

THE THERMODYNAMIC PROPERTIES OF SOLID COBALT–TIN ALLOYS

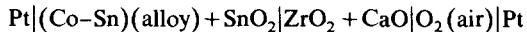
H. CÖMERT * and J.N. PRATT

Department of Metallurgy and Materials, University of Birmingham, P.O. Box 363, Birmingham B15 2TT (Gt. Britain)

(Received 11 September 1984)

ABSTRACT

Reversible potentials of galvanic cells of the form



have been measured between 873 and 1323 K. The results have been used to derive the thermodynamic activities and the partial and integral free energies, enthalpies and entropies of formation of the γ , γ' , CoSn and CoSn_2 intermediate phases. Exothermic heats of formation and negative entropies of formation are observed throughout the system. The enthalpies of formation are compared with independent calorimetric and theoretical values and underlying factors influencing their values are considered. The possible contributions to the entropies of formation of the solid phases are discussed and their Debye temperatures are estimated; θ_D values of approximately 273, 256 and 169 K are suggested for Co_3Sn_2 (γ), CoSn and CoSn_2 , respectively.

INTRODUCTION

In a recent paper [1], systematic studies of the thermodynamic properties of alloys of transition metals with B-subgroup elements [2–7] were extended to the cobalt–zinc system. A similar investigation of cobalt–tin alloys is now described.

The equilibrium diagram of the cobalt–tin system, as assessed by Hansen and Anderko [8], is shown in Fig. 1. Solid-state phase equilibria are not well established; generally the extent of the cobalt-rich terminal solution and the exact positions of the γ -phase boundaries are subject to some uncertainty (shown as broken lines in Fig. 1). The high-temperature γ -phase, which has a partially filled NiAs (B8_2) type of structure [9], is formed congruently from the liquid at 1170°C and transforms to the more ordered γ' -phase at 550°C.

* Present address: School of Mathematics and Physics, University of East Anglia, Norwich NR4 7TJ, Gt. Britain.

Two possible structures have been suggested [10] for the γ' -phase. One is based on a hexagonal lattice, with parameters $a = 16.39 \text{ \AA}$, $c = 5.208 \text{ \AA}$, and the other on an orthorhombic unit cell, $a = 8.20 \text{ \AA}$, $b = 7.09 \text{ \AA}$, $c = 5.21 \text{ \AA}$, but as single crystals could not be obtained, it was not possible to determine the structure definitely. The phase CoSn is formed peritectically from the liquid and γ -phases at $936 \pm 9^\circ\text{C}$. It has a hexagonal B35 type of structure, isotypic with PtTi and with the lattice parameters $a = 5.279 \text{ \AA}$, $c = 4.259 \text{ \AA}$ [10]. The phase CoSn_2 is also formed peritectically, from the liquid and

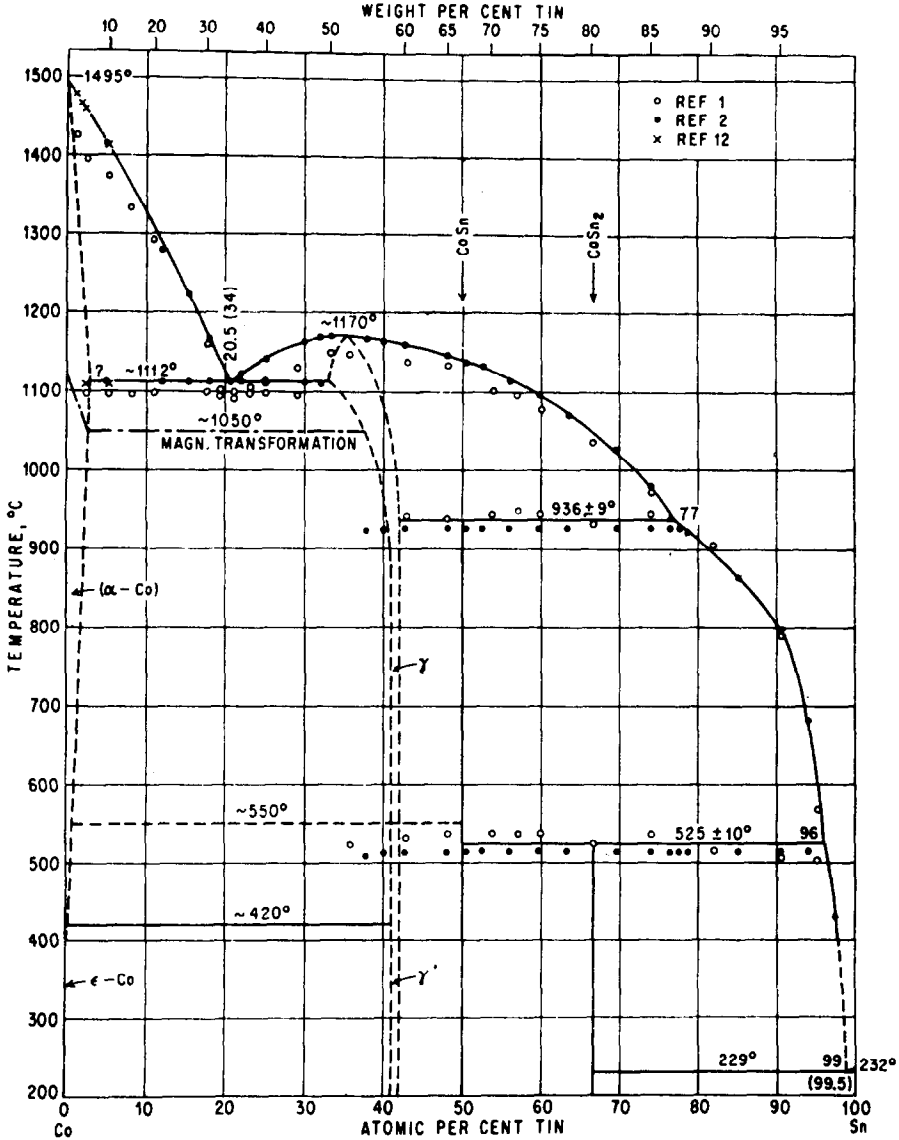


Fig. 1. The cobalt-tin equilibrium diagram.

CoSn, at $525 \pm 10^\circ\text{C}$. The structure of CoSn_2 is tetragonal, of the CuAl_2 (C16) type, with $a = 6.361 \text{ \AA}$, $c = 5.451 \text{ \AA}$ [10].

The earliest investigation of the thermodynamic properties of cobalt–tin alloys is that reported by Körber and Oelsen [11]. Using a simple calorimetric technique, based on the direct mixing of the liquid metals, they determined the heats of formation of both liquid and solid alloys containing between 11 and 80 atomic% Sn at 293 and 1773 K. For the solid phases their values are exothermic, showing compositional symmetry, that is with the maximum negative value occurring at the phase CoSn. They also observed exothermic heats of formation in the liquid alloys containing up to 60 atomic% tin, but reported endothermic values beyond this composition.

Eremenko et al. [12] also investigated the thermodynamic properties of the liquid alloys, at 1573 K, over the entire composition range using the Knudsen effusion method. They again reported exothermic heats of formation in the cobalt-rich alloys and endothermic values in the tin-rich alloys; entropies of formation were reported to be positive throughout. Conflicting behaviour is, however, indicated by the results of a subsequent calorimetric determination of partial and integral entropies in cobalt–tin alloys at 1850 K made by Esin et al. [13]. They report endothermic values up to 80 atomic% tin and exothermic values at the higher tin contents.

The most recently published measurements on this system are those made by Predel and Vogelbein [14] who have employed tin-solution calorimetry to determine the heats of formation of the solid phases Co_3Sn_2 and CoSn; large exothermic values are reported.

The above examination of the literature shows that thermodynamic knowledge of the system is somewhat contradictory and, in respect of the solid state, very limited. It was noted, in particular, that no information existed on the free energies of formation of the solids. A solid-electrolyte galvanic-cell technique has therefore been employed to obtain such data for the solid phases of the cobalt–tin system.

EXPERIMENTAL DETAILS

Alloy preparation

The alloys were prepared from 99.99% pure cobalt (Centre d'Information du Cobalt Brussels) and 99.999% pure tin (Capper Pass Ltd.), using two different procedures. Cobalt-rich alloys, containing less than 40 atomic% tin, were prepared by induction melting of the elements in a recrystallised alumina boat and under an atmosphere of gettered argon. They were rapidly cooled after melting, by the water-cooled hearth, so as to give fine-grained samples and to minimise segregation. The resulting ingots were resealed in argon-filled silica capsules and homogenised at 1000°C for 14 days.

Initially, alloys containing more than 40 atomic% tin were melted using the same method as used for the cobalt-rich alloys. However, metallographic examination and EMF results showed that inhomogeneity persisted even after prolonged annealing at the highest practicable solid-state temperatures. An alternative method of preparation, which may be described as a "rotating-melting" technique, was therefore adopted. This method involved sealing the weighed, chemically cleaned and dried quantities of the pure metals in silica capsules, after evacuating to better than 10^{-5} atm and re-filling with argon to a pressure of 0.3–0.4 atm. The sealed capsule was placed inside a closed-end silica tube which was attached, by means of an adaptor, to a small electric motor capable of one revolution per minute. A silica spacer-tube was inserted between the adaptor and the sample capsule to prevent the capsule moving during rotation. A schematic diagram of the rotating assembly is shown in Fig. 2. Alloys were prepared by placing the silica tube in a horizontal, resistance-heated furnace. The sample was rotated, and the temperature was raised gradually to 50°C below the liquidus temperature of the alloy, where it was kept for 48 h; after this the temperature was raised to 50°C or more above the liquidus temperature where it was held for a period of 48–72 h, depending on the melting point of the alloy. Following this, the alloy was cooled slowly to 800°C , allowing time for transformation, if any, and kept there for at least 1 week to homogenise. Finally, the alloys were quenched into cold water. There was no evidence of alloy contamination or reaction with capsules, and compositions were monitored by careful weighing at each stage of preparation. Phase structure and sample homogeneity were confirmed by metallographic and Debye-Scherrer X-ray examination of samples taken from several different parts of the ingots.

Galvanic-cell studies

The EMF apparatus was identical to that employed in the thermodynamic study of the cobalt-zinc system described previously [1]. Sieved (200 mesh)

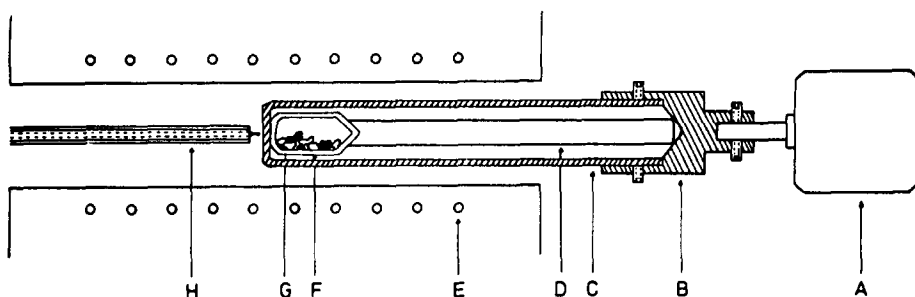
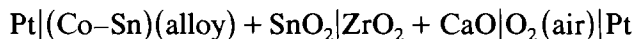


Fig. 2. The rotating-melting apparatus. (A) motor; (B) adaptor; (C) rotating sample holder; (D) supporting tube; (E) heating coil; (F) sealed silica-alloy capsule; (G) alloy charge; (H) thermocouple.

powder samples of the alloys, prepared by filing with a diamond file or by crushing in a pestle and mortar, were mixed with SnO₂ (99.5% purity) in an approximately 7:1 (w/w) ratio of alloy/oxide and tamped down into the small electrolyte crucible to form the electrodes. A platinum disc was placed on the tamped powder in the crucible in order to ensure good electrical contact between platinum lead-wire and sample. After assembly, the sealed system was alternately evacuated and flushed with argon at room temperature before degassing at 200°C overnight. The purified argon atmosphere was then re-established and kept at a pressure slightly greater than atmospheric to avoid contamination of the cell by air. The cell was then rapidly heated to the highest temperature to be investigated. Cell potentials were then monitored until stable values were observed. Potentials were measured at approximately 20°C intervals on both heating and cooling cycles. Reversibility of the cells was demonstrated by the stability of the measured potentials, their insensitivity to temperature cycling or electrical disturbance and their reproducibility in repeated experiments with new samples.

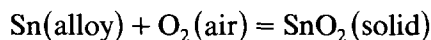
RESULTS

Fourteen alloys containing from 1 to 60 atomic% tin were investigated over temperature ranges between 873 and 1323 K using cells of the form



EMF data collected from multiple runs on each alloy composition were treated by least-squares analysis to yield the linearly temperature-dependent cell-potential equations recorded in Table 1.

For the basic cell reaction



the free energy, ΔG , at any temperature T (K)

$$\Delta G = -nFE \quad (1)$$

$$= \Delta G_{\text{SnO}_2}^0 + RT \ln \frac{a_{\text{SnO}_2}}{a_{\text{Sn}} a_{\text{O}_2}} \quad (2)$$

where E is the cell potential (mV), $n = 4$ and $F = 96.483 \text{ J mV}^{-1} \text{ g-equiv}^{-1}$, $\Delta G_{\text{SnO}_2}^0$ is the standard free energy of formation of SnO₂, a_{Sn} is the activity of Sn in the alloy. Since $a_{\text{SnO}_2} = 1$ and $a_{\text{O}_2} = P_{\text{O}_2}(\text{air})$, the above equations are re-arranged to yield the partial free energies of solution of Sn, and hence

$$\Delta \bar{G}_{\text{Sn}} = RT \ln a_{\text{Sn}} = \Delta G_{\text{SnO}_2}^0 + nFE - RT \ln P_{\text{O}_2}(\text{air}) \quad (3)$$

Required values for $\Delta G_{\text{SnO}_2}^0$ were calculated from the relation

$$\Delta G_{\text{SnO}_2}^0 (\text{J mol}^{-1}) = -573462 + 204.451T \quad (4)$$

TABLE 1

Temperature dependence of the EMF of the cells Pt|(Co-Sn)+SnO₂|ZrO₂+CaO|O₂(air)|Pt

x_{Sn}	EMF (mV)	Phase
0.01		
0.02		
0.10	$1391.8 \pm 0.260 - (0.5260 \pm 0.0003) T (\text{K})$	$\alpha + \gamma$
0.15		
0.30		
0.3895	$1391.8 \pm 0.260 - (0.5260 \pm 0.0003) T (\text{K})$ ^a	$\alpha + \gamma$
0.3895	$1274.3 \pm 1.407 - (0.4336 \pm 0.0011) T (\text{K})$ ^b	γ
0.405	$1358.4 \pm 0.152 - (0.4856 \pm 0.0001) T (\text{K})$	γ
0.411	$1359.3 \pm 0.107 - (0.4782 \pm 0.0001) T (\text{K})$	γ
0.413	$1354.9 \pm 0.212 - (0.4718 \pm 0.0002) T (\text{K})$	γ
0.415	$1345.7 \pm 0.155 - (0.4601 \pm 0.0001) T (\text{K})$	γ
0.415	$1146.9 \pm 1.698 - (0.2130 \pm 0.0022) T (\text{K})$	γ'
0.450		$\gamma + \text{CoSn}$
0.499	$1339.1 \pm 0.133 - (0.4513 \pm 0.0001) T (\text{K})$	
0.511		$\text{CoSn} + \text{liq}$
0.600		
0.499	$1559.1 \pm 2.284 - (0.6283 \pm 0.0018) T (\text{K})$	$\gamma + \text{liq}$
0.511		
0.600		
0.600	$1255.7 \pm 0.933 - (0.2762 \pm 0.0012) T (\text{K})$	$\text{CoSn} + \text{CoSn}_2$

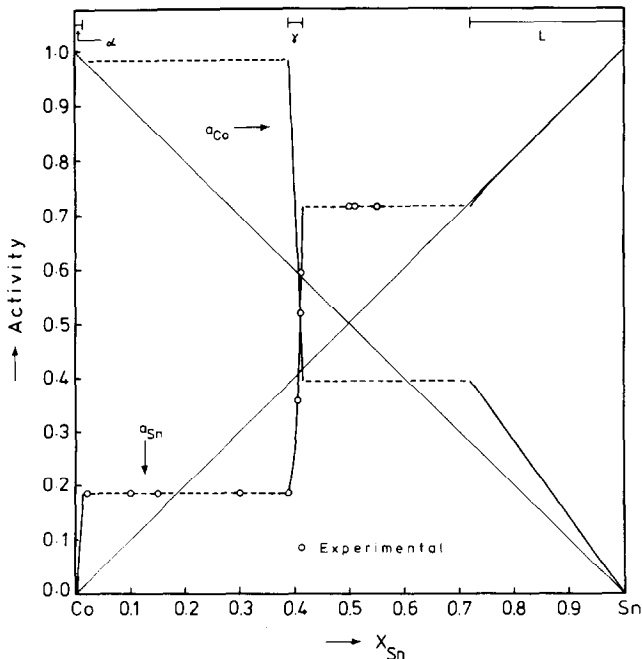
^a $T < 1270 \text{ K}$.^b $T > 1270 \text{ K}$.

Fig. 3. Thermodynamic activities of cobalt and tin at 1273 K. (Reference states: Co (FCC) and Sn (liq)).

TABLE 2

Activities, partial free energies of solution and integral free energies of formation Co-Sn alloys at 1273 K (reference states: Co (FCC) and Sn (liq))

x_{Sn}	a_{Sn}	a_{Co}	$\Delta\bar{G}_{\text{Sn}}$ (J g- atom ⁻¹)	$\Delta\bar{G}_{\text{Co}}$ (J g- atom ⁻¹)	ΔG (J g- atom ⁻¹)	Phase
0.0125–0.389	0.185	0.988	-17860	-130		$\alpha + \gamma$
0.395	0.236	0.846	-15280	-1770	-7110	γ
0.400	0.290	0.735	-13100	-3260	-7195	γ
0.405	0.360	0.633	-10810	-4840	-7260	γ
0.410	0.475	0.525	-7880	-6820	-7255	γ
0.4145–0.7175	0.715	0.395	-3545	-9830		$\gamma + \text{liq}$
0.74	0.737 ^a	0.367	-3230	-10610	-5150	liq
0.77	0.770 ^a	0.325	-2765	-11895	-4865	liq
0.80	0.800 ^a	0.283	-2360	-13360	-4560	liq
0.85	0.850 ^a	0.212	-1720	-16415	-3925	liq
0.90	0.900 ^a	0.141	-1115	-20730	-3080	liq
0.95	0.950 ^a	0.071	-545	-27995	-1915	liq

^a Extrapolated.

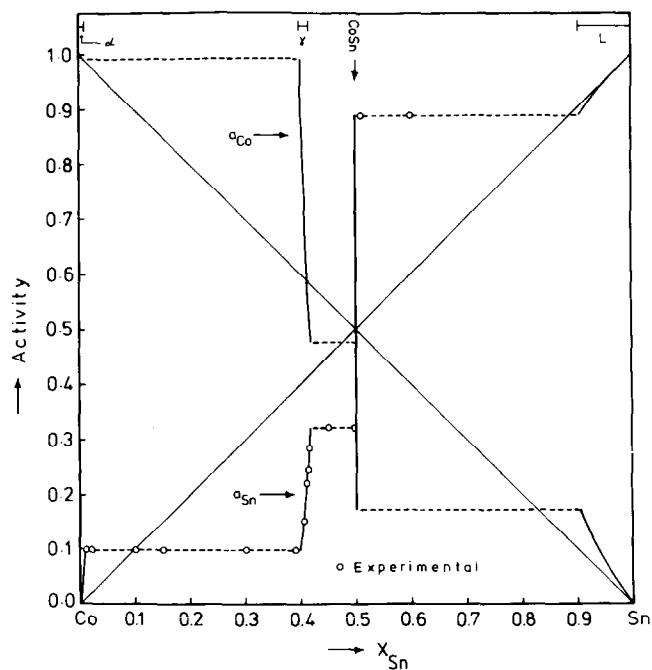


Fig. 4. Thermodynamic activities of cobalt and tin at 1073 K. (Reference states: Co (FCC) and Sn (liq)).

This assessment of the standard free energies of formation of SnO_2 was obtained by combining the free energies of the reaction $\frac{1}{2}\text{Sn(l)} + \text{NiO(s)} = \text{Ni(s)} + \frac{1}{2}\text{SnO}_2\text{(s)}$, calculated by averaging the results reported by Petot-Ervas et al. [15] and Seetharaman and Staffansson [16], with measurements of the

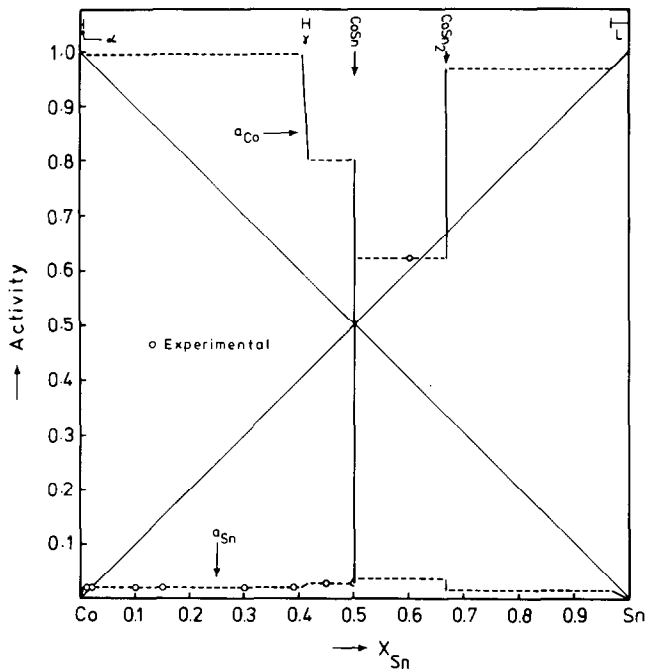


Fig. 5. Thermodynamic activities of cobalt and tin at 773 K. (Reference states: Co (FCC) and Sn (liq)).

TABLE 3

Activities, partial free energies of solution and integral free energies of formation of Co-Sn alloys at 1073 K (reference states: Co (FCC) and Sn (liq))

x_{Sn}	a_{Sn}	a_{Co}	$\Delta\bar{G}_{\text{Sn}}$ (J g- atom ⁻¹)	$\Delta\bar{G}_{\text{Co}}$ (J g- atom ⁻¹)	ΔG (J g- atom ⁻¹)	Phase
0.0091-0.399	0.098	0.991	-20720	-80		$\alpha + \gamma$
0.405	0.151	0.800	-16865	-1990	-8015	γ
0.410	0.205	0.653	-14140	-3800	-8040	γ
0.415	0.282	0.521	-11290	-5815	-8090	γ
0.417-0.500	0.321	0.476	-10135	-6620		$\gamma + \text{CoSn}$
0.500-0.905	0.890	0.172	-1040	-15700		$\text{CoSn} + \text{liq}$
0.92	0.911 ^a	0.136	-830	-17800	-2190	liq
0.93	0.925	0.114	-695	-19370	-2000	liq
0.95	0.95 ^a	0.076	-460	-22980	-1585	liq
0.98	0.98 ^a	0.030	-180	-31175	-800	liq

^a Extrapolated.

standard free energy of formation of NiO made in the present studies in order to test the apparatus. The values obtained for NiO [$\Delta G^0(\text{J mol}^{-1}) = -232542 + 83.517T$] are in excellent agreement with the many previous studies and provide confirmation of the satisfactory operation of the apparatus. An oxygen partial pressure of 0.2095 atm was assumed throughout for the air reference electrode; the effect of variations in atmospheric pressure on the oxygen potential was found to be negligible.

Using the above relationships and cell potentials derived from Table 1, activities and partial free energies of solution of Sn at 1273 K were calculated. The corresponding quantities for the cobalt component were then obtained by integration of the Gibbs–Duhem relation and the integral free energies of formation of the alloys were yielded by the normal summation of the partials. The resulting activities are plotted in Fig. 3, whilst smoothed values of all the quantities are assembled in Table 2. Similar treatments were

TABLE 4

Activities, partial free energies of solution and integral free energies of formation of Co–Sn alloys at 773 K (reference states: Co (FCC) and Sn (liq))

x_{Sn}	a_{Sn}	a_{Co}	$\Delta\bar{G}_{\text{Sn}}$ (J g- atom ⁻¹)	$\Delta\bar{G}_{\text{Co}}$ (J g- atom ⁻¹)	ΔG (J g- atom ⁻¹)	Phase
0.0042–0.4040	0.020	0.996	–25 140	–25		$\alpha + \gamma$
0.41	0.024 ^a	0.892	–23 970	–735	–10 260	γ'
0.416–0.500	0.028	0.800	–22 980	–1435		$\gamma' + \text{CoSn}$
0.500–0.667	0.622	0.036	–3050	–21 365		$\text{CoSn} + \text{CoSn}_2$
0.667–0.967	0.967 ^b	0.015	–215	–26 990		$\text{CoSn}_2 + \text{liq}$

^a Interpolated.

^b Extrapolated.

TABLE 5

Partial and integral entropies and heats of formation of Co–Sn alloys (reference states: Co (FCC) and Sn (liq))

x_{Sn}	$\Delta\bar{S}_{\text{Sn}}$ (J K ⁻¹ g- atom ⁻¹)	$\Delta\bar{S}_{\text{Co}}$ (J K ⁻¹ g- atom ⁻¹)	ΔS (J K ⁻¹ g- atom ⁻¹)	$\Delta\bar{H}_{\text{Sn}}$ (J g- atom ⁻¹)	$\Delta\bar{H}_{\text{Co}}$ (J g- atom ⁻¹)	ΔH (J g- atom ⁻¹)	Phase
0.0091	–14.38	+0.09	–0.04	–36 150	+20	–310	^a
0.405	–30.01	+10.65	–5.82	–49 060	+9440	–14 250	γ
0.410	–31.74	+11.73	–6.08	–48 160	+8790	–14 560	γ
0.415	–39.84	+17.46	–6.32	–54 040	+12 920	–14 870	γ
0.500			–12.80			–22 100	CoSn
0.667			–7.23 ^b			–14 730 ^b	CoSn ₂

^a $\alpha/\alpha + \gamma$ phase boundary.

^b Interpolated.

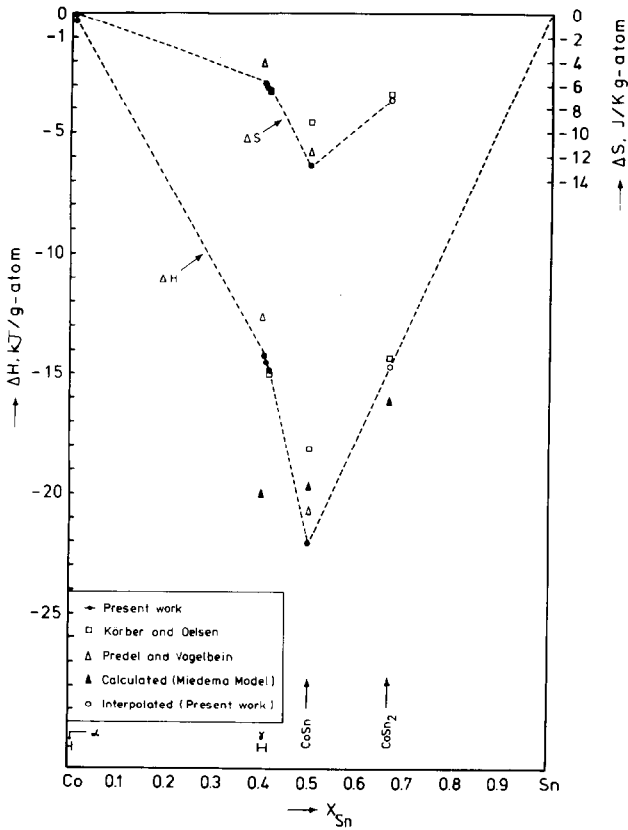


Fig. 6. Enthalpies and entropies of formation of solid cobalt-tin alloys. (Reference states: Co (FCC) and Sn (liq)).

made of data for 1073 and 773 K in order to obtain information for the CoSn and CoSn₂ phases; the corresponding results for these temperatures are presented in Figs. 4 and 5 and Tables 3 and 4. Partial entropies of solution and integral entropies of formation were derived by analogous procedures starting from the temperature coefficients of Table 1 and of eqn. (4). Finally, partial and integral heats of formation were obtained from the free-energy and entropy data by means of the Gibbs-Helmholtz relation. The various entropy and enthalpy values are given in Table 5 and shown in Fig. 6.

DISCUSSION

Since the solid solubility of tin in cobalt is less than 1.5 atomic% Sn, it may be assumed in treating the data that the activities of tin throughout the α -solid solution obey Henry's law. The activities of cobalt show positive

deviations from ideality in the cobalt-rich composition range, but these are negative in the central regions of the system. Deviations of the activity of tin are of variable sign. The large changes in activity on crossing the single-phase regions of CoSn and CoSn_2 are characteristic of the behaviour of ordered line compounds. Similar rapid variations of activity across the γ -phase field are also indicative of a highly ordered but less rigidly stoichiometric intermediate phase. The composition dependence of the free energies of formation is essentially symmetrical with maximum negative values corresponding to the CoSn compound.

Heats of formation values obtained in the present investigations are compared, in Fig. 6, with the results of the calorimetric studies by Körber and Oelsen [11] and Predel and Vogelbein [14], and with values calculated using the Miedema model [17]. The agreement of present results with calorimetrically determined values is satisfactory and demonstrates the general reliability of the EMF investigation.

The maximum exothermicity in the cobalt-tin alloys is of a similar magnitude to that previously observed in the cobalt-zinc system [1], but it is noteworthy that this now occurs at a lower concentration of the 4-valent element. This is consistent with the more rapid filling of the Co d -states in the present case. This is also indicated by the more rapid decrease in magnetic susceptibility with tin content exhibited by the phases of this system [18,19]. Though quantitative values are not well established, the magnetic studies suggest that few Co d -states remain to be filled beyond CoSn . Thus, while intercomponent electron transfer will have been increasing up to this stage, continuously enhancing the degree of heteropolar (exothermic) bonding, contributions to the molar heats of formation from this mechanism will fall with decreasing cobalt content for compositions where the d -states are completely filled. Hence, one may account for the fall in enthalpy of formation from CoSn to CoSn_2 . It is interesting to note the quite rapid variation of the heats of formation across the limited homogeneity range of the γ -phase which indicates a high degree of sensitivity to the state of occupation of the trigonal interstitial sublattice involved in the "filled" NiAs-type structures.

For the phases CoSn_2 and CoSn the Miedema model yields heats of formation in very reasonable agreement with experiment, but in the case of the γ -phase the calculated value deviates considerably from that observed. It is suggested that the failure of the model to reflect the observed trend completely may be a consequence of its treatment of the $sp-d$ hybridisation effects, which the model, like the above discussion, postulates to be responsible for large negative enthalpy contributions in systems such as this. In the Miedema calculations the hybridisation energy, present in alloys of transition metals with a polyvalent non-transition-element partner, is described by means of a single-valued parameter, determined solely by the combination of elements involved. The thermodynamic and magnetic data on the present

and previously investigated systems [1,5,6], however, demonstrate that electron transfer/hybridisation effects require to be recognised as inherently variable with composition even within individual systems.

Entropies of formation derived solely from the EMF temperature coefficients of the present study are compared in Fig. 6 with the corresponding values calculated by combining present free energies of formation with the independent calorimetrically based enthalpies of formation. The system is seen to be characterised by pronounced negative entropies of formation and it is of interest to examine these with respect to their possible origins.

With their adherence to rigid stoichiometries and precipitous activity variations, CoSn and CoSn₂ may be assumed to be maximally ordered phases and so to have zero configurational entropies. While a high degree of order is similarly indicated for the γ -phase, it is nevertheless to be expected that the entropy of this "partially filled" NiAs structure will have a configurational component. Having compositions around Co₃Sn₂, the structure will comprise Sn atoms occupying a close-packed, hexagonal sublattice with an equal number of Co atoms filling positions corresponding to its octahedral interstitial sites; the remaining Co atoms will be distributed, presumably randomly, throughout the trigonal interstices of the Sn sublattice. The configurational entropy for such a distribution may be shown to be given by the relation

$$S_{\text{conf}} = -R \left[(1 - 2x_{\text{Sn}}) \ln(1 - 2x_{\text{Sn}}) + (3x_{\text{Sn}} - 1) \ln(3x_{\text{Sn}} - 1) - x_{\text{Sn}} \ln x_{\text{Sn}} \right]$$

which yields a value of 2.335 J K⁻¹ mol⁻¹ at Co₃Sn₂.

Electronic entropies have been calculated using the relation, $S_{\text{elec}} = \int_0^T \gamma_0 dT$, using temperature-independent electronic specific heat coefficients (γ_0). Values for the latter were calculated using the free-electron approximation, $\gamma_0 = 9.62 \times 10^{-5} (V_A/n)^{2/3} \text{ J K}^{-2} (\text{mol elec})^{-1}$, where V_A is the atomic volume and n the number of free electrons per atom. Atomic volumes were derived from the lattice-parameter values reported by Nial [10]. Valencies of zero for Co and 4 for Sn were assumed throughout, although magnetic properties [18,19] suggest that Co could effectively exhibit negative valencies in the higher Sn phases; however, γ_0 estimates are not significantly affected by such an alternative assumption. The values derived assuming free-electron behaviour may nevertheless be overestimates, remembering the hybrid nature of the bonding of these phases.

Magnetic entropies may be calculated using the half-integral, localised-spin model whence $S_{\text{mag}} = R \ln(2S + 1)$ [20]. A value for the γ (Co₃Sn₂) phase has been obtained using the magnetic data of Asumana [18] which indicates for the high-temperature γ -form a Curie temperature of 680 K and, assuming quenching of the orbital moments, a localised spin, $S = 0.9/2$ per Co atom. Work by Michel [19] shows a rapid, progressive decrease in magnetic susceptibility from γ to CoSn to CoSn₂ and on the basis of the relatively low values shown by the last two, their magnetic entropies have been assumed to

TABLE 6

Analysis of the entropies of Co-Sn intermediate phases (entropy units, $\text{J K}^{-1} \text{mol}^{-1}$)

	Co_3Sn_2 (1000 K)	CoSn (1000 K)	CoSn_2 (750 K)
S_{elements}	80.12	82.98	79.88
S_{alloy}	73.80	70.18	72.65
S_{config}	2.34	0	0
S_{elec}	0.7	0.8	0.68
S_{mag}	3.03	0	0
$S_{\text{vib+dil}}$	67.73	69.38	71.97
$\theta_{\text{Debye}} \text{ (K)}$	273	256	169
$\theta_{\text{D}} \text{ (Lindemann)}$	270	230	172

be negligible. Michel's results do, however, suggest complex magnetic behaviour for all three intermediate phases, involving significant variation with temperature of the numbers of unpaired Co spins, and it is possible that magnetic entropies could be larger than the above estimates.

Total entropies of the phases at the selected temperatures were calculated from the present experimental entropies of formation and the corresponding entropies of the elements as assessed by Hultgren et al. [21]. After deducting the foregoing estimates of the configurational, electronic and magnetic contributions, Debye temperatures have been derived from the remainders by using the Debye entropy function [22] and Debye internal energy function ($\times 10^{-4}$) to describe the vibrational and dilatational entropies, respectively. The results of this entropy analysis are assembled in Table 6.

While most uncertainty in this treatment attaches to the electronic and magnetic entropy values, the effect on the subsequently derived Debye temperatures is probably slight, since these contributions are mostly comparatively small and, fortuitously, the likely associated errors are of opposite sign. Some support for the validity of the Debye temperatures obtained is provided by the corresponding values indicated by application of the Lindemann formula [23], $\theta_{\text{D}} = C_{\text{L}} T_{\text{m}}^{1/2} V_{\text{A}}^{-1/3} M^{-1/2}$, where V_{A} is the atomic volume, M the molar mass, T_{m} the melting temperature and C_{L} a constant; a value of $C_{\text{L}} = 160 \text{ cm g}^{1/2} \text{ K}^{1/2} \text{ mol}^{-5/6}$, suggested by Kaufman [24] for metallic phases, was employed. Since CoSn and CoSn_2 do not melt congruently, their peritectic decomposition temperatures were used as first approximations for T_{m} for these phases.

REFERENCES

- 1 H. Cömert and J.N. Pratt, *Thermochim. Acta*, 59 (1982) 267.
- 2 A.W. Bryant, W.G. Bugden and J.N. Pratt, *Acta Metall.*, 18 (1970) 101.
- 3 J.B. Darby, K.M. Myles and J.N. Pratt, *Acta Metall.*, 19 (1971) 7.

- 4 J.M. Bird, A.W. Bryant and J.N. Pratt, *J. Chem. Thermodyn.*, 7 (1975) 577.
- 5 S. Martosudirjo and J.N. Pratt, *Thermochim. Acta*, 17 (1976) 183.
- 6 N. Ahmad and J.N. Pratt, *Thermochim. Acta*, 45 (1981) 139.
- 7 N. Ahmad and J.N. Pratt, unpublished work, University of Birmingham, 1979.
- 8 M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
- 9 W.B. Pearson, *Lattice Spacings of Metals and Alloys*, Pergamon, London, 1967.
- 10 O. Nial, *Z. Anorg. Chem.*, 238 (1938) 287.
- 11 F. Körber and W. Oelsen, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch.*, Dusseldorf, 19 (1937) 209.
- 12 V.N. Eremenko, G.M. Lukashenko and V.L. Pritula, *Izv. Akad. Nauk SSSR, Met.*, 3 (1971) 82; *Russ. J. Phys. Chem.*, 45 (1971) 1131.
- 13 Yu.O. Esin, M.G. Valishev, V.M. Baev and P.V. Gel'd, *Zh. Fiz. Khim.*, 51 (1977) 2524; *Russ. J. Phys. Chem.*, 51 (1977) 1480.
- 14 B. Predel and W. Vogelbein, *Thermochim. Acta*, 30 (1979) 201.
- 15 G. Petot-Ervas, R. Farhi and C. Petot, *J. Chem. Thermodyn.*, 7 (1975) 1131.
- 16 S. Seetharaman and L.-I. Staffansson, *Metall. Trans.*, 10B (1979) 299.
- 17 A.R. Miedema, R. Boom and F.R. de Boer, *J. Less-Common Met.*, 41 (1975) 283.
- 18 M. Asumana, *J. Phys. Soc. Jpn.*, 17 (1962) 300.
- 19 W. Michel, *Ann. Phys.*, 11 (1963) 321.
- 20 R.A. Oriani and W.K. Murphy, *Acta Metall.*, 10 (1962) 879.
- 21 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser and K.K. Kelley, *Selected Values of the Thermodynamic Properties of the Elements and Alloys*, American Society for Metals, Metals Park, OH, 1973.
- 22 Landolt-Bornstein Tables, Vol. 2, 6th edn., Springer, Heidelberg, 1961, pp. 747, 749.
- 23 F.A. Lindemann, *Phys. Z.*, 11 (1910) 609.
- 24 L. Kaufman, *Trans. Metall. Soc. AIME*, 244 (1962) 1006.