

## THERMODYNAMIC PROPERTIES OF BINARY LIQUID THALLIUM–SELENIUM SOLUTIONS

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### ABSTRACT

The e.m.f. of liquid solutions of thallium and selenium with respect to thallium was investigated in the temperature range 663–763 K, thallium being the more electropositive component. Activities and the partial molar properties  $G$ ,  $H$ , and  $S$  of both components at 738 K are reported.

### INTRODUCTION

Much work has been devoted to the determination of the Tl–Se phase diagram [1–7]. The integral enthalpy of formation of the melts has been measured by calorimetry [8–11], and the heat capacities at constant pressure of TlSe and Tl<sub>2</sub>Se have also been measured [12–15].

To study the thermodynamic properties of liquid alloys a useful procedure is the measurement of the electrochemical potential of the solution with respect to the more electropositive metal. Compared with other methods usable at moderately elevated temperatures, this has proved to be an exceptionally precise means for determining the partial molar free energy, entropy, and heat content of a component [16–20].

The purpose of this paper is to present the results of an electrode potential study of the liquid binary solutions of thallium and selenium.

### APPARATUS

#### *Principles*

The cell used in the temperature range 663–763 K was  
 $(-)\text{Tl}(l)/\text{Tl}^{n+}(1, \text{soln}, \text{KCl} + \text{LiCl})/\text{Se}_x\text{Tl}_{1-x}(1)(+)$

At the electrodes the following equilibria are established:

anode



cathode



where Tl(l) represents pure liquid thallium, Tl(l, soln) represents thallium in a liquid alloy.

The driving force for the transfer of thallium from the anode to the cathode is represented by the e.m.f. of the reversible cell given by

$$G(\text{Tl, soln, l}) = RT \ln a(\text{Tl, soln, l}) = -nFE \quad (1)$$

$G(\text{Tl, soln, l})$  is the free energy change of one mole of thallium isothermally transferred from the pure state into a very large quantity of alloy of the cathode composition, i.e. the partial molar free energy of thallium in the alloy, with respect to pure liquid thallium at the same temperature as the reference state.  $F$  is the Faraday equivalent or  $96485.309 \text{ C mol}^{-1}$  [21],  $a(\text{Tl, soln, l})$  is the activity of thallium in the cathode alloy,  $T$  is the absolute temperature in Kelvin, and  $n$  the valence of metal ions (here  $\text{Tl}^{+}$ ) in the electrolyte.

The entropy change for the transfer of thallium is obtained from the temperature coefficient of the cell potential

$$S(\text{Tl, soln, l}) = nF(\delta E/\delta T) \quad (2)$$

and the change of the heat content may be calculated by substituting eqns. (1) and (2) into the Gibbs–Helmholtz equation

$$H(\text{Tl, soln, l}) = nF[T(\delta E/\delta T) - E] \quad (3)$$

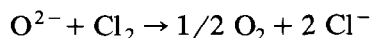
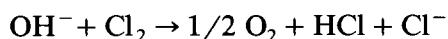
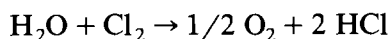
### *Experimental procedure*

#### *Preparation of the electrolyte*

The supporting electrolyte is a eutectic mixture ( $T_{\text{fus}} = 631 \text{ K}$ ) of 48.5 mole% KCl and 51.5 mole% LiCl. The procedure used here is derived from methods described by Boston and Smith [22], Maricle and Hume [23] and Hayer [24].

To avoid side reactions special care was taken to prepare the salt mixture free of water or oxide. At 723 K the mixture of reagent grade KCl and LiCl (Prolabo, 99.5% purities) is placed on a fritted disk and melted under purified argon over 1 h. Then chlorine is passed through the melt until the cloudiness of the molten mixture disappears, the gas being dispersed by the

fritted disk into a stream of fine bubbles. Chlorine gas at 723 K removes water,  $\text{OH}^-$ , and  $\text{O}^{2-}$  according to the following reactions



To remove excess chlorine argon was then bubbled through the melt for 1 h.

The eutectic mixture was filtered through the disk into a tube to remove insoluble impurities. The tube containing the mixture was then sealed under purified argon and stored for later use.

The electrolyte is a mixture of KCl–LiCl eutectic and a small amount of TiCl (less than 1%). TiCl is a Koch–Light product with impurities of less than  $10^{-3}$  %.

### *Preparation of the alloys*

In order to prevent oxidation, alloys were prepared by direct fusion of the pure elements in a silica tube sealed under vacuum (1 hPa). Thallium and selenium are Koch–Light chemicals with a purity of 5N. Thallium was treated with 0.1N  $\text{H}_2\text{SO}_4$ , and selenium was cleaned prior to use (to remove the oxide surface layer) by melting in vacuum and filtering through silica wool under purified argon.

### *The electrochemical cell*

The electrochemical cell used in all the experiments was made of silica glass. Its general design is shown in Fig. 1.

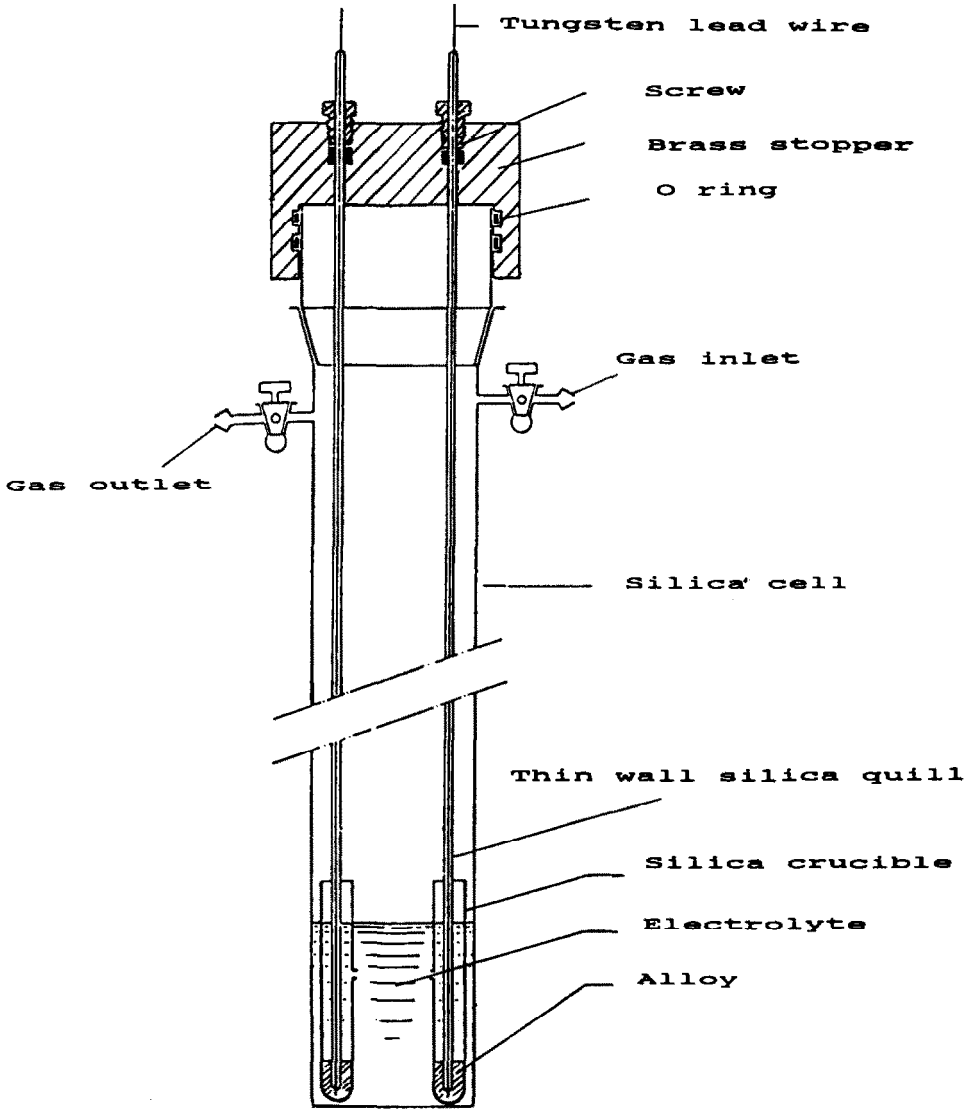
During a run the cell was positioned in a vertical tube furnace ROK/F (Heraeus) equipped with a Kelvitron temperature controller (Eurotherm).

Alloys and pure thallium metal were placed in silica crucibles and these positioned in the silica cell. The tungsten lead wires were enclosed in thin-wall silica quills. In preparing for a run, the tips of the tungsten leads were cleaned by electrolyzing them as anode in a concentrated aqueous solution of NaOH.

### *E.m.f. measurements*

E.m.f. and temperature are continuously measured with a Keithley model 193 multimeter, combined with a Keithley model 705 scanner, equipped with a field-installable low current multiplexer model 7059 plug-in card. This multiplexer is capable of switching up to 10 channels in a programmable sequence.

Both scanner and multimeter use the IEEE-488 standard interface bus for control and data read-out. It is therefore possible to incorporate the



**Electrochemical cell**

Fig. 1. Cell design.

scanner/multimeter combination described into any measurement system that uses programmed control through the IEEE-488 bus.

In this manner the single model 193 multimeter and the scanner could monitor the e.m.f. of up to 10 electrochemical cells synchronously.

By connecting the trigger inputs of the two instruments with a micro-computer (Olivetti M19, with an IBM IEEE-448 card) a complete measurement sequence could be performed automatically. E.m.f. data obtained at each

temperature point measured were first stored by the multimeter in data store mode and then transferred to the computer via the IEEE-448 bus.

The electrodes were immersed in the molten electrolyte and the cell was held at 670 K for several hours until the e.m.f. had reached a stable state. Temperature was then increased to 770 K at a rate of 6 K h<sup>-1</sup> and cooled down again at the same rate. The e.m.f. of each cell was read continuously as programmed by the scanner. At temperature steps of approximately 30 K the silica cell was held at constant temperature for 4 h and the e.m.f. was recorded during this period. These isothermal measurements agreed with those determined on heating and on cooling.

Temperature was measured with a Pt/Pt-10% Rh thermocouple connected to the multiplexer/scanner. Before reading each e.m.f. value, the temperature channel of the scanner was selected and the temperature was recorded. The temperature difference between two measurements was less than 0.4 K in the range 663–763 K.

To determine the experimental error of the e.m.f. data, two standard anodes were placed in a single cell, and the potential difference between them was measured. Voltages measured were approximately 0.3 mV or less.

The model 193 multimeter was verified with a voltage calibrator (Weston cell): 200 mV and 2 V inputs led to multimeter readings between 199.982 and 200.018 mV or 1.99984 and 2.00016 V, respectively.

Software for measurement control and data acquisition has been developed in the BASIC programming language in our laboratory.

## EXPERIMENTAL RESULTS, DISCUSSION AND CONCLUSION

E.m.f. measurements were carried out on 8 alloys. For all these alloys the data showed very little scatter and varied linearly with temperature within the precision of the measurements and the temperature range studied.

TABLE 1

Cell voltages as a linear function of temperature. Coefficients obtained by least squares fitting of experimental data

$X_{Ti}$	$E$ (mV) = $a + bT$ (K) between 663 and 764 K
0.10	$E = (474.85 \pm 0.70) + (0.376 \pm 0.007)T$
0.20	$E = (517.91 \pm 1.75) + (0.240 \pm 0.015)T$
0.30	$E = (534.32 \pm 2.41) + (0.160 \pm 0.011)T$
0.40	$E = (535.47 \pm 1.20) + (0.070 \pm 0.012)T$
0.50	$E = (536.34 \pm 0.98) - (0.111 \pm 0.011)T$
0.60	$E = (408.63 \pm 0.83) - (0.010 \pm 0.008)T$
0.63	$E = (336.65 \pm 5.55) - (0.124 \pm 0.062)T$
0.67	$E = (354.06 \pm 1.43) - (0.159 \pm 0.016)T$

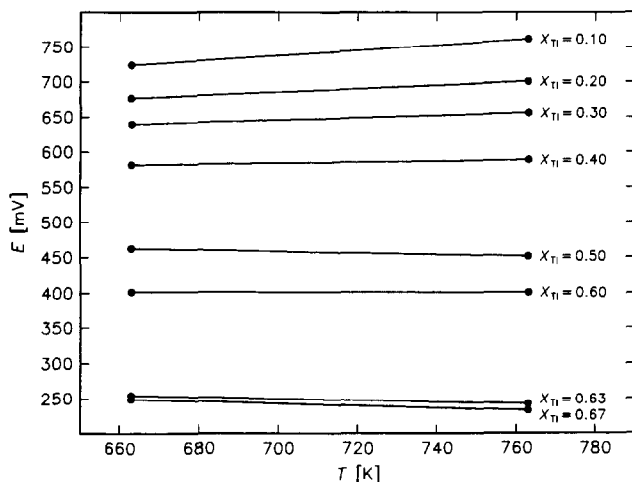


Fig. 2. Experimental cell voltages as a function of temperature.

E.m.f. data were subjected to a linear regression according to the equation  $E = a + bT$ . By means of least squares fitting, the coefficients  $a$  and  $b$  were obtained. Table 1 lists the measured data, and the fitted lines are shown in Fig. 2. The activity  $a(\text{Tl}, \text{l}, \text{soln})$  of thallium in liquid alloys, from equations  $E = f(T)$ , is obtained for 738 K.

From the activity values  $a(\text{Tl}, \text{l}, \text{soln})$  at this temperature we calculated the partial molar free enthalpy  $G(\text{Tl}, \text{l}, \text{soln})$ , and the partial molar enthalpy  $H(\text{Tl}, \text{l}, \text{soln})$  of thallium with respect to pure liquid thallium at 738 K as the reference state.

By integration of the Gibbs–Duhem equation [25] it was also possible to determine the respective values for selenium, i.e.  $a(\text{Se}, \text{l}, \text{soln})$ ,  $G(\text{Se}, \text{l}, \text{soln})$  and  $H(\text{Se}, \text{l}, \text{soln})$  referred to pure liquid selenium at 738 K.

Table 2 lists the activity values of thallium and selenium in the liquid alloys  $\text{Se}_x\text{Tl}_{1-x}$ .

TABLE 2

Cell voltages and activities of thallium and selenium in the liquid alloys  $\text{Se}_x\text{Tl}_{1-x}$  at 738 K

$X_{\text{Tl}}$	$E$ 738 K (V)	$a(\text{Tl}, \text{l}, \text{soln})$	$a(\text{Se}, \text{l}, \text{soln})$
0.10	0.7523	$7.279 \times 10^{-6}$	0.8959
0.20	0.6950	$1.793 \times 10^{-5}$	0.7614
0.30	0.6524	$3.505 \times 10^{-5}$	0.6020
0.40	0.5871	$9.785 \times 10^{-5}$	0.3405
0.50	0.4552	$7.788 \times 10^{-4}$	0.0616
0.60	0.4013	$1.818 \times 10^{-3}$	0.0206
0.63	0.2481	$2.023 \times 10^{-2}$	0.0004
0.67	0.2360	$2.445 \times 10^{-2}$	0.0003

TABLE 3

Partial and integral free enthalpy data for Tl–Se liquid alloys derived from e.m.f. measurements at 738 K (referred to the pure liquid components)

$X_{\text{Tl}}$	$G(\text{Tl, l, soln})$ (kJ mol <sup>-1</sup> )	$G(\text{Se, l, soln})$ (kJ mol <sup>-1</sup> )	$\Delta G_{\text{mix}}$ (kJ mol <sup>-1</sup> )
0.10	-72.591	-0.674	-7.866
0.20	-67.061	-1.673	-14.750
0.30	-62.948	-3.114	-21.064
0.40	-56.648	-6.611	-26.625
0.50	-43.920	-17.100	-30.510
0.60	-38.717	-23.814	-32.755
0.63	-23.935	-47.389	-32.613
0.67	-22.770	-49.589	-31.620

Table 3 gives the partial and integral free enthalpies of both components in the liquid alloys  $\text{Se}_x\text{Tl}_{1-x}$  with respect to the pure liquid elements.

The respective values of the partial and integral enthalpies are shown in Table 4.

From the free enthalpy data obtained by e.m.f. measurements and from enthalpy data measured earlier by calorimetry [4] we were able to calculate the integral entropy of mixing from the relation  $\Delta G_{\text{mix}}(\text{e.m.f.}) = \Delta H_{\text{mix}}(\text{calorimetry}) - T * \Delta S_{\text{mix}}$ . Table 5 lists the molar entropy of mixing at 738 K.

The complete set of integral thermodynamic functions obtained (mixing, ideal, and excess) is listed in Table 6 and plotted as a function of composition in Fig. 3.

The comparison of the integral molar enthalpies of mixing of the alloys  $\text{Se}_x\text{Tl}_{1-x}$  at 738 K with those obtained by us by calorimetry [4] shows good agreement between both series of results. The difference between the en-

TABLE 4

Partial and integral enthalpy data for Tl–Se liquid alloys derived from e.m.f. measurements at 738 K (referred to the pure liquid components)

$X_{\text{Tl}}$	$H(\text{Tl, l, soln})$ (kJ mol <sup>-1</sup> )	$H(\text{Se, l, soln})$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{mix}}$ (kJ mol <sup>-1</sup> )
0.10	-45.817	0.071	-4.518
0.20	-49.971	0.821	-9.337
0.30	-51.554	1.358	-15.058
0.40	-51.663	1.418	-19.815
0.50	-51.753	1.493	-25.130
0.60	-39.429	-13.011	-28.862
0.63	-32.479	-24.131	-29.390
0.67	-34.163	-20.991	-29.820

TABLE 5

Entropy of mixing at 738 K obtained from the relation  $\Delta G_{\text{mix}}(\text{e.m.f.}) = \Delta H_{\text{mix}}(\text{cal}) - T \cdot \Delta S_{\text{mix}}$  (referred to the pure liquid components)

$X_{\text{Tl}}$	$\Delta G_{\text{mix}}(\text{e.m.f.})$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{mix}}(\text{cal})$ (kJ mol <sup>-1</sup> )	$\Delta S_{\text{mix}}$ (J mol <sup>-1</sup> )
0.10	-7.866	-4.468	4.604
0.20	-14.750	-10.644	5.564
0.30	-21.064	-16.271	6.495
0.40	-26.625	-21.572	6.847
0.50	-30.510	-25.679	6.546
0.60	-32.755	-29.560	4.329
0.63	-32.613	-30.330	3.093
0.67	-31.620	-31.223	0.538

TABLE 6

Summary of thermodynamic values for Tl-Se liquid alloys at 738 K

$X_{\text{Tl}}$	$\Delta G_{\text{mix}}$ (J mol <sup>-1</sup> )	$\Delta H_{\text{mix}}$ (J mol <sup>-1</sup> )	$T\Delta S_{\text{mix}}$ (J mol <sup>-1</sup> )	$\Delta G_{\text{id}}$ (J mol <sup>-1</sup> )	$\Delta G_{\text{ex}}$ (J mol <sup>-1</sup> )	$T\Delta S_{\text{ex}}$ (J mol <sup>-1</sup> )
0.00	0	0	0	0	0	0
0.10	-7866	-4468	3398	-1995	-5871	1403
0.20	-14750	-10644	4106	-3070	-11680	1036
0.30	-21064	-16271	4793	-3748	-17316	1045
0.40	-26625	-21572	5053	-4129	-22496	924
0.50	-30510	-25679	4831	-4253	-26257	578
0.60	-32755	-29560	3195	-4129	-28626	-934
0.63	-32613	-30330	2283	-4043	-28570	-1760
0.67	-31620	-31223	397	-3891	-27729	-3494

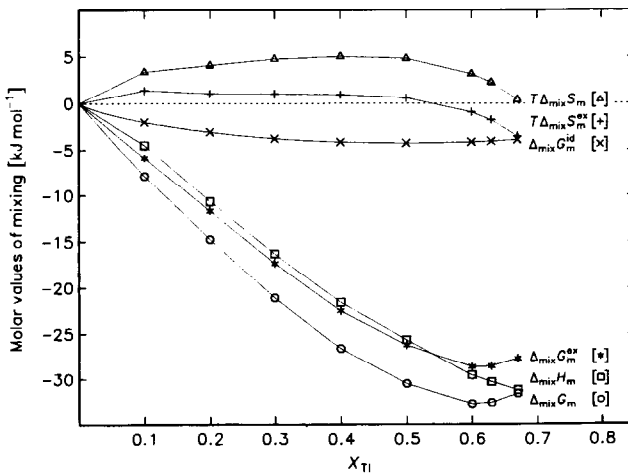


Fig. 3. Thermodynamic values (integral, ideal, excess) of liquid alloys  $\text{Tl}_x\text{Se}_{1-x}$ .



TABLE 7

Comparison between integral molar enthalpies of mixing obtained by e.m.f and those obtained by calorimetry at 738 K (referred to the pure liquid components)

$X_{Tl}$	$\Delta H_{mix}(emf)$ (kJ mol <sup>-1</sup> )	$\Delta H_{mix}(cal)$ (kJ mol <sup>-1</sup> )	$\delta\Delta H_{mix}$ (kJ mol <sup>-1</sup> )	$R(\%)$
0.10	-4.518	-4.468	0.050	1.1
0.20	-9.337	-10.644	-1.307	12.3
0.30	-15.058	-16.271	-1.213	7.5
0.40	-19.815	-21.572	-1.722	8.0
0.50	-25.130	-25.679	-0.549	2.1
0.60	-28.862	-29.560	-0.698	2.4
0.63	-29.390	-30.330	-0.940	3.1
0.67	-29.820	-31.223	-1.403	4.5

thalpies obtained by different methods was less than 1.5 kJ mol<sup>-1</sup> for all the alloys investigated, the absolute error being always less than 12.3% referred to calorimetric data. These results are summarized in Table 7. The good agreement of both data sets confirms the validity of our results.

The results of the activity measurements are in good agreement with the values found by Zaleska et al. [16].

The plots of excess molar thermodynamic functions of mixing ( $\Delta G_{mix}^{ex}$ ,  $\Delta H_{mix}$ ,  $T * \Delta S_{mix}^{ex}$ ) versus  $X_{Tl}$  in Fig. 3 show a minimum for the composition corresponding to the existence of the most stable compound  $Tl_2Se$ .

Excess entropy of mixing has positive values up to a thallium concentration of  $X_{Tl} = 0.55$ . This could be explained by the neighbourhood of the miscibility gap in the concentration range around  $X_{Tl} = 0.1$  found by Kanda et al. [2], Brättner et al. [5], and Pettit and Camp [26]. They report a critical temperature of 727, 729.5, and 721.6 K, respectively. Obviously, the forces giving rise to demixing are responsible for the positive entropy effect in this concentration range since our data apply to a temperature only about 10 K above the reported critical point. On the other hand  $C_p$  measurements of solid and liquid  $Tl_2Se$  carried out in our laboratory [15] show a rapid decrease of excess  $C_p$  of the liquid alloy with increasing temperature. This could be understood by assuming the presence of associates in the melt. This view is supported by the strong exothermic enthalpy of mixing of the liquid alloys. Obviously the strong negative enthalpy effect of the formation of associates of formulae  $TlSe$  and  $Tl_2Se$  overwhelms the small positive entropy effect of the miscibility gap, resulting in excess enthalpy and entropy of unlike sign.

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## REFERENCES

- 1 A.P. Obukhov and N.S. Bubyrrera, *Iz. Sektora Fiz. Khim. Anal.*, 19 (1949) 276.
- 2 A.F. Kanda, R.C. Faxon and D.V. Keller, *Phys. Chem. Liquids*, 1 (1968) 61.
- 3 T.S. Kabre, Thèse de Doctorat d'état es sciences physiques, Université Paris VI, Paris, 1974.
- 4 A. Tausend and D. Wobig, *Z. Phys. Chem., Neue Folge*, 96 (1975) 199.
- 5 P. Brättner, H. Busse, M. Scheiba and D. Wobig, *Z. Phys. Chem., Neue Folge*, 110 (1978) 29.
- 6 M. Mushiage, K. Tamura, H. Hoshino and H. Endo, *J. Phys. Soc. Jpn.*, 48 (1980) 1702.
- 7 G. Morgant, B. Legendre, S. Maneglier-Lacordaire and C. Souleau, *Ann. Chim. Fr.*, 6 (1981) 315.
- 8 E.Y. Turkina and G.M. Orlova, *Zh. Neorg. Khim.*, 28 (1983) 1351.
- 9 T. Maekawa, T. Yokokawa and K. Niwa, *J. Chem. Thermodyn.*, 3 (1971) 707.
- 10 T. Maekawa, T. Yokokawa and K. Niwa, in S. Takeuchi (Ed.), *Properties of Liquid Metals*, Proc. 2nd. Int. Conf., 1972, Taylor and Francis, London, 1972, pp. 501–505.
- 11 G. Morgant, B. Legendre, C. Souleau and J.-R. Didry, *Ann. Chim. Fr.*, 6 (1981) 661.
- 12 V.P. Vasil'ev, A.V. Nikol'skaya, A.G. Bachinskaya and Ya.I. Gerasimov, *Dokl. Akad. Nauk SSSR*, 176 (1967) 1335.
- 13 G. Brekow, M. Meibner, M. Scheiba, A. Tausend and D. Wobig, *J. Phys. C, Solid State Phys.*, 6 (1973) L462.
- 14 G. Brekow, M. Meibner, M. Scheiba, A. Tausend and D. Wobig, *J. Phys. C, Solid State Phys.*, 8 (1975) L456.
- 15 G. Morgant, B. Legendre and C. Souleau, *Ann. Chim. Fr.*, 7 (1982) 301.
- 16 E. Zaleska and J. Terpilowski, *Rocz. Chem.*, 39 (1965) 527.
- 17 J. Terpilowski, E. Zaleska and W. Gawel, *Rocz. Chem.*, 42 (1968) 1845.
- 18 Y. Nakamura and M. Shimoji, *Trans. Faraday Soc.*, 65 (1969) 1509.
- 19 V.P. Vasil'ev, A.V. Nikol'skaya and Ya.I. Gerasimov, *Dokl. Akad. Nauk SSSR*, 188 (1969) 1318.
- 20 V.P. Vasil'ev, A.V. Nikol'skaya and Ya.I. Gerasimov, *Zh. Fiz. Khim.*, 45 (1971) 2061.
- 21 I. Mills, *Quantities, Units and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Oxford, 1988.
- 22 C.B. Boston and G.P. Smith, *J. Phys. Chem.*, 62 (1958) 409.
- 23 D.L. Maricle and D.N. Hume, *J. Electrochem. Soc.*, 107 (1960) 354.
- 24 E. Hayer, Thesis, University of Vienna, 1969.
- 25 L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953.
- 26 R.B. Pettit and W.J. Camp, *Phys. Rev. Lett.*, 32 (1974) 369.