

# Thermodynamic properties of Cu-Ni alloys: measurements and assessment

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*The activity of nickel in solid Cu-Ni alloys has been measured at 1000 K using a solid state galvanic cell incorporating calcia stabilised zirconia as the solid electrolyte. The activity of nickel shows positive deviation from Raoult's law over the entire range of concentration. Partial molar entropy of nickel in solid Cu-Ni alloys has been measured directly using a newly developed twin solid state thermocell apparatus. A consistent set of thermodynamic data for the Cu-Ni system has been derived by combining the results of the present study with selected data on enthalpy and free energy of mixing of liquid alloys and the phase diagram. The miscibility gap and the chemical spinodal boundaries obtained from the evaluated data are in good agreement with X-ray and diffuse neutron scattering studies reported in the literature.*

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## Introduction

Copper-nickel alloys are of great theoretical and practical interest. The sizes of copper and nickel atoms in solution differ by only 2% and the two elements are very close to each other in Pauling's electronegativity scale. Hence, a thermodynamic investigation of solid Cu-Ni alloys would provide an indication of the electronic interactions that occur on alloying. Substitution of copper atoms for nickel in solid Cu-Ni alloys results in extra electrons (one electron per atom) in the nickel lattice, since the lattice remains unaltered except at lower temperatures. These extra electrons increase the Fermi energy. Since the density of states in the d band of nickel is much greater than in the s band, the additional electrons will enter into the d band until this band is completely filled.<sup>1,2</sup> The number of vacancies in the d band of nickel is reported in the literature<sup>1,2</sup> as 0.6 per atom based on magnetic measurements. Hence, on alloying copper to nickel, for  $X_{\text{Cu}} < 0.6$  the d band is filled and for  $X_{\text{Cu}} > 0.6$  the energy states of the narrow 4s band are occupied. Various physical properties in solid Cu-Ni alloys such as specific heat, electrical conductivity, and optical properties substantiate this theory.<sup>1</sup> However, based on measurements of conductivity, thermoelectric power, and Hall effect, Schmidt<sup>3</sup> concludes that the 3d band is filled to somewhat higher concentrations of copper, i.e.  $X_{\text{Cu}} \sim 0.7$ . It is expected that the thermodynamic functions for solid Cu-Ni alloys would provide valuable indication of the electronic configuration of these alloys.

The practical relevance of Cu-Ni alloys comes from the extensive use of cupronickels in several applications. Cupronickels have superior mechanical and corrosion resistance properties at high temperatures. They have potential application in marine structures and desalination and nuclear plants, hence the requirement for the establishment of accurate thermodynamic data for Cu-Ni alloys and a complete phase diagram.

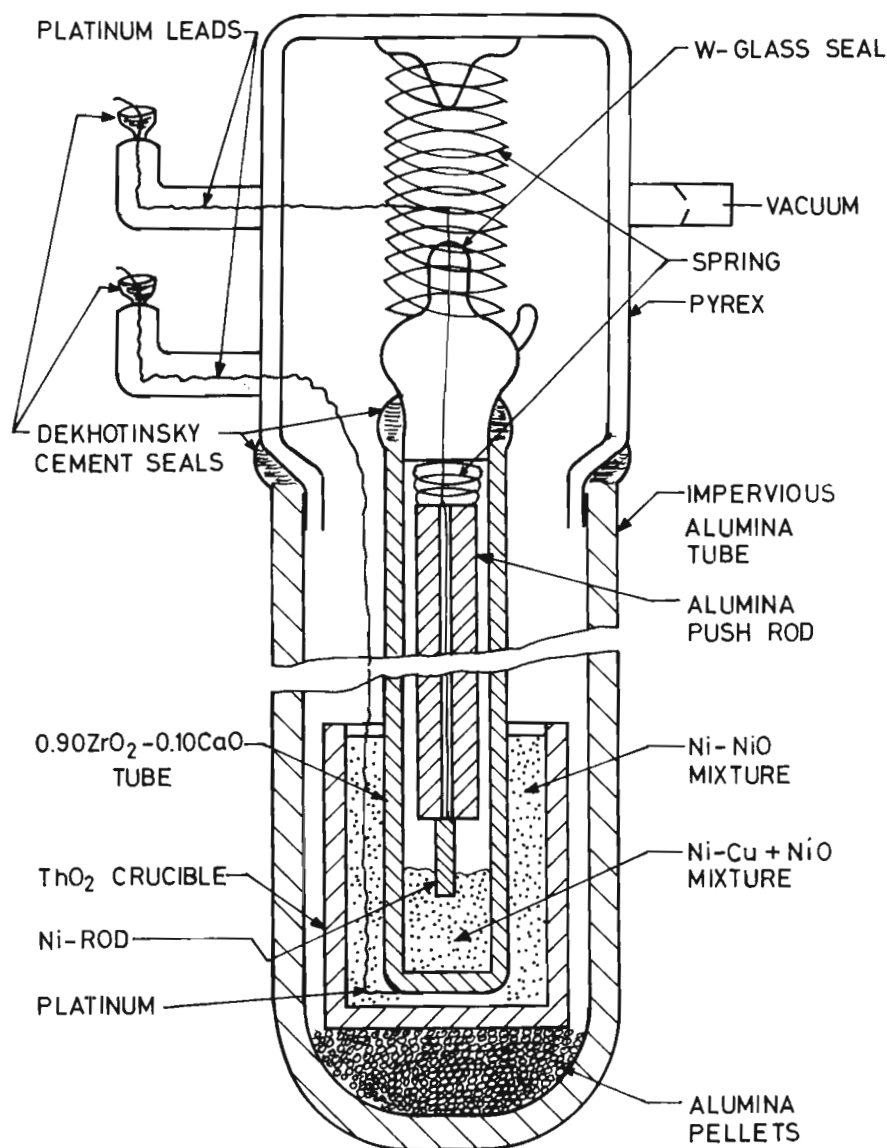
Activity data for solid Cu-Ni alloys have been reported by several investigators.<sup>4-9</sup> Vecher and Gerasimov<sup>4</sup> used an electromotive force (EMF) technique using an iodide salt bath to measure the activity of copper ( $X_{\text{Cu}} = 0.104-0.935$ ) in solid Cu-Ni alloys at 1000 K. They report large positive deviation from Raoult's law. The activity of nickel in solid Cu-Ni alloys has been determined using a solid state galvanic cell by Rapp and Maak<sup>5</sup> ( $X_{\text{Ni}} = 0.1-0.9$ ) at 973 and 1273 K, by Moser *et al.*<sup>6</sup> ( $X_{\text{Ni}} = 0.05-0.85$ ) between 1173 and 1373 K, by Notin *et al.*<sup>7</sup> ( $X_{\text{Ni}} = 0.02-0.95$ ) at 1000 and 1300 K, by Katayama *et al.*<sup>8</sup> ( $X_{\text{Ni}} = 0.2-0.85$ ) at 1273 K, and by Kontopoulos<sup>9</sup> ( $X_{\text{Ni}} = 0.18-0.82$ ) between 1073 and 1273 K. All these investigators report large positive deviations from ideality and their results are in general

agreement within the limits of experimental uncertainty when compared at 1273 K.

There is considerable discrepancy between experimental values on the enthalpy of formation in solid Cu-Ni alloys reported in the literature.<sup>10-13</sup> Oriani and Murphy<sup>10</sup> used a differential solution calorimeter using liquid tin as the solvent to measure enthalpy of mixing in solid Cu-Ni alloys at 1113 K. Their study gives a maximum value of 1590 J mol<sup>-1</sup> at  $X_{\text{Ni}} \sim 0.7$ . Kubaschewski *et al.*<sup>11</sup> obtained a value of 2260 J mol<sup>-1</sup> for the enthalpy of formation of equiatomic Cu-Ni solution at 1000 K by means of an adiabatic reaction calorimeter. Elford *et al.*<sup>12</sup> observed a sudden drop in the enthalpy of mixing in the concentration range  $X_{\text{Ni}} = 0.5-0.75$  at 973 K using a high temperature adiabatic calorimeter. They attribute this deviation to a magnetic transformation. Their results also show a large scatter. Leach and Bever<sup>13</sup> used liquid tin solution calorimetry to study the enthalpy of mixing of solid Cu-Ni alloys. Their investigation yields significantly higher values for the enthalpy of mixing than those reported by the other workers.<sup>10-12</sup> Values for the enthalpy of formation of solid Cu-Ni alloys have also been derived by various investigators<sup>4-7,9</sup> from the temperature coefficient of EMF.

Several authors conclude that either clustering or a miscibility gap occurs in the Cu-Ni system at low temperatures, based on conductivity,<sup>3,14</sup> magnetic susceptibility,<sup>15</sup> and specific heat measurements<sup>16,17</sup> and from thermodynamic calculations.<sup>12,18</sup> However, there is disagreement about the temperature and composition range over which the clustering or the miscibility gap occurs. Accurate experimental determination of the miscibility gap is extremely difficult because of the slow kinetics at low temperatures. The only experimental determination of the solid state miscibility gap boundaries is that of Sachtler and co-workers.<sup>19,20</sup> They used an X-ray study of alloy films at 473 K and suggest segregation into two fcc phases having compositions of 10 and 95%Ni, respectively. The miscibility gap reported in the literature<sup>21</sup> is based on the thermodynamic calculations of Elford *et al.*<sup>12</sup> Vrijen and Radelaar<sup>22</sup> used diffuse neutron scattering experiments to study the clustering behaviour in solid Cu-Ni alloys. They determined the spinodal curve from the diffuse neutron scattering results using the model of Clapp and Moss.<sup>23-25</sup>

Recently, Mey<sup>26</sup> carried out a thermodynamic evaluation of the Cu-Ni system. By adopting an optimisation procedure and using experimental information on the thermodynamic properties and the equilibrium phase diagram of the Cu-Ni system, a set of coefficients was obtained for the representation of the thermodynamic properties of solid and liquid Cu-Ni alloys. However, the suggested values for liquid Cu-Ni alloys do not compare well with the activity measurements for liquid alloys reported in the literature.<sup>27</sup>



1 Static vacuum apparatus used for measurement of electromotive force (EMF)

It is intended in the present study to characterise completely the thermodynamic properties of solid Cu-Ni alloys. This would establish the extent of the miscibility gap. A consistent set of data for the Cu-Ni system is obtained by combining the results of the present study with selected data for liquid alloys and the phase diagram.

## Experimental technique

### MATERIALS

The starting materials for the preparation of the alloys were nickel and copper of 99.99% purity. Nickel and copper rods of 3 mm dia. and puratonic grade powders of copper, nickel, and nickel oxide were obtained from Johnson Matthey Chemicals, Birmingham. The alloys were prepared by induction melting and casting in a purified argon atmosphere. The alloys were homogenised at 1250 K and fine powders were prepared by filing. Steel particles in the powder were removed magnetically. The composition of the alloys was determined by chemical analysis. The reference electrode consisted of an equimolar mixture of nickel and nickel oxide. Electrode pellets for the entropy meter appar-

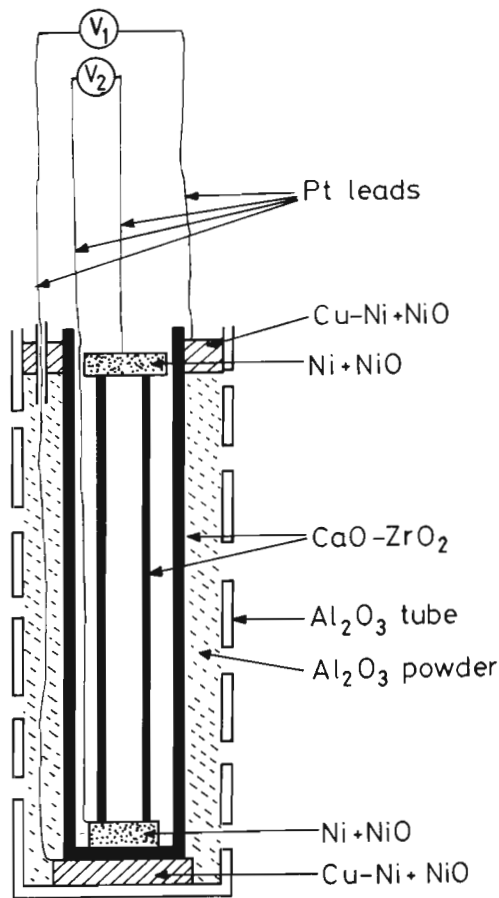
atus were prepared by compaction and sintering at 1250 K for 12 ks. Argon gas, used to provide an inert atmosphere over the electrodes in the twin thermocell, was of 99.998% purity. The argon gas was further dried by passing through anhydrous magnesium perchlorate and deoxidised by passage through copper at 700 K.

## APPARATUS AND PROCEDURE

### Activity measurements

The cell apparatus used for measurements of activity is shown in Fig. 1. It is similar to the electrochemical cell designed by Charette and Flengas<sup>28</sup> to investigate the thermodynamic properties of metal oxides. It consisted of two half cell compartments separated by a calcia stabilised zirconia tube, both sealed under vacuum. The alloy electrode comprising of the alloy-nickel oxide powder is tightly packed inside the closed end calcia stabilised zirconia solid electrolyte tube. The top of this tube is closed by a tight fitting bell-shaped Pyrex tube which supports a tungsten electrode connection sealed into the glass. The bell is connected to the zirconia tube with deKhotinsky cement.\* A 3 mm dia. nickel rod is pressed against the alloy-nickel

\*deKhotinsky is a tradename of CENCO, Chicago, USA.



2 Section of twin differential thermocell used in present investigation;  $V_1$  and  $V_2$  are EMFs

oxide mixture by means of a spring and an alumina insulating push rod, ~6 mm in diameter.

The assembled alloy electrode half cell is first evacuated using a side arm tube, heated to 400–500 K, and then the tube is flame sealed under vacuum. The outer half cell contains the Ni + NiO reference mixture and an inert platinum foil electrode. The firmly packed Ni + NiO mixture is contained in a thoria crucible placed inside a closed end impervious alumina tube. The crucible is supported on alumina granules. The top of this alumina tube is again sealed with deKhotinsky cement to a larger bell-shaped Pyrex tube which has two tungsten lead wire connectors sealed into glass.

The entire cell is assembled by inserting the alloy electrode half cell into the empty thoria crucible, pressing against the reference electrode, and packing the free volume of the crucible with the Ni + NiO mixture. The zirconia tube is maintained tightly against the reference electrode by means of a second metal spring inserted between the inner and outer bells. The outer bell is cemented in place by melting the deKhotinsky cement in the ring container, as shown in Fig. 1, and the cement is allowed to solidify while the outer bell is pressed against the spring. Then the outer compartment is also evacuated using a side arm tube and flame sealed under vacuum. The cell was suspended in a vertical Kanthal resistance furnace. The cell was electrically shielded by a Kanthal tape wound around the outer alumina tube and earthed. The temperature of the furnace was controlled to  $\pm 1$  K. Temperatures were measured at the outer wall of the cell at the level of the alloy-nickel oxide mixtures using a calibrated Pt/Pt-13Rh thermocouple. Cell potentials were measured by a Kiethley digital electrometer with an impedance exceeding  $10^{12} \Omega$ . The

Table 1 Activities in Cu-Ni alloys at 1000 K

Concentration of nickel $X_{Ni}$	Electromotive force $E$ , mV	Activity of nickel $a_{Ni}$	Activity of copper $a_{Cu}$
0.10	50.5	0.3103	0.9128
0.20	30.8	0.4894	0.8463
0.30	22.1	0.5985	0.7926
0.40	16.3	0.6856	0.7376
0.50	12.4	0.7506	0.6856
0.60	9.9	0.7953	0.6391
0.70	7.9	0.8322	0.5873
0.80	6.1	0.8686	0.5141
0.90	3.7	0.9185	0.3649

advantages of using a static vacuum closed cell arrangement are the elimination of mixed potential, rapid cell response, and highly stable EMFs over long periods.<sup>28</sup>

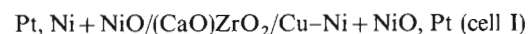
### Entropy meter apparatus

A schematic diagram of the twin differential thermocell used in the present study for partial entropy measurements is shown in Fig. 2. It consists of two concentric calcia stabilised zirconia tubes of identical composition. Electrodes of Ni + NiO are pressed against each end of the inner tube and electrodes of alloy and oxide (Cu-Ni + NiO) are placed in contact with the outer tube. The two zirconia tubes are placed in an identical temperature gradient. The entire assembly is placed inside a flat bottom alumina tube as shown in the figure and the free volume between the outer alumina and zirconia tubes is packed with dry  $Al_2O_3$  powder. The cell is suspended inside a two zone, vertical Kanthal resistance furnace. The even temperature zones extended to ~8 cm at the high temperature end and to ~4 cm at the low temperature end of the thermocells giving temperature differentials up to 200 K. The cell is electrically shielded by a Kanthal tape wound around the outer alumina tube and earthed. Temperatures in each zone are controlled to within  $\pm 1$  K and measured using calibrated Pt/Pt-13Rh thermocouples. The differential EMF of the two thermocells was monitored using a Kiethley digital electrometer.

## Results

### MEASUREMENTS OF ACTIVITY

The solid state galvanic cell used in the present study for activity measurements can be represented as

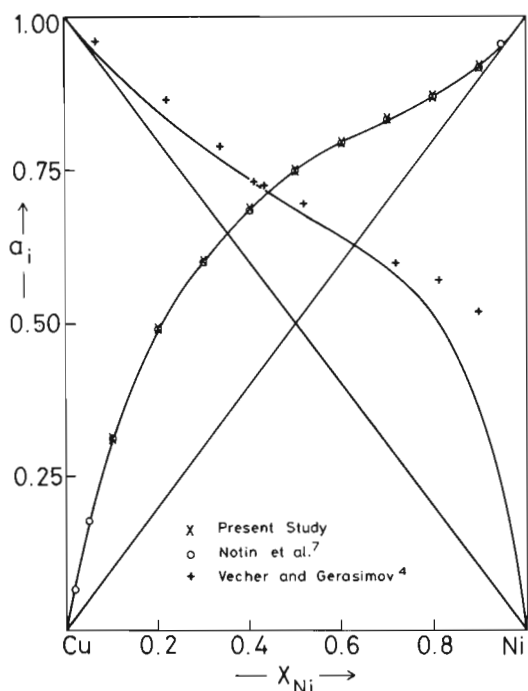


A summary of the values of electromotive force  $E$  of cell I at 1000 K, measured as a function of concentration of nickel in the metallic solid solution, is given in Table 1. From the measured values of  $E$  the activity of nickel was calculated using the relationship

$$\ln a_{Ni(\text{alloy})} = -2EF/RT \quad \dots \quad (1)$$

where  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is the absolute temperature. The calculated values of activity are given in Table 1 and plotted as a function of concentration of nickel in Fig. 3. From the activity coefficients of nickel in the binary Cu-Ni solid solution, the activity coefficients of copper at 1000 K, with respect to fcc copper as standard state, are derived by Gibbs-Duhem integration using the  $\alpha$ -function

$$\ln \gamma_{Cu} = -\alpha_{Ni} X_{Cu} X_{Ni} - \int_{X_{Cu}=1}^{X_{Cu}} \alpha_{Ni} dX_{Cu} \quad \dots \quad (2)$$



3 Relationship between activity  $a_i$  and concentration of nickel  $X_{Ni}$  in solid Cu-Ni alloy at 1000 K

The variation of the function  $\alpha_{Ni} = \ln \gamma_{Ni}/X_{Cu}^2$  as a function of  $X_{Cu}$  at 1000 K is shown in Fig. 4. The calculated values of activity for copper as a function of composition are given in Table 1 and plotted in Fig. 3. The activity data for both components indicate positive deviations from ideal behaviour. The excess integral molar free energy  $\Delta G^E$  calculated at 1000 K using the expression

$$\Delta G^E = RT(X_{Cu} \ln \gamma_{Cu} + X_{Ni} \ln \gamma_{Ni}) \quad (3)$$

as a function of concentration is shown in Fig. 5. This relationship can be represented by an empirical equation

$$\Delta G^E = X_{Ni}(1 - X_{Ni})[12025 - 1352(1 - 2X_{Ni}) + 1080(1 - 2X_{Ni})^2] \text{ J mol}^{-1} \quad (4)$$

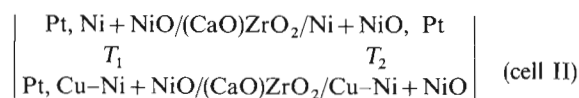
The respective excess partial molar free energies of nickel and copper at 1000 K are

$$\Delta G_{Ni}^E = (1 - X_{Ni})^2[12025 - 1352(1 - 4X_{Ni}) + 1080(1 - 6X_{Ni})(1 - 2X_{Ni})] \text{ J mol}^{-1} \quad (5)$$

$$\Delta G_{Cu}^E = X_{Ni}^2[12025 - 1352(3 - 4X_{Ni}) + 1080(5 - 6X_{Ni})(1 - 2X_{Ni})] \text{ J mol}^{-1} \quad (6)$$

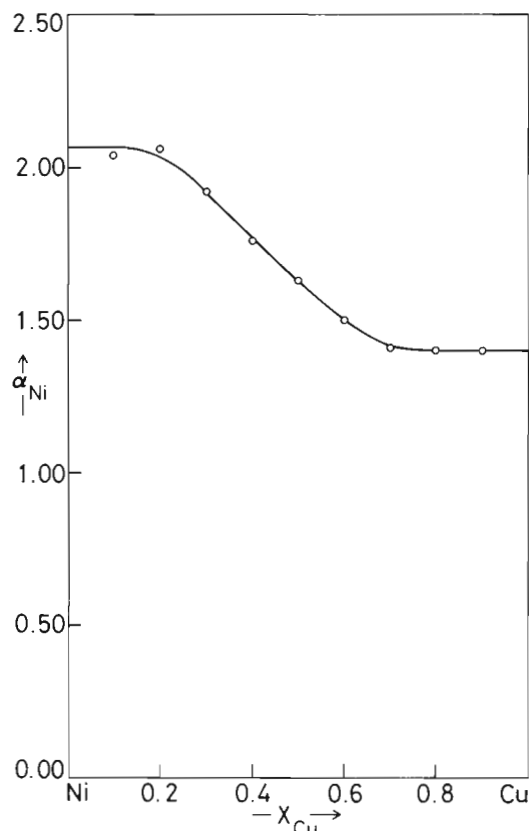
### MEASUREMENT OF PARTIAL ENTROPY

Partial molar entropy of nickel in solid Cu-Ni alloys was measured using a twin solid state thermocell or an entropy meter apparatus represented by



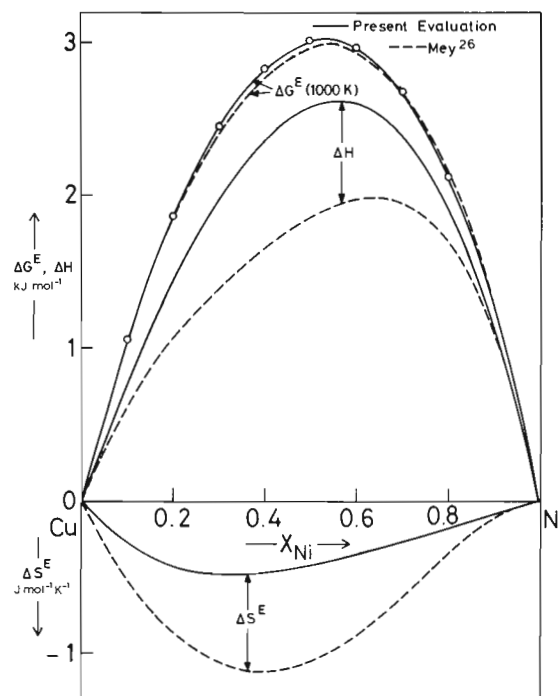
The entropy meter apparatus is based on the principle that the difference in Seebeck coefficients  $\phi$  of the two thermocells is related directly to the difference in the partial entropy of oxygen around each thermocell<sup>29</sup>

$$\begin{aligned} \phi_1 - \phi_2 &= (dE_1/dT - dE_2/dT) \\ &= [\Delta S_{O_2(2)} - \Delta S_{O_2(1)}]/4F \quad (7) \end{aligned}$$



4 Variation of  $\alpha$ -function  $\alpha_{Ni}$  with concentration of copper  $X_{Cu}$  for solid Cu-Ni alloys at 1000 K

where  $\phi_1$  and  $\phi_2$  are the Seebeck coefficients of thermocells with Ni + NiO and Cu-Ni + NiO electrodes, respectively, and  $\Delta S_{O_2(1)}$  and  $\Delta S_{O_2(2)}$  are the respective partial molar entropies. The partial entropy of oxygen defined by a



5 Variation of excess integral molar free (Gibbs) energy  $\Delta G^E$ , enthalpy  $\Delta H$ , and entropy of mixing  $\Delta S^E$ , respectively, with  $X_{Ni}$  for solid Cu-Ni alloys at 1000 K

mixture of Ni + NiO is given by



$$\Delta S_{\text{O}_2}(\text{Ni} + \text{NiO}) = 2\Delta S_f^\circ(\text{NiO}) \quad \dots \quad (9)$$

where  $\Delta S_f^\circ(\text{NiO})$  is the standard entropy of formation of NiO. For the alloy electrode containing a mixture of alloy and oxide,



$$\Delta S_{\text{O}_2}(\text{Cu-Ni} + \text{NiO}) = 2\Delta S_f^\circ(\text{NiO}) - 2\Delta S_{\text{Ni}} \quad \dots \quad (11)$$

where  $\Delta S_{\text{Ni}}$  is the partial molar entropy of mixing of nickel in the solid Cu-Ni alloy. Thus, for the twin thermocell shown in Fig. 2 the difference in Seebeck coefficients is directly related to  $\Delta S_{\text{Ni}}$

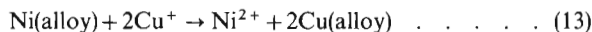
$$\phi_1 - \phi_2 = (dE_1/dT - dE_2/dT) = -\Delta S_{\text{Ni}}/2F \quad \dots \quad (12)$$

The Seebeck coefficient of calcia stabilised zirconia is not a strong function of temperature.<sup>29</sup> Hence  $dE/dT$  can be replaced by  $\Delta E/\Delta T$  in equation (12). The results obtained using the twin thermocell are shown in Fig. 6. Small negative deviations from ideal entropy are observed. The uncertainty limits shown in the plot occur because of the experimental uncertainty in the Seebeck coefficients of the two thermocells. Although the two zirconia tubes were fabricated from the same batch of raw materials and were subjected to identical processing and heat treatments, occasionally there were small variations in their Seebeck coefficients, presumably of microstructural origin. The entropy meter apparatus based on twin thermocells operated in differential mode has not been used in earlier thermodynamic investigations of alloys.

## Discussion

### COMPARISON WITH LITERATURE

Values for activity of nickel in solid Cu-Ni alloys at 1000 K derived in the present study are in excellent agreement with the EMF measurements of Notin *et al.*<sup>7</sup> at the same temperature as shown in Fig. 3. Values for activity of copper derived from Gibbs-Duhem integration in the present study are somewhat lower than the measurements of Večer and Gerasimov.<sup>4</sup> They used a melt of sodium and potassium iodides with a small amount of copper iodide. Since the standard Gibbs' energies of formation of CuI and  $0.5\text{NiI}_2$  differ by only 39 kJ mol<sup>-1</sup> (Ref. 30) at 1000 K, it is possible that their measurements may be affected by the displacement reaction

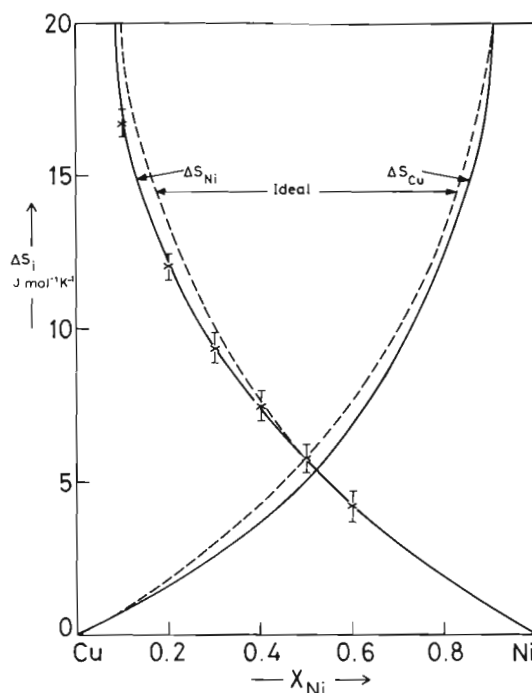


The presence of small amounts of Cu<sup>2+</sup> ions may also have resulted in an electronic contribution to the conductivity of the fused salt, resulting in smaller EMF and higher activity values.

### THERMODYNAMIC EVALUATION AND ASSESSMENT

#### Thermodynamic properties of liquid Cu-Ni alloys

Activity data for liquid Cu-Ni alloys have been reported by Kulkarni and Johnson,<sup>27</sup> Tomiska and Neckel,<sup>31</sup> and Hultgren *et al.*<sup>32</sup> based on the vapour pressure measurements of Schultz *et al.*<sup>33</sup> and data for copper rich alloys have been reported by Melnikov and Novoselov.<sup>34</sup> Kulkarni and Johnson<sup>27</sup> used a solid electrolyte galvanic cell to measure oxygen activities in liquid Cu-Ni melts at several temperatures. The values of activity for nickel in the liquid Cu-Ni system were calculated using the EMF data on oxygen saturated melts at 1673 K. Tomiska and Neckel<sup>31</sup> determined the thermodynamic properties of

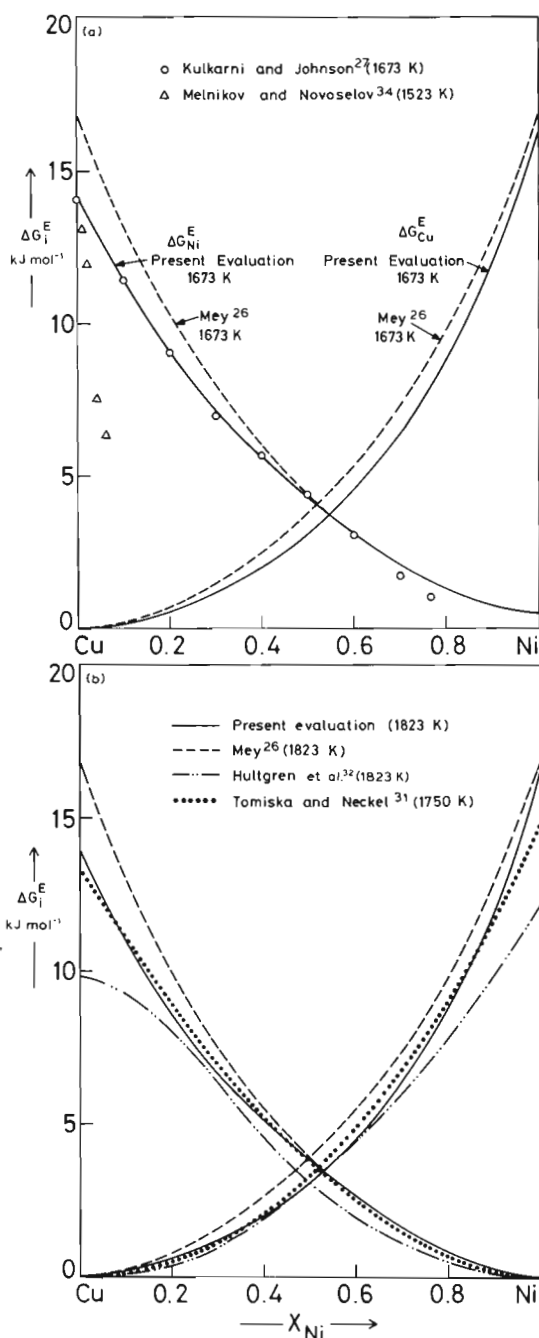


6 Variation of partial molar entropy of nickel and copper  $\Delta S_{\text{Ni}}$  and  $\Delta S_{\text{Cu}}$ , respectively, with  $X_{\text{Ni}}$  in solid Cu-Ni system obtained using entropy meter apparatus shown in Fig. 2 (data points); solid curve represents data evaluated in present work

liquid Cu-Ni alloys by means of Knudsen cell-mass spectrometer combination. Their results obtained at 1750 K are in reasonable agreement with those of Kulkarni and Johnson.<sup>27</sup> Schultz *et al.*<sup>33</sup> measured the vapour pressure of copper over liquid Cu-Ni alloys ( $X_{\text{Cu}} = 0.052-0.9$ ) in the temperature range 1796-1867 K by means of the transpiration method. Their data at 1823 K are given in the compilation of Hultgren *et al.*<sup>32</sup> Values of activity lower than the true value can be obtained using the transpiration method if the carrier gas is unsaturated with respect to melt vapour and if diffusion gradients exist in the melt. Melnikov and Novoselov<sup>34</sup> used a liquid electrolyte ( $\text{Na}_2\text{O}-\text{SiO}_2 + 5\%\text{NiO}$ ) to measure the activity of nickel for dilute alloys ( $X_{\text{Ni}} = 0.002-0.06$ ) between 1393 and 1523 K. Their data suggest values of activity much lower than those reported by other investigators. Further, their results lead to  $\Delta H < 0$ , in contradiction to experimental calorimetric data. The excess partial Gibbs' energies in liquid Cu-Ni alloys reported by various investigators are plotted for comparison in Fig. 7a (Refs. 26, 27, 34) with respect to solid nickel and liquid copper as standard states and in Fig. 7b (Refs. 26, 31, 32) with respect to liquid metal standard state for both copper and nickel. Values for excess partial Gibbs' energies in liquid Cu-Ni alloys evaluated by Mey<sup>26</sup> are not in very good agreement with those reported by Kulkarni and Johnson<sup>27</sup> at 1673 K and the reported values of Hultgren *et al.*<sup>32</sup> at 1823 K as shown in Figs. 7a and b, respectively. The EMF measurements of Kulkarni and Johnson<sup>27</sup> have been chosen in the present evaluation because of higher precision. At 1673 K, the evaluated Gibbs' energy for liquid Cu-Ni alloys can be represented by an equation of the form

$$\Delta G^E = X_{\text{Ni}}(1 - X_{\text{Ni}})[13\,565 - 1270(1 - 2X_{\text{Ni}}) + 1402(1 - 2X_{\text{Ni}})^2] \text{ J mol}^{-1} \quad \dots \quad (14)$$

with respect to pure liquid components as standard states. The excess Gibbs' energy evaluated in the present study is plotted as a function of concentration at 1673 K in Fig. 8 together with the evaluated results of Mey.<sup>26</sup> The values of

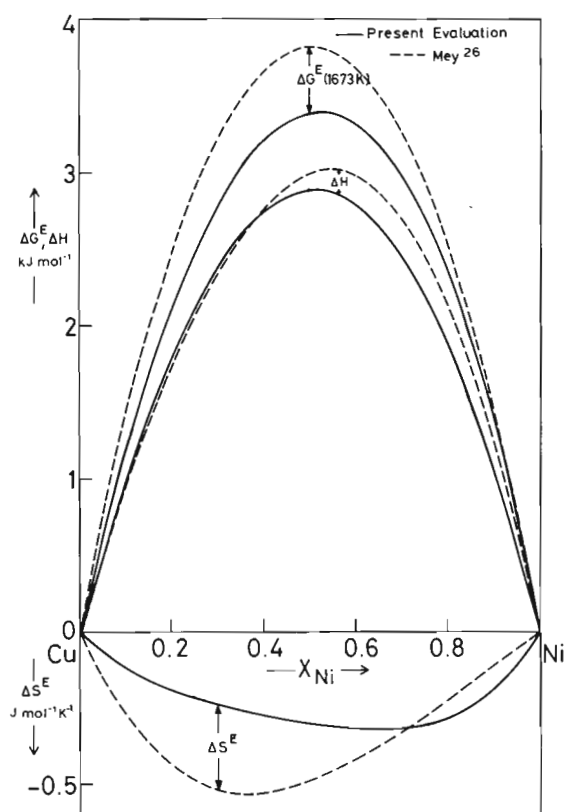


a solid nickel and liquid copper as standard states; b liquid nickel and copper as standard states

**7 Excess partial Gibbs' energies of nickel and copper  $\Delta G_{Ni}^E$  and  $\Delta G_{Cu}^E$ , respectively, with  $X_{Ni}$**

$\Delta G_{Ni}^E$  evaluated by Mey<sup>26</sup> are represented incorrectly in Fig. 3 of her paper. The enthalpies and entropies of fusion for pure copper and nickel for the conversion of standard states were taken from the compilation of Barin and Knacke.<sup>35</sup>

The partial or integral enthalpy of mixing of liquid Cu-Ni alloys have been measured calorimetrically by a number of investigators.<sup>36-40</sup> Values determined by Dokken and Elliott<sup>36</sup> and by Benz and Elliott<sup>37</sup> are in agreement with each other, while those of Predel and Mohs,<sup>38</sup> El'Khasan *et al.*,<sup>39</sup> and Von Samson-Himmelstjerna<sup>40</sup> deviate from these. Dokken and Elliott<sup>36</sup> used a high temperature solution calorimeter to measure directly the partial molar enthalpy of mixing of nickel ( $X_{Ni} = 0.0-0.15$ ) at 1473 K. Their experimental method was an improvement over the earlier procedure of Benz and



**8 Variation of  $\Delta G^E$ ,  $\Delta H$ , and  $\Delta S^E$  with  $X_{Ni}$  for liquid Cu-Ni alloys**

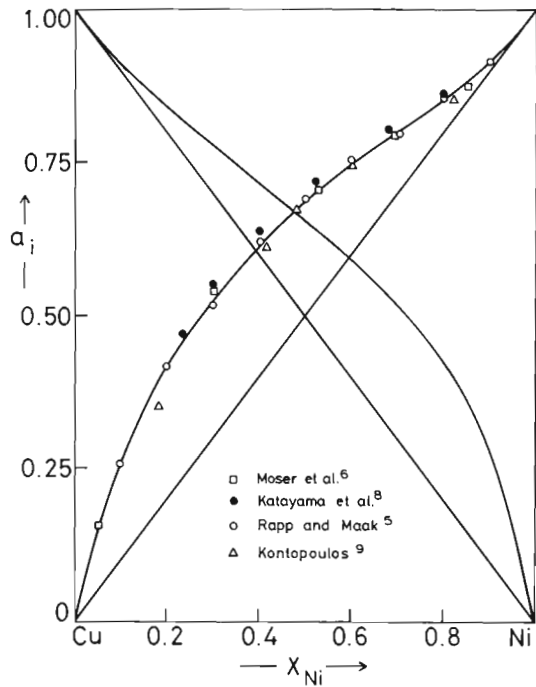
Elliott.<sup>37</sup> The values of enthalpy for liquid Cu-Ni alloys reported by Predel and Mohs<sup>38</sup> show large scatter and are lower than the data reported by Dokken and Elliott.<sup>36</sup> Von Samson-Himmelstjerna<sup>40</sup> measured heat contents of liquid alloys by pouring the alloys into a calorimeter at room temperature. However, this method is somewhat crude. El'Khasan *et al.*<sup>39</sup> report high exothermic values for the enthalpy of mixing ( $\Delta H_{max} = 8 \text{ kJ mol}^{-1}$ ) at 1773 K and their results are not compatible with other calorimetric studies. They used a graphite resistance tube for heating which possibly contaminated the nickel with carbon. Hence, the values of enthalpy of mixing given by Von Samson-Himmelstjerna<sup>40</sup> and El'Khasan *et al.*<sup>39</sup> are rejected. The values for the enthalpy of mixing chosen in the present evaluation are based on the calorimetric studies of Dokken and Elliott<sup>36</sup> extended to the entire concentration range by a subregular solution model. It can be represented by an empirical expression of the form

$$\Delta H = X_{Ni}(1 - X_{Ni})[11577 - 523(1 - 2X_{Ni})] \text{ J mol}^{-1} \quad (15)$$

with reference to pure liquid components as standard states. Combining equations (14) and (15) an expression for the excess entropy in liquid Cu-Ni alloys is derived as

$$\Delta S^E = X_{Ni}(1 - X_{Ni})[-1.189 + 0.445(1 - 2X_{Ni}) - 0.838(1 - 2X_{Ni})^2] \text{ J mol}^{-1} \text{ K}^{-1} \quad (16)$$

The integral enthalpy and excess entropy for liquid Cu-Ni alloys are shown as a function of composition in Fig. 8. The values of partial excess Gibbs' energy at 1673 K can be combined with the values of partial enthalpy obtained in the present evaluation to derive values of excess partial Gibbs' energy at other temperatures. Values for excess partial Gibbs' energy derived from the present evaluation at two temperatures are shown in Fig. 7 in comparison with those reported in the literature. It can be seen that the results of the present evaluation on liquid alloys are in



9 Relationship between  $a_i$  and  $X_{Ni}$  in solid Cu-Ni alloy at 1273 K

better agreement with those of Tomiska and Neckel<sup>31</sup> than those suggested by Mey.<sup>26</sup>

Thermodynamic properties of solid alloys

Values of enthalpy and entropy of solid Cu-Ni alloys were derived using the thermodynamic properties of liquid alloys evaluated in the present study, the equilibrium phase diagram reported in the literature,<sup>21</sup> and the results of activity and partial entropy measurements on solid alloys obtained in the present study using an optimisation procedure. The enthalpies, entropies, and temperatures of fusion of pure copper and nickel required for the conversion of standard states were taken from the compilation of Barin and Knacke.<sup>35</sup> The optimised values of enthalpy and excess entropy for solid Cu-Ni alloys can be represented, respectively, by the empirical expressions

$$\Delta H = X_{Ni}(1 - X_{Ni})[10\,321 - 2625(1 - 2X_{Ni}) + 544(1 - 2X_{Ni})^2] \text{ J mol}^{-1} \quad (17)$$

$$\Delta S^E = X_{Ni}(1 - X_{Ni})[-1\,706 - 1\,272(1 - 2X_{Ni}) - 0\,538(1 - 2X_{Ni})^2] \text{ J mol}^{-1} \text{ K}^{-1} \quad (18)$$

The values of integral enthalpy and excess entropy for solid Cu-Ni alloys are shown in Fig. 5 in comparison with those given by Mey.<sup>26</sup> Values of partial entropy of mixing obtained in this evaluation are compared in Fig. 6 with the direct measurements using the entropy meter apparatus.

The values of excess integral entropy for solid Cu-Ni alloys derived in the present work are negative over the entire concentration range with a minimum ( $-0\,49 \text{ J mol}^{-1} \text{ K}^{-1}$ ) at  $X_{Ni} \sim 0\,3$ . Integral enthalpies for solid Cu-Ni alloys evaluated in the present study reach a maximum value of  $2620 \text{ J mol}^{-1}$  at  $X_{Ni} \sim 0\,56$ . This compares well with the value of  $2260 \text{ J mol}^{-1}$  for an equiatomic alloy reported by Kubaschewski *et al.*<sup>11</sup> The values of the integral enthalpy of mixing derived in the present study are higher than those reported by Oriani and Murphy<sup>10</sup> and Elford *et al.*,<sup>12</sup> but are lower than the values reported by Leach and Bever.<sup>13</sup> The experimental data of Elford *et al.*<sup>12</sup> are associated with large scatter. They observed a non-characteristic drop in the enthalpy of mixing in the composition range  $X_{Ni} \sim 0\,5-0\,7$ , because of

a magnetic transformation. Results in this composition range were derived by interpolation in their study. Positive values for  $\Delta H$  and negative values for  $\Delta S^E$  are consistent for a system that exhibits clustering or immiscibility at lower temperatures.

Activity data for solid Cu-Ni alloys obtained in the present study at 1000 K can be extrapolated to higher temperatures using the evaluated values of partial enthalpy. It is of interest to compare the activity data obtained at 1273 K using this method with direct measurements. Activity of nickel reported by Rapp and Maak,<sup>5</sup> Moser *et al.*,<sup>6</sup> Katayama *et al.*,<sup>8</sup> and Kontopoulos<sup>9</sup> at 1273 K are in good agreement within the limits of experimental uncertainty with the evaluated data as shown in Fig. 9.

The behaviour of the  $\alpha_{Ni}$  function with composition (Fig. 4) obtained in the present study shows a change in slope at  $X_{Ni} \sim 0\,3$ . A similar behaviour in the  $\alpha_{Ni}$  function for solid Cu-Ni alloys was also observed by Rapp and Maak.<sup>5</sup> The change in slope signifies a slight increase in the activity coefficients of nickel and copper when the vacant states in the 3d band are occupied. The excess entropy function for solid Cu-Ni alloys obtained in the present study (Fig. 5) also has a minimum value when  $X_{Ni} \sim 0\,3$ . These observations on the thermodynamic behaviour for solid Cu-Ni alloys are consistent with the suggestion of Schmidt<sup>3</sup> that the vacancies in the 3d band of nickel are filled up to copper concentrations of 70 at.-%. It can be inferred from the behaviour of excess entropy that as the 3d band of nickel is filled, the excess entropy decreases, corresponding to a minimum value for a completely filled 3d band, and subsequently increases as the electrons occupy the energy levels of the 4s band. The 4s band in nickel has lower energies than the 3d band, characteristic of transition metals. However, since the 3d band of nickel has a much higher density of states than the 4s band, alloying of copper to nickel results in the filling of the former.

Solid state miscibility gap and chemical spinodal boundary

Using the thermodynamic properties of solid alloys evaluated in the present study, the binodal and spinodal boundaries can be calculated by standard methods reported in the literature.<sup>41</sup> At the binodal boundaries the equilibrium conditions are

$$\mu_{Ni}(X_1, T) = \mu_{Ni}(X_2, T) \quad (19)$$

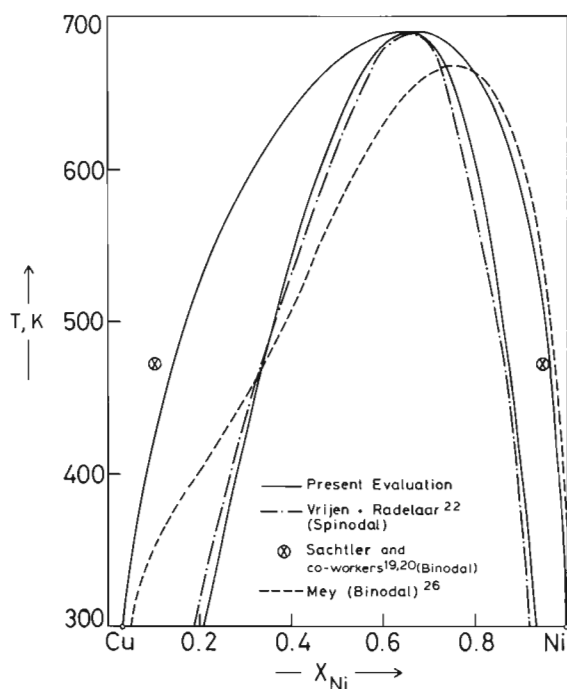
$$\mu_{Cu}(X_1, T) = \mu_{Cu}(X_2, T) \quad (20)$$

where  $\mu_i$  indicates the chemical potential of component  $i$  and  $X_1$  and  $X_2$  indicate the mole fractions of Ni at the boundaries of the miscibility gap at temperature  $T$ . Equations (19) and (20) can be solved simultaneously at specific values of  $T$  to determine the binodal points. The spinodal curve is the locus of the solution of the equation

$$(\partial^2 G^m / \partial X_{Ni}^2)_T = 0 \quad (21)$$

for various values of temperature  $T$ . The binodal and spinodal curves are shown in Fig. 10 for the Cu-Ni system using the thermodynamic properties of solid alloys evaluated in the present study.

The only available experimentally determined limits of the solid state miscibility gap in Cu-Ni system are those reported by Sachtler and co-workers<sup>19,20</sup> from their X-ray study of alloy films at 473 K. They report segregation into two fcc phases at this temperature, one containing  $>95\%$  Ni, the other containing 10% Ni. Results of the present evaluation at 473 K are in good agreement with those of Sachtler and co-workers<sup>19,20</sup> as shown in Fig. 10. The thermodynamic evaluation of the solid state miscibility gap has been carried out by many investigators.<sup>5,12,18,26</sup> Rapp and Maak<sup>5</sup> used the enthalpy values derived from the values of free energy at 973 and 1273 K to evaluate the



10 Binodal and spinodal curves for fcc phase in Cu-Ni system calculated in present work compared with data measured by various authors

boundary of the binodal curve. Values of enthalpy derived using this procedure are associated with a large uncertainty. Elford *et al.*<sup>12</sup> used their measured values of enthalpy and the values of free energy of Rapp and Maak<sup>5</sup> for solid Cu-Ni alloys to calculate the binodal curve. However, as mentioned earlier, the values of enthalpy of mixing derived in Ref. 12 show a sharp drop between  $X_{Cu} = 0.5$  and  $0.7$ , and values in this concentration range have been obtained by interpolation. Meijering<sup>18</sup> used a regular solution approximation for the free energy of mixing to calculate the solid state miscibility gap in the ternary Ni-Cr-Cu system and in the constituent binaries. Mey<sup>26</sup> calculated the limits of the miscibility gap using her assessed data. The results obtained in some of these studies are compared in Fig. 10. Vrijen and Radelaar<sup>22</sup> used a diffuse neutron scattering technique, combined with the model of Clapp and Moss,<sup>23-25</sup> to determine the spinodal boundary and the critical point. The present evaluation of the spinodal boundary and the critical point yields values in good agreement with those of Vrijen and Radelaar.<sup>22</sup> The critical point in the present evaluation is located at  $X_{Ni} = 0.67$  and  $T_c = 690$  K.

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