

Phenomenological Relations between Solid Phases and a Liquid Phase of a Metal

By

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Part I

This report consists of two sections; one concerns the melting curves maxima, the entropy changes maxima during melting and the other concerns the electric resistances of bismuth as functions of pressure and temperature, which were observed in our experiments. The melting curves maxima can be explained phenomenologically by the two species model of Rapoport. Even though this model cannot be applied directly to bismuth, because the phase diagram is too complicated, the observed results of the electrical resistances seem to support the Rapoport's view concerning to the relations between solid phases and a liquid phase.

Introduction

There are a few theories which predict the melting curves. One of them is the Simon's equation¹⁾. With the assumption that the Grüneisen ratio is indeed constant, Slater²⁾ reformulated theoretically the equation from the Lindeman³⁾ law of melting. Recently Kraut and Kennedy⁴⁾ proposed the empirical equation to give the melting curves of the alkali metals except cesium. Following Ross⁵⁾, these equations can be derived by the statistical-mechanical manner and we can see that the difference of the forms of the two equations are due to the types of the potentials.

These equations do not predict the correct melting curves and give considerably high melting temperatures for most substances at high pressure. Moreover, since they are monotonous in the word of mathematics, they cannot explain the melting curves maxima.

Quite recently, Rapoport^{6) 7) 8)} proposed the unique model for molten metals. It is called the two species model and defined as follows⁹⁾. Suppose the liquid consists of two species, in the broad sense of the word, the one corresponding to the low pressure solid phase and the other to the high pressure phase respectively, and a species therefore is characterized by coordination number, nearest neighbor distance and bond type, the liquid is looked upon as a quasilattice with an average coordination number and can be treated by statistical mechanical methods by use of Bragg-Williams and Quasichemical approximations.

In this report we shall not give any criticisms to the two species model but derive some important facts. The phenomenological explanation of the melting curves maxima is included in them.

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The observed results of the electrical resistances of bismuth as functions of pressure and temperature seem to support the Rapoport's view. Here, the words "Rapoport's view" mean that a liquid consists of "Species".

Melting Curves Maxima on The Two Species Model

We shall restrict the detailed treatments to cesium and tellurium, because we can apply the numerical results of Rapoport^{7) 8)} directly to them. Following the two species model, the chemical potentials of two species (say A and B) are given by

$$\mu_A = \mu_A^\circ + RT \ln(1-x) + x^2 \omega \quad (1)$$

and

$$\mu_B = \mu_B^\circ + RT \ln x + (1-x)^2 \omega \quad (2)$$

respectively. The equilibrium condition is

$$\mu_A = \mu_B.$$

Hence we have

$$\Delta\mu^\circ = RT \ln \frac{x}{1-x} + (1-2x)\omega, \quad (3)$$

where

$$\Delta\mu^\circ = \mu_A^\circ - \mu_B^\circ.$$

Rapoport determined the relation between x , the mole fraction of the species B and pressure P from eq.(3), under the assumption for ω to satisfy the selfconsistency between $\Delta\mu^\circ$ and the electrical properties of the liquid under consideration.

The Gibbs' free energy of the liquid at pressure P and temperature T is

$$\begin{aligned} G &= \mu_A(1-x) + \mu_B x \\ &= \mu_A^\circ(1-x) + \mu_B^\circ x + RT \{(1-x) \ln(1-x) + x \ln x\} + x(1-x)\omega. \end{aligned} \quad (4)$$

If the pressure dependence of ω is negligible compared with others, the volume of the liquid is given by

$$V_l = \left(\frac{\partial G}{\partial P} \right)_T = (V_A)_l - x(\Delta V)_l, \quad (5)$$

where

$$\frac{\partial \mu_A^\circ}{\partial P} = (V_A)_s, \quad \frac{\partial \mu_B^\circ}{\partial P} = (V_B)_s$$

and

$$(\Delta V)_l = (V_A)_l - (V_B)_l > 0.$$

Hereafter l, s denote liquid and solid respectively.

Now, we shall introduce the assumption for the volume relation between the partial molar volume of a species and the volume of the corresponding solid phase, i, e ,

$$(V_A)_l = \frac{(V_A^\circ)_l}{(V_A^\circ)_s} \cdot (V_A)_s, \quad (6)$$

where $^\circ$ denotes the value at zero pressure. Moreover we assume that the ratio $(V_A^\circ)_l / (V_A^\circ)_s$ is indeed constant and independent of species and solid phases. $(\Delta V)_l$ then becomes

$$(\Delta V)_l = (V_A)_l - (V_B)_l = \frac{(V_A^\circ)_l}{(V_A^\circ)_s} \{(V_A)_s - (V_B)_s\}, \quad (7)$$