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Ambient Heat Capacities and Entropies of Ionic Solids: A Unique View Using the Debye Equation

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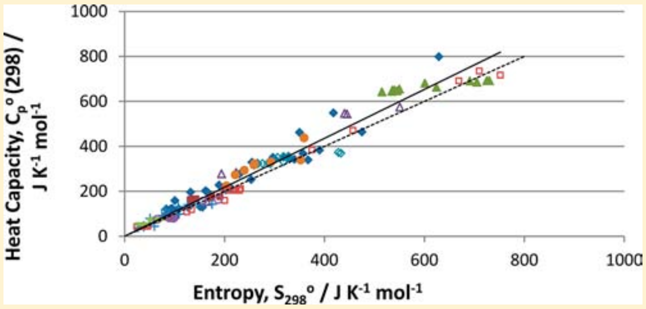
Supporting Information



ABSTRACT: Entropies of solids are obtained experimentally as integrals of measured heat capacities over the temperature range from zero to ambient. Correspondingly, the Debye phonon distribution equation for solids provides a theoretical connection between these two chemical thermodynamic measures. We examine how the widely applicable Debye equation illuminates the relation between the corresponding experimental measures using more than 250 ionic solids. Estimation of heat capacities for simple ionic solids by the Dulong−Petit heat capacity limit, by the Neumann−Kopp elemental sum, and by the ion sum method is examined in relation to the Debye equation. We note that, and explain why, the ambient temperature heat capacities and entropies of ionic solids are found to be approximately equal, and how deviations from equality may be related to the Debye temperature, Θ_D, which characterizes the Debye equation. It is also demonstrated that Debye temperatures may be readily estimated from the experimental ratio of ambient heat capacity to entropy, C_p/S_p, rather than requiring resort to elaborate theoretical or experimental procedures for their determination. Correspondingly, ambient mineral entropies and heat capacities are linearly correlated and may thus be readily estimated from one another.

■ INTRODUCTION

Over the past decade or so, colleagues and I have developed predictive methods for the common parameters of the chemical thermodynamics of ionic solids, namely, heat capacity,[1] entropy,[2] lattice energy,[3] formation enthalpy and Gibbs energy,[4] and even the thermoelastic property of compressibility.[5] These predictive methods have been based on either the development of additive single-ion values for a property or empirical linear correlation between the property and formula unit volume (values of which are readily available from crystal structure determination, experimental density, or even estimated) in the process that we have termed Volume-Based Thermodynamics, VBT.[6]

In particular, we have observed that the ambient values of isobaric heat capacity, $C_{p,m}$,[1a] and of entropy, $S_{p,m}$,[2a] of ionic solids are each strongly linearly correlated with formula volume, V_m. This implies that heat capacity and entropy are correspondingly linearly correlated with each other. The function of the present communication is to investigate this latter correlation from a fundamental viewpoint, noting that these properties are related not only experimentally but also through the Debye phonon distribution equation. In this way, we intend to develop a deeper understanding of the underlying source of the correlation. Compared with the standard approaches to the Debye equation, where individual materials are considered, in this new approach we examine the relation across an extensive range of ionic solids, from simple binary materials to complex minerals.

We have only be able to locate one other consideration of the relation between ambient heat capacity and entropy. In that early analysis, Landiya[7] reported an empirical relation based on the assumption of approximate linearity of heat capacity with inverse absolute temperature

$$C_{v,at}/\mathrm{J\,K^{-1}\,mol^{-1}} = 20.5 - (15.1/S_{at})$$

where the subscript "at" refers to values per mole of atoms. A test of current values of heat capacity and entropy shows this not to be a usefully reliable relation.

■ THERMODYNAMIC RELATIONS

Heat capacity is usually considered under conditions of either constant volume, C_v, or of constant pressure, C_p

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \quad \text{and} \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{1}$$

with U = energy and H = enthalpy.

Entropy is an integrated function of heat capacity

$$S°(T) = \int_0^{T°} \frac{C(T)}{T}\,\mathrm{d}T = \int_0^{T°} C(T)\,\mathrm{d}\ln T \tag{2}$$

The Debye equation[8] estimates the phonon contribution to the isochoric (constant volume) heat capacity, $C_v(T)$, of a solid

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as a function of temperature, for a simple phonon distribution, based on a parameter termed the Debye temperature, Θ_D. For a mole of atoms, the equation for heat capacity has the form:

$$C_v(\tau)/\mathrm{J\,K^{-1}\,(mol\,of\,atoms)^{-1}} = 9R\tau^3 \int_0^{1/\tau} \frac{x^4 e^x}{(e^x - 1)^2}\,dx \tag{3}$$

where R is the gas constant and $\tau \equiv T/\Theta_D$ is a normalized (or reduced) temperature. Θ_D corresponds to the temperature at which the most energetic of the phonon modes is excited. Since the integral has no analytic solution, it has to be evaluated numerically.[9]

This equation correctly describes the low-temperature dependence of the heat capacity as proportional to T^3 and also asymptotes at high temperatures to the Dulong–Petit value of about $3R \cong 25$ J K^{-1} (mol of atoms)$^{-1}$, but takes no account of possible phase transitions, magnetic contributions, metallic electrical conductivity through electron motion, anisotropy, dispersion, or varied optic vibrational modes.[10] In considering the following analysis, these limitations should be noted.

The Debye equation may also be integrated[8] to yield the energy, U, and entropy, S,

$$U(T, \Theta_D)/\mathrm{J\,(mol\,of\,atoms)^{-1}} = \frac{9R\Theta_D}{8} + \frac{9RT^4}{{\Theta_D}^3} \int_0^{\Theta_D/T} \frac{x^3\,dx}{e^x - 1} \tag{4}$$

$$S_v(\tau)/\mathrm{J\,K^{-1}\,(mol\,of\,atoms)^{-1}} = 9R\tau^3 \int_0^{1/\tau} \left[\frac{x}{e^x - 1} - \ln(1 - e^{-x})\right] x^2\,dx \tag{5}$$

These equations yield the Debye energy, heat capacity, and entropy for solids under conditions of constant volume. Figure 1 is a plot of both Debye heat capacity and entropy as a function of the normalized temperature.

The following are important points to note with regard to the curves in Figure 1. Initially, heat capacity rises more rapidly with temperature than does entropy, but is overtaken at $\tau \equiv T/\Theta_D \cong 0.58(6)$, when each has the value 21.6(5) J K^{-1} (mol of atoms)$^{-1}$. Thereafter, entropy increases smoothly while heat capacity asymptotes toward the Dulong–Petit value of approximately 25 J K^{-1} (mol of atoms)$^{-1}$. For an ambient temperature of 300 K, the crossover point corresponds to a Debye temperature of about 510 K. While the Debye equation relies on one Debye temperature only, the best fit of heat capacity to the equation for real materials requires Debye temperatures which vary somewhat with temperature.[8] For the current approximate considerations, this complication will be ignored.

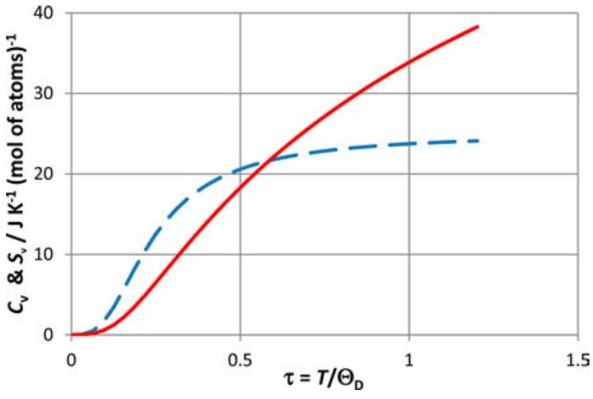

Figure 1. Heat capacity, C_v (broken blue curve), and entropy, S_v (solid red curve), per mole of atoms, according to Debye eqs 4 and 5, respectively,[9] plotted against the normalized temperature, $\tau \equiv T/\Theta_D$. The equivalence (crossover) point lies at $T/\Theta_D \cong 0.58(6)$, when each quantity plotted has the value 21.6(5) J K^{-1} (mol of atoms)$^{-1}$.

Figure 2 shows, from the Debye equation, that heat capacities and entropies lie within 10% of one another in the normalized temperature range $0.50 < \tau < 0.68$, provided that there are no intruding low-temperature phase changes.

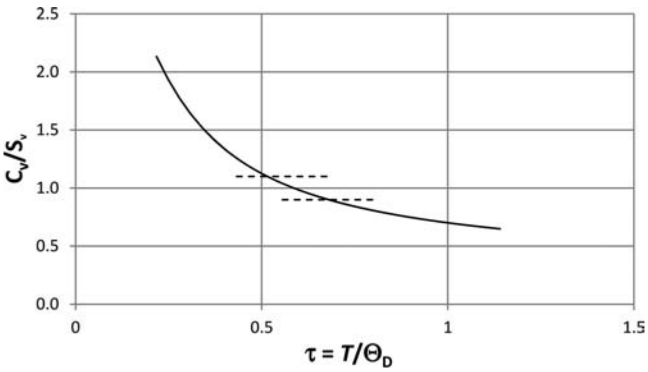

Figure 2. Ratio of Debye heat capacity and entropy, C_v/S_v, plotted against normalized temperature, $\tau \equiv T/\Theta_D$. The range where the values lie within 10% of one another, $0.50 < \tau < 0.68$, is delimited by the horizontal lines.

The Debye phonon distribution is, as noted above, only an approximation to the real properties of materials, omitting many features of actual materials, so that more sophisticated (and complex) spectral distributions than implied by the simple Debye distribution have been devised to better represent many materials.[10,11] However, there is little need, for present purposes, to delve into these details since "the thermodynamic functions are integrals over the frequency distribution [so that] they are insensitive to details of the spectrum."[10]

■ EXPERIMENTAL OBSERVATIONS

Most values of heat capacity and entropy for solids are reported under conditions of fixed pressure rather than fixed volume since ambient fixed pressure measurements are much more straightforward. The positive heat-capacity difference

$$C_p - C_v = VT\frac{\alpha^2}{\beta_T} \tag{6}$$

where α = coefficient of thermal expansion, and β_T = isothermal compressibility, may be regarded as negligible for ionic solids for present purposes.

In the current paper, we examine the relation between ambient heat capacity and ambient entropy for many ionic solids and demonstrate that there is much to be learned by consideration of this relation with reference to the Debye equation, well beyond the obvious integral connection between the two properties.

■ IONIC SOLIDS

The simplest method for estimation of heat capacities under ambient conditions for nonelementary solids is as a sum of the

Dulong–Petit value of ~25 J K^{-1} per mole of constituent atoms. The commonly applied Neumann–Kopp method[12] of summing the heat capacities of the constituent elements provides improved accuracy. In Figure 3, which plots the ambient heat capacities for 161 simple ionic solids against their entropies (data in the Supporting Information, Table S1), we see that the values for binary ionic solids do, indeed, asymptote toward (2 × 25) J K^{-1} mol^{-1} as their entropy increases, while those for ternary ionic solids asymptote more slowly to (3 × 25) J K^{-1} mol^{-1}. Those materials in a given class having smaller ions (e. g., MgO) have smaller entropies, while entropies increase as lattice vibrations become freer with larger ions (such as CsI). For these simple solids, ambient heat capacities and entropies do not correlate except as limiting low entropy values for the most rigid materials.

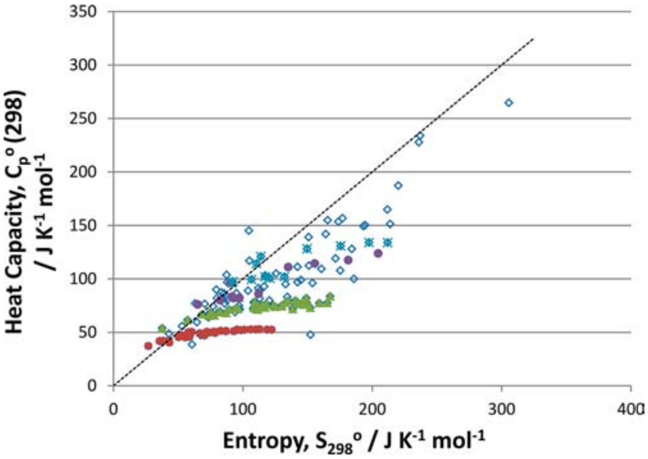

Figure 3. Heat capacity, C_p° (298)/J K^{-1} mol^{-1} plotted versus entropy, S_{298}°/J K^{-1} mol^{-1}, for 161 simple ionic solids. The red squares represent binary ionic solids, ranging from MgO at left to CsI at right; the green triangles represent ternary ionic solids, ranging from Li_2O at left to BaI_2 at right; the purple circles represent ionic carbonates, grouped into the alkaline-earth carbonates, starting with $MgCO_3$ at left, to the alkali metal carbonates with Cs_2CO_3 on the right; while the blue stars represent sulfates, similarly grouped from $MgSO_4$ at left to Cs_2SO_4 on the right. The remaining open blue diamonds represent nitrates, phosphates, and a range of other ionic solids which do not demonstrate such clearly systematic behavior. The following outliers have been omitted from the graph: $CuCl_2$: C_p°(298) = 71.9, S°(298) = 108.1 (magnetic transition); Li_2S: C_p°(298) = 38.6, S°(298) = 60.7. The broken diagonal line represents equality of heat capacity and entropy.

As the complexity of the materials increases, the reliability of the Neumann–Kopp prediction decreases. In this situation, additive single-ion values should preferably be used to predict the heat capacities.[1b]

Lambert and Leff[13] have recently published a correlation of enthalpy, ΔH°(298), versus standard entropy, S°(298), for a wide range of materials, based on the definition

$$\Delta H^\circ = \int_0^{T^0} C_p(T)\, \mathrm{d}T \qquad (7)$$

According to this correlation, $S^\circ \cong 0.066\ \Delta H^\circ\ K^{-1}$, with excellent linearity. As these authors have demonstrated, the assumption of an essentially linear C_p versus T relation for many materials over the temperature range from low to ambient temperature yields just this slope of 0.066 K^{-1} when the enthalpy integral is correlated with ambient entropy, yielding a mean Debye temperature of about 150 K. Moreover, the Debye relation 4 and 5 (with this Debye temperature of 150 K) remarkably yields a ratio of S/U = 0.0067 K^{-1}. However, this correlation has little fundamental significance since it simply represents the same data set (of C_p values) plotted against each other with different weightings (i.e., eq 7 versus eq 2). The alternative weighting does, of course, show up some minor anomalies.[13] It is unfortunate that this relation has been characterized elsewhere as an "entropy-enthalpy compensation effect",[14] which has itself been described as "two variables [which] are very largely the same variable looked at in two different ways".[15]

We here further develop the heat capacity versus entropy correlation by plotting the ambient heat capacities against their ambient entropies for 109 silicate and aluminate minerals, together with oxides, hydroxides, and carbonates, from the recent internally consistent database of Holland and Powell,[16] (see the Supporting Information, Table S2, for data).

The plot of Figure 4 not only confirms the expected correlation between ambient heat capacity and entropy for the more complex ionic solids, but also yields the intriguing result that the ambient temperature heat capacities and entropies of the minerals and other materials included are almost equal to one another (slope of 1.089), even though the heat capacity is a room-temperature value while the entropy is a heat capacity value integrated to room temperature. In terms of Figure 2, with heat capacities averaging about 9% larger than the corresponding entropies, this implies that the Debye temper-

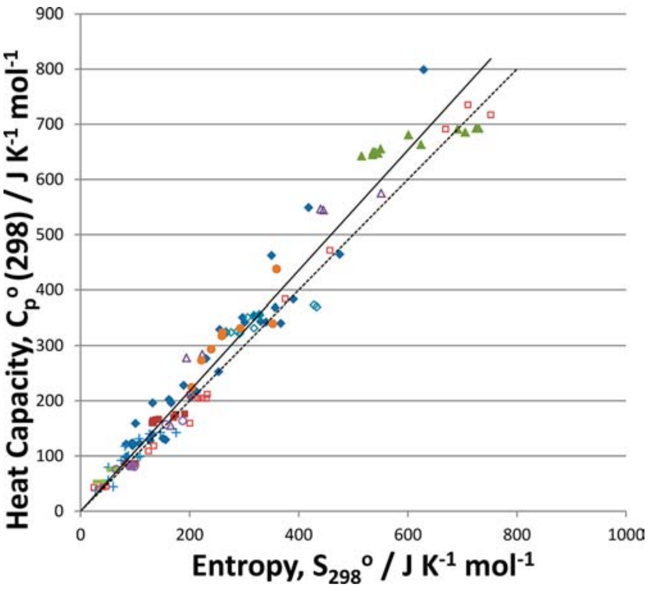

Figure 4. Heat capacity, C_p° (298)/J K^{-1} mol^{-1} plotted versus entropy, S_{298}°/J K^{-1} mol^{-1}, for 109 silicate and aluminate minerals, together with oxides, hydroxides and carbonates, from the most recent internally consistent database of Holland and Powell.[16] Ortho- and ring-minerals: filled blue diamonds; pyroxenes: filled red squares; amphiboles: filled green triangles; chain silicates: open triangles; micas: open diamonds; filled orange circles: other sheet silicates; open red squares: framework silicates; blue pluses: oxides; green dashes: hydroxides; purple open circles: carbonates. The fitted linear correlation has the formula C_p° (298) = 1.089 (±0.012) S_{298}°; R^2 = 0.955 (with an almost identical fit without the constraint of zero intercept). The broken diagonal line represents equality of heat capacity and entropy.

atures of these materials are close to $\tau \cong 0.5$, or $\Theta_D \cong 600$ K since the data plotted refer to a temperature of about 300 K. Most of the mineral groups are scattered along the correlation line, perhaps reflecting the presence of the rather rigid silicate tetrahedra. On the other hand, the amphiboles (filled green triangles) have rather constant heat capacities, tending toward a limiting value, reflecting the similarity in their basic structure, which consists of double chains of SiO_4 tetrahedra linked at the vertices, but with a broad range of Debye temperatures. On the scale of Figure 4, the deviations (near the origin) noted in Figure 3 for the simple (binary, ternary) ionic solids do not show.

A heuristic explanation for this approximate equality of ambient heat capacity and entropy values again follows from Lambert and Leff's[13] assumption of a linear increase of heat capacity with temperature:

$$
\begin{aligned}
C_p^\circ(T^\circ)/S^\circ(T^\circ) &= AT^\circ\Big/\int_o^{T^\circ} \frac{C_p^\circ(T)}{T}\,\mathrm{d}T \\
&= AT^\circ\Big/\int_o^{T^\circ} \frac{AT}{T}\,\mathrm{d}T = AT^\circ\Big/\int_o^{T^\circ} A\,\mathrm{d}T \\
&= T^\circ\Big/\int_o^{T^\circ} 1\,\mathrm{d}T = T^\circ/T^\circ = 1
\end{aligned}
\tag{8}
$$

Thus, the assumed linearity ensures cancellation of the variation when the ratio of the quantities is taken. This observation should by no means be considered a proof of such a relation between heat capacity and entropy, but simply indicative. The near equality of heat capacity and entropy values may have been remarked upon before but does not seem to have received any explanation.

Materials whose data are to the right of the equivalence line have greater entropy than heat capacity and so lie closer to the Dulong–Petit heat-capacity value (the high temperature limit), having a correspondingly lower Debye temperature, while materials whose data are to the left of the equivalence line have higher Debye temperatures. From the position of most data points for simple ionic solids to the right of the line in Figure 3, we can conclude that most such materials have low Debye temperatures.

Debye temperatures can now be readily assessed using only ambient values of heat capacity and entropy. For example, using CsI as an example, C_p/S_p (at 300 K) = 52.5/122.5 = 0.43; using the Debye equation (and Supporting Information Table S3 is provided for ease of reference[9]), this corresponds to a normalized temperature $\tau \equiv T/\Theta_D \cong 300/\Theta_D \cong 2.6$. Thus, $\Theta_D \cong 113$ K. This low Debye temperature implies that the lattice vibrations of this soft material are substantially excited at room temperature. For MgO, C_p/S_p (at 300 K) = 37.2/26.9 = 1.38, $\tau = 0.385$, and $\Theta_D \cong 774$ K. By contrast, this rather high Debye temperature corresponds to incomplete excitation of the lattice vibrations of this harder material near room temperature. The Debye temperatures evaluated in this way correspond well with the (sometimes variable) literature values,[17] which require quite elaborate theoretical or experimental procedures for their determination.[18]

■ CONCLUSION

We have here examined the relation between ambient heat capacity and entropy for a large range of ionic solids. Most simple ionic solids have entropies which are larger than their heat capacities, corresponding to low Debye temperatures. Conversely, more complex ionic solids, such as minerals, have heat capacities only about 9% larger than their entropies, yielding Debye temperatures close to 600 K for these materials. Debye temperatures may be estimated using only available values of C_p/S_p at a given temperature, and Supporting Information Table S3 facilitates this estimation.

Similarly, the linear correlation in Figure 4, C_p° (298) = 1.089 S_{298}°, permits rough estimation of either one of these thermodynamic properties from the other, for silicate and aluminate minerals.

These results follow from the fact that heat capacity and entropy for ionic solids are both properties dependent largely upon the phonon contribution to the energy of the material and are, in turn, directly related through the Debye equation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1 lists ambient heat capacity and entropy data for 161 small ionic solids derived from the HSC database.[19] Table S2 lists similar data from the database of Holland and Powell[16] for 105 minerals plus related materials. Table S3 lists data for the Debye equation, including Debye temperatures calculated from ambient values of C_p/S_p. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Glasser, L.; Jenkins, H. D. B. *Inorg. Chem.* **2011**, *50*, 8565–9. (b) Glasser, L.; Jenkins, H. D. B. *Inorg. Chem.* **2012**, *51*, 6360–6366.

(2) (a) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2003**, *42* (26), 8702–8708. (b) Glasser, L.; Jenkins, H. D. B. *Thermochim. Acta* **2004**, *414* (2), 125–130. (c) Glasser, L.; Jenkins, H. D. B. *Inorg. Chem.* **2009**, *48* (15), 7408–7412.

(3) (a) Glasser, L.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2000**, *122* (4), 632–638. (b) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2002**, *41* (17), 4378–4388.

(4) Glasser, L. *Inorg. Chem.* **2013**, *52* (2), 992–998.

(5) (a) Glasser, L. *Inorg. Chem.* **2010**, *49*, 3424–3427. (b) Glasser, L. *J. Phys. Chem. C* **2010**, *114*, 11248–11251.

(6) (a) Glasser, L.; Jenkins, H. D. B. *J. Chem. Eng. Data* **2011**, *56* (4), 874–880. (b) Glasser, L.; Jenkins, H. D. B. *Chem. Soc. Rev.* **2005**, *34* (10), 866–874.

(7) (a) Landiya, N. A. *Zh. Fiz. Khim.* **1953**, *27*, 495–501. (b) Landiya, N. A. *Zh. Fiz. Khim.* **1951**, *25*, 927–941.

(8) Gopal, E. S. R. *Specific heats at low temperatures*; Plenum Press: New York, 1966.

(9) *Mathcad 14*; Parametric Technology Corporation (PTC): Needham, MA, 2007.

(10) Kieffer, S. W. *Rev. Geophys.* **1979**, *17* (1), 35–59.

(11) Otero-de-la-Roza, A.; Abbasi-Pérez, D.; Luaña, V. *Comput. Phys. Commun.* **2011**, *182* (10), 2232–2248.

(12) (a) Leitner, J.; Voňka, P.; Sedmidubský, D.; Svoboda, P. *Thermochim. Acta* **2010**, *497*, 7–13. (b) Leitner, J.; Chuchvalec, P.; Sedmidubský, D.; Strejc, A.; Abrman, P. *Thermochim. Acta* **2003**, *395* (1–2), 27–46.

(13) Lambert, F. L.; Leff, H. S. *J. Chem. Educ.* **2009**, *86* (1), 94−98.

(14) (a) Starikov, E. B.; Nordén, B. *Chem. Phys. Lett.* **2012**, *538*, 118−120. (b) Starikov, E. B.; Nordén, B. *Appl. Phys. Lett.* **2012**, *100*, 193701.

(15) Cornish-Bowden, A. *J. Biosci.* **2002**, *27*, 121−126.

(16) (a) Powell, R.; Holland, T. J. P.; White, R. *THERMOCALC*; http://www.metamorph.geo.uni-mainz.de/thermocalc/; (b) Holland, T. J. B.; Powell, R. *J. Metamorphic Geol.* **2011**, *29*, 333−383.

(17) (a) Sirdeshmukh, D. B.; Subhadra, K. G. *J. Mater. Sci.* **2005**, *40* (7), 1553−1570. (b) Chopelas, A. *Phys. Chem. Miner.* **1990**, *17*, 142−148.

(18) Narain, S. *Phys. Status Solidi B* **1994**, *182*, 273−278.

(19) Outotec Research Oy *HSC Chemistry 7*; Outotec Research Oy: Finland, 2009.