Note

Rationale on the Thermodynamic Properties of Elements and Binary Compounds

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1. Introduction

As a sequel to the author's recent publication of a short paper in *ISIJ International*,¹⁾ this latest study was undertaken to explore the broader aspects of rationale on the thermodynamic properties of elements and several binary compounds. The results of this study are presented in this Note.

The thermodynamic data used are those of Hultgren *et al.*^{2,3)} on elements and binary alloys and by Barin *et al.*^{4,5)} on a wide range of inorganic substances.

2. Free Energies at mp and bp Temperatures

The free energies G_{mp} at the melting point temperatures of elements are plotted in Fig. 1(a). With the exception of Lanthanoid and Actinoid series of elements, the data points for most other elements are randomly scattered about the direct proportionality line. The data in Fig. 1(b) clearly show that the free energies G_{bp} are directly proportional to the absolute boiling point temperature of these elements.

Fig. 1. Free energies G_{mp} and G_{bp} related to the absolute melting point and boiling point temperatures, respectively.

The G_{mp} values for a series of oxides, sulphides and nitrides in Fig. 2 are again directly proportional to the absolute melting point temperature. A similar trend appears in Fig. 3 for the G_{mp} values of solid borides and silicides. Most of the data points for the G_{mp} values of silicates and titanates in Fig. 4 are also in direct proportionality to the absolute melting point temperature.

3. Isothermal Free Energy G_T Relation to $(H/S)_T$ Ratio

As shown in Fig. 5, the free energies of solid and liquid elements at 1000 K increase with an increasing heat content/entropy ratio (H/S) at 1000 K. Similar relations are found for 2000 K with much lower G_T and higher H/S values.

For solid oxides and sulphides the G_T vs. $(H/S)_T$ relations

Fig. 2. G_{mp} values are directly proportional to the absolute melting point temperature of binary solid compounds.

Fig. 3. G_{mp} values are directly proportional to the absolute melting point temperature of solid silicide and boride compounds.

Fig. 4. G_{mp} values are directly proportional to the absolute melting point temperature of solid silicates and titanates.

Fig. 5. G_T relations to $(H/S)_T$ ratios for solid and liquid elements at 1000 K.

Fig. 6. G_T relations to $(H/S)_T$ ratios for solid oxides and sulphides at 1000 and 2000 K.

in Fig. 6 are well represented by straight lines for 1000 and 2000 K. Similar linear relations in Fig. 7 are for solid borides, carbides and nitrides at 1000 and 2000 K.

4. Temperature Dependence of G_T and $(H/S)_T$ Ratio

The free energies and heat content/entropy ratios are

Fig. 7. G_T relations to $(H/S)_T$ ratios for solid borides, carbides and nitrides at 1000 and 2000 K.

Fig. 8. Temperature dependence of G_T and $(H/S)_T$ values for Mo, W, Ta and elements in the Lanthanoid and Actinoid series.

functions of temperature in a systematic manner as illustrated in Fig. 8 for Mo, W, Ta and for elements in the Lanthanoid and Actinoid series. The $(H/S)_T$ ratios increase linearly with an increasing temperature. There is a non-linear decrease in the values of G_T with an increasing temperature. It should be noted that for the Lanthanoid and Actinoid series of elements, the G_T values are much lower than other elements. Uncertainties appear on the G_{mp} and $(H/S)_{mp}$ values for Th.

5. (H/S) Ratios Related to mp and bp Temperatures

In Fig. 9, the heat content/entropy ratios show to be directly proportional to the melting point and boiling point temperatures of liquid and gaseous elements, respectively. In Fig. 10, the enthalpies of fusion and enthalpies of vapourisation of elements are observed to be linear functions of the melting point and boiling point temperatures, respectively. For the latter case, a very slight curve may well be represented by the broken straight line.

6. Concluding Remarks

The regularities found in the free energies and heat content/entropy ratios as functions of temperature may be considered to constitute the essence of the concept of a series of rationales on some of the thermodynamic properties of elements and their binary compounds. Perhaps the most

Fig. 9. Ratios $(H/S)_l$ and $(H/S)_g$ are directly proportional to the melting point and boiling point temperatures of liquid and gaseous elements, respectively.

Fig. 10. Enthalpies of fusion and vapourisation of elements at the melting point and boiling point temperatures, respectively.

significant aspect of the rationale is in the direct proportionality of the G_T and $(H/S)_T$ values to the absolute melting point and boiling point temperatures.

These findings could be helpful in assessing assuredly the thermodynamic properties of elements and their compounds at higher temperatures beyond the experimental range.

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