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Note

Thermodynamic investigation of the Rh–Ge and Ir–Ge binary alloys

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Abstract

The enthalpies of formation $\Delta_f H_m$ of the Ir–Ge and Rh–Ge alloys were measured at 1266 K with respect to composition by direct reaction calorimetry (drop method) with the help of high temperature Calvet-type calorimeters. The values lead to the following equation valid for $0 < x_{Ir} < 0.21$ and $0 < x_{Rh} < 0.32$

$$\Delta_f H_m/\mathrm{kJ\,mol^{-1}} = x_{Ir}(1 - x_{Ir})(-112.47 - 372.44x_{Ir} + 1095.47x_{Ir}^2)$$

$$\Delta_f H_m/\mathrm{kJ\,mol^{-1}} = -121.2x_{Rh}$$

a6 The thermodynamic behaviour of the melts is characterized by strong negative deviations from ideality suggesting some chemical short-range order. It will be interesting to investigate in future work the thermodynamic properties of these two binaries in the concentrated range and their temperature dependence.

INTRODUCTION

Thermodynamic data concerning the two systems investigated are very scarce. The phase diagram of the iridium–germanium binary is unknown and that of the rhodium–germanium was only tentatively established in 1956 [1]. There are many intermediate compounds in both systems (IrGe, Ir_3Ge_4 (?), Ir_3Ge_7 and Ir_4Ge_5, Rh_3Ge_4, RhGe, Rh_5Ge_3 and Rh_2Ge) according to [2] and [3], but their melting temperatures are unknown. To our knowledge there is no information about the thermodynamic function of formation of the liquid and solid phases. Therefore we carried out calorimetric determinations of the enthalpy of formation of the two systems. These binary systems occur among the alloys formed by transition

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metals with elements of group IVA of the Periodic Table, i.e. systems showing strong departures from ideality (for example, Pt–Ge and Pd–Ge [4], Pd–Pb [5] and Pt–Pb [6]) and whose behaviour is mainly due to short-range order in the melt [7, 8].

CALORIMETRIC METHOD

The apparatus used was a high-temperature ($T/\mathrm{K} < 1400$) Calvet-type calorimeter built in the laboratory many years ago. The drop method used (direct reaction calorimetry) has already been described [9]. The enthalpy of formation $\Delta_f H_m$ was deduced from the heat effects corresponding to successive additions of small quantities of iridium or rhodium (about 20 to 100 mg according to the concentration range) at T_0 (near 298 K) to an Ir_xGe_{1-x} or Rh_xGe_{1-x} binary alloy placed in an alumina crucible at the bottom of the calorimetric cell at temperature T. Before the first addition of Ir or Rh the melt was pure Ge (about 800 mg).

The thermal effects in the case of Ir–Ge correspond to the reaction

$$n\,\mathrm{Ir(cr, 298\,K)} + m\,\mathrm{Ir}_x\mathrm{Ge}_{1-x}(L, T) \rightarrow (n+m)\mathrm{Ir}_{x+dx}\mathrm{Ge}_{1-x-dx}(L, T)$$

and they lead to the integral enthalpy of formation of the alloys with respect to the content of iridium x. The enthalpy variation used to change the reference state from solid Ir or Rh to liquid Ir or Rh was taken from [10].

The pure metals used were purchased from Koch–Light with metallic impurities less than 10^{-3} mass%. The calibration of the calorimeter was performed by adding some small pieces of α-alumina (U.S. National Bureau of Standards), the enthalpy change of which from T_0 to T is well known [11].

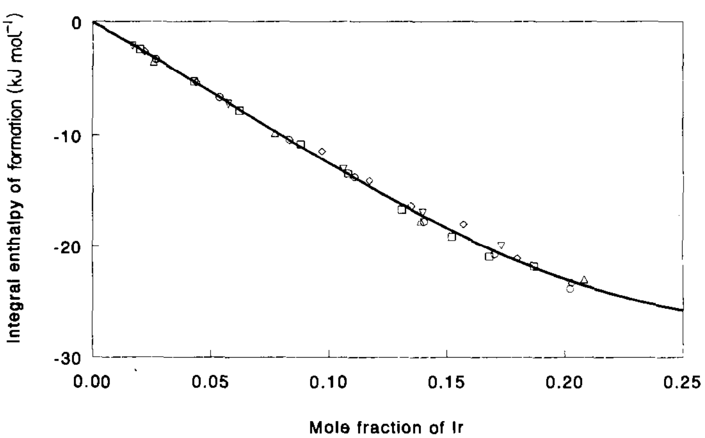

Fig. 1. Molar integral enthalpy of formation of Ir–Ge alloys at 1266 K referred to both liquid components (experimental results). Each symbol corresponds to one measurement.

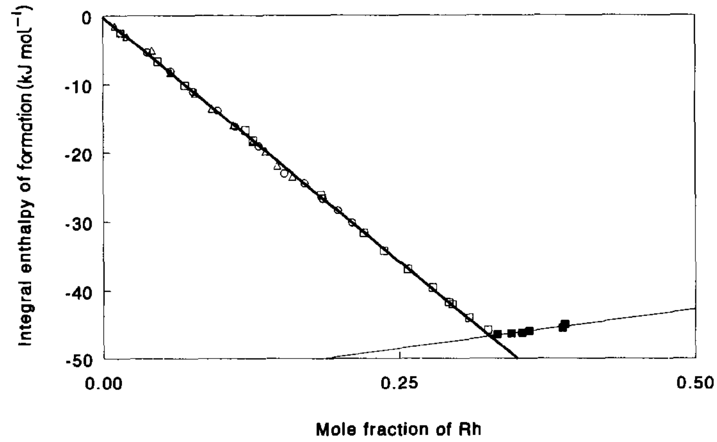

Fig. 2. Molar integral enthalpy of formation of the Rh–Ge alloys at 1266 K referred to both liquid components (experimental results). Each symbol corresponds to one measurement. Open symbols: single liquid phase; solid symbols: two phase region.

TABLE 1

Integral molar enthalpy of formation of Ir–Ge alloys at 1266 K with reference to pure liquid components (experimental results)

x_{Ir}	$\Delta_f H_m$/ kJ mol^{-1}	x_{Ir}	$\Delta_f H_m$/ kJ mol^{-1}
Series 1		Series 2	
0.027	−3.28	0.026	−3.51
0.054	−6.65	0.077	−9.81
0.083	−10.41	0.139	−17.77
0.111	−13.81	0.208	−23.01
0.140	−17.79		
0.170	−20.71	Series 4	
0.202	−23.86	0.022	−2.60
0.020	−2.41	0.044	−5.34
		0.097	−11.50
Series 3		0.117	−14.15
0.043	−5.26	0.135	−16.38
0.062	−7.79	0.157	−18.04
0.088	−10.83	0.180	−21.09
0.108	−13.52	0.203	−23.36
0.131	−16.73		
0.152	−19.14	Series 5	
0.168	−20.93	0.017	−2.10
0.187	−21.83	0.057	−7.22
		0.106	−13.10
		0.140	−16.97
		0.173	−19.96

TABLE 2

Integral molar enthalpy of formation of Rh–Ge alloys at 1266 K with reference to pure liquid components (experimental results)

x_{Rh}	$\Delta_f H_m$/ kJ mol^{-1}	x_{Rh}	$\Delta_f H_m$/ kJ mol^{-1}
Series 1		Series 3	
0.015	−2.52	0.015	−2.54
0.037	−5.35	0.046	−6.71
0.057	−8.12	0.069	−10.16
0.076	−11.03	0.120	−16.73
0.097	−13.78	0.126	−18.20
0.111	−16.19	0.184	−26.06
0.131	−19.00	0.220	−31.63
0.153	−22.96	0.237	−34.21
0.170	−24.35	0.257	−36.92
0.185	−26.58	0.278	−39.58
0.198	−28.34	0.292	−41.70
0.210	−30.11	0.295	−42.04
		0.309	−44.04
Series 2		0.325	−45.79
0.010	−1.51	0.333	−46.45
0.020	−3.03	0.345	−46.31
0.041	−5.10	0.354	−46.23
0.057	−8.30	0.360	−45.99
0.078	−11.27	0.388	−45.52
0.092	−13.48	0.390	−44.98
0.110	−15.97		
0.126	−18.38		
0.137	−19.79		
0.147	−21.82		
0.160	−23.42		

TABLE 3

Selected values of the integral molar enthalpy of formation of Ir–Ge and Rh–Ge melts referred to both liquid components

x_{Ir} or x_{Rh}	$\Delta_f H_m$/kJ mol^{-1}	
	Ir–Ge	Rh–Ge
0.05	−6.10	−6.06
0.10	−12.49	−12.12
0.15	−18.32	−18.18
0.20	−22.90	−24.24
0.21	−23.62	–
0.25	–	−30.30
0.30	–	−36.36
0.32	–	−38.78

RESULTS

The enthalpy of formation of the Ir–Ge and Rh–Ge liquid alloys was determined at 1266 K with respect to the mole fraction of Ir and Rh. Figures 1 and 2 show the molar intergral enthalpy formation of the alloys with reference to the pure liquid components. The corresponding data are given in Tables 1 and 2. They lead to the following equations valid for $0 < x_{\mathrm{Ir}} < 0.21$ and $0 < x_{\mathrm{Rh}} < 0.32$

$$\Delta_f H_m/\mathrm{kJ\,mol^{-1}} = x_{\mathrm{Ir}}(1 - x_{\mathrm{Ir}})(-112.47 - 372.44x_{\mathrm{Ir}} + 1095.47x_{\mathrm{Ir}}^2)$$

$$\Delta_f H_m/\mathrm{kJ\,mol^{-1}} = -121.2x_{\mathrm{Rh}}$$

and to the smoothed data given in Table 3.

As can be seen on Fig. 1, the enthalpy of mixing of the Ir–Ge melts is linear with respect to concentration up to about $x_{\mathrm{Ir}} = 0.1$. At higher Ir content the experimental results are more scattered and the enthalpy exhibits a positive curvature. The enthalpy of mixing of the Rh–Ge melts is linear in the whole range of concentration investigated (Fig. 2). The molar partial enthalpies of Ir and Rh at infinite dilution are, respectively, −112.5 and −121.2 kJ mol^{-1}.

CONCLUSION

The thermodynamic behaviour of the Ir–Ge and Rh–Ge liquid phases investigated exhibits very large negative departures from ideality, corresponding probably to very strong chemical order. Indeed, among the Me–Ge systems, where Me is a noble metal of the Group VIII of the Periodic Table, the more negative partial molar enthalpy at infinite dilution corresponds to rhodium (−121.2 kJ mol^{-1}) and then to iridium (−112.5 kJ mol^{-1}) since we found previously [4] values of −107.4 and −79.0 kJ mol^{-1} for Pt–Ge and Pd–Ge respectively. It will be interesting to investigate in the future the thermodynamic properties of these two alloy systems in the concentrated range and their temperature dependence.

REFERENCES

1 N.N. Zhuravlev and G.S. Zhdanov, Kristallografiya, 1 (1956) 205.
2 M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York, 1958.
3 R.P. Elliott, Constitution of Binary Alloys, 1st Suppl., McGraw-Hill, New York, 1965.
4 R. Castanet, J. Chem. Thermodyn., 14 (1982) 639.
5 M.L. Michel, H. Bros and R. Castanet, Z. Metallkde., in press.
6 A. Amzil and R. Castanet, Ber. Bunsenges. Phys. Chem., in press.
7 R. Castanet and R. Chastel, Z. Metallkde., 78 (1987) 97.
8 R. Castanet, Z. Metallkde., 80 (1989) 737.

9 T. Kang and R. Castanet, J. Less Common Met., 51 (1977) 125.
10 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, American Society of Metals, Metals Park, OH, 1973.
11 Certificate of Standard Reference Material 720, Synthetic Sapphire, U.S. Department of Commerce, N.B.S., Washington, DC, USA.