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A Method to Estimate Entropies and Heat Capacities Applied to Alkali Oxides

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We present a method that is useful in the estimate and assessment of heat capacity data. The approach is based on an analysis of the logarithmic average of the phonon frequencies. In this quantity, that may be easily derived from experimental data on the vibrational entropy, the influence of atomic masses can be exactly accounted for even in polyatomic solids. Our method is applied to Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O. In particular, literature data for K_2O are critically examined.

KEY WORDS: alkali oxides; Debye temperature; entropy; heat capacity.

1. INTRODUCTION

There are several collections of thermodynamic data giving heat capacities C_p of solids as a function of temperature, e.g., the JANAF tables [1] and tables by Barin [2]. To some extent they are based on a critical assessment of direct experimental results, but when such information is lacking the authors have often resorted to estimates. One example of the procedure for such estimates is as follows. At intermediate and high temperatures T, C_p is dominated by the harmonic vibrational part, amounting to $3k_B$ per atom, where k_B is Boltzmann's constant. In a real solid, C_p increases above $3k_B$ per atom at high T because of anharmonic effects. This anharmonic contribution to C_p is then sometimes estimated from the measured value for another similar solid. For instance, the C_p of K_2O has been modeled in this way by comparison with the C_p of Na_2O [1]. In this paper we suggest an alternative method that has a higher reliability.

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2. THE $\theta_S(T)$ METHOD

Let $S(T)$ be the entropy of a solid, calculated from $C_p(T)$ as

$$S(T)=\int_0^T \frac{C_p(T')}{T'}\,dT' \tag{1}$$

Further, let $S_D(T/\theta_S)$ be the entropy in a Debye model for the lattice vibrations, with a Debye temperature θ_S. For each temperature T, we get an experimentally determined "entropy Debye temperature" $\theta_S(T)$ from the equation

$$S(T)=S_D(T/\theta_S) \tag{2}$$

The solution to Eq. (2) may be readily obtained by interpolation in Debye function tables in Ref. 3 or from the following rapidly converging series expansion for $\theta_S(T)$:

$$\theta_S(T)=T\left[\varepsilon+\frac{1}{40}\varepsilon^3+\frac{1}{896}\varepsilon^5+\frac{1}{17{,}046}\varepsilon^7+\cdots\right] \tag{3}$$

It gives θ_S to better than 0.1% when $T>0.45\theta_S$. Here ε is related to the vibrational entropy $S(T)$ of 1 mol of a compound having n atoms per formula unit as

$$\frac{1}{\varepsilon}=\exp\left\{\left[\frac{S(T)}{3nR}\right]-\frac{4}{3}\right\} \tag{4}$$

The properties of $\theta_S(T)$ have been illustrated in several previous papers from our group [4–9]. Here it suffices to note the following. For harmonic lattice vibrations and at high temperatures (often $T>\theta_S/3$ suffices), the quantity θ_S measures the logarithmically averaged phonon frequency $\omega_{\log}$ over the full frequency spectrum, through

$$\theta_S=(h/k_B)\exp(\tfrac{1}{3})\,\omega_{\log} \tag{5}$$

The interatomic forces and the atomic masses normally mix in a complicated way in the individual phonon frequencies ω. However, the atomic masses enter only through a multiplicative factor in $\omega_{\log}$ [4]. Thus we can write

$$\theta_S=(h/k_B)(k_S/M_{\text{eff}})^{1/2} \tag{6}$$

M_{eff} is the logarithmic average of all the atomic masses in the solid, and k_S is a quantity with the dimension of a force constant that is a complicated average over all the interatomic forces.

In a plot of $\theta_S(T)$ versus T, there is usually a variation with T at low temperatures, because the true phonon spectrum is not of the Debye form. For strictly harmonic vibrations, $\theta_S(T)$ would tend to a constant at high temperatures, given by Eq. (5). For real solids, $\theta_S(T)$ usually decreases in a regular manner with T, because of anharmonic softening of the phonon frequencies. In the approximate temperature range $\theta_S/2$–$3\theta_S/2$, the temperature is high enough to make the temperature dependence of θ_S caused by the form of the phonon spectrum small. The temperature is also low enough for anharmonic effects to be rather small. The result is that $\theta_S(T)$ varies only little with T from $T \approx \theta_S/2$ to $T \approx 3\theta_S/2$. Hence we may use experimental entropy data at $T \approx \theta_S$ and Eqs. (2) and (6) to derive an average effective force constant k_S that well describes the "harmonic" phonon spectrum of the solid.

We have previously noted some striking regularities in $\theta_S(T)$ and k_S that will form the basis for the θ_S method used here. Within a group of chemically similar solids, k_S shows a very regular variation, which is even more pronounced if we consider a quantity E_S with the dimension of energy,

$$E_S = k_S \Omega^{2/3} \tag{7}$$

Ω is the average volume per atom in the compound. As an example [9], in 20 ionic compounds of the type AB_2, with $A =$ Be, Mg, Ca, Sr, and Ba and $B =$ Li, K, Rb, and Cs, E_S (with θ_S evaluated at $T \approx \theta_S$) is constant to within ±9% (rms deviation). If Ω is now known, and since also M_{eff} is trivially obtained, Eqs. (6) and (7) imply that we can account for θ_S of all the 20 compounds in this example to within ±4% (rms deviation).

The temperature dependence of $\theta_S(T)$ at high T also shows a very regular behavior for chemically similar systems [5–8]. According to low-order perturbation theory of anharmonic lattice vibrations, $\theta_S(T)$ decreases linearly with T at high T. As the melting temperature T_{m} is approached, a more or less pronounced additional decrease in $\theta_S(T)$ sets in, which often gives a significant deviation from the linear temperature dependence of θ_S above $3T_{\mathrm{m}}/2$.

3. APPLICATION TO ALKALI OXIDES

The thermal properties of the alkali oxides are of particular interest because these solids exhibit fast ion conduction and other unusual properties at high temperatures. Figure 1 shows $\theta_S(T)$ derived as described above, from entropy data given in the JANAF tables [1] and the table by Barin [2]. For K_2O, the JANAF and Barin tables give Debye temperatures θ_S

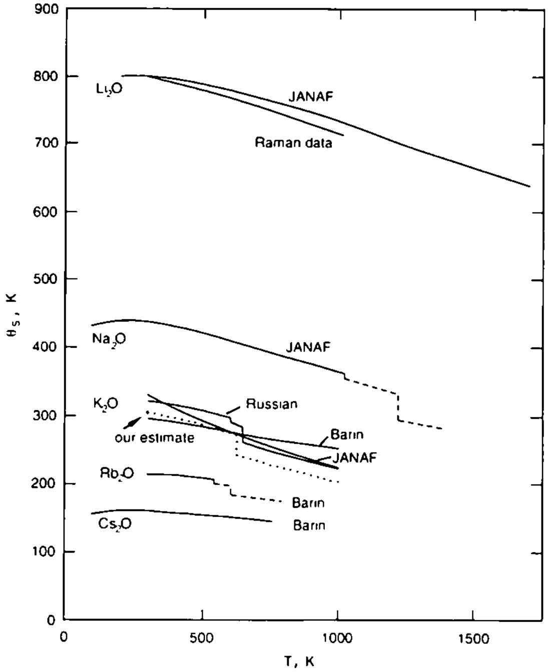

Fig. 1. The entropy Debye temperature $\theta_S(T)$ for alkali oxides, based on reported experimental data. The asterisk and the dotted curve for K_2O represent an estimate using the methods presented in this paper.

at room temperature that differ by about 8%, and the temperature dependence of their θ_S is significantly different. $\theta_S(T)$ derived from a Russian table [10] of entropy data is also shown in Fig. 1. We now use the method presented in this paper to discuss critically the thermodynamic properties of K_2O, as they are reflected in θ_S. We deal first with the magnitude of θ_S at room temperature, then with the temperature dependence of θ_S and, finally, trace one reason for the difference between the $\theta_S(T)$ curves of K_2O in Fig. 1.

At room temperature $T \approx \theta_S$ for K_2O and E_S can be derived as described above. The atomic volume Ω is calculated from crystallographic data [11]. We get for E_S of K_2O (in 10^{-18} J) 5.73 (Barin's data), 7.17 (JANAF's data), and 6.74 (Russian data [10]). Li_2O, Na_2O, K_2O, and Rb_2O all have the CaF_2-type crystal structure. From the regularities noted for many other systems of the same crystal structure, we expect them to have similar E_S, values, within say ±10%. The corresponding E_S of Li_2O, Na_2O, and Rb_2O, evaluated from θ_S at $T \approx \theta_S$, are 6.10 (Li_2O), 6.50

(Na_2O), and 5.52 (Rb_2O), giving an average $E_S = 6.04$ for these three compounds. In comparison with this value, E_S values of K_2O from the JANAF and Russian tables appear to be too high, which suggests that these sources underestimate the entropy at room temperature. If one adopts the average $E_S = 6.04$ value for K_2O, one obtains the θ_S value marked with an asterisk in Fig. 1. We finally note that CsO_2, with the $CdCl_2$-type crystal structure, has $E_S = 4.93$.

We next turn to the temperature dependence of $\theta_S(T)$. It is qualitatively similar for Li_2O, Na_2O, Rb_2O, and Cs_2O, with $\theta_S(T)$ being curved downward, as found for other solids [5–8]. The temperature dependence of θ_S for Li_2O is similar to that observed in Raman scattering data on the softening of phonons [12]; see Fig. 1, where the Raman data have been normalized so as to coincide with θ_S at room temperature. Many compounds of the CaF_2-type crystal structure show some kind of phase transition at high temperatures. A latent heat associated with such a transformtion will show up as a step in the θ_S-versus-T curve, as in Fig. 1 for Na_2O and Rb_2O. It is important to stress that the lower θ_S after such a step (Fig. 1) may reflect an entropy contribution that is associated with some lattice disorder. Then an interpretation of θ_S directly in terms of phonon frequencies is incorrect at temperatures above the steps.

The general agreement in the temperature dependence of $\theta_S(T)$ for Li_2O, Na_2O, Rb_2O, and Cs_2O, and the agreement with Raman data for Li_2O, makes us confident that also $\theta_S(T)$ of K_2O should show the same behavior. Molybdenum and tungsten have been shown to have almost-identical temperature dependences of $\theta_S(T)$ when the normalized quantity $\theta_S(T)/\theta_S(T')$ is plotted versus T/T_m and $T' \approx \theta_S$ [13]. Also, for a large number of nontransition metals, the decrease of $\theta_S(T)/\theta_S(T')$ from T' to T_m is approximately the same within groups of elements in the same column in the Periodic Table [5]. One can also argue for such a behavior in terms of dimensional analysis, when the potentials describing the interatomic foces in a class of solids all have the same shape but vary in strength and in a length parameter that scales with lattice parameter (Grimvall, unpublished). The decrease in $\theta_S(T)/\theta_S(T')$ from T' to T_m for Li_2O and Na_2O is 24 (± 3)% if we neglect the steps and assume a smooth extrapolation in $\theta_S(T)$. Assuming the same temperature dependence in $\theta_S(T)$ for K_2O, and inserting one step of the same magnitude as the two steps in the Russian data, we arrive at the dotted curve in Fig. 1. It is very similar to that from the Russian data, except for the almost-constant displacement in the magnitude of θ_S. Such a displacement results if the Russian table somewhat underestimates S (300 K). We suggest that our dotted curve well represents the entropy of K_2O.

The data reported by Barin for K_2O agree to a large extent with the expected $\theta_S(T)$, although one would also expect a downward step in θ_S corresponding to a disorder transition. It remains to understand why the JANAF values are so different, in spite of the fact that they are said to be modeled by comparison with experimental data for Na_2O. One then notes that the JANAF tables of 1985 report data for K_2O that were assessed already in 1963. The experimental data for Na_2O then available, and used in the estimate for K_2O, are considerably different from those reported for Na_2O in the 1985 edition.

The variation in $\theta_S(T)$ with T for Cs_2O is smaller than for the other alkali oxides. This is not likely to be explained solely by the fact that Cs_2O has a different crystal structure. We therefore suggest that Barin's heat capacity increases too slowly with T for high T.

4. DISCUSSION

The method described in this paper is now compared with some other semiempirical methods to estimate Debye temperatures and vibrational entropies. We first give some advantages in using the entropy Debye temperature $\theta_S(T)$ and the quantity E_S. They are both uniquely related to the vibrational entropy of solids. The most important feature of E_S, derived with a θ_S as in Eq. (5), is that it depends only on the chemical bonding in the solid. Therefore regularities in E_S can be directly related to similarities in the electronic structure in a class of chemically related compounds. E_S has no dependence on the atomic masses, unlike θ_S itself or thermodynamic quantities such as the heat capacity. Representing the anharmonic effects through the temperature dependence of $\theta_S(T)$ also has several advantages. For instance, compare a direct study of the heat capacity $C_p(T)$ with a study of $\theta_S(T)$ derived from the same $C_p(T)$. $C_p(T)$ increases with T at low temperatures due to quantum statistical effects and at high temperatures due to anharmonicity. At temperatures of the order of, and somewhat above, the Debye temperature, the two effects combine to give an inflexion point in a $C_p(T)$-versus-T curve. This fact makes a separation and extrapolation of the anharmonic effect difficult [8], in particular when $C_p(T)$ of one solid is modeled by comparison with another solid with known $C_p(T)$. In contrast, $\theta_S(T)$ shows a smoother behavior, and in a strict Debye spectrum for the phonons there would be no temperature dependence in $\theta_S(T)$ caused by quantum statistical effects. (The expected smoothness in the variation in $\theta_S(T)$ was used in a critical discussion of C_p of Ca [6].) Further, θ_S at high T is tantamount to the logarithmic average of the phonon frequencies. Therefore, the temperature dependence of $\theta_S(T)$ can be compared with the temperature dependence of some phonon modes measured in other ways, e.g., through the Debye–Waller factor, inelastic neutron scattering, or (as done above for Li_2O) Raman scattering.

After the reason for the anomalous behavior of $\theta_S(T)$ in K_2O based on the JANAF data was clarified above, $\theta_S(T)$ values of all the alkali oxides in Fig. 1 show a mutually consistent behavior that also has the qualitative temperature dependence found for other classes of chemically similar compounds [5–8] (if the steps in θ_S due to premelting disorder phenomena are disregarded). This mutual agreement lends credibility to the experimental data we have used to derive $\theta_S(T)$. It also suggests that we could have obtained a good estimate of $\theta_S(T)$ for K_2O even if experimental thermodynamic data on K_2O had been entirely lacking.

We next turn to other estimation methods. The most common empirical procedure to estimate Debye temperatures θ is the Lindemann relation among θ, the melting temperature T_m, a lattice parameter a, and an atomic mass M, *viz.*,

$$Ma^2\theta^2/T_m = C$$

where C is a constant that is supposed to be the same within a group of related solids. This relation is often well obeyed for the elements. In compounds with large atomic mass differences (such as those considered in this paper), there is no theoretically and empirically well defined way to form an average mass M to be used in the Lindemann relation. Further, the alkali oxides show premelting effects that make the use of T_m to deduce room temperature properties dubious.

Voronin [14] has proposed a semiempirical method to estimate the vibrational contribution to standard entropies S^0_{298}. He has given results for 14 alkali oxides, sulphides, selenides and tellurides, including Li_2O, Na_2O, K_2O, and Rb_2O. His equation for the Debye temperature θ has two free parameters to fit and, also, has a mass dependence given by the arithmetically averaged atomic mass in a compound. The parameters relate to a particular form of an interatomic potential. When Voronin's standard entropies S^0_{28} are converted to θ_S, one gets 826 K (Li_2O), 457 K (Na_2O), 333 K (K_2O), and 266 K (Rb_2O). These values are higher than the experimental values in Fig. 1 by 3% (Li_2O), 5% (Na_2O), 10% (K_2O, the "star"), and 24% (Rb_2O). We note that the discrepancy increases with the mass ratio in a compound. It might be explained by the fact that Voronin uses the molecular weight (the average atomic mass) as a parameter, while theory shows that the entropy at high T depends on the logarithmically averaged atomic mass.

Latimer's rule [15, 16] offers another method to estimate standard entropies S^0_{298}. It correctly introduces the logarithmically averaged mass

[17, 18]. It also contains purely empirical constants. If they are fitted to experimental data of a restricted class of compounds, as was done in this paper, one may predict an unknown S_{298}^{0} (e.g., for K_2O) with about the same accuracy as we would achieve. However, the empirical parameters in Latimer's rule are not explicitly related to fundamental physical quantities of the compound.

The "zero-entropy-of-formation" method [18] assumes that the entropy of a compound is a weighted average of the entropy of the constituent pure elements in solid form. Then the correct logarithmic mass dependence is obtained but the prediction is uncertain since it does not include any information on the type of bonding in the compound.

In conclusion, we have demonstrated the application of a semiempirical method that relies on a single parameter (θ_S or E_S) to represent a complex phenomenon (the total contribution to the thermodynamic functions from all vibrational modes). This gives an inherent limitation to the accuracy of the predictions that we share with other one-parameter approximations. However, the quantities we work with are physically well motivated and defined, and the approximations involved in the one-parameter representation may in principle be traced exactly to the fundamental physics of the system. Therefore our method offers a suitable framework for the estimation and critical assessment of data related to the vibrational properties of compounds.

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