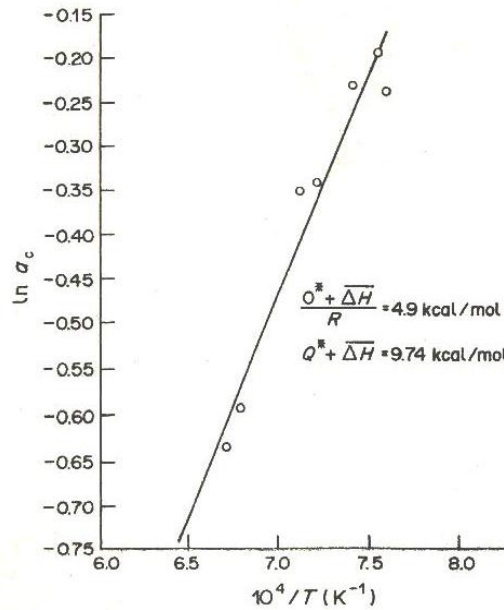
x Metals Handbook data (25)

Fig. 4: Least squares plot of *In a_c* as a function of *I/T* for the 0.22 wt%C alloy.

Combining this with equation (19) we obtain

$Q^*_{thermal}$ + 52.154 KJ/mol = 40.753 KJ/mol

$Q^*_{thermal}$ = - 11.40 KJ/mol

Our value of $\overline{\Delta H}$ = 52.15 KJ/mol determined for the partial molar enthalpy of carbon in F_c - 32.5 wt% Ni deserves further discussion.

In their work, Wada *et al.*[25] had reported a partial molar enthalpy of $\overline{\Delta H}^{Fe}$ = 44 KJ/mol for carbon in pure iron. In a later work, Elliott and Chipman[26] reported a partial molar enthalpy of ΔH_c^{Ni} = 56 KJ/mol for carbon in pure nickel. These results suggest that as nickel is added into iron, the partial molar enthalpy of carbon increases. The thermodynamic behaviour can be interpreted by the atomistic model developed by Wagner[27] for liquid alloys. The carbon atoms in the austenitic alloys can be situated in different types of sites with 6 - i iron atoms and i (= 0 to 6) nickel atoms as next nearest neighbours in the octahedron around the interstitial site.

Assuming random distribution of the metal atoms and a change of the partial molar enthalpy of carbon in the different sites according to

$$\Delta H_c = \frac{6-i}{6}\Delta \overline{H}_c^{Fe} + \frac{i}{6}\Delta H_{ci}^{Ni} - \frac{(6-i)}{6}ih \quad [28]$$

where $\overline{\Delta H}^{Fe}_c$ = 44 KJ/mol, $\overline{\Delta H}^{Ni}_c$ = 56 KJ/mol and h = —3.8 KJ/mol, the value for the partial molar enthalpy of carbon in the iron-nickel alloy ($\Delta H_c^{Fe-32.5wt\%Ni}$ = 52.15 KJ.mol) determined from this work becomes most reasonable, and in accordance with the above formulation.

The sign of $Q^*_{thermal}$ is consistent with the reported carbon migration to the hotter portion of the sample.[10] The near equality between this value of Q^* = (-11.40±0.23)KJ/mol and that of -11.70 KJ/mol obtained for the single phase 0.22 wt% carbon alloy (Table 1) gives credence to our value of - 11.40 ± 0.23 KJ/mol which assumes non-ideality. It was established in an earlier work,[10] that there is no concentration dependence on Q^* in this alloy. The large difference of 14% between this Q^* value (-11.40±0.23)KJ/mol reported[10] earlier for both single and two-phase alloys could be attributable to enthalpy contributions.

Furthermore, this method of analysis yields a reliable value for heat of solution (enthalpy) of the solute in the matrix.

CONCLUSION

1. The measured heat of transport Q^* can be broken into two parts namely the activation energy for solute migration and the enthalpy (heat of solution) contribution.

2. Results for Q^* measurements obtained from plots of In c vs I/T differ appreciably from those obtained from ln a_c vs I/T plots, even when micro-structural studies suggest ideality conditions.

3. A difference of about 14% is observed to exist between the values of Q^* obtained from two differing plots - In a vs l/T and In c vs 1/T. The In a vs *I/T plot* yields lower and more reliable results. And the higher value obtained from the Inc vs *I/T* plot appears to contain contributions due to enthalpy.

4. The heat of solution of carbon in γ - phase Fe-Ni-C system has been determined to be 52.15 KJ/mol. This is in conformity with a projected value for such an alloy.

5. The use of *In a* vs *I/T* plots the place of In c vs *I/T* plots has the added advantage of providing for the determination of the heat of solution ($\overline{\overline{\Delta H}}$)

REFERENCES

1. K. Natesan and T. F. Kassrier, Metall. *Trans,* 2008; 4: 2557.
2. K. J. Irvine, T. Gladman and F. B. Pickering, *J. Iron Steel Inst.,* 1998; 207: 1017.

3. J. E. White and J. W. freeman, *Trans. A.S.M.E.. J. Engng Power,* 2010; 85: 119.

4. R. Nakagawa and Y. Givguro, *Tetsu-tu-Hagne,* 2009; 47: 1169.

5. J. T. Barnby and F. M. Peace, *Acta matell.,* 2009; 19: 1351.

6. H. B. Huntington, *ASM Seminar Book on Diffusion* p. 155. Am. Soc. Metals, Metals Park, Ohio, 2007.

7. H. B. Huntington, in *Diffusion in Solids: Recent Developments* p. 303. Academic Press, New York, 2007.

8. O.N Cartson Metall. Trans 12A, 1999; 1795.

9. H. Nakajma and K. Hirano. *J. appl. Phys.,* 2010; 48; 1793.

10. O.N Cartson and DM Martin, Metall. Trans, 1999; 13A: 1713.

11. R. S Sorbello, *Comments Solid St. Phys.,* 2001; 6: 117.

12. A. R. Allwatt and A. V. Chadwick, *Chem. Rev.,* 1999; 67: 681.

13. L. Onsager, *Phys. Rev.,* 2004; 37: 405.

14. S. R. de Groot, *The Thermodynamics of Irreversible Processes,* Inter-science, New York, 2007.

15. D. O. Raleigh and A. W. Sommer, *J. chem. Phys.,* 1999; 36: 381.

16. J. O. Denbigh, *The- Thermodynamics of the Steady State, Methuens Monographs on Chemical Subject.* London, 1997.

17. P. Shewmon, *Acta metal,* 2006; 8: 605.

18. P. Shewmom, *J. chem.. phys.,* 2006; 29: 1032.

19. O. N. Carlson and D.M Martin, *Metall. Trans,* 2001; 9A: 1615.

20. S R. de Groot. *Physica,* 1999; 9: 699.

21. J. A. Bierlein, *J. chem. Phys.,* 1999; 23: 10.

22. Cahn R.W, *Metall. Trans.,* 2000; 13A: 1748.

23. J.J Moore, "Chemical metallogy" Bietter Werth – Heinemawn 2nd Edition, 2001.

24. D. J. Fray and J. Chipmun. *Trans, metall. Soc. A.I.M.E.* 2003; 245: 1143.

25. T. Wada, H. Wada, J. F, Elliot *Metall. 'Trans.,* 2009; 2: 2199.

26. F, Shewmon and Acta Metall, 2005; 9: 603.

27. C. Wiener. *Acta metal.,* 2010; 21: 1297.

28. S. K. Bose and H. J. Grabke, Z. *Metal K.,* 2009; 69(8).