7408 Inorg. Chem. 2009, 48, 7408–7412
DOI: 10.1021/ic9009543

Inorganic Chemistry
Article

Single-Ion Entropies, S°_{ion}, of Solids—A Route to Standard Entropy Estimation

Leslie Glasser*

Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia

H. Donald Brooke Jenkins*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, West Midlands, United Kingdom

Received May 14, 2009

Single-ion standard entropies, S°_{ion}, are additive values for estimation of the room-temperature (298 K) entropies of ionic solids. They may be used for inferring the entropies of ionic solids for which values are unavailable and for checking reported values, thus complementing the independent method of estimation from molar volumes (termed volume-based thermodynamics). Current single-anion entropies depend on the charge of the countercation, and so are difficult to apply to complex materials, such as minerals. The analysis of reported data here presented provides a self-consistent set of entropies for cations and charge-independent values for anions. Although the S°_{ion} values presented encompass only a limited set of ions, the retrieval of values for ions not listed is straightforward and is described. An unexpected and significant observation is that cation entropies are related to the molar volumes of the corresponding (neutral) condensed-phase metals.

Introduction

The standard chemical thermodynamic quantities (heat capacity, enthalpy, entropy, Gibbs energy) provide the fundamental information essential to the understanding of the stability of materials and thus the capability of their syntheses and of their possible chemical reactions. Although there are many thermodynamic database resources currently available,[1] they actually provide a rather limited set of data, indeed, often replicating the same information (or even conflicting), and of course, they are necessarily retrospective, without information on materials either not yet measured, not synthesized, or even hypothetical. Furthermore, the rate of thermodynamic measurement is slow since it is both difficult and demanding work requiring considerable expertise. Regrettably, it is not, currently, a topic receiving much attention, except in a few important laboratories.

For these reasons, reliable predictive methods are essential, and of growing interest and importance. In recent years, we have made contributions to these methods through the introduction and development of volume-based thermodynamics (VBT), whereby the values of many thermodynamic quantities can readily be predicted from knowledge of the molar volume (whether by X-ray determination, from density, or by simple estimation) of the material of concern.[2] This contrasts with the considerably more demanding (although potentially more reliable) processes of modeling the materials and calculating their properties by empirical or quantum mechanical computer programs.

The present paper adds to current procedures for estimating the room-temperature (298 K) entropies of ionic solids by providing an optimized set of additive values for the entropies of many ions constituting such solids and provides new, unexpected and significant correlations against volume.

Estimation of Entropy

The VBT method for entropy estimation relies on a rather close linear correlation between the entropy and molar volume of condensed materials. Thus, the standard entropy,

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*To whom correspondence should be addressed. Tel.: + 61 8 9266-3126 (L.G.), +44 2476-523-265 or +44 2476-466-747 (H.D.B.J.). Fax: + 61 8 9266-4699 (L.G.), + 44 2476-524-112 (H.D.B.J.). E-mail: l.glasser@curtin.edu.au (L.G.), h.d.b.jenkins@warwick.ac.uk (H.D.B.J.).

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S°_{298}, is related to molar volume, V_m, by[3]

$$S^\circ_{298}/\mathrm{J\,K^{-1}\,mol^{-1}} \approx k(V_\mathrm{m}/\mathrm{nm^3\ formula\ unit^{-1}}) + c \quad (1)$$

where k and c are constants. The relation can equivalently be expressed in terms of density, ρ:

$$S^\circ_{298}/\mathrm{J\,K^{-1}\,mol^{-1}} \approx k'[(M/\mathrm{g\,mol^{-1}})/(\rho/\mathrm{g\,cm^{-3}})] + c \quad (2)$$

where k' is a related constant and M is the formula mass of the ionic material.

While the VBT linear correlation may be considered generally satisfactory, it is desirable to have an independent confirmatory procedure. A long-established alternative method due to Latimer, without overt volume dependence, uses the summation of single-ion entropies. Latimer[4] initially suggested that the contribution for each element in a compound was given by

$$S_\mathrm{Latimer} = 3N_\mathrm{A}k_\mathrm{B}\left[k_\mathrm{L} + \frac{1}{2}\ln M_\mathrm{r}\right] \quad (3)$$

where k_L is an empirical dimensionless constant of order unity, N_A is Avogadro's constant, k_B is Boltzmann's constant, and M_r is the relative atomic mass. Grimvall[5] has demonstrated, on the basis of lattice dynamical theory, that this expression gives fair estimates of the entropy of ionic solids at room temperature, provided that very light atoms are absent and interatomic forces are not excessively variable. Later developments of additive single-ion entropies,[4b,6−8] largely influenced by Latimer's early work, have been of a more empirical bent, generating single cation entropies together with anion entropies which differ according to the charge on the countercation.

This charge dependence of the anion values was incorporated in order to obtain a better fit to the reported data; unfortunately, this becomes a problem when dealing with complex ionic materials where it is not always clear which of the (possibly many) single ion entropy values, S°_ion, for the countercations may be relevant. We have, instead, now proceeded to obtain a set of additive ion entropies which are *independent* of countercation charge. This simplifies application of the S°_ion values when applied to complex materials, simultaneously reducing the number of parameters needing to be generated.

At first sight, the agreement between reported and estimated values (as viewed in Figure 1 and in the Supporting Information) may not seem outstanding. However, in thermodynamics, standard entropy most usually enters the arena in the form of its contribution to the evaluation of the "$T\Delta S$" term—in its role as a key contributer to the overall arbiter of thermodynamic feasibility for reactions, ΔG, the Gibbs energy change. As such, its value (in J K^{-1} mol^{-1}) is multiplied by T and *divided by 1000* (i. e., the factor is 298/1000) to necessarily convert the units to kilojoules per mole. This means that both the values and their errors are reduced to about one-third near room temperature, so that the precision with which S°_ion is reported can tolerate moderate uncertainties while still providing satisfactory guidance as to the magnitude of the thermodynamic relationships under prediction.

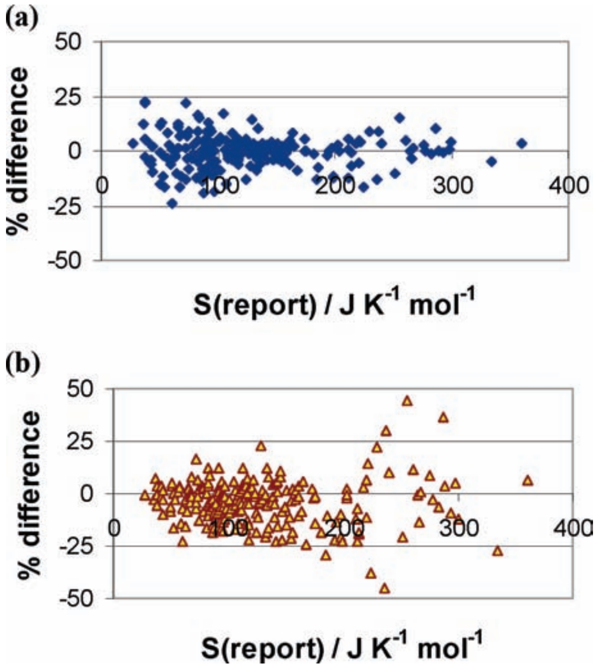

Figure 1. The percentage difference between ion entropy sums versus the reported entropy for 214 ionic solids: (a) for the optimized ion entropies (diamonds) and (b) for the summed values from Spencer (triangles).[8] The average deviation of the difference and their mean is 5.6 J K^{-1} mol^{-1} and −0.5 J K^{-1} mol^{-1}, respectively, for the optimized ion entropies and 7.0 J K^{-1} mol^{-1} and −3.9 J K^{-1} mol^{-1}, respectively, for the corresponding Spencer-based sums (for which his dication values have been selected for the anions).

Generation of Internally-Consistent Single Ion Entropies

A search of current databases[1] has provided us with the standard entropies at room temperature of 214 ionic solids and hydrates, ranging from simple halides to complex minerals, involving 19 cations (from singly charged alkali metal ions to quadrupally charged silicon ions) and 13 anions (from halides to phosphate) plus water of crystallization. The value of "S°_ion" for H_2O was fixed during optimization at the value taken by $\Theta_S{}^\circ\{\mathrm{H_2O,\ s{-}s}\} = 40.9$ J K^{-1} mol^{-1} (see Table 1, ref 9) in our "Difference Rule" studies.[9] The ions selected are those present in common ionic solids and in a range of minerals.[10,11] Where a particular material contained a very large number of ions, the numbers were reduced by an appropriate divisor to avoid excessive weighting of that material in the data set (for example, the entropy for tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$, having 39 contributory ions, was divided by 2 in the fitting data set). The ion entropy sums

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Table 1. Single-Ion Entropies, S°_{ion} (J K^{-1} mol^{-1}) As Optimized against a Set of 214 Ionic Solids, Where *n* Is the Total Number of Ions in the Data Set

ion	S°_{ion} optimized/J K^{-1} mol^{-1}	std. error[a]/J K^{-1} mol^{-1}	*n*[b]	S°_{ion}, Spencer[c]/J K^{-1} mol^{-1}	S°_{ion}, R&V[13]/J K^{-1} mol^{-1}
NH_4^+	67.0	4	9.0		
Li^+	19.4	3	15.0	14.6	19.7
Na^+	37.2		24.0	37.2	34.0
K^+	50.5	2	24.0	46.4	46.4
Rb^+	63.1	3	10.0	59.2	55.9
Cs^+	69.2	3	10.0	67.9	62.1
Mg^{2+}	20.5	4	50.3	23.4	26.7
Ca^{2+}	32.5	4	46.0	39.1	39.5
Sr^{2+}	37.9	4	13.0	48.7	52.9
Ba^{2+}	55.1	5	10.0	62.7	59.3
Fe^{2+}	38.6	4	21.0	35.0	52.2
Zn^{2+}	37.3	5	8.0	42.8	47.9
Cu^{2+}	33.5	5	8.0	44.0	41.5
Ni^{2+}	29.6	5	9.0	35.1	33.3
Co^{2+}	39.5	5	8.0	34.1	
Fe^{3+}	28.2	6	19.0	35.0	
Al^{3+}	17.3	5	57.0	23.4	
Si^{4+}	24.5	8	101.4	35.2	
Ti^{4+}	35.2	9	4.0	39.3	
F^-	20.6	2	26.0	18.6	
Cl^-	36.1	2	29.0	30.5	
Br^-	48.6	2	25.0	47.0	
I^-	56.8	2	24.0	53.9	
N_3^-	54.8	7	2.0		
O^{2-}	7.4	4	396.5	2.5	
OH^-	20.7	2	61.2	18.3	
S^{2-}	22.1	4	11.0	18.1	
CO_3^{2-}	52.6	4	15.0	44.4	
NO_3^-	78.5	3	14.0	66.1	
PO_4^{3-}	71.8	6	6.0	60.3	
SO_4^{2-}	74.3	4	19.0	68.7	
ClO_4^-	105.8	4	6.0	105.8	
H_2O	40.90[d]		7.5		

[a] The standard errors were determined using Billo's SolvStat Excel macro.[12] The value for Na^+ was fixed, as a reference base, at the value determined by Mills,[7,8] in the optimization. The final two columns list other published single-ion entropies. [b] *n* = number of ions included in the fitting set of ionic materials; fractions appear because of the normalization factors used to reduce the number of ions per material to comparable values (i. e., range: $2 \leq n \leq 22.9$). [c] For anions, the values for doubly charged cations from Spencer[7,8] are listed; these best match the current optimized set. [d] The value of 40.9 J K^{-1} mol^{-1} for water of crystallization[13] was kept fixed during the optimization. This ensures that the features of our difference rule[9] for prediction of the standard entropy, S°_{ion}, for hydrates in the form $[S^\circ_{\text{ion}}(M_pX_q \cdot nH_2O, s) - S^\circ_{\text{ion}}(M_pX_q, s)]$/J K^{-1} mol^{-1} $\approx n\Theta_S°\{H_2O, s{-}s\} = 40.9n$ are preserved.

for each of these solids was generated using initial values for the individual ion entropies from Spencer's tables.[8] A nonlinear minimization of the error in the least-squares sum of the calculated ion sum entropies against the reported entropies was undertaken (using the Microsoft Excel routine Solver), by allowing the contributing ion entropies to vary. This yielded a stable minimum, even when a variety of arbitrary initial values was used, but with the individual optimized ion entropies differing by amounts of up to 10% for the singly charged ions, and increasing with charge. Any optimized set of single-ion entropies from this analysis provides a satisfactory set of entropy sums; the set selected (on the basis of small sum-of-squares errors between the reported and summed entropies) appears in Table 1, which also lists single ion entropies from published sources. A set[6] of single ion entropies derived from published entropies of dissolution[6b] is omitted since it provides values poorly consistent with those reported here.

Observations

Figure 1a,b show the percentage differences between both our optimized ion entropy sums and using the tabulated values from Spencer[8] (supplemented by our optimized values for the missing NH_4^+ and N_3^- values) plotted against the reported entropies. It is observed that the percentage errors

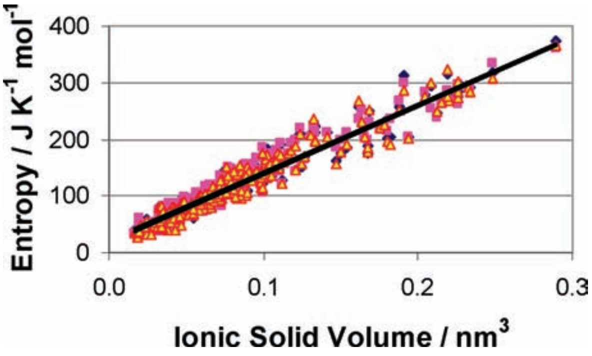

Figure 2. Ionic solid entropies plotted against the molar (that is, formula unit) volumes of 214 ionic solids, for reported entropies (squares), optimized single ion entropy sums (diamonds), and Spencer sums (triangles).[8] The least-squares line shown is for the reported entropies and has a slope = 1186.0 ± 22 J K^{-1} mol^{-1} nm^{-3} and an intercept = 24.2 ± 22 J K^{-1} mol^{-1}. For the optimized single-ion entropy sums, the values are 1199.6 J K^{-1} mol^{-1} nm^{-3} and 22 J K^{-1} mol^{-1}, respectively, and for the Spencer-based sums, 1202.3 J K^{-1} mol^{-1} nm^{-3} and 18 J K^{-1} mol^{-1}. These values should be compared with our generalized values of 1360 ± 56 J K^{-1} mol^{-1} nm^{-3} and 15 ± 6 J K^{-1} mol^{-1}. The largest diamond outlier which can be observed is for almandine ($Fe_3Al_2Si_3O_{12}$; we are using the disorder-corrected value[11] of 299.8 J K^{-1} mol^{-1}, but reported values[3a] extend[1e] up to 342.9 J K^{-1} mol^{-1}).

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Table 2. Entropy Sums Compared with Reported Entropies for Some Complex Ferric Minerals

mineral	formula as listed	volume/nm^3	S°_{298}/J K^{-1} mol^{-1}(ref 14)	S°_{298}/J K^{-1} mol^{-1} (predicted)	% error
iron sulfate 5-hydrate[14a]	$Fe_2(SO_4)_3 \cdot 5.03H_2O$	0.3266	488.2	485.0	−0.7
coquimbite[14a]	$(Fe_{1.47}Al_{0.53})(SO_4)_3 \cdot 9.65H_2O$	0.4405	638.3	668.2	4.7
ferricopiaptite[14a]	$Fe_{4.78}(SO_4)_6(OH)_{2.34} \cdot 20.71H_2O$	0.9544	1449.2	1476.0	1.8
rhomboclase[14a]	$(H_3O)_{1.34} \cdot Fe(SO_4)_{2.17} \cdot 3.06H_2O$[a]	0.2411	380.1	369.4	−2.8
yavapaiite[14b]	$KFe(SO_4)_2$	0.1649[b]	224.7	227.2	1.1
natrojarosite[14c]	$NaFe_3(SO_4)_2(OH)_6$	0.2595[b]	382.4	394.5	3.2
Mg-staurolite[14d]	$Mg_{3.5}Al_{18}Si_{7.75}O_{44}(OH)_4$	0.7333	937.9	979.4	4.4

[a] In the absence of H_3O^+ from our set of optimized ion entropies, the value for H_2O was used in this sum. [b] Molar volumes from "Mineralogy Database" (http://www.mindat.org/index.php).

Table 3. Estimation of Single-Ion Entropy Contribution, $S^\circ(Cd^{2+})$/J K^{-1} mol^{-1}, for Cd^{2+} Cation in Cd Compounds Arbitarily Selected from Ref 1i

solid compound	S°_{298}/J K^{-1} mol^{-1} (reference 1i)	value of $S^\circ(Cd^{2+})$/ J K^{-1} mol^{-1} obtained by subtraction of single ion values, S°_{ion}, in Table 1
CdO	54.8	47.4
CdF_2	77.4	36.4
$CdCl_2 \cdot 2.5H_2O$	227.2	53.0
$CdBr_2$	137.2	40.3
$CdSO_4 \cdot 8/3H_2O$	229.63	46.4
average value for $S^\circ(Cd^{2+})$/J K^{-1} mol^{-1}		44.7 ± 6.5

tend to decrease with the increasing volume and complexity of the materials concerned, in spite of their increasing entropies, with values generally within 15% of the reported entropy. In general, the Spencer sums tend to be slightly lower than the reported values, while the optimized sums tend to have slightly smaller errors (it is acknowledged that the optimization process was against this set, but the wide range of materials included precludes individual entries from dominating the values obtained).

In Figure 2, we note that both the ion entropy sums retain the excellent linear correlation with volume earlier noted in the VBT procedures.[2]

We have tested the reliability of our ion summation on a small set of recently presented mineral entropies,[14] as seen in Table 2 (note: small differences can occur between the listed values, calculated in the Excel spreadsheet, for materials containing large numbers of ions, and those calculated from the data in Table 1 simply because of rounding in the presentation of the values in Table 1).

Prediction of S°_{ion}/J K^{-1} mol^{-1} for Ions Not Listed in Table 1

Cations. Consider the standard entropies, S°_{298}/J K^{-1} mol^{-1}, for the arbitrarily chosen Cd compounds listed in Table 3. For each of the listed compounds, S°_{ion}/J K^{-1} mol^{-1} is known for all of the component ions except Cd^{2+}. Hence, $S^\circ_{298}(Cd^{2+})$/J K^{-1} mol^{-1} can be estimated by subtraction. The value found can then be used, as in Table 4, to predict values for other Cd materials. The compounds listed in Table 4 also have known[1i] standard entropies, S°_{298}/J K^{-1} mol^{-1}, so that the predictions can be tested.

Table 4. Estimation of Standard Entropy, S°_{298}/J K^{-1} mol^{-1}, for the Cd Compounds Listed, Whose Experimental S°_{298}/J K^{-1} mol^{-1} Values Are Known from Ref 1i

solid compound	S°_{298}/J K^{-1} mol^{-1} (predicted)	S°_{298}/J K^{-1} mol^{-1} (reported)[1i]	% error
$CdSO_4 \cdot H_2O$	159.8 ± 6.5	154.0	3.7
$(NH_4)_2Cd_2(SO_4)_3$	446.0 ± 9.2	485.7	− 8.2
$CdCO_3$	97.1 ± 6.5	92.5	5.0

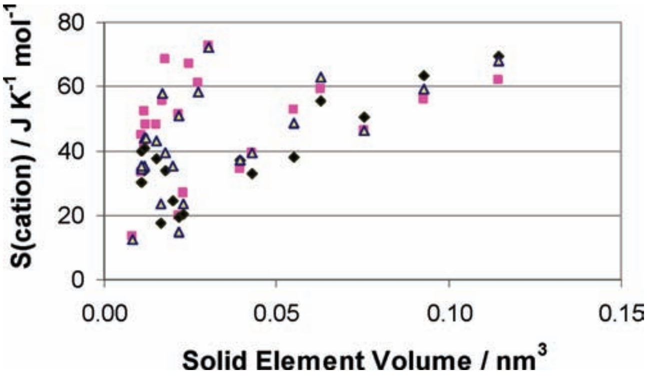

Figure 3. Single cation entropies plotted against the molar volumes of the solid elements,[1] for (a) for the current optimized set (diamonds), (b) the set of Richter and Vruels[13] (squares), and (c) for the Spencer-based set[7,8] of the same cations (triangles).

The results in Table 4 indicate that this approach gives reasonable estimates for the materials, where the predictions usually—although, not always—encompass the experimental results when uncertainties are considered. By contrast, for only two of these compounds, $CdCO_3$ and $CdSO_4 \cdot H_2O$, could Latimer's original approach[4b] have been applied. The predicted entropies (and errors) are found to be 101.7 (− 9.9%) and 165.3 J K^{-1} mol^{-1} (−7.3%), respectively.

Anions. An exactly analogous procedure can be adopted for determining the single entropy contribution of an anion.

Relation to Element Volumes

Figure 3 demonstrates an unexpected, intriguing, and significant relation between the cation entropies and the molar volumes of the corresponding solid elements. (Such a relation is not apparent between these ion entropies and either the molar masses or densities of the elements.)

It is seen that there are two branches in the relation (an upper branch proceeding along a near vertical direction and a lower, more diagonal branch, each developing from a more-or-less common intersection). The lower branch corresponds to the alkali and alkaline earth metals (having relatively low single ion entropies), while the upper branch includes the

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[14] (a) Majzlan, J.; Navrotsky, A.; McCleskey, R. B.; Alpers, C. N. *Eur. J. Mineral.* **2006**, *18*, 175–186. (b) Forray, F. L.; Douet, C.; Navrotsky, A. *Geochim. Cosmochim. Acta* **2005**, *69*, 2133–2140. (c) Stoffregen, R. E. *Geochim. Cosmochim. Acta*, **1993**, *57*, 2417–2429 (estimate). (d) Grevel, K.-D.; Navrotsky, A.; Fockenberg, T.; Majzlan, J. *Am. Mineral.* **2002**, *87*, 397–404.

transition metals and the closely related, so-called "basic" metals (Pb, Sn, Tl) (each having large single ion entropies relative to their volumes). The branches converge for those metals with smaller single ion entropies and smaller molar volumes (such as Fe; our pair of ion entropy values for Fe^{2+} and Fe^{3+} both lie in this region). This convergence may be related to Grimvall's observation[5] that the Latimer approach may be less useful for smaller, lighter atoms. A value of this observation is that it provides a new relation between the entropies of the atoms and of their ions in the solid state by means of which single cation entropies may readily be estimated from the molar volume of the solid metal. For example, we may (very tentatively) suggest from the graph that the entropy of the Cd^{2+} ion is about 40 J K^{-1} mol^{-1} on our optimized scale since Cd is a transition metal with a molar volume of 0.0215 nm^3 (cf. the estimated value of 44.7 ± 6.5 J K^{-1} mol^{-1} in Table 2).

Conclusions

Additive single-ion entropies, independent of charge, for a range of cations and anions are optimized against 214 ionic solids. Entropies generated by summing these quantities are usually within ~15% of reported values, and such error is reduced by about one-third when the entropies are used in $T\Delta S$ form in the calculation of Gibbs energies near room temperature. Unexpectedly, it is found that cation entropies are related to the molar volumes of the elemental metals. The present work provides an *independent*, *nonvolume-based* procedure by which the entropies of ionic solids may readily and reliably be estimated.

Acknowledgment. The assistance and advice of Prof. E. J. Billo[12] in the use of his Excel routine SolvStat is gratefully acknowledged. H.D.B.J. acknowledges the support of the University of Warwick for the continuation of this work.

Note Added after ASAP Publication. This article was released ASAP on July 6 with minor errors in reference 1c and Table 1. The correct version was posted on July 9, 2009.

Supporting Information Available: Table S1 lists the 214 ionic materials used in the single-ion optimization, together with their reported room-temperature entropies and the corresponding ion entropy sums, together with entropy estimates from our linear entropy−volume correlations,[3] as well as the differences from the reported entropies. Figure S1 plots the estimates versus the reported entropies. Table S2 lists the sums of squares of errors between the reported entropies and their estimates. Table S3 lists the data for Figure 3. This material is available free of charge via the Internet at http://pubs.acs.org.