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Abstract

Full Text

Physical Chemistry

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Investigation of the Thermodynamic Properties of Platinum-Lead Alloys

The thermodynamic functions of the Pt–Pb system were studied in the range 700–875°. Within the indicated temperature limits, the phase diagram of the Pt–Pb system includes two intermetallic compounds, PtPb and Pt₃Pb; a region of liquid solutions (L) within lead concentrations from 1.0 to 0.65–0.47; and four heterogeneous regions: L + PtPb, L + Pt₃Pb, Pt₃Pb + PtPb, and Pt + Pt₃Pb ⁽¹⁾. By the method of measuring saturated vapor pressure (Knudsen effusion method), we determined the activities of lead in alloys with platinum. The apparatus and experimental procedure are described in ⁽²⁾.

To prepare the alloys, platinum of 99.9% purity and spectrally pure lead were used.

The activity a_i , determined by the method of measuring the vapor pressure of one of the components of the alloy–lead—is related to the change in chemical potential by the equation:

$$\Delta\mu_i = RT \ln a_i = RT \ln \frac{p_i}{p_i^0},$$

where a_i is the activity of lead in the alloy, p_i is the saturated vapor pressure of lead over the alloy, and p_i^0 is the saturated vapor pressure of pure lead at the same temperature.

The rate of evaporation of lead from the alloy (the evaporation rate, in accordance with the procedure we used, is proportional to the vapor pressure) was measured in the temperature interval 700–875°; the activity of lead in the alloys was calculated for temperatures 700–790°. The data are given in Table 1.

Table 1

Activity of lead in lead-platinum alloys

Atomic fraction of lead in the alloy, N_{Pb}	Activity of lead a_i , $T = 973^\circ\text{K}$	Activity of lead a_i , $T = 1063^\circ\text{K}$	Atomic fraction of lead in the alloy, N_{Pb}	Activity of lead a_i , $T = 973^\circ\text{K}$	Activity of lead a_i , $T = 1063^\circ\text{K}$
1.0	1.0	1.0	0.514	0.347	0.148
0.921	0.891	0.891	0.385	0.049	0.135
0.832	0.776	0.741	0.193	0.006	0.016
0.734	0.550	0.389	0.113	0.006	0.016
0.545	0.347	0.148			

Next, using known formulas, the partial enthalpies and entropies of formation of the alloys were found and, by graphical integration of the Duhem–Margules equation, the integral enthalpies and entropies of formation of alloys from pure metals. The data on the integral values of enthalpy and entropy for the mean temperature of the interval 700–790° made it possible to calculate changes in the isobaric-isothermal potential.

Table 2

Partial and integral thermodynamic functions for alloys of the lead-platinum system (in the range 973–1063 °K)

Atomic fraction of lead in the alloy, N_{Pb}	$\Delta\bar{H}_{\text{Pb}}$, kcal/g-at	$\Delta\bar{S}_{\text{Pb}}$, cal/g-at · deg	ΔH , kcal/g-at	ΔS , cal/g-at · deg	ΔG , kcal/g-at
1.00	0.00	0.00	0.00	0.00	0.00
0.921	0.20	0.22	1.00	1.60	−0.63
0.832	1.06	1.56	1.40	3.28	−1.94
0.800	2.02	2.71	1.36	3.50	−2.20
0.734	7.90	9.10	0.70	2.90	−2.25
0.700	9.73	11.30	−0.90	2.10	−3.04
0.650	12.60	14.83	−2.94	0.26	−3.20
0.600	16.28	18.55	−5.36	−2.00	−3.32
0.545	19.48	21.70	−8.53	−5.20	−3.23
0.514	19.48	21.70	−10.43	−7.03	−3.27
0.500	19.48	21.70	−11.30	−7.85	−3.31
0.385	−23.11	−17.50	−8.67	−5.64	−2.93
0.250	−21.81	−12.06	−5.47	−3.00	−2.44
0.193	−21.81	−12.06	−4.20	−2.31	−1.85
0.113	−21.81	−12.06	−2.40	−1.35	−1.03

The temperature interval 700–790° was chosen for calculating the thermodynamic properties because here it is convenient to calculate the heats and iso-

Fig. 1. Integral enthalpy of formation of lead-platinum alloys

Figure 1: Fig. 1. Integral enthalpy of formation of lead-platinum alloys

Fig. 2. Integral entropy of formation of lead-platinum alloys

Figure 2: Fig. 2. Integral entropy of formation of lead-platinum alloys

baric potentials of the reactions $3\text{Pt} + \text{Pb} = \text{Pt}_3\text{Pb}$ and $\text{Pt}_3\text{Pb} + 2\text{Pb} = 3\text{PtPb}$, and from these the values for the reactions of formation of Pt_3Pb and PtPb from the metals in the intervals $N_{\text{Pb}} = 0.00 \div 0.25$ and $0.25 \div 0.50$. In the same temperature interval, at $N_{\text{Pb}} > 0.65$, the partial heats of solution of liquid lead in the melt are calculated. The values for melts in the concentration interval $N_{\text{Pb}} = 0.65\text{--}0.55$ are inaccurate, since here the investigated temperature interval includes the liquidus curve.

Fig. 1. Integral enthalpy of formation of lead-platinum alloys

Fig. 2. Integral entropy of formation of lead-platinum alloys

Table 2 gives the partial and integral thermodynamic functions. The error in determining the activity of lead is about 1%, the error in calculating the enthalpy of formation of the alloys is $\sim 20\%$, and that of the entropy is $\sim 25\%$.

It is interesting to note that the integral enthalpy and entropy of formation of the alloy change sign at $N_{\text{Pb}} = 0.65\text{--}0.70$ (Figs. 1 and 2). This is evidently associated with the transition from the region of liquid solutions to heterogeneous regions.

For more accurate calculations of the thermodynamic functions of the melt, especially in the region from ~ 0.65 to 0.545 (in atomic fractions of lead), it would be necessary to ...

to study the melts in greater detail within the indicated concentration limits. It would then have been possible to extrapolate $\Delta\bar{H}_{\text{Pb}}$ from the homogeneous region into the heterogeneous one and to determine these quantities near the liquidus curves.

It must be emphasized, however, that the aim of the work was to determine ΔH and ΔS for solid compounds of lead with platinum.

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Note: Figure translations are in progress. See original paper for figures.

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