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Energetics of Silver Alloys. Enthalpies of Mixing and Formation in the Systems Silver–Aluminium and Silver–Tin†

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The paper presents values of the enthalpies of mixing and formation in the systems Ag–Al and Ag–Sn. Appropriate polynomial functions for the composition dependence of the enthalpies of mixing and formation and their partial molar quantities are given. The behaviors of the integral and partial molar enthalpies of mixing and formation are discussed. The trend of the enthalpy of formation in the system silver–tin points out the existence of the compound Ag_3Sn in the solid state. The enthalpy of formation in the system Ag–Sn depends insignificantly on the temperature, while that in the system Ag–Al displays a pronounced temperature dependence which is attributed to lattice defects in the structure. A pronounced temperature dependence of the enthalpy of formation seems, therefore, not to be a general property of all metallic alloys.

Recent studies[1–4] on liquid and solid metallic systems disclosed the following points concerning the behavior of the thermodynamic functions:

(i) The behaviors of the thermodynamic functions depends on the chemical bonding which in turn depends on the mole fraction, (ii) the valence electron concentration (C_{ve}) predicts the trends of the partial molar quantities (refer to Refs. 5 and 6), (iii) the stability of the phases present and the behavior of the thermodynamic functions depend on the ratio of the atomic radii of the components, (iv) the trends of the thermodynamic functions predict the presence of intermetallic phases and compounds in the liquid and solid state. The last point is of considerable importance not only in the fundamental research, but also in the industries producing materials of high value. Thus, the study on the behavior of thermodynamic functions seemed of interest.

Although the above given factors may contribute to suggestions about systematic statements for the behavior of the enthalpy of formation of solid solutions, we still have to depend on model systems (free from miscibility gaps and phases of different structures). Useful statements for the enthalpy of formation in solid solutions could be obtained by studying systems of elements from homologous series. These can be obtained by combination of a metal (selected according to theoretical standpoints) with all possible neighbors to binary systems. The first work in this direction began in the previous paper.[7] The present paper deals with the trends of mixing and formation enthalpies in the systems Ag–Al[8] and Ag–Sn.[9] These systems have been selected due to their somewhat large range of miscibility in the solid state and due to the nonexistence of miscibility gaps in the liquid state. From the trends of the enthalpies of mixing and formation, it would be possible to detect eventual presence of compounds.

Another point of interest is to confirm our previous conclusion concerning the relation of the enthalpy of formation in solid solution to temperature (see Ref. 7).

Experimental

Sample. The metals used were of E. Merck extra purity grade. The preparation, treatment and testing of the alloy samples were all the same as described before.[1] The Ag–Al samples were tempered for 12 h at 825 K and 196 h at 773 K, while those of Ag–Sn were tempered for 7 h at 700 K and 89 h at 823 K.

Measurements of the enthalpy differences of Ag, Al, and Sn were carried out as follows: solid samples of silver with different masses lying between 1.781 and 2.055 g were heated at the initial temperature used and dropped in the calorimeter being heated at even temperature interval of 10 K in the range of 700 to 1300 K (Tables 1 and 2 gives the enthalpy differences for selected temperatures). The same is true for the aluminium samples with different masses lying between 1.206 and 1.895 g. Determination of the enthalpy differences of tin are based on C_p measurements in the range 323 to 1300 K[1,2] using Wittig's calorimeter (see Ref. 1).

The measurements of the enthalpy of mixing were carried out using the drop-calorimetry method: samples of silver with different masses (12.981—0.368 g) were dropped in liquid samples of tin (1.611 g) at 1220 K, or in liquid aluminium (1.129 g) at 1225 K. Measurements of the enthalpy difference of the single miscible phase were carried out using the same method: the solid alloy samples of Ag–Al system with different masses lying between 0.953 and 1.105 g were dropped at 773 and 825 K in a liquid phase of Ag–Al system (of the same composition as that of the alloy sample) at 1225 K. The same is true for the samples of Ag–Sn system: samples of different masses (1.602—1.589 g) of Ag–Sn system at 700 and 823 K were dropped in liquid phase of Ag–Sn system at 1220 K.

In order to prevent oxidation, argon gas was used as a protector during the measurement process.

Apparatus. The calorimetric apparatus and measurement technique have been described in detail[4,7] along with results for the enthalpy difference of a standard sample of tin. However, some modifications on the calorimeter are made: i.e. increasing the sensibility by using a set of fifteen differential thermocouples for measurement of the temperature drifts of the shield from calorimeter.

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† Dedicated to Prof. Dr. Franz Wittig (Phys. Chem. Inst., University of Munich) for the occasion of his 70th birthday.

Results and Discussion

(i) Enthalpies. Table 1 collects values of

$H^\circ_{\mathrm{Al}}(T)-H^\circ_{\mathrm{Al}}(773\ \mathrm{K})$; $H^\circ_{\mathrm{Al}}(T)-H^\circ_{\mathrm{Al}}(825\ \mathrm{K})$ and
$H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(773\ \mathrm{K})$; $H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(825\ \mathrm{K})$,

which were determined in the present study for the enthalpy differences of Al and Ag in the system Al-Ag.

In Table 2 are listed the enthalpy differences of Ag and Sn:

$H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(700\ \mathrm{K})$; $H^\circ_{\mathrm{Sn}}(T)-H^\circ_{\mathrm{Sn}}(700\ \mathrm{K})$ and
$H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(823\ \mathrm{K})$; $H^\circ_{\mathrm{Sn}}(T)-H^\circ_{\mathrm{Sn}}(823\ \mathrm{K})$

which were measured in the present study on the system Ag-Sn.

The deviations are 0.35% and 0.42% for a single measurement in the systems Al-Ag and Ag-Sn, respectively.

Table 3 illustrates the present values of the enthalpy differences of the alloy Al-Ag:

$H^\circ_{\mathrm{AgAl}}(1225\ \mathrm{K})-H^\circ_{\mathrm{AgAl}}(773\ \mathrm{K})$ and
$H^\circ_{\mathrm{AgAl}}(1225\ \mathrm{K})-H^\circ_{\mathrm{AgAl}}(825\ \mathrm{K})$.

The deviation is 0.43% for a single measurement.

Table 4 summarizes values of the enthalpy differences of the Ag-Sn alloy:

$H^\circ_{\mathrm{AgSn}}(1220\ \mathrm{K})-H^\circ_{\mathrm{AgSn}}(823\ \mathrm{K})$ and
$H^\circ_{\mathrm{AgSn}}(1220\ \mathrm{K})-H^\circ_{\mathrm{AgSn}}(700\ \mathrm{K})$.

The estimated standard deviation is 0.4% for a single measurement.

(ii) Enthalpies of Mixing. Equations which could be used for determining the enthalpy of mixing have been given elsewhere.[2)]

Table 5 presents values of the enthalpy of mixing in the system Al-Ag at 1225 K in the whole range of composition. A number within parenthesis is the estimated standard deviation (e.s.d.). The present

Table 1. Experimentally Determined Enthalpy Differences of Silver and Aluminium in kJ mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Al)=26.982 g mol^{-1}

T/K	$H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(773\ \mathrm{K})$	$H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(825\ \mathrm{K})$	$H^\circ_{\mathrm{Al}}(T)-H^\circ_{\mathrm{Al}}(773\ \mathrm{K})$	$H^\circ_{\mathrm{Al}}(T)-H^\circ_{\mathrm{Al}}(825\ \mathrm{K})$
800	0.759	—	0.832	—
900	3.680	2.160	4.081	2.371
1000	6.772	5.080	17.852	16.290
1100	10.034	7.870	21.053	19.382
1200	13.467	10.770	24.210	22.560
1300	27.330	25.793	27.393	25.751

Table 2. Experimentally Determined Enthalpy Differences of Silver and Tin in kJ mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Sn)=118.69 g mol^{-1}

T/K	$H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(700\ \mathrm{K})$	$H^\circ_{\mathrm{Ag}}(T)-H^\circ_{\mathrm{Ag}}(823\ \mathrm{K})$	$H^\circ_{\mathrm{Sn}}(T)-H^\circ_{\mathrm{Sn}}(700\ \mathrm{K})$	$H^\circ_{\mathrm{Sn}}(T)-H^\circ_{\mathrm{Sn}}(823\ \mathrm{K})$
800	2.790	—	9.987	—
900	5.779	2.222	12.432	9.207
1000	8.901	5.257	14.805	11.691
1100	12.235	8.242	16.998	13.870
1200	15.739	11.859	18.992	16.089
1300	29.601	25.871	20.790	18.007

Table 3. Enthalpy Difference of the Alloys in the System Silver-Aluminium in kJ mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Al)=26.98 g mol^{-1}

x_{Ag}	$H^\circ_{\mathrm{AgAl}}(1225\ \mathrm{K})-H^\circ_{\mathrm{AgAl}}(773\ \mathrm{K})$	$H^\circ_{\mathrm{AgAl}}(1225\ \mathrm{K})-H^\circ_{\mathrm{AgAl}}(825\ \mathrm{K})$
0.45	17.056	14.343
0.50	18.245	15.599
0.60	20.475	17.491
0.70	22.088	19.128
0.80	22.812	19.621
0.90	22.511	19.063

Table 4. Enthalpy Difference of the Alloys in the System Silver-Tin in kJ mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Sn)=118.69 g mol^{-1}

x_{Sn}	$H^\circ_{\mathrm{AgSn}}(1220\ \mathrm{K})-H^\circ_{\mathrm{AgSn}}(700\ \mathrm{K})$	$H^\circ_{\mathrm{AgSn}}(1220\ \mathrm{K})-H^\circ_{\mathrm{AgSn}}(823\ \mathrm{K})$
0.15	15.146	11.353
0.20	15.294	11.527
0.25	15.281	11.825

Table 5. Experimentally Determined Enthalpy of Mixing of Liqid Ag-Al Alloys at 125 K Together with That Determined by Hultgren et al.[10] in kJ mol^{-1}. Estimated Standard Deviations in Parenthesis in J mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Al)=26.98 g mol^{-1}

$x_{\rm Ag}$	$\Delta_{\rm S}H^\circ$ Present study	$\Delta_{\rm S}H^\circ$ Hultgren et al.[10]	$\Delta_{\rm S}H^\circ_{\rm Al}$	$\Delta_{\rm S}H^\circ_{\rm Ag}$
0.00	0	0	0	−36.319
0.10	−3.140(25)	−3.182	−0.570	−26.270
0.20	−5.054(26)	—	−2.562	−15.021
0.30	−5.660(22)	−6.001	−5.653	−4.876
0.40	−5.164(24)	—	−8.877	+0.406
0.50	−3.950(18)	−3.913	−11.059	+3.160
0.60	−2.471(15)	—	−11.260	+3.388
0.70	−1.140(12)	−1.171	−9.208	+2.318
0.80	−0.217(5)	—	−5.743	+1.164
0.90	+0.295(6)	−0.280	−3.250	+0.689

accuracy obtained for determination of the enthalpy of mixing is excellent: 0.4%. The present value is in good agreement with that reported by Hultgren et al.[10] (see Table 5).

The results have been fitted by the method of least squares in the following polynomial function of mole fraction of Ag, $x_{\rm Ag}$:

$$\Delta_{\rm S}H^\circ = -36.319x_{\rm Ag} + 39.457x_{\rm Ag}^2 + 117.555x_{\rm Ag}^3 - 211.243x_{\rm Ag}^4 + 91.316x_{\rm Ag}^5. \quad (1)$$

The curves of the integral and partial molar enthalpies of mixing against the composition are shown in Fig. 1. The integral enthalpy of mixing, $\Delta_{\rm S}H^\circ$ in the system Al-Ag is negative in the range 10 to 80% Ag. After reaching the minimum at $x_{\rm Ag}$=0.3, $\Delta_{\rm S}H^\circ$ increases with the increase of the composition of Ag and becomes slightly positive above the composition 85 at% Ag. Such a behavior of the enthalpy of mixing in the system Al-Ag has also been observed for $\Delta_{\rm S}H^\circ$ in the system Ag-In.[7] With this in view, we conclude that the enthalpies of mixing in binary systems of Ag and elements of the third main group of the periodic table nearly exhibit the same behavior as described above.

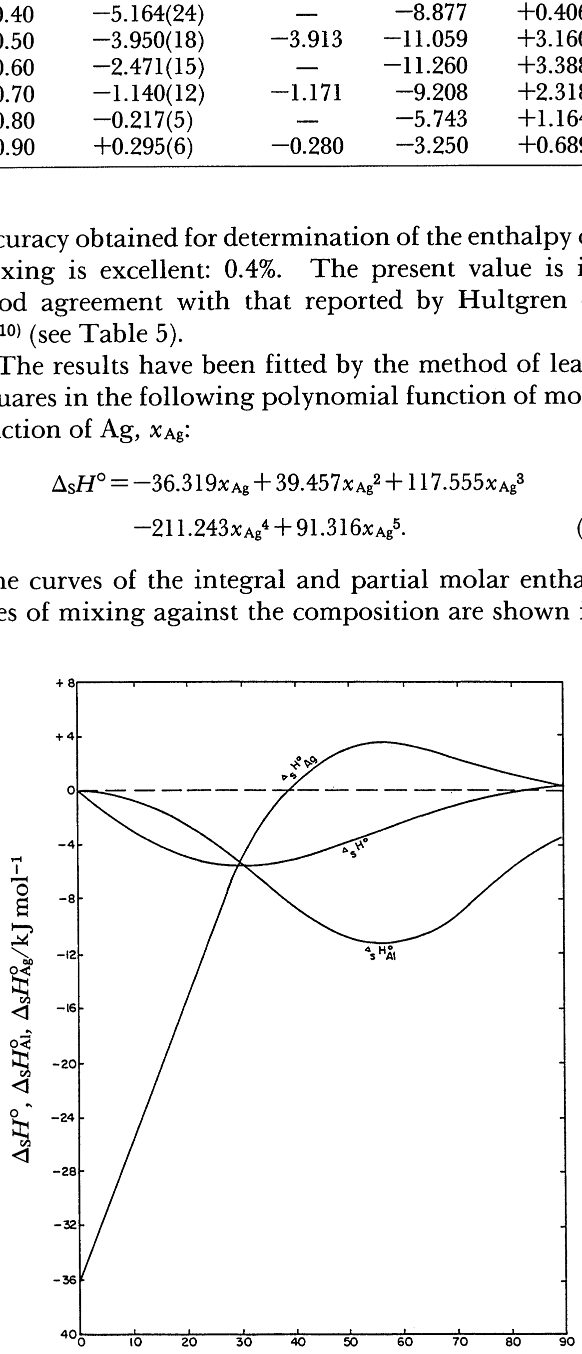


Fig. 1. The integral and partial molar enthalpies of mixing at 1225 K in the system Ag-Al.

With reference to Eq. 1, we obtain through the definition of the partial molar quantities (see Ref. 2) the following polynomial functions for $\Delta_{\rm S}H^\circ_{\rm Al}$ and $\Delta_{\rm S}H^\circ_{\rm Ag}$:

$$\Delta_{\rm S}H^\circ_{\rm Al} = -39.475x_{\rm Ag}^2 - 235.110x_{\rm Ag}^3 + 633.729x_{\rm Ag}^4 - 165.264x_{\rm Ag}^5, \quad (2)$$

$$\Delta_{\rm S}H^\circ_{\rm Ag} = -36.319 + 78.914x_{\rm Ag} + 313.208x_{\rm Ag}^2 - 1080.082x_{\rm Ag}^3 + 1090.309x_{\rm Ag}^4 - 365.264x_{\rm Ag}^5. \quad (3)$$

As shown in Fig. 1, the partial molar enthalpy of mixing of aluminium takes a minimum at the composition 55 at% Ag. This is due to the transfer of electrons from aluminium to silver. Such a transfer of electrons increases with the increase of silver mole fraction. Consequently, $\Delta_{\rm S}H^\circ_{\rm Al}$ becomes more negative and takes a minimum at $x_{\rm Ag}$=0.55. Figure 1 also illustrates that the partial molar enthalpy of mixing of silver, $\Delta_{\rm S}H^\circ_{\rm Ag}$ is negative in the range 0 to 40 at% Ag but increases with increasing composition and takes positive values above 40 at% Ag with a maximum at $x_{\rm Ag}$=0.55. This may be explained through the following view: the insertion of the somewhat larger silver atom in the structure causes a positive deformation work which increases with the increase of the

Table 6. Experimentally Determined Enthalpy of Mixing of Liqid Ag-Sn Alloys at 1220 K Together with That Determined by Hultgren et al.[10] in kJ mol^{-1}. Estimated Standard Deviations in Parenthesis in J mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Sn)=118.69 g mol^{-1}

$x_{\rm Ag}$	$\Delta_{\rm S}H^\circ$ Present study	$\Delta_{\rm S}H^\circ$ Hultgren et al.[10]	$\Delta_{\rm S}H^\circ_{\rm Ag}$	$\Delta_{\rm S}H^\circ_{\rm Sn}$
0.00	0[a]	0	0	−32.137
0.10	−2.254(16)	−2.202	−0.863	−14.774
0.20	−2.970(12)	—	−2.706	−4.026
0.30	−2.689(09)	−2.617	−4.532	+1.613
0.40	−1.888(11)	—	−5.574	+3.641
0.50	−0.961(08)	−0.909	−5.383	+3.462
0.60	−0.195(4)	—	−3.927	+2.294
0.70	+0.255(6)	+0.206	−1.672	+1.081
0.80	+0.382(4)	—	+0.340	+0.364
0.90	+0.358(3)[a]	+0.307	+2.172	+0.364

a) Extrapolated value.

composition of Ag due to higher tension suffered by the structure. The above described relations for $\Delta_S H^\circ$ have also been deduced for $\Delta_S H^\circ$ in the system Ag-In,[7] however, the position of the maxima or minima differs in both systems.

In Table 6 are listed the values of the integral and partial molar enthalpy of mixing in the system Ag-Sn together with those obtained by Hultgren et al.[10] The accuracy obtained is 0.5%. The present value is in acceptable agreement with that obtained by Hultgren et al.[10] who give an accuracy of about 1% for their measurements.

For the integral enthalpy of mixing its partial molar quantities, the following equations are derived:

$$\Delta_S H^\circ = -32.1371x_{Sn} + 105.670x_{Sn}^2 - 98.8385x_{Sn}^3 + 6.8999x_{Sn}^4 + 18.8596x_{Sn}^5, \quad (4)$$

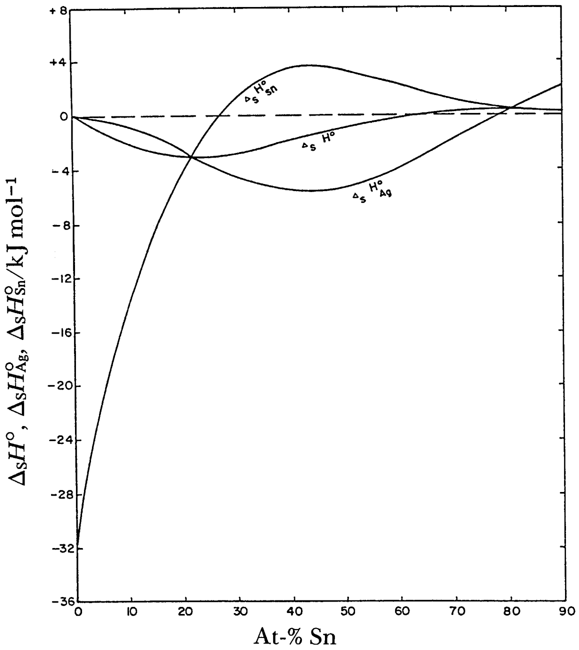


Fig. 2. The integral and partial molar enthalpies of mixing at 1220 K in the system Ag-Sn.

$$\Delta_S H^\circ_{Ag} = -105.767x_{Sn}^2 + 197.677x_{Sn}^3 - 20.699x_{Sn}^4 - 73.438x_{Sn}^5, \quad (5)$$

$$\Delta_S H^\circ_{Sn} = -32.137 + 211.534x_{Sn} - 402.282x_{Sn}^2 + 225.277x_{Sn}^3 + 73.598x_{Sn}^4 - 75.438x_{Sn}^5 \quad (6)$$

These equations produce the curves of the integral and partial molar enthalpies of mixing against the composition of Sn, x_{Sn} as shown in Fig. 2. It is clearly observable that the trends of the integral and partial molar enthalpy of mixing in the system Ag-Sn are similar to those of the integral and partial molar enthalpy of mixing in the system Ag-Al. However, the minimum of $\Delta_S H^\circ$ in the system Ag-Sn is shifted to the composition $x_{Sn}=0.2$. This is due to the somewhat large difference in the electronegativity between Ag and Sn if compared with that between Ag and Al in the system Ag-Al. Furthermore, the minimum of $\Delta_S H^\circ_{Ag}$ and also the maximum of $\Delta_S H^\circ_{Sn}$ are shifted to the composition $x_{Sn}=0.4$.

(iii) Enthalpies of Formation. Equations which could be used to calculate the enthalpy of formation from that of mixing were derived before.[2].

The present values of the integral and partial molar enthalpies of formation at 773 and 823 K in the system Ag-Al are given in Table 7 for the compositions 30 to 90 at% Ag. A number within parenthesis is the e.s.d. The average error of the individual measurements was found to be 0.4% for the enthalpy of formation at 773 and 0.5% for that at 825 K. The present value is in fair agreement with that obtained by Wittig[11] who studied the heat of formation in the system Ag-Al at 603, 643, and 703 K, however, using a different procedure.

The following polynomial functions for $\Delta_f H^\circ$, $\Delta_f H^\circ_{Al}$, and $\Delta_f H^\circ_{Ag}$ were derived to produce the curves of these quantities against x_{Ag} as illustrated in Fig. 3:

$$\Delta_f H^\circ = -8.402x_{Ag} + 0.502x_{Ag}^2 + 12.178x_{Ag}^3, \quad (7)$$

$$\Delta_f H^\circ_{Al} = -0.502x_{Ag}^2 - 24.356x_{Ag}^3, \quad T=773\text{ K} \quad (8)$$

$$\Delta_f H^\circ_{Ag} = -8.402 + 1.004x_{Ag} + 36.032x_{Ag}^2 - 24.345x_{Ag}^3. \quad (9)$$

Table 7 and Fig. 3 illustrate the negative trend of the

Table 7. Enthalpy of Formation in the System Silver-Aluminium in kJ mol^{-1}. Estimated Standard Deviation in Parenthesis in J mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Al)=26.98 g mol^{-1}

x_{Ag}	T=773 K			T=825 K		
	$\Delta_f H^\circ$	$\Delta_f H^\circ_{Al}$	$\Delta_f H^\circ_{Ag}$	$\Delta_f H^\circ$	$\Delta_f H^\circ_{Al}$	$\Delta_f H^\circ_{Ag}$
0.30	−2.147[a)]	−0.703	−5.516	−1.857[a)]	−0.773	−4.387
0.40	−2.501[a)]	−1.640	−3.794	−2.079[a)]	−1.803	−2.493
0.45	−2.570	−2.321	−2.321	−2.070	−3.461	−1.480
0.50	−2.553(10)	−2.919	−1.937	−1.969(9)	−3.487	−0.449
0.60	−2.230(11)	−5.442	−0.089	−1.312(7)	−5.986	+1.583
0.70	−1.458(8)	−8.600	+1.602	−0.443(10)	−9.450	+3.444
0.75	−0.882[a)]	−10.558	+2.344	+0.290(5)	−11.613	+4.260
0.80	−0.165(5)[a)]	−12.792	+3.193	+1.162[a)]	−14.050	+4.973
0.85	+0.700[a)]	−15.320	+3.527	+2.198[a)]	−19.773	+5.562
0.90	+1.722(7)[a)]	−18.162	+3.932	+3.407[a)]	−19.953	+6.008

a) Extrapolated value.

enthalpy of formation. $\Delta_f H^\circ$ increases slightly with the composition of Ag. This is due to the insertion of the silver atom, which is not much larger than the aluminium atom, in the structure. This causes a small negative deformation work so that the enthalpy of formation exhibits a slight composition dependence.

The enthalpy of formation in the system Ag-Al takes a minimum at the composition $x_{Ag}=0.45$. This would be clear from the extrapolated trend of $\Delta_f H^\circ_{Al}$ at the compositions 0.4 and 0.3 (Fig. 3).

Figure 3 shows the negative trend of $\Delta_f H^\circ_{Al}$ which becomes more negative at higher composition of Ag.

The partial molar enthalpy of formation of silver is negative, but increases with increasing composition to take positive values at the composition 60 at%Ag. This behavior is also understandable: the insertion of the somewhat larger silver atom in the structure leads to higher tension due to a small deformation work being associated with the insertion of the aluminium atom in the structure.

Table 7 and Fig. 4 illustrate the enthalpy of formation at 773 and 825 K in the system Ag-Al. The following polynomial function produces the curve of $\Delta_f H^\circ$ at 825 K:

$$\Delta_f H^\circ = -7.562x_{Ag} + 0.552x_{Ag}^2 + 13.396x_{Ag}^3. \tag{10}$$

It is clearly observable that the enthalpy of formation displays a pronounced temperature dependence. This has also been recognised by Wittig[11] in his study on the enthalpy of formation in the same system. According to Wittig's explanation, such a temperature dependence of $\Delta_f H^\circ$ may be attributed to lattice defects of greater expansion of the aluminium lattice in the alloy compared with the expansion in pure aluminium metal.

The values of the partial molar enthalpies of formation of aluminium and silver at 825 K are given in Table 7. These values are obtained from calculations according to the equations being derived with reference to the definition of the partial molar quantities (see Ref. 2) and through Eq. 10:

$$\Delta_f H^\circ_{Al} = -0.552x_{Ag}^2 - 26.792x_{Ag}^3, \tag{11}$$

$$\Delta_f H^\circ_{Ag} = -7.562 + 1.104x_{Ag} + 39.639x_{Ag}^2 - 26.792x_{Ag}^3. \tag{12}$$

These equations would produce curves for $\Delta_f H^\circ_{Al}$ and $\Delta_f H^\circ_{Ag}$ with trends similar to those of the same partial molar quantities at 773 K.

Values of the integral and partial molar enthalpies of formation at 700 and 823 K in the range of the ξ phase of the system Ag-Sn are presented in Table 8. The average error of the individual measurements was found to be 0.5% for the enthalpy of formation at both temperatures. There exists no report on the data of the enthalpy of formation for the system Ag-Sn in the literature. Hence a comparison with the present data cannot be made.

From curve-fitting calculations, the following equations are derived for the enthalpy of formation

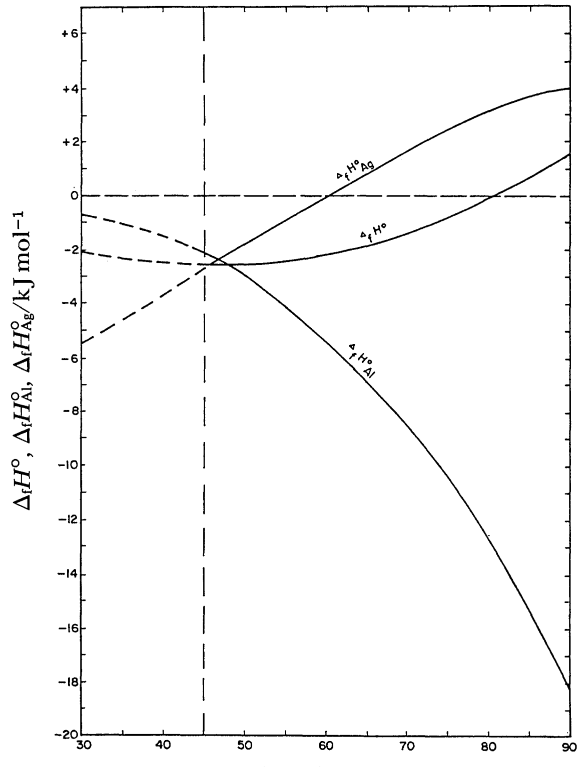


Fig. 3. The integral and partial molar enthalpies of formation at 773 K in the system Ag-Al.

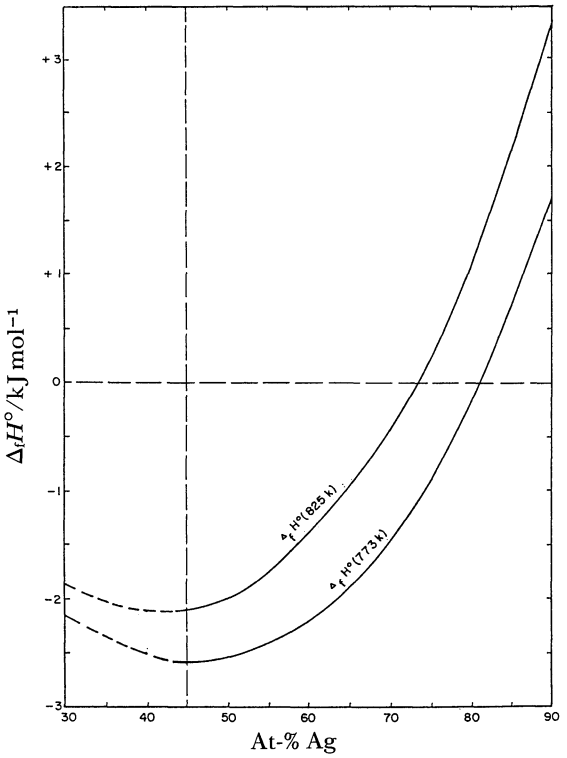
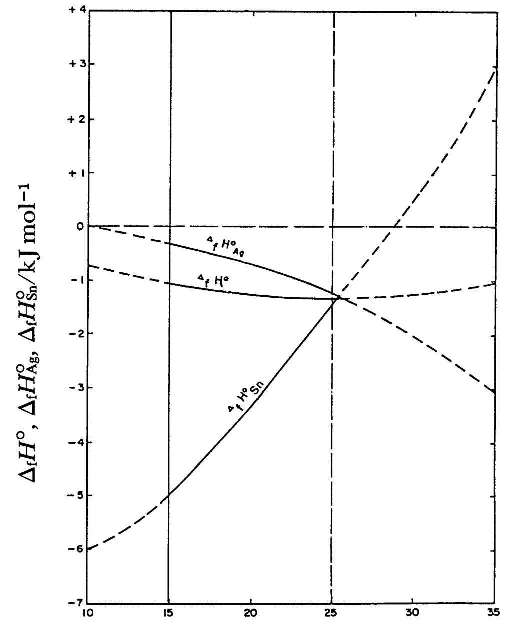


Fig. 4. The enthalpies of formation at 773 and 825 K in the system Ag-Al.

Table 8. Enthalpy of Formation in the System Silver–Tin in kJ mol^{-1}. Estimated Standard Deviation in Parenthesis in J mol^{-1}. M(Ag)=107.868 g mol^{-1}; M(Sn)=118.69 g mol^{-1}

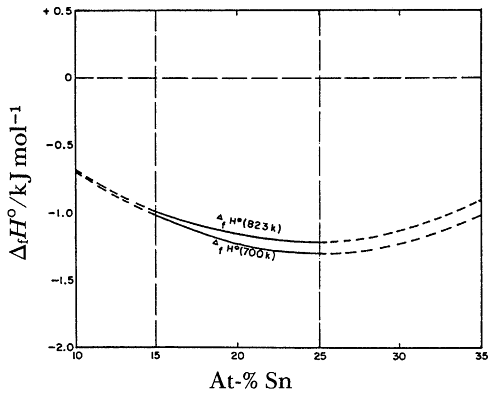
x_{Sn}	T=700 K			T=823 K		
	$\Delta_f H^\circ$	$\Delta_f H^\circ_{Ag}$	$\Delta_f H^\circ_{Sn}$	$\Delta_f H^\circ$	$\Delta_f H^\circ_{Ag}$	$\Delta_f H^\circ_{Sn}$
0.10	−0.775[a)]	−0.013	−6.013	−0.720[a)]	−0.120	−6.175
0.15	−1.026(8)	−0.323	−5.007	−0.980(9)	−0.337	−4.713
0.20	−1.211(8)	−0.679	−3.339	−1.157(4)	−0.696	−3.003
0.25	−1.285(6)	−1.224	−1.467	−1.212(6)	−1.351	−5.699
0.30	−1.228[a)]	−1.992	+0.468	−1.133[a)]	−3.447	+1.003
0.35	−1.022[a)]	−3.041	+3.041	−0.900[a)]	−2.049	+3.217

a) Extrapolated value.



At-% Sn

Fig. 5. The integral and partial molar enthalpies of formation at 700 K in the range of the ξ phase in the system Ag–Sn.



At-% Sn

Fig. 6. The enthalpies of formation at 700 and 823 K in the range of the ξ phase in the system Ag–Sn.

and its partial quantities in the system Ag–Sn:

$$\Delta_f H^\circ = -8.402x_{Sn} + 6.502x_{Sn}^2 + 26.178x_{Sn}^3, \quad (13)$$

$$\Delta_f H^\circ_{Ag} = -6.502x_{Sn}^2 - 52.356x_{Sn}^3, \quad T = 700\ \mathrm{K} \quad (14)$$

$$\Delta_f H^\circ_{Sn} = -8.402 + 13.004x_{Sn} + 72.032x_{Sn}^2 - 52.356x_{Sn}^3, \quad (15)$$

and

$$\Delta_f H^\circ = -8.193x_{Sn} + 6.665x_{Sn}^2 + 26.836x_{Sn}^3, \quad (16)$$

$$\Delta_f H^\circ_{Ag} = -6.665x_{Sn}^2 - 53.672x_{Sn}^3, \quad T = 823\ \mathrm{K} \quad (17)$$

$$\Delta_f H^\circ_{Sn} = -8.193 + 13.330x_{Sn} + 73.843x_{Sn}^2 - 53.672x_{Sn}^3. \quad (18)$$

The plot of the integral and partial molar enthalpies of formation at 700 K versus the composition is shown in Fig. 5. The enthalpy of formation is negative and decreases with increasing composition of Sn to reach a minimum at the composition 25 at% Sn; after that the enthalpy of formation increases with the increase of the composition of Sn. Such a trend of $\Delta_f H^\circ$ points out the presence of a compound. Using Wagner's theory[12)] for a heteropolar compound where Ag is considered to be the donor and Sn the acceptor, the composition of a compound with the form Ag_3Sn should lie $x_{Sn}=1-3/(1+3)=0.25$. Since the minimum of $\Delta_f H^\circ$ also lies at the same composition, the existence of such a compound seemed to be reliable. More evidence for the presence of the compound Ag_3Sn is the previous diffraction study by Pearson.[13)]

The partial molar enthalpy of formation of Ag is negative and becomes more negative at higher composition of Sn. The partial molr enthalpy of formation of tin is also negative but increases with increasing composition of Sn. The negtive trend of $\Delta_f H^\circ$ indicates the stability of the structure. However, this stability decreases at higher composition of Sn due to the increasing insertion of Sn atom in the structure: the deformation work increases due to higher tension suffered by the structure.

A comparison of the trend of $\Delta_f H^\circ$ at 700 K with that at 823 K (see Fig. 6) leads to the following conclusions: the enthalpy of formation in the system Ag–Sn depends insignificantly on the temperature. This is in contrast to that for the enthalpy of formation in the system Ag–Al where $\Delta_f H^\circ$ displays a pronounced temperature dependence due to lattice defect in the structure (see Ref. 11). Low and high temperature diffraction studies[13)] on the system Ag–Sn revealed nearly the same values of the interlayer distance, d, and consequently excluded lattice defects in the structure. Hence a pronounced temperature dependence of $\Delta_f H^\circ$ seemed not to be a general property of all metallic alloys. This also confirms our previous conclusion concerning the relation of $\Delta_f H^\circ$ in metallic systems to temperature (see Ref. 7).

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