Communications

Standard Free Energy of Formation of Tin Telluride

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Thermodynamic properties of tin telluride, the only stable compound in the Sn-Te system, have been investigated by a number of workers.[1-8] The standard free energy of formation of this compound has been determined, in most of the cases, by using the data obtained from calorimetric measurements. The direct determination of this property by emf method using molten salt electrolyte has been in the lower temperature range (533 to 668 K)[1] only. In the present work, using galvanic cells with calcia stabilized zirconia (CSZ) as the solid electrolyte, the standard free energy of formation of SnTe has been determined in the temperature range 930 to 1030 K.

The cell used had the following scheme:

$$Pt,Air//ZrO_2(+CaO)//SnTe,Te,SnO_2/W.$$

Tin and tellurium were of 99.99 pct purity while SnO_2 was 99.5 pct pure. The compound SnTe was prepared by melting together the constituents in the required ratio in inert atmosphere. The electrolyte was in the form of one end closed CSZ tubes, 400 mm long and 5 mm ID. The mixture of SnTe, Te and SnO_2 was filled into the CSZ tube up to a height of about 50 mm. Purified argon gas flowed through the CSZ tube at about 20 ml/min. The cell assembly was placed in a Kanthal-wound vertical furnace which could be controlled to ±2°C. The measurements were carried out in the temperature range 930 to 1030 K. As the vapor pressure of tellurium is very high (10^{-2} atm at 890 K), it was found necessary to add tellurium into the zirconia tube so as to ensure unit activity of tellurium in the electrode mixture. When this was not done, the cell emf remained steady for some time, drifted afterwards and became steady again but at a different value. Addition of tellurium at this stage restored the emf to original steady value. Thermal emf generated by W-Pt junction was measured in purified argon atmosphere in a separate experiment. The emf varied approximately linearly from 8.3 to 10.4 mV as the temperature varied from 930 to 1030 K.

The cell emf, after applying correction for thermal emf of W-Pt junction, is plotted in Fig. 1 as a function of temperature. In the temperature range of investigation, the emf (mV) *vs* temperature (K) relationship is found to be linear and can be represented by the following equation obtained by least-square method:

$$E = 1274.0 - 0.4568T \ (\pm 8.5 \text{ mV}). \qquad [1]$$

The error limits given in parentheses above (and also in subsequent equations) represent $\pm 2\sigma$ (± two sigma) limits, *i.e.*, approximately 95 pct confidence limits, where σ is the standard deviation of the measurements. The deviation in any observed emf value from that obtained, at the same temperature, using the above expression does not however exceed ±7 mV.

For the cell used, the virtual reaction, in the temperature range of study, can be written as:

$$SnTe(s) + O_2(\text{air}) = SnO_2(s) + Te(l). \qquad [2]$$

If ΔG_R be the free energy change accompanying the above reaction, then,

$$\Delta G_R = -4EF = \Delta G^o_{SnO_2} - \Delta G^o_{SnTe} - RT \ln pO_2(\text{air}) \qquad [3]$$

where F is Faraday and R the universal gas constant. $\Delta G^o_{SnO_2}$ and ΔG^o_{SnTe} are the standard free energies of formation of SnO_2 and SnTe, respectively. Rearranging the terms in Eq. [3], one gets:

$$\Delta G^o_{SnTe} = \Delta G^o_{SnO_2} + 4EF - RT \ln pO_2(\text{air}). \qquad [4]$$

Linear regression analysis of the free energy of formation data of SnO_2 compiled by Barin, Knacke and Kubaschewski[9,10] gives:

$$\Delta G^o_{SnO_2} \ (\text{J/mole}) = -568{,}605 + 194.28T \ (900 \text{ to } 1900 \text{ K}).$$
$$\pm 1600 \qquad \pm 2185 \qquad \pm 1.52 \qquad [5]$$

The standard free energy of formation of SnTe from liquid tin and liquid tellurium is obtained by combining Eqs. [1], [2], [4] and [5] and is given by:

$$\Delta G^o_{SnTe}(s) \ (\text{J/mole}) = -76{,}927 + 30.94T \quad (930 \text{ to } 1030 \text{ K}).$$
$$\pm 4880 \qquad [6]$$

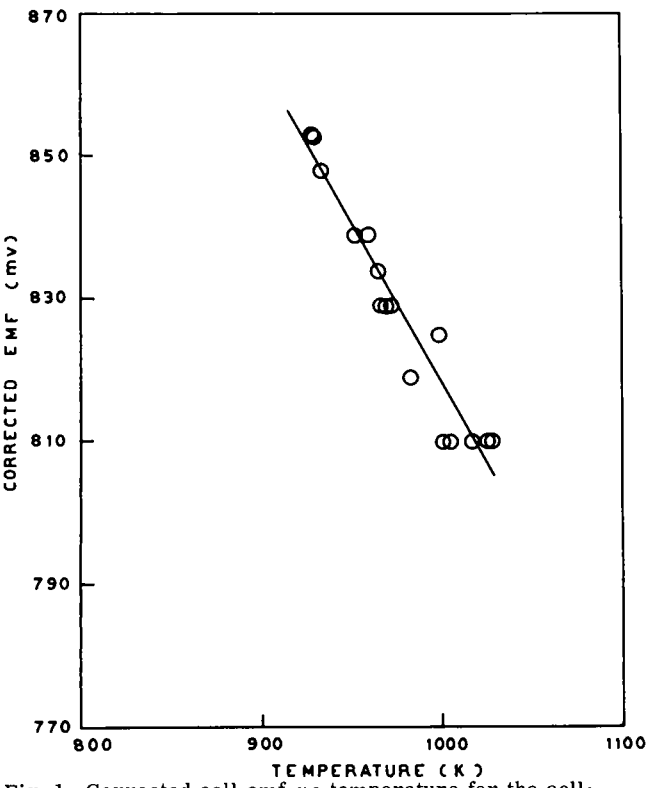

Fig. 1—Corrected cell emf *vs* temperature for the cell: $Pt,Air//ZrO_2(+CaO)//SnTe,Te,SnO_2/W$.

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At the mean temperature of 980 K, one gets from the above expression for ΔG^o_{SnTe} a value of $-46{,}606 \pm 4880$ J/mole. This is in very good agreement with the value of $-43{,}661$ J/mole calculated (at 980 K) from the data compiled by Barin, Knacke and Kubaschewski.[10]

Hultgren *et al*[11] have critically evaluated the available thermodynamic data on Sn-Te system. Based on this evaluation, at 600 K, the standard free energy of formation of SnTe from solid tin and solid tellurium is given by:

$$\Delta G^o_{SnTe} = -60{,}584 - 1.397T \quad \text{(J/mole)}. \qquad [7]$$
$$\pm 418.4 \quad \pm 418.4 \quad \pm 0.837$$

Assuming that the heats of melting of tin (7029 J/g·atom) and tellurium (17,489 J/g·atom) are temperature independent and that $\Delta C_p \simeq 0$ for the formation of SnTe, which is supported by the evaluated data,[11] one may write, starting with Eq. [7], for the formation of SnTe from liquid tin and liquid tellurium according to the reaction:

$$Sn(l) + Te(l) = SnTe(s)$$

$$\Delta G^o_{SnTe}(s) = -85{,}102 + 36.71T \text{ J/mole}. \qquad [8]$$

At 980 K, Eq. [8] yields for ΔG^o_{SnTe} a value of $-49{,}126$ J/mole which is in very good agreement with the value of $-46{,}606 \pm 4880$ J/mole obtained from this work.

Uncertainties in the standard enthalpy and entropy of formation in Eq. [6] can be calculated from the knowledge of the standard deviation of intercept and slope in Eq. [1]. The standard deviation of intercept is found to be 32 mV while that of the slope is 0.0335 mV/K. The uncertainties in ΔH^O and ΔS^O values, estimated from these standard deviations, are quite large which may be because of the very narrow temperature range of investigation.

In writing down the virtual cell reaction (Eq. [2]) and therefore in making further calculations, it has been assumed that the activity of SnO_2 in the electrode mixture SnTe + Te + SnO_2 is unity. One may, however, also consider the possibility of the reaction:

$$SnTe + SnO_2 = 2SnO + Te. \qquad [9]$$

As the activity of tin in SnTe (in contact with tin oxide) is very small, Eq. [9] will be pushed in the direction right to left. Moreover, it has been pointed out by Shunk[14] that SnO disproportionates to Sn and SnO_2 at ~175°C. The assumption of unit activity of SnO_2 is, therefore, justified.

The free energy of formation of the compound SnTe can be calculated from the equilibrium diagram applying Jordan's regular associated solutions model.[12] Taking the heat and entropy of fusion of SnTe data from Barin, Knacke and Kubaschewski's compilation[10] and the liquidus of the equilibrium diagram of the Sn-Te system from Hansen,[13,14] one obtains a value of $-32{,}635$ J for the free energy of formation of one mole of $Sn_{0.5}Te_{0.5}$ at its melting point from liquid tin and tellurium. This value is smaller than the one obtained from Eq. [6]. The difference is possibly due to the assumptions and approximations involved in Jordan's model.

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On the Rate Limiting Step in the Decarburization of Iron Droplets in an Oxidizing Slag

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Particularly since the work of Meyer and his coworkers,[1] it has been realized that a substantial part of the carbon elimination and other refining[2] that takes place in top blown steelmaking processes occurs in the slag-metal-gas emulsion. Modeling of the carbon elimination process has yielded two conflicting opinions about the rate controlling mechanism at high carbon concentration. Okhotskii[3] has concluded that the chemical reaction at the metal/slag interface is rate determining, whereas Acheson and Hills[4] consider that the process is controlled by the rate at which CO bubbles can escape from the foaming slag.

Two substantial studies have been made of the nature of the reaction of iron droplets with oxidizing slags. Mulholland *et al*,[5] observed the physical nature of the decarburization reaction by direct X-ray fluoroscopy and, most recently, Gaye and Riboud[6] quantitatively determined the rate of decarburization of droplets by continuous measurement of the flow rate of evolved gas. These latter authors also obtained some information on the rates of S and P transfer by the analysis of quenched droplets.

It is the purpose of the present communication to show that the measured maximum rates of decarburization of iron droplets, containing concentrations of sulfur typical of commercial steels, are consistent with interfacial chemical reaction control at the *metal-gas* interface of the slag-metal-gas system.

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