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*, 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.

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 $(H/S)_T$ 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...
in Fig. 6 are well represented by straight lines for 1 000 and 2 000 K. Similar linear relations in Fig. 7 are for solid borides, carbides and nitrides at 1 000 and 2 000 K.

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

The free energies and heat content/entropy ratios are 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
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.

REFERENCES

1) E. T. Turkdogan: ISIJ Int., 47 (2007), 1232.

2) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelly: Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, Ohio, (1973).

3) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelly: Selected Values of the Thermodynamic Properties of Binary Alloys, American Society for Metals, Metals Park, Ohio, (1973).

4) I. Barin and O. Knacke: Thermodynamic Properties of Inorganic Substances, Springer-Verlag, Berlin, (1973).

5) I. Barin, O. Knacke and O. Kubaschewski: Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, (1977).