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to the Equation of State*

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A GENERIC MODEL FOR THE IONIC CONTRIBUTION TO THE EQUATION OF STATE

by

J. D. Johnson

ABSTRACT

We have formulated a model that yields the thermodynamics for the ionic contribution to general materials from the low temperature solid region, through melting, to ideal gas. We use the Debye model for the solid. Melting is determined by the Lindemann formula with standard rules of thumb used to determine density and energy discontinuities. The model interpolates through the liquid regime to ideal gas assuming that the specific heat drops monotonically from about $3R$ at melting, to $9R/4$ at five times melting, and continuing to $3R/2$ at high temperatures. The area under the specific heat curve is constrained in the model to reproduce the correct high temperature entropy. Thus, for a compound the extra contribution from the entropy of mixing forces into the model, in a crude way, the extra specific heat due to dissociation.

Introduction

In the modeling of equations of state in those cases where the region of interest is several decades of density and temperature, it is standard to divide the problem into three contributions: the zero temperature isotherm, the thermal contribution from the electrons, and the thermal contribution from the motion of the ions. In this paper we consider only the latter. Furthermore, it is customary to use a generic model for all materials that, in outline, is a Debye model in the solid region but interpolates through melting

and the liquid region to ideal gas. The melting is usually determined by the Lindemann rule¹ normalized to data. Examples of this approach are the models of Cowan² and Thompson.³

We seek here to develop a similar model that incorporates more details of melting, improves the temperature dependence of the specific heat in the liquid regime, and reproduces the correct ideal gas entropy even for mixtures of species. All this we have done, and we present two versions of such a model. We should point out that we are focusing in this paper on the temperature dependence of the ionic thermodynamics. This, in particular, means we will assume that the Debye temperature as a function of density is known.

Constraints

Since we use the Debye model¹ for the solid regime, we need the Debye temperature $\theta(\rho)$ as a function of density ρ . We assume $\Gamma = \frac{\rho}{\theta} \frac{d\theta}{d\rho}$ is given to us, and we integrate Γ to obtain θ . The constant of integration is determined at the ambient density ρ_0 from the experimental melting temperature and the Lindemann criterion. In applying this procedure one should correct for the change in the melting temperature from the melting density to ambient. A crude, but good, operational rule is to multiply the experimental melt temperature by 1.1. This was arrived at by a study of about fifty pure elements. Of course, for any given material the true melting temperature at ambient density is preferred.

The Lindemann rule has one undetermined constant, namely a in

$$T_m = \theta^2 / (a\rho^{2/3}) \quad . \quad (1)$$

We have estimated α again from a study of about fifty pure elements. We find, in units of eV for temperatures (11604.5 is the conversion factor to kelvin) and g/cm^3 for density, that $\alpha = 1.25/\bar{A}^{5/3}$, where \bar{A} is the average atomic weight of the compound. We should note that for this study we are not using the low temperature determination for θ , but instead we calculate θ from the entropy at the melting point. We feel this is better for the uses to which our equations of state are put because the low temperature region is not of much importance in those cases. We then use Eq. (1) with the so determined α to specify T_m as a function of density. (Remember that $\theta(\rho)$ is given as described in the previous paragraph.)

We now go above the melting point, keeping the density fixed, and discuss our constraints in terms of C_v , the constant volume specific heat. We want C_v to go smoothly and monotonically from $3R$ at T_m , the high temperature Debye value, to $3R/2$, the ideal gas limit, at high temperatures. The exception to this is we do add to C_v a contribution that represents the heat of fusion between T_m and $1.2T_m$. This extra contribution, linear in temperature, is determined such that the entropy increases an extra $0.6R$ in going from T_m to $1.2T_m$. The 0.6 and 1.2 are chosen again from studies of real materials.

From Grover⁴ it is typical that the specific heat drops linearly in T from $3R$ to $9R/4$ from T_m to $5T_m$. Above $5T_m$ from Debye-Hückel theory,⁵ we expect that C_v should approach $3R/2$ smoothly and monotonically as $T^{-3/2}$. However, we find it is a good approximation to let C_v go to $3R/2$ at some finite values $T = \alpha$ linearly in $\ln T$.

Our final constraint, an integral one, follows from the entropy. One knows at high temperature, for compounds T needs to be high enough to dissociate, that

$$S/Nk = \frac{3}{2} \ln(S_0 T) + \dots, \quad (2)$$

where S_0 is known and independent of T , and the higher order terms behave as T to a negative power. Since

$$S = \int_0^T C_v/T' \, dT' \quad (3)$$

the known S_0 is an integral constraint on C_v . This in our modeling determines one parameter in the functional form used for C_v above melting. Other parameters are determined by the continuity of C_v , internal energy E , and Helmholtz free energy A at T_m .

The Model

We present two versions of a model that implements the above. There are common features in the two versions, and we present them first. We will repeat some previous points.

The Debye temperature is calculated from integrating $\Gamma = \frac{\rho}{\theta} \frac{d\theta}{d\rho}$. The reference θ_0 , the integration constant, is obtained from

$$\theta_0 = (a \rho_0^{2/3} T_{m,0})^{1/2} \quad (4a)$$

and

$$a = 1.25/\bar{A}^{5/3}, \quad (4b)$$

where ρ_0 is the ambient density, and $T_{m,0}$ is the melt temperature at that density. Remember to correct the melting temperature from the melt density to ρ_0 . The T_m for general density now follows from

$$T_m = \theta^2 / (a\rho^{2/3}) \quad (5)$$

We define a reduced variable $\psi = T/T_m$. For $\psi \leq 1$ we use the standard Debye model for both versions.

If

$$D(x) = \frac{3}{x} \int_0^x y^3 / (e^y - 1) dy \quad (6a)$$

then the internal energy and Helmholtz free energy are

$$E = E_D = NkT \left[\frac{9}{8} \frac{\theta}{T} + 3D\left(\frac{\theta}{T}\right) \right] \quad (6b)$$

and

$$A = A_D = NkT \left[\frac{9}{8} \frac{\theta}{T} + 3 \ln(1 - e^{-\theta/T}) - D\left(\frac{\theta}{T}\right) \right] \quad (6c)$$

with

$$PV = P_D V = \Gamma E_D \quad (6d)$$

For $1 \leq \psi$ the two versions diverge from each other. Version 1 is the preferred one, and we present that now. The physics of Version 2 is perhaps a little better than Version 1, but there is little difference in the final equations of state and Version 1 is simpler.

Version 1

For $1 \leq \psi$ there are two regions, $1 \leq \psi \leq 1.2$, the melting region, and

$1.2 \leq \psi$, with different analytic forms due to the heat of fusion in each. We define a number of auxiliary quantities first. First, let

$$a_1 = -5.7 - \sum_{\text{species}} n_i \ln[(A_i/\bar{A})^{3/2}/n_i] \quad , \quad (7a)$$

where n_i are number fractions and A_i are the atomic weights of the various species. The sum exists only for compounds and is where the entropy of mixing for the high temperature ideal gas enters the model. Because of the highly coupled nature of thermodynamics, the entropy of mixing forces extra area under the C_v curve that corresponds, in a crude way, to the energy of dissociation. Continuing,

$$y = (201[1600a_1^2 + 2398(4a_1 + 5)]^{1/2} - 40(5 - 197a_1))/[3980(4a_1 + 5)] \quad , \quad (7b)$$

$$a_2 = \frac{3}{2} (1 + a_3)^3 / [a_3(1-y)(a_3y + 2-y)] \quad , \quad (7c)$$

$$a_3 = 200 \quad , \quad (7d)$$

and

$$a_4 = -\frac{8}{5} [a_1 + a_2/(1+a_3)] \quad . \quad (7e)$$

Define

$$\epsilon_1 = \frac{3}{2}(\psi - \psi^{-1}) \quad , \quad (8a)$$

$$\epsilon_2 = 0.66/\psi \quad , \quad (8b)$$

$$\alpha_1 = \frac{3}{2} (2 - \psi - \psi^{-1}) \quad , \quad (8c)$$

and

$$\alpha_2 = 0.66/\psi - 0.6 \quad . \quad (8d)$$

Also let

$$E_o = -\frac{3}{2} + \frac{3}{2} a_4 [1 - 1/(2\psi^{1/2})] / \psi^{3/2} \\ + a_2 (a_3 y + \psi^{1-y}) / [\psi^y (a_3 + \psi^{1-y})^2] \quad , \quad (9)$$

and

$$A_o = \frac{3}{2} \ln \psi + a_1 + a_2 / [\psi^y (a_3 + \psi^{1-y})] \\ + a_4 [1 - 3/(8\psi^{1/2})] / \psi^{3/2} \quad . \quad (10)$$

Then for $1 \leq \psi \leq 1.2$,

$$A = A_D + NkT (A_o + \alpha_1) \quad , \quad (11a)$$

$$E = E_D + NkT (E_o + \epsilon_1) \quad , \quad (11b)$$

and

$$PV = \Gamma E_D + (2\Gamma - \frac{2}{3}) NkT (E_o + \epsilon_1) \quad . \quad (11c)$$

For $1.2 \leq \psi$,

$$A = A_D + NkT (A_o + \alpha_2) \quad , \quad (12a)$$

$$E = E_D + NkT (E_0 + \epsilon_2) \quad , \quad (12b)$$

and

$$PV = \Gamma E_1 + (2\Gamma - \frac{2}{3})NkT(E_0 + \epsilon_2) \quad . \quad (12c)$$

This completes Version 1. For the interested reader, the parameters y , a_1 , a_2 , a_3 , and a_4 are determined from demanding continuity of C_v , E , and A at T_m and from the entropy constraint. The ϵ and α terms put in the extra contributions from the heat of fusion.

Version 2

In this case we consider four regions, $1 \leq \psi \leq 1.2$, $1.2 \leq \psi \leq 5$, $5 \leq \psi \leq \alpha$, and $\alpha \leq \psi$. In each region C_v is linear in T except the third where it is linear in $\ln T$. We integrate to obtain E and A and differentiate A to obtain P . The constants of integration are calculated by requiring E and A to be continuous. The α is calculated by forcing the entropy to limit correctly at high temperature. We now give another list of auxiliary quantities. We still use a_1 from Eq. (7a) and ϵ_1 , ϵ_2 , α_1 , and α_2 from Eqs. (8). We define

$$b = 9/[32(a_1 + 3/4 + \frac{27}{16}\ln 5)] \quad (13a)$$

and

$$\alpha = 5e^{-3/(4b)} \quad . \quad (13b)$$

It is convenient to have

$$E_1 = 3/16 - 3\psi/32 - 3/(32\psi) , \quad (14a)$$

$$A_1 = -\frac{3}{16} \ln\psi - 3\psi/32 - 3/(32\psi) , \quad (14b)$$

$$E_2 = -3/4 + b \ln(\psi/5) - b + 5(b + 9/20)/\psi , \quad (14c)$$

$$\begin{aligned} A_2 = & \frac{3}{4} \ln\psi + b \ln\psi + 5(b + 9/20)/\psi \\ & + b (\ln 5)(\ln\psi) - \frac{b}{2} \ln^2\psi - \frac{b}{2} \ln^2 5 \\ & - b \ln 5 - b - \frac{15}{16} \ln 5 , \end{aligned} \quad (14d)$$

$$E_3 = -\frac{3}{2} + 5(b + 9/20)/\psi - ab/\psi , \quad (14e)$$

and

$$A_3 = \frac{3}{2} \ln\psi + 5(b + 9/20)/\psi - ab/\psi + a_1 . \quad (14f)$$

Then for $1 \leq \psi \leq 1.2$,

$$E = E_D + NkT (E_1 + \epsilon_1) , \quad (15a)$$

$$A = A_D + NkT (A_1 + \alpha_1) , \quad (15b)$$

and

$$PV = \Gamma E_D + (2\Gamma - \frac{2}{3})NkT(E_1 + \epsilon_1) . \quad (15c)$$

For $1.2 \leq \psi \leq 5$,

$$E = E_D + NkT (E_1 + \epsilon_2) , \quad (16a)$$

$$A = A_D + NkT (A_1 + \alpha_2) , \quad (16b)$$

and

$$PV - \Gamma E_D + (2\Gamma - \frac{2}{3}) NkT (E_1 + \epsilon_2) \quad . \quad (16c)$$

For $5 \leq \psi \leq \alpha$,

$$E - E_D + NkT(E_2 + \epsilon_2) \quad , \quad (17a)$$

$$A - A_D + NkT (A_2 + \alpha_2) \quad , \quad (17b)$$

and

$$PV - \Gamma E_D + (2\Gamma - \frac{2}{3}) NkT (E_2 + \epsilon_2) \quad . \quad (17c)$$

And for $\alpha \leq \psi$,

$$E - E_D + NkT(E_3 + \epsilon_2) \quad , \quad (18a)$$

$$A - A_D + NkT(A_3 + \alpha_2) \quad , \quad (18b)$$

and

$$PV - \Gamma E_D + (2\Gamma - \frac{2}{3}) NkT(E_3 + \epsilon_2) \quad . \quad (18c)$$

This completes Version 2.

Discussion

We have given two versions of a model that incorporates the thinking of this paper. The first version is the recommended one, although the second is just fine also. We now explain our reasoning on that choice. We will refer to Versions 1 and 2 just as 1 and 2. In 2 the C_v is somewhat more physical even though it does not have the Debye-Hückel tail. This is because 2 is

better for $1 \leq \psi \leq 10$ and the tail does not influence the thermodynamics very much. As a result 2 also has a better energy, and to understand this we need a side discussion. At high temperature one has the internal energy behaving as $\frac{3}{2} NkT + \text{constant}$, and one has some feel for the constant. Version 2 matches the constant a factor of five better than Version 1. But still, all this does not influence the resulting thermodynamics in any meaningful way. Now 1 has two advantages over 2. First, it is simpler, with $1 \leq \psi$ broken up into fewer regions. Also, both 1 and 2 have structure in P as a function of ρ whenever $\Gamma(\rho)$ has structure. These features can run up to quite high temperatures before being washed out by the ideal gas term. The structure may or may not be physical to such high temperatures, but we are somewhat more comfortable with it being minimized. Version 1 has less structure. Thus, based on these last two pluses for 1 and the lack of influence from the pluses of 2, we recommend Version 1. But Version 2 is still a good model, and a person should use it if there is justification to switch.

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