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On the Temperature Dependence of the Heat of Formation of the Compound AgMg

by

A. K. Jena and M. B. Bever

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Department of Metallurgy and Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts

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A. K. Jena and M. B. Bever
Department of Metallurgy and Materials Science
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The heats of formation ΔH at $273^{o}K$ of the compound AgMg as a function of composition have been measured by solution calorimetry.[1] The value at the stoichiometric composition is -4.41 kcal/g-atom. From e.m.f. measurements[2,3] the heat of formation at $773^{o}K$ of stoichiometric AgMg has been determined as -5.19 kcal/g-atom.[4] The combination of these two values results in an unusually high negative temperature coefficient of the heat of formation $d\Delta H/dT = \Delta C_p = -1.6$ cal/g-atom-^{o}K. By contrast, published heat contents of the compound AgMg and the component elements above room temperature[5] indicate that the temperature coefficient of the heat of formation of AgMg is nearly zero. In this communication calorimetrically measured heats of formation of AgMg below room temperature are reported and the temperature dependence of the heat of formation is discussed.

The heat effects of additions of samples of the compound AgMg containing 50.1 at. pct Mg to liquid tin-rich solutions at $623^{o}K$ were measured in a solution calorimeter.[6] The heat effects of additions plotted against the average of the atom fractions of solutes in the solution before and after each addition were a linear function of composition from which the heat effect at infinite dilution was obtained (Table I). The calorimeter was calibrated by additions of tin; the heat content ($H_{623^{o}K} - H_{273^{o}K}$) of tin was taken as 4.08 kcal/g-atom.[4]

The heat effect at infinite dilution of an addition of AgMg is

$$h_{x_{Sn} \rightarrow 1} = -\Delta H_{AgMg,T} + \sum_i X_i \left[(H_{623^o} - H_T)_i + \Delta\bar{H}_{i,x_{Sn} \rightarrow 1} \right] \qquad (1)$$

where $\Delta H_{AgMg,T}$ = heat of formation of AgMg at T^oK

T = temperature from which samples are added (78^o, 195^o and 273^oK)

X_i = atom fraction of i in AgMg

$\Delta\bar{H}_i$ = relative partial gram-atomic enthalpy of i in tin-rich solution

x_{Sn} = atom fraction of tin in the tin-rich solution

i stands for Ag and Mg

In order to find the heat of formation $\Delta H_{AgMg,T}$ by Eq (1), the heat contents $(H_{623^o} - H_T)$ of silver and magnesium and the gram-atomic enthalpies of silver and magnesium in liquid tin relative to solid silver and magnesium at 623^oK are required. Published values of the heat contents were used.[4] The partial gram-atomic enthalpy of magnesium has been reported as -5.615 ± 0.060 kcal/g-atom.[7] The partial gram-atomic enthalpy of silver was obtained from the heat effects at infinite dilution on addition of silver to liquid tin-rich solutions measured in this investigation (Table I) and published heat contents of silver.[4] The resulting value of 3.63 kcal/g-atom is consistent with values for other temperatures.[8]

The heats of formation of AgMg at 78^o, 195^o and 273^oK are listed in Table I. Any errors in the heat contents of magnesium and silver[4] and in the partial gram-atomic enthalpy of magnesium[7] are systematic errors

in the reported heats of formation. The measured heat of formation at 273°K of -4.48 kcal/g-atom of AgMg containing 50.1 at. pct Mg compares with -4.41 ± 0.03 kcal/g-atom.(1) At least part of the difference between these two values may be attributed to systematic errors. Since these errors affect the heats of formation at 78° and 195°K in a similar manner, the temperature dependence $d\Delta H/dT$ is relatively unaffected.

The heats of formation are plotted in Fig. 1 against temperature. The temperature coefficient of ΔH is negative and appreciable near 78°K, but with increasing temperature it decreases gradually to a small value near room temperature. Such behavior of the heat of formation below room temperature has been found for the compounds InSb and InTe.(9) At and above room temperature, the published heat capacities of most intermetallic compounds deviate from the Kopp-Neumann rule by only a few percent(10) and consequently the temperature coefficient of ΔH is generally small.

Heats of formation of AgMg above room temperature have been calculated from the measured heat of formation at 273°K and published heat contents(5) of AgMg, Ag and Mg between 298°K and 800°K, by the equation

$$\Delta H_T = \Delta H_{273^\circ} + (H_T - H_{273^\circ})_{AgMg} - 0.499(H_T - H_{273^\circ})_{Ag} - 0.501(H_T - H_{273^\circ})_{Mg} \quad (2)$$

The dashed line in Fig. 1 represents this equation. The temperature dependence of the heat of formation of AgMg above room temperature is consistent with the temperature dependence of the measured heats of formation at 78°, 195° and 273°K, as shown by the continuity of the slopes of the two parts of the curve. It can be seen that the heats of formation based on the e.m.f. measurements are likely to be in error.

The large cohesive energy of AgMg to be inferred from its negative heat of formation suggests that the bonds are stronger in the compound than in the component elements. Stronger bonds are characterized by higher frequencies of vibration of the lattice and higher Debye temperatures. The contribution of the lattice heat capacities to ΔC_p, therefore, is negative. Since near $78^{\circ}K$ all contributions to the ΔC_p of AgMg are small compared with that of the lattice, the temperature dependence of ΔH should have an appreciable negative value. With increasing temperature the difference between the lattice heat capacities becomes small and other terms become increasingly important so that the temperature dependence of ΔH may approach zero at higher temperatures.

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Table I

Heat Effects of Additions of AgMg, Ag and Mg to Liquid Tin-Rich Solutions at Infinite Dilution at 623°K and Heat of Formation of AgMg at 78°, 195° and 273°K.

Additions	Temperature from which Samples were Added, T°K	Measured Heat Effect at Infinite Dilution, kcal/g-atom	Heat of Formati at T°K, kcal/g-atom
AgMg(X_{Mg} = 0.501)	273°	5.69 ± 0.02 (1)*	-4.48
AgMg(X_{Mg} = 0.501)	195°	6.11 ± 0.04 (2)	-4.45
AgMg(X_{Mg} = 0.501)	78°	6.51 ± 0.05 (2)	-4.28
Ag	273°	5.82 ± 0.03 (1)	
Mg	273°	-3.39 ± 0.06**	

Note: * Number of runs in parentheses

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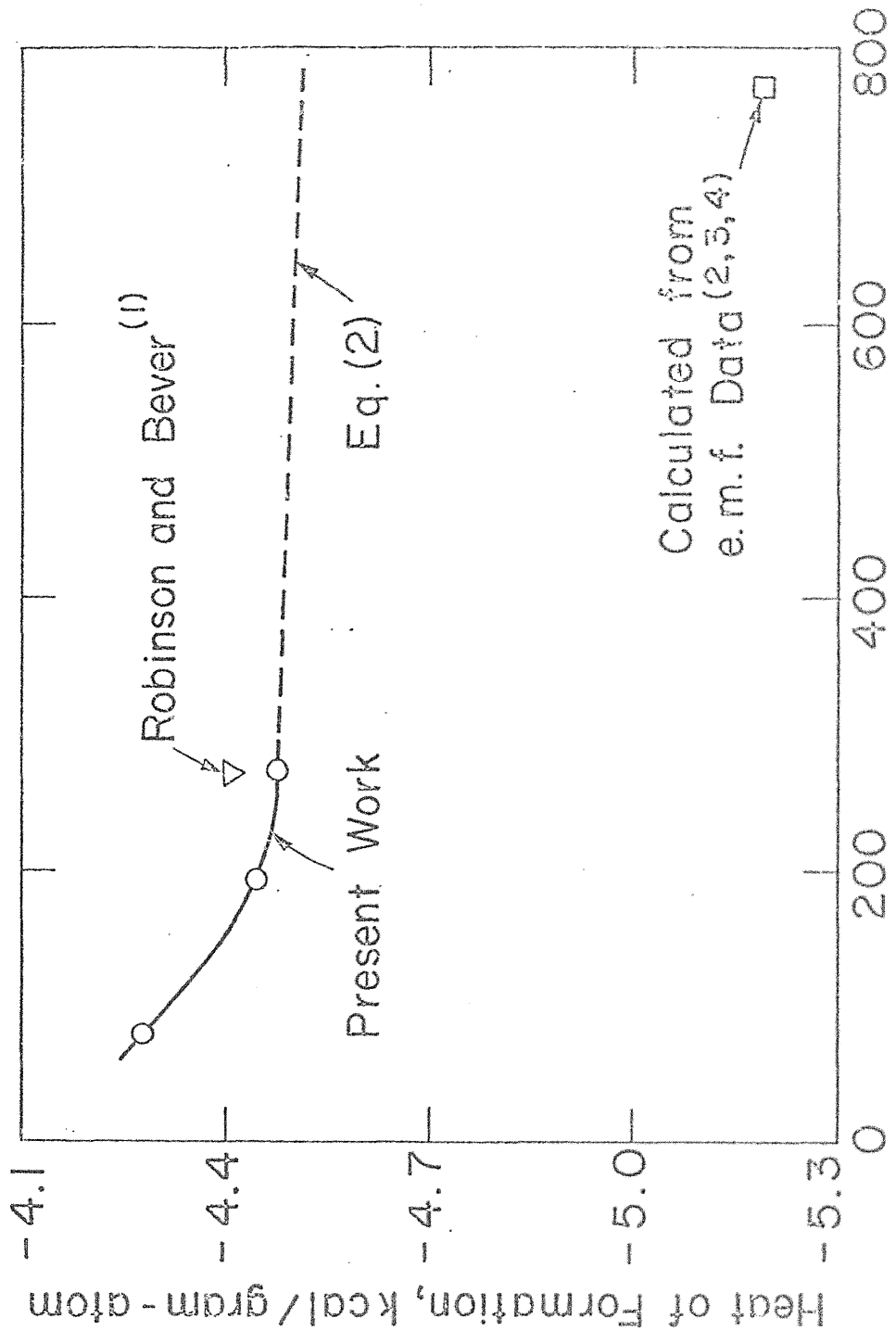

Fig. 1 Heat of Formation of the Compound AgMg Containing 50.1 at. pct. Mg as a Function of Temperature.

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Heats of formation at 78°, 195° and 273°K of the compound AgMg containing 50.1 at. pct Mg have been measured by metal solution calorimetry. The relative partial gram-atomic enthalpy of silver in liquid tin-rich solutions at infinite dilution has also been measured. The temperature coefficient of the heat of formation is negative and appreciable near 78°K, but with increasing temperature it decreases gradually to a small value near room temperature. This is consistent with the reported high-temperature heat contents of AgMg, Ag and Mg It is suggested that such behavior of the temperature dependence of the heat of formation can be explained on the basis of the contributions from lattice heat capacities.

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