

Thermodynamic Properties of Liquid Ag-Si Alloys

HIROSHI SAKAO AND JOHN F. ELLIOTT

The thermodynamic properties of silicon in liquid Ag-Si alloys in the range of 1100 to 1325°C have been measured by an electrochemical cell employing silica-saturated lithium silicate as the electrolyte. The range of composition studied is $0.015 < x_{\text{Si}} < 0.29$. For the change in standard state from pure liquid silicon to silicon at infinite dilution with the composition in atom fraction:

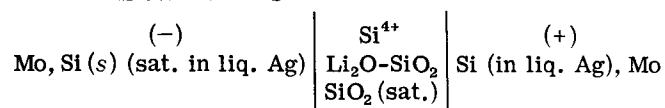
$$\text{Si}(l) = \text{Si}(\text{inf. dil.}): \Delta G^\circ = 5,000 + 5.47 T, (\text{J/g-atom})$$

The results of the study are in good agreement with the measurements on the phase diagram by Hager.

THE thermodynamic properties of silicon in liquid silver-silicon alloys has been a subject of interest for determining the activity of silicon in liquid iron by the distribution method. In this method, the equilibrium distribution of silicon between immiscible layers of liquid iron and liquid silver is measured.¹ The system is also of general interest because it shows only slight deviations from ideal behavior, even though the two components differ materially in chemical and physical properties. This behavior was described by Hager² who determined the liquidus lines and eutectic temperature of the phase diagram, and who used the phase diagram to calculate activities in the system. Measurements of the partial pressure of silver by O'Keefe,³ by Vermandé, Ansara and Desré,⁴ and by Robinson and Tarby⁵ provide information on the whole system. However, these measurements are not of sufficient precision to provide accurate values for the activity of silicon at dilute concentrations. Measurements utilizing the solubility of silicon carbide^{6,7} or silicon nitride⁸ also are relatively imprecise because of the imprecision in our knowledge of the standard free energies of formation of these compounds. A study of possible experimental methods that might be used showed that an electrochemical method was the most promising way for measuring the activity of silicon at dilute concentrations. This paper describes the result of a study using the Emf method.

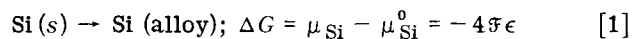
THE EXPERIMENTS

The cell utilized was



The overall process in the cell with the passage of positive current from the left electrode to the right in the cell is the transfer of silicon from a chemical potential of pure solid silicon on the left, μ_{Si}^0 , at its

chemical potential in the Ag-Si solution, μ_{Si} , on the right.



The charge transfer reactions per atom of silicon at each electrode with a silicate electrolyte involved 4 electrons⁹ ($Z = 4$). \mathcal{F} is Faraday's constant, 96,487 coulombs per equivalent. The activity, a_{Si}^s , activity coefficient, γ_{Si}^s , and excess relative partial molar entropy of silicon in the alloys, S_{Si}^{Xs} , all relative to pure solid silicon as indicated by the superscript s , are obtained directly from the reversible potential of the cell, ϵ , as follows:

$$\ln a_{\text{Si}}^s = -Z\mathcal{F}\epsilon/RT \quad [2]$$

$$\ln \gamma_{\text{Si}}^s = -Z\mathcal{F}\epsilon/RT - \ln x_{\text{Si}} \quad [3]$$

$$S_{\text{Si}}^{Es} = Z\mathcal{F}\partial\epsilon/\partial T - R \ln x_{\text{Si}} \quad [4]$$

x_{Si} is the atom fraction of silicon in the liquid alloy.

The design of the cell is shown in Fig. 1. Lithium-silicate was selected as the electrolyte primarily because the standard free energy of formation of Li_2O (per mole of O_2) is approximately 120 kJ more negative than that of silica. Thus, the reduction of lithium into the electrodes by the reaction between silicon and Li_2O is essentially avoided. It is to be noted that preliminary measurements with a sodium-silicate electrolyte met with failure because of the exchange reaction involving silicon and sodium. A second reason for selecting lithium silicate melts for the electrolyte is that there is a eutectic at 19 wt pct Li_2O and 1030°C.¹⁰ Accordingly, the electrolyte can be a mixture of the eutectic liquid and solid particles of pure silica over the temperature range of interest, *i.e.*, 1100 to 1325°C. An electrolyte saturated with silica permitted use of silica as the refractory material for the cell. The average composition of the electrolyte was from 10.5 to 12 wt pct Li_2O .

The electrolyte was prepared by mixing pure powdered silica and ground $\text{Li}_2\text{O-SiO}_2$ of the eutectic composition (19 wt pct Li_2O). The silica powder was prepared by igniting silicic acid (Mallinkrodt analytical reagent grade) in air at 1000°C. The $\text{Li}_2\text{O-SiO}_2$ eutectic powder was prepared by mixing the required amounts of lithium carbonate and silicic acid (Mallinkrodt analytical reagent grade) and igniting them in

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a platinum dish at 1000°C in air. Subsequently, the temperature was raised to 1230°C and the mixture was fused. The cold glassy product was milled to a fine powder in an alumina ball mill. The electrolyte was placed in the cell as a mixed powder or in some cases the mixture was sintered into a cylindrical block in a silica crucible of the size used in the cell. Subsequently, recesses and holes were drilled in the block so that the cell could be assembled with all of the electrodes and leads positioned exactly as required and with the electrolyte in place. Both methods were satisfactory but the second allowed a larger amount of electrolyte to be placed in the cell.

The design of the cell is shown in Fig. 1. The cell crucible, 55 mm I.D. × 50 mm high, and the electrode crucibles, 10 mm I.D. × 15 mm high, were clear quartz glass. The assembly was wrapped in molybdenum foil to protect the furnace tube (porcelain) from attack by possible leakage of the electrolyte or by Li₂O fumes. Radiation shields spaced at intervals of 25 mm above the cell also held the electrode leads in position and prevented serious convective flow of gases in the system. Each cell had four electrodes, one or two were saturated with silicon and served as reference electrodes. The other two or three were Ag-Si cathodes, and in some cells there were one or two Fe-Si cathodes in place of Ag-Si cathodes.

The electrodes were prepared by melting the appropriate weights of silver (99.99 pct pure) and silicon (99.99 pct pure). These electrodes were solidified and then placed within the cell when it was assembled. The compositions of all of the cathode electrodes were determined by chemical analysis of each button on completion of an experiment. The leads were withdrawn from the electrodes prior to shutting down the cell. Seven of the twelve cathode alloys were cut in half and two determinations were made of the compositions. For alloys below 2.0 pct Si, the agreement was within 0.02 wt pct, *i.e.*, 1.79 and 1.77 wt pct. The analyzed compositions were also within a few hundredths percent of the compositions as weighed out, but the average of the chemical determinations was taken as the composition of the alloy. At the higher compositions, the silicon precipitated on cooling and floated to the top of the metal button. Thus, it was unlikely that duplicate determinations would be in good agreement because the silicon might not have been uniformly distributed and some

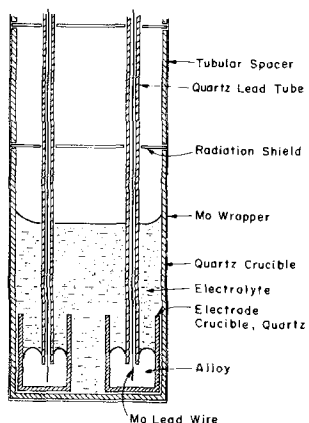


Fig. 1—Cell design for Ag-Si alloys.

might have been lost in cutting the button. Anode 13-1 was cut and the determinations were 3.57 and 3.69 wt pct and the average was used.

Several cells were run with only Ag-Si electrodes. A check of possible contamination of the electrodes by iron and molybdenum was made by analyzing one electrode (No. 11-2) for these elements, 0.0003 pct Fe and less than 0.0001 pct Mo were found. Another electrode contained 0.005 pct Mo. Several of the Ag-Si cathodes were contained in cells which also had Fe-Si cathodes, one such Ag-Si alloy (17-1) was found to contain 0.0009 pct Fe. The electrolyte in cells containing both Fe-Si and Ag-Si alloys showed between 0.04 and 0.05 pct Fe. These impurity levels were considered to indicate that there were no serious problems with exchange reactions in these cells.

To prevent contamination of the electrodes with molybdenum from the lead wire, the tip of each wire was immersed briefly in a molten Ag-Si alloy. A thin silicide coating resulted which prevented solution of the wire and also depletion of silicon from the electrodes during the experiments. The analyses of the electrodes described above indicate that the prior treatment of the leads was effective. The atmosphere in the cell was argon containing 3 pct hydrogen at a pressure slightly greater than atmospheric. Each gas was purified separately; the argon by passing it successively through columns of ascarite, copper at 500°C and iron at 700°C, and hydrogen by passing it through a platinum catalyst, drierite and ascarite. Initially, the cold cell system was evacuated by mechanical pumping and then it was filled with the purified gases. A slight flow of gas was maintained through the cell.

The temperature of the cell was determined by a Pt-Pt/10 pct Rh thermocouple located immediately below the tube containing the cell. The reading of this thermocouple was calibrated by making simultaneous measurements over the experimental temperature range with another thermocouple of the same type placed within the cell assembly. For this set of measurements, the cell was assembled exactly as for an experiment except that the electrolyte and electrodes were omitted. A thermal survey of the cell assembly showed the temperature gradients to be less than 0.7°C, the variation of temperature because of cycling of the controller to be approximately 0.5°C, and the drift over several hours was not more than 1°C. The thermocouples were calibrated against the gold and palladium points by the wire method. It is assumed that the total uncertainty in the temperature of a set of readings of the cell potentials was not more than 1.3°C. Thermocouple potentials were measured with a Rubicon-type B potentiometer.

Cell potentials were measured with a Keithley model 630 potentiometer which has an impedance of 10¹⁴ ohms. The readings of the cell were also checked occasionally with the Rubicon potentiometer to test the quality of the measurements by passing very small positive and negative currents through the cell for short periods. For most checks of this type, the potential returned smoothly from either side to its original value within 20 to 40 s. When it did not, adjustment of the position of the lead usually corrected the condition. It appeared that the potential of an electrode settled down to a constant value as rapidly as thermal equi-

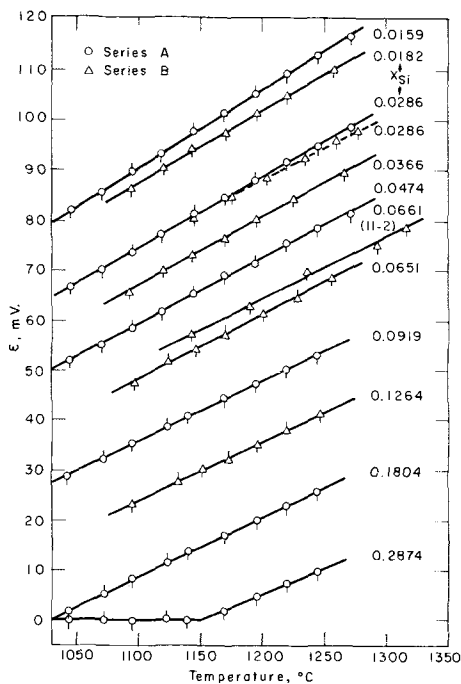


Fig. 2—Experimental data on emf of cells: Series A, Ag-Si only; Series B, Ag-Si electrodes in cells that also contained Fe-Si electrodes.

librium in the cell was attained. This usually required approximately one hour after the temperature setting on the controller was changed. The temperatures at which measurements were obtained were in an overlapping sequence alternating with an increase in temperature, followed by a decrease in temperature. The life-time of a cell was approximately 48 h because of devitrification of the quartz crucible and damage to the connecting leads because of attack by silicon.

Coulometric determinations of the value of Z in Eq. [2] were attempted. These efforts met with failure, apparently because the current required to produce the transfer of sufficient metal in the time of an experiment also caused some silicon to deposit on the lead wire. Hence, a quantitative relationship of adequate precision between electrical transport and mass transport was not possible.

THE MEASUREMENTS

The cell potentials were steady and reproducible and they are plotted in Fig. 2. Series A are those electrodes from cells containing only Ag-Si cathodes; series B are from cells containing some Fe-Si cathodes as well. (The results of the work with Fe-Si alloys will be reported later.) The data for each cathode are fitted by a least-squares equation of the form:

$$\epsilon = A + BT, \quad [5]$$

the coefficients of which are given in Table I. The potentials for electrode 11-2 appear to be high by approximately 3.5 mv, but there is no apparent reason for excluding them.

The values of the activity of silicon relative to pure solid silicon at 1200°C were calculated by Eq. [2] from the data in Table I. Corresponding values of a_{Ag} were

Table I. Equations of ϵ for Electrodes, $\epsilon = A + BT$

Electrode No.	Composition, x_{Si}	A , volts	$B \times 10^4$ volts/K
18-4	0.0159	-0.1245	1.564
15-1	0.0182	-0.1130	1.457
18-2	0.0286	-0.1216	1.426
17-1	0.0286	-0.1025	1.292
14-1	0.0366	-0.1229	1.380
18-1	0.0474	-0.1222	1.321
11-2	0.0661	-0.1176	1.233
12-1	0.0651	-0.1316	1.307
4-4	0.0917	-0.1287	1.198
13-1	0.1264	-0.1374	1.174
4-3	0.1804	-0.1543	1.187
4-2	0.2874	-0.1481	1.040

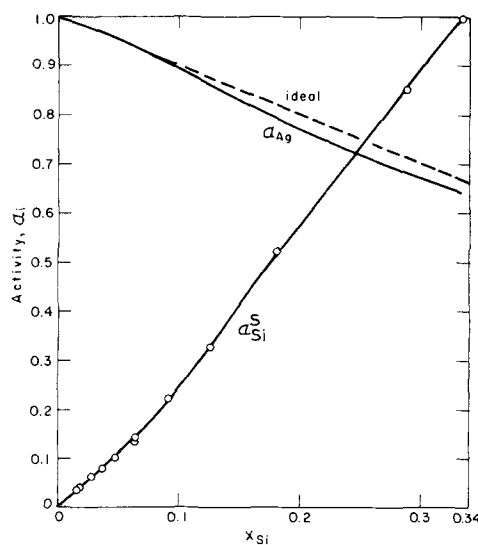


Fig. 3—Activity of Si relative to pure solid Si and of Ag relative to liquid Ag at 1200°C.

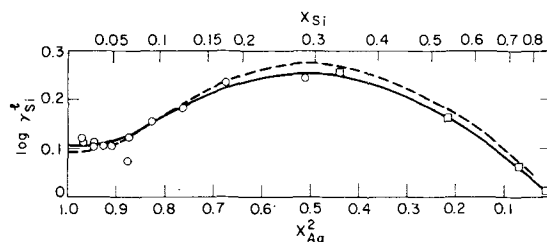


Fig. 4—Activity coefficient of Si referred to pure liquid Si as standard state. Solid line: 1200°C; circles: observed points; squares: calculated from Hager's liquidus; broken line: 1100°C.

obtained by integrating the Gibbs-Duhem equation. The results are shown in Fig. 3.

It is more meaningful to consider the properties of silicon relative to pure liquid silicon. The transformation of standard states is accomplished using data on the normal melting point of silicon, $T_m = 1687$ K; the heat of fusion at the normal melting point, $\Delta H_m = 50,550$ J/g-atom; and the heat capacities, $C_p^l = 25.5$ J/g-atom K and $C_p^s = 28.3 + (T - T_m) 25 \times 10^{-4}$ J/g-atom K, for the pure liquid and solid states, respectively.¹¹ Using these data, the equation for the conversion of pure solid silicon to pure liquid silicon (under-

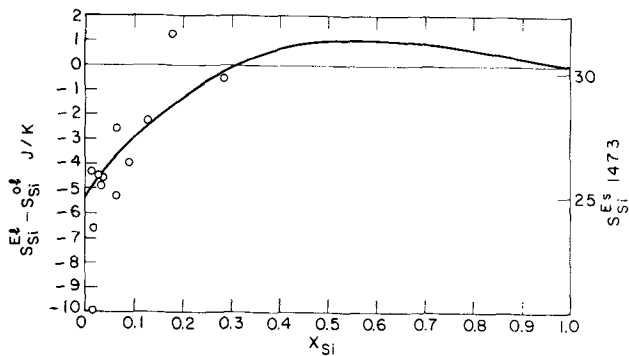


Fig. 5—Excess relative partial molar entropy of Si in Ag. The standard state is pure liquid Si.

Table II. Partial Molar Properties of Si and Ag at 1200°C Relative to the Liquid*

x_{Si}	$\log \gamma_{Si}^l$	$G_{Si}^{El} - G_{Si}^l$ J/g-at.	$S_{Si}^{El} - S_{Si}^l$ J/g-at.K	$H_{Si}^l - H_{Si}^l$ kJ/g-at.	$\log \gamma_{Ag}$	a_{Ag}	$H_{Ag} - H_{Ag}^o$ kJ/g-at.
0.0 ^a	0.105	2960	-5.4	-4.99	0.000	1.000	0.0
0.05	0.115	3242	-4.1	-2.80	-0.001	0.948	0.0
0.1	0.160	4511	-3.0	+0.09	-0.004	0.892	-0.3
0.15	0.214	6033	-2.1	+2.94	-0.012	0.827	-0.7
0.2	0.235	6625	-1.3	+4.71	-0.016	0.770	-1.1
0.3	0.255	7190	-0.1	+7.04	-0.022	0.666	-1.9
0.4	0.225	6343	+0.6	+7.23	-0.005	0.593	-1.9
0.5	0.180	5075	+1.0	6.55	+0.032	0.538	-1.3
0.6	0.130	3665	+1.0	5.14	+0.094	0.496	+0.2
0.7	0.080	2255	+0.9	3.58	+0.185	0.459	+3.6
0.8	0.035	986	+0.6	1.87	+0.314	0.412	+8.0
0.9	0.010	280	+0.3	0.70	+0.475	0.300	+15.0
1.0	0.000	0	0.0	0.0	+0.660	0.000	+25.0

*Under-cooled liquid silicon.

cooled) in the vicinity of 1473 K (1200°C) is:

$$Si(s) = Si(l); \Delta G (J/g\text{-atom}) = 51,130 - 30.34 T \quad [6]$$

and the activity of silicon relative to the pure liquid state is given by

$$\log a_{Si}^l = \log a_{Si}^s - 2670/T + 1.585 \quad [7]$$

The values of $\log \gamma_{Si}^l$ calculated from the equations given in Table I by Eqs. [3] and [7] are shown in Fig. 4. Below $x_{Si} = 0.05$ the values of $\log \gamma_{Si}^l$ at 1200°C are approximately constant at 0.1, and the line is drawn to connect this value smoothly with the curve through the results at higher concentrations. The points above $x_{Si} = 0.3$ were calculated from Hager's liquidus points² using the data on entropy that are developed in the next paragraph. Values of $\log \gamma_{Si}^l$ at 1100°C are slightly below the 1200°C line below $x_{Si} = 0.1$, and above the line at the higher concentrations.

The excess partial molar entropy of Si calculated from values of B in Table I are shown in Fig. 5. The data are not completely consistent, but at low concentrations they appear trustworthy within ± 1 J/g-atom K or ± 0.25 e.u. At higher concentrations, there are no data and the line is extended on the assumption that the solution becomes more nearly regular as x_{Si} increases. The effects of temperature on the excess free energy and the activity coefficient were calculated from this line. The partial molar properties of both components at 1200°C are given in Table II. These data are obtained by use of the curves in Figs. 3, 4,

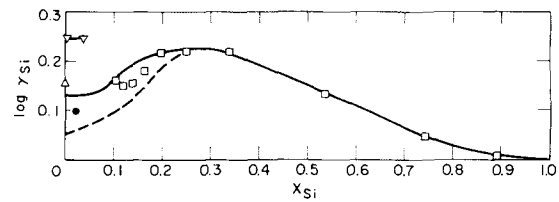


Fig. 6—Activity coefficient of Si at 1420°C. Solid line: present data extrapolated; dotted line: Hager's data assuming regular solution. Squares calculated from Hager's points using our entropy. Δ Chipman and Baschwitz,¹ ∇ Turkdogan and Grieveson,⁸ \bullet Smith and Taylor.⁷

and 5. As an approximation, it is assumed that S_{Si}^E and H_{Si} are independent of temperature.

At infinite dilution $\log \gamma_{Si}^l$ is 0.105 at 1473 K and $S_{Si}^{El} = -5.4$. From these data the free energy for the change in standard state is

$$Si(l) = Si(\text{indif. dil.}); \Delta G_{Si}^l (J/g\text{-atom}) = -5000 + 5.4 T \quad [7]$$

and

$$\log \gamma_{Si}^o = -2613/T + 0.282 \quad [8]$$

DISCUSSION

A plot of $\log \gamma_{Si}$ at 1420°C that was obtained by extrapolating the results of this study is shown in Fig. 6. Values of $\log \gamma_{Si}$ calculated by Hager from points on his phase diagram² and the assumption of regularity are also shown. Hager's individual data points calculated to 1420°C by means of the values of the entropy from Fig. 5 are shown by squares. Above $x_{Si} = 0.2$ they agree well with our line. The only divergence is at concentrations just above the eutectic where the liquidus curve is exceedingly steep and the data may be strongly influenced by slight errors in determining the composition. However, further confirmation of Hager's results is found in the following points. Hager's solubility of $x_{Si} = 0.334$ at 1200°C fits the activity data of Fig. 3. Our line for the emf of the cell $x_{Si} = 0.2874$ in Fig. 2 shows a break at 1152°C which is within 5°C of Hager's liquidus temperature for this alloy, 1157°C.

Fig. 6 permits comparison of the results of previous work with that of the present study. Chipman and Baschwitz¹ pointed out that the entropy of mixing in the Ag-Si system probably is not ideal and they suggested an arbitrary correction of +0.10 in Hager's value of $\log \gamma_{Si}$ at low concentrations. Their value is shown at $x_{Si} = 0$. The same correction was applied by D'Entremont and Chipman⁶ to derive the free energy of β -SiC from its measured solubility in liquid silver. Smith and Taylor⁷ confirmed D'Entremont's value for the solubility of SiC in Ag and used this with their value for the free energy of formation of the carbide to obtain the activity coefficient. Their value of $\log \gamma_{Si}$ at $x_{Si} = 0.02$ is also shown in Fig. 6. With the aid of the new measurements, it might be profitable to reverse this calculation to obtain the free energy of formation of SiC. Turkdogan and Grieveson⁸ measured the solubility of Si_3N_4 in liquid silver, and from their data and the free energy of formation of the compound they concluded that $\gamma_{Si} = 1.76$ at 1400°C within the

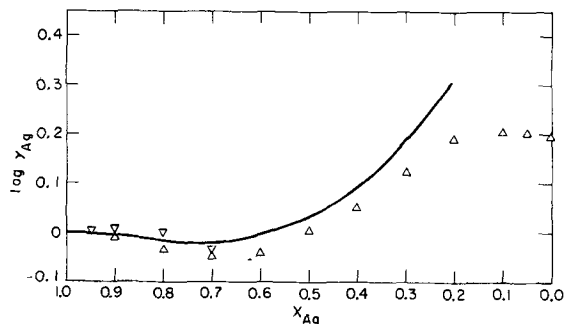


Fig. 7—Activity coefficient of Ag at 1420°C. Lines (this study): ∇ Vermande *et. al.*,⁴ Δ - Robinson and Tarby.⁵

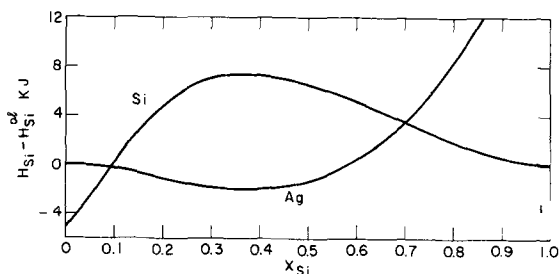


Fig. 8—Relative partial molar enthalpy of Si and of Ag. The standard states are the pure liquids.

range $0.005 < x_{Si} < 0.038$. The correction to 1420°C is insignificant and their values is shown as $\log \gamma_{Si}^0 = 0.245$. Our value for $\log \gamma_{Si}^0$ is given in Eq. [8], from which its value at several experimental temperatures is as follows: 0.105 at 1200°C, 0.128 at 1420°C, and 0.137 at 1530°C.

Tupkary¹² measured the emf of the cell Ag-Si (l)/CaO-B₂O₃-SiO₂ (SiO₂ sat.)/Pt/O₂ (g) at 1150°C and from the results calculated the activity of Si in the alloy. The calculation depends upon the value adopted for the free energy of formation of SiO₂ and in view of uncertainties in this datum, the results are of only relative significance. They are not far from our results at 1200°C and display a minimum at a concentration less than $x_{Si} = 0.1$, implying a minimum in the curve for $\log \gamma_{Si}$.

The activity coefficient of silver at 1420°C, as found by Gibbs-Duhem integration, is shown in Fig. 7. Shown for comparison are the direct observations of Vermandé, Ansara, and Desré,⁴ interpolated to 1420°C. The former show a slight rise above the ideal at $x_{Ag} = 0.9$, a difference which is qualitatively in agreement with the minimum $\log \gamma_{Si}$ shown by Tupkary. Robinson

and Tarby's⁵ results are somewhat more negative than are ours.

From the activity coefficients (Figs. 6 and 7) and the relative partial molar entropy of Si (Fig. 5), the relative partial molar enthalpy of each component was calculated and is shown in Fig. 8.

SUMMARY

A reversible electrochemical cell has been devised using a silica-saturated lithium silicate electrolyte in which reproducible emf data at temperatures of 1050 to 1325°C have been obtained for liquid Ag-Si alloys relative to pure solid Si. The thermodynamic properties have been derived for the temperatures of 1100 and 1200°C and for concentrations up to saturation ($x_{Si} = 0.334$ at 1200°C). Deviations from ideality are slight, the activity coefficient of Si relative to the pure liquid being larger than unity at all concentrations. Derived values for entropy and enthalpy permit calculation of excess free energy and of $\log \gamma_{Si}$ from the phase diagram. The results of this calculation, together with our data, form a continuous line across the whole composition range $0 < x_{Si} < 1.0$. The data are corrected to 1420°C for comparison with published values of $\log \gamma_{Si}$ and $\log \gamma_{Ag}$.

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