

Resolution of Heat-Capacity Curves for Crystalline Substances*

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Resolution of excess heat capacities of many types of transitions – whether structural or electronic, or otherwise – requires a reliable estimate of the lattice contribution. This besetting problem has confronted thermophysicists for decades. Corresponding state theories have been less than satisfactory; Lindemann schemes are suggestive. For chemical thermodynamic purposes use of a volume-weighted scheme over the range where entropy development largely occurs is demonstrated to provide resolution of Schottky contributions for $\text{Ln}(\text{OH})_3$ and LnCl_3 systems and has been shown to be superior to other approaches. Application to estimation of heat capacities (entropies, *etc.*) and to extrapolation of results to pure end-member composition in geothermodynamic problems are considered.

INTRODUCTION

Because the heat capacity of a system is determined by the energy levels of that system, heat capacity measurements themselves are often used to deduce those energy levels. Very often one has a model of a system and can calculate the resultant excess heat capacity associated with the model. Unfortunately, the heat capacity of interest is often superimposed on a background contribution and the separation of the excess contribution must be made from that of the background. All too often, this resolution is made by good judgment only. The relevant background contribution is usually the so-called lattice contribution and inasmuch as it typically represents 80 to 100% of the total measured heat capacity, if it is going to be estimated, the procedure must be one of relatively

high precision. Consequently, whenever resolution of transitions (be they magnetic, structural, Schottky, order-disorder) is to be done, one is confronted with the necessity of an evaluation of the lattice contribution. When estimates are made of the heat capacity and/or the thermodynamic functions of substances, the lattice represents the bulk of the quantity. Moreover, when adjustment of thermophysical properties, *e.g.* of minerals or of petrological materials is involved, the same problem arises. Consequently, an urgent need exists for evaluation of the lattice contribution.

We consider that we have recently made significant progress in this matter and that the volume of the crystal over an important portion of the temperature scale is clearly involved. Nonetheless, mass and the structure-type are also relevant parameters.

Historically, the story begins with the 1961 Grönvold/Westrum paper on the correlation of entropies for transition-element chalcogenides¹⁾ and the graphical representation of the surprising result of this endeavor at a 1977 Moscow Plenary lecture^{2,3)} reproduced this endeavor against the Latimer^{4,5)} scheme for entropy contributions for cations in Figure 1. Latimer considered that these contributions were proportional to the logarithm of the mass of the cation. Two aspects surprising to me were

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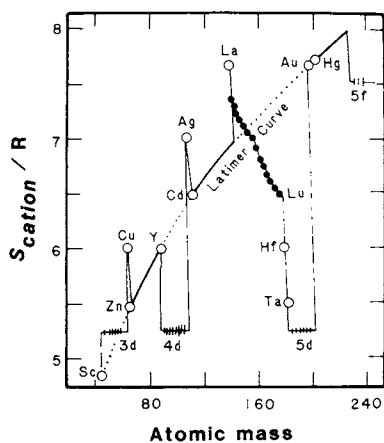


Fig. 1. The Grønvd-Westrum scheme¹⁾ superimposed on the d-f electron portion of the Latimer⁵⁾ scheme.

The main stream 3d, 4d, and 5d-cations all show the same contribution to the entropy rather than a Latimer-like mass dependence.^{4,5)} Borderline transition-element chalcogenides are possibly intermediate.

The entropy values for 4f (lanthanide) cations were diametrically perpendicular to the mass dependence predicted by the Latimer scheme⁶⁾ suggesting that although masses and volumes change by roughly the same fractional magnitude through the system, the heat-capacity trend here clearly favored volume rather than mass dependence.

Although the first surprise hides much of interest, the second is the one of immediate concern and shows clearly the consequences of the lanthanide contraction.

On the basis of these abstracts, we have chosen to study lanthanide systems. We early investigated the sesquioxides, Ln_2O_3 ,⁷⁻¹²⁾ then more recently moved on to the trichlorides, LnCl_3 ,¹³⁻¹⁵⁾ and have most recently considered the trihydroxides, $\text{Ln}(\text{OH})_3$ ¹⁶⁻²⁰⁾ which have the great advantage of being isostructural throughout the series.

In the discussion which follows, frequent reference is made to Schottky contributions – interesting in their own right – but here used as a means of testing the success of the evaluation of the lattice contribution.

THE LANTHANIDE SYSTEM

Lanthanide Sesquioxides

Recognition of the importance of the Schottky thermophysical contribution came with a series of papers by Justice and Westrum⁷⁻¹¹⁾ who studied the lanthanide sesquioxides and obtained an unusually rich yield of data concerning the energetics of the trivalent ions in these compounds. Although the Schottky contributions may also be studied spectroscopically, the general unavailability of single crystal samples for absorption spectroscopy or for paramagnetic resonance experiments had tended to favor the calorimetric approach. Our initiatory measurements⁷⁾ on neodymium sesquioxide yielded results in levels more than an order of magnitude smaller than those estimated by Penny²¹⁾ from crystal-field splittings. But any discredit was of short duration, since spectroscopy²²⁾ confirmed, in this instance, the values that had been obtained by calorimetry. The quantitative comparison is made in table 1.

Table 1. Stark levels/cm⁻¹ for Nd_2O_3

Level	g_i	Calc. ^a	Calorimetry ^b	Spectroscopy ^c
0	2	0	0	0
1	2	492	21	22
2	2	1476	81	83
3	2	2952	400	390
4	2	4920	---	---

^a Penny Reference 21.

^b Justice and Westrum Reference 7.

^c Henderson *et al.* Reference 22.

The method of approach involved measurement of the total heat capacity of Nd_2O_3 , of a diamagnetic analog, La_2O_3 , and the resolution of the difference in heat capacity of the two compounds in terms of a sequence of Schottky levels of the degeneracies predicted by crystal-field theory. The power of the cryogenic calorimetric approach thus demonstrated was later extended by the same authors to include most other lanthanide sesquioxides, even those containing C_2 and C_{31} sets of levels. It was demonstrated that the levels were valid not only for the cryogenic heat capacity contribution, but as well for temperatures in excess of 1000 K. Unfortunately, the sesquioxides crystallized in A-, B-, and C- forms thus making it harder

to recognize the underlying trends. A recent paper extends this fitting and correlation to new electronic Raman scattering data.²³⁾

Lanthanide Trichlorides

The desirability of extending such studies to other systems led Sommers and Westrum to examine the lighter lanthanide trichlorides.^{13,14)} Their study further heightened the understanding of the trend and regularities involved and showed the importance of the Schottky contribution to the thermophysical functions. The latter were in excellent accord with those predicted by the scheme of Westrum²⁴⁾ based upon the treatment of Grønvdold and Westrum.¹⁾ The quality of the accord can be seen in Table 2.

Lanthanide Pnictides

The heat capacities of a set of lanthanide mononitrides has been achieved by Stuttius²⁵⁾ on materials less well characterized than desirable. We are presently undertaking a reinterpretation of these data. His work is interesting in that he did utilize crystal parameters in interpolating lattice heat capacities across the lanthanide series.

Lanthanide Hexaborides

Several of these compounds have been studied over the cryogenic range by Westrum *et al.*²⁶⁾ These studies are interesting and will be examined critically.

Lanthanide Sesquisulfides

Exceedingly interesting spectroscopic studies, together with heat-capacity measurements at very low temperatures, are beginning to probe lanthanide sesquisulfides, Ln_2S_3 , which are being prepared as stoichiometric single crystals, as well as in the hyper- and hypo-stoichiometric forms. Since most of this work is as yet unpublished in definitive form, one can only herald the endeavors of Professors Gschneidner and Gruber and their collaborators for these pioneering studies. Schottky functions at the higher cryogenic temperatures are being explored by this author and his co-workers in a collaborative endeavor with the Ames Laboratory.

OTHER INTERPOLATION SCHEMES

In principle, the best way to evaluate C_{latt} is from the phonon dispersion relation, $k(\omega)$, determined by inelastic neutron scattering.

However, occasionally Einstein functions (in which $\omega_E = \text{constant}$) or Debye functions (in which $\omega_D = \nu_0 k$) can be used to get results reliable within about 10 per cent.

Attempts to get an experimental estimate of C_{latt} in X compound by measuring the heat capacity of an isostructural diamagnetic (ID) compound are frequent. Here the corresponding states assumption

$$C_{\text{latt}}(\text{X cpd})(T) = C_{\text{latt}}(\text{ID}) \times (k \cdot T)$$

Table 2. Comparison of some trichloride entropy estimation schemes

Compound	$\{S^\circ(298.15\text{K}) - S^\circ(0)\} / \text{cal K}^{-1} \text{mol}^{-1}$			
	Latimer	Latimer augmented ^a	Westrum augmented ^b	Experimental Refs. 13, 14
LaCl_3	34.5	34.5	33.1	32.88
CeCl_3	34.5	38.1	36.1	(36.0) ^c
PrCl_3	34.5	38.9	36.8	36.64 ^d
NdCl_3	34.6	39.2	36.8	36.67
PmCl_3	34.7	39.5	36.8	(37.0) ^c
SmCl_3	34.8	38.4	35.7	35.88
EuCl_3	34.8	37.3	34.5	34.43
GdCl_3	35.0	39.1	36.0	36.19

^a By $R \ln(2J+1)$: the $(\text{Cl}_3)^{3-}$ ion contribution is taken as 20.7 cal $\text{K}^{-1} \text{mol}^{-1}$.
^b By $R \ln(2J+1)$: the $(\text{Cl}_3)^{3-}$ ion contribution is taken as 17.9 cal $\text{K}^{-1} \text{mol}^{-1}$.
^c Parentheses denote interpolated lattice and calculated Schottky contributions.
^d Based on 0.294 K.

in which k is experimentally deduced is often employed.

Alternatively, the Debye theta approximation is couched in the masses (M) of the molecules

$$\frac{\theta_D(X)}{\theta_D(ID)} = \left[\frac{M(ID)}{M(X)} \right]^{1/2}$$

The more refined Lindeman's relationship using melting points, T_m , and molal volumes, V is also used.

$$\theta_D^2 = \frac{k' T_m}{MV^{2/3}}$$

Corresponding states approaches are often used.

For nearly half a century the Latimer scheme^{4,5)} has been a favorite way of taking into account the differences between compounds in iso-anionic series. This time-honored scheme – devised primarily for entropy estimates – is not without its flaws, despite the several times it has been adjusted by Latimer himself.

THE VOLUMETRIC SCHEME

The scheme that we advocate involves linear interpolation on the basis of the molal volumes of the compounds in question. In particular, the formula by which the lattice heat capacity of the praseodymium trihydroxide may be calculated is indicated below:

$$C_p [\text{Pr}(\text{OH})_3 \text{ lattice}] = x C_p [\text{La}(\text{OH})_3] + (1-x) C_p [\text{Gd}(\text{OH})_3] \text{ and in which } x \text{ is the fractional molal volume increment, i.e.} \\ x = \{V[\text{Pr}(\text{OH})_3] - V[\text{La}(\text{OH})_3]\} / \{V[\text{Gd}(\text{OH})_3] - V[\text{La}(\text{OH})_3]\}$$

It should be noted that utilization of other than linear interpolations would have involved only second order effects. The importance of volume was appreciated^{2,3)} on recognition of the fact that for the lanthanide chalcogenides the lattice contribution decreased with increasing atomic number and was, therefore, diametrically opposed to the trend in the Latimer scheme based on mass. The lanthanide contraction provided the clue. Other authors^{27,28)} have been engaged in a polemic as to the relevance of *volume versus mass* in providing interpolation schemes for lattice contributions. Moreover, Kieffer²⁹⁻³²⁾ has undertaken a theoretical and experimental correlation of the lattice vibrations of minerals. This takes into account the many factors involved and discusses particularly

the analysis of the vibrational contribution, which has been discussed also by Sommers and Westrum.¹⁴⁾

But does the volumetric scheme really work? Perhaps the best way of testing the validity of a lattice contribution scheme is in the calculation of the calorimetric Schottky contribution and the comparison of this excess heat capacity with that calculated from spectroscopic data on the sample itself. However, this comparison can only be made when one utilizes the Stark levels of the *concentrated* compounds. Measurements made on *doped* lanthanide halides, for example, need to be extrapolated by some technique (discussed elsewhere)¹⁵⁾ or by calculations based on crystal-field parameters.

TESTS OF GOODNESS OF LATTICE CONTRIBUTION BY COMPARISON OF SPECTROSCOPIC AND CALORIMETRIC SCHOTTKY CONTRIBUTIONS

Since resolution of Schottky contributions from the generally much larger vibrational (lattice) heat capacities of lanthanide compounds has been limited by the uncertainty in the magnitude of the lattice contribution, such subtle effects as dependence of the Stark levels on temperature and host lattice have been heretofore undetected calorimetrically. Since the lanthanide trihydroxides are an iso-anionic series having relatively small lattice contributions and their lower-lying Stark levels have been spectroscopically deduced for many of the concentrated compounds, this series is the most nearly ideal system yet studied in an attempt to resolve Schottky contributions in the 5 to 350 K range. Three examples illustrate the success of the scheme described on $\text{Ln}(\text{OH})_3$ systems; moreover, two examples from LnCl_3 systems demonstrate that excellent agreement obtains here as well.

Eu(OH)₃

The Schottky contribution to the heat capacity of the Eu(III) analog is unique in that it arises entirely from thermal populations of excited $[SL]$ J -manifolds. This invariably results in the lowest excited Stark levels being much higher in energy for the Eu(III) analog than for any other series member. The calculated Schottky heat capacity is consequently relatively insensitive to small shifts in the Stark level energies and, therefore, is expected to be the most accurate approximation to

the true Schottky heat capacity within any lanthanide series.

The energy levels of concentrated $\text{Eu}(\text{OH})_3$ were determined by Cone and Faulhaber³³⁾ from absorption and fluorescence spectra at 4.2 and 7.7 K. Stark levels arising from the 7F_0 , 7F_1 , 7F_2 , and 7F_3 manifolds all contribute to the Schottky heat capacity below 350 K. The derived calorimetric Schottky contribution shown in figure 2 is seen to be in excellent accord with that calculated from the spectroscopic data.¹⁷⁾

$\text{Pr}(\text{OH})_3$

The crystal-field splitting of the 3H_4 manifold of $\text{Pr}(\text{OH})_3$ has been determined from the absorption spectra of mulls at 95 K.³⁴⁾ The observed spectra were not as highly resolved as one might obtain from measurements on single crystals. This lack of resolution is reflected in a $\pm 3 \text{ cm}^{-1}$ uncertainty in the Stark level energies. As seen in figure 3 the calorimetric and spectroscopic Schottky curves are in very good agreement between 15 and 230 K. Below 25 K a cooperative magnetic contribution of unknown magnitude plus the uncertainty in the energy of the lowest excited Stark level preclude any attempt to accurately determine the Schottky contribution in this temperature region. Above 260 K the calorimetric curve trends below the calculated band. Such a decrease in the high-temperature calorimetric Schottky curve could be due to a gradually decreasing crystal field intensity within the $\text{Pr}(\text{OH})_3$ crystals as the lattice expands with temperature. (A gradual shift to lower energies of 5 to 10 cm^{-1} by the four highest Stark components of the 3H_4 -manifold between 100 and 350 K would account for the observed deviation.)

$\text{Tb}(\text{OH})_3$

The energy levels of the lowest four manifolds of concentrated $\text{Tb}(\text{OH})_3$ and Tb^{+3} doped $\text{Y}(\text{OH})_3$ were determined by Scott, Meissner, and Crosswhite.³⁵⁾ The observed Schottky below 350 K is due almost entirely to population of the 7F_6 manifold. The availability of spectroscopically determined energy levels for both the $\text{Tb}(\text{OH})_3$ and $\text{Y}(\text{OH})_3$ host lattices provides an opportunity to directly observe the sensitivity of the new lattice approximation technique in differentiating

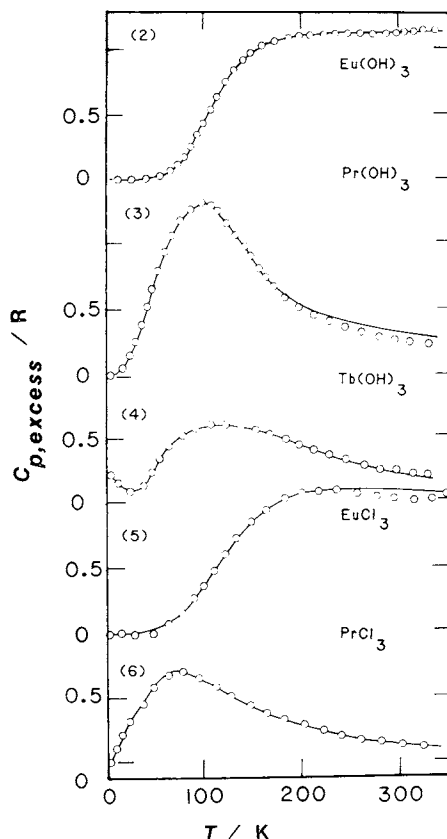


Fig. 2-6. Calorimetrically (—) and spectroscopically (oooo) determined Schottky contributions. (2) for $\text{Eu}(\text{OH})_3$ ¹⁷⁾; (3) for $\text{Pr}(\text{OH})_3$ ¹⁶⁾; (4) for $\text{Tb}(\text{OH})_3$ ¹⁸⁾; (5) for EuCl_3 ¹⁵⁾; and (6) for PrCl_3 .¹⁵⁾ (The successive curves are displaced by 1 unit of C/R .)

between such systems. Heretofore the general assumption has been that any calorimetrically derived Schottky contribution is too crude to detect the effect of any differences in the Stark level energies of such systems.

As seen in figure 4 the calorimetric and calculated $\text{Tb}(\text{OH})_3$ Schottky curves are in excellent agreement below 160 K, while at higher temperatures the calorimetric curve trends below that deduced from the spectral data.¹⁸⁾ The calorimetric Schottky curve is clearly in far better agreement with the spectroscopic curve calculated from the Stark levels of concentrated $\text{Tb}(\text{OH})_3$ rather than with that of Tb^{+3} doped $\text{Y}(\text{OH})_3$. (Above 160 K the difference between the calorimetric and calculated curves may be accounted for if the Stark

levels are assumed to undergo an approximately 6 per cent shift to lower energies between 77 and 350 K. Such a shift may be postulated to be occasioned by the decrease of the crystal-field intensity as the lattice expands with increasing temperature.)

EuCl₃

The Schottky heat-capacity contribution of EuCl_3 is unique – like that of $\text{Eu}(\text{OH})_3$ – in that it arises entirely from thermal population of excited $[SL]J$ -manifolds. The first excited states are near 355 and 405 cm^{-1} . The Schottky contribution was calculated from energy levels of (1 and 4 per cent) Eu^{+3} doped LaCl_3 determined from the absorption spectrum at 4 K and the fluorescence spectrum at 4 and 77 K studied by Deshazer and Dieke.³⁶⁾ The energy levels of concentrated EuCl_3 are not expected to be identical to those of Eu^{+3} doped LaCl_3 . The stronger crystal field in concentrated EuCl_3 – compared to that in the LaCl_3 host – is expected to increase the Stark splitting and simultaneously to lower the center of gravity of the 7F_1 -manifold, *i.e.*, to lower the energy of the $\mu = 1$ doublet and to leave the $\mu = 0$ level essentially unchanged. The effect of the stronger crystal field will be countered to some extent by expansion of the EuCl_3 lattice at higher temperatures (*i.e.*, in the region of the Schottky maximum); however, this is anticipated to be insuffi-

cient to fully nullify the effect. Because the energies of the Stark levels contributing to the Schottky heat capacity are relatively high, a shift of the $\mu = 1$ doublet by as much as 10 to 15 cm^{-1} will have but a small effect on the calculated Schottky contribution. The derived *calorimetric* Schottky heat capacity shown in figure 5 is seen to be in excellent accord with that derived from the *spectroscopic* data.¹⁵⁾

PrCl₃

The analysis of the Schottky contribution to the heat capacity of PrCl_3 is complicated by unusual shifts in the Stark level energies as the intensity of the crystalline field is varied. However, the basic arguments remain essentially unchanged from those applied to the preceding compounds. The energy levels of Pr^{+3} doped LaCl_3 were determined from absorption and fluorescence spectra by Sarup and Crozier.³⁷⁾ Although the wealth of spectroscopic data may be best deduced by reference to the definitive paper,¹⁵⁾ both figure 6 and table 3 attest to the good agreement between the two Schottky contributions.¹⁵⁾

THE ROLE OF MASS

The continuous and dashed curves of figure 7 represent $[C_p\{\text{Gd}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ and $[C_p\{\text{Y}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ with the cooperative magnetic contribution to the $\text{Gd}(\text{OH})_3$ heat capaci-

Table 3. Energy levels/ cm^{-1} for 3H_4 -state of PrCl_3

State	$\text{Pr}^{+3} : \text{LaCl}_3$	Concentrated PrCl_3				
		Calorimetry	CEF	ERS'	ERS''	Absorp.
Technique	Abs. Fluor.					
	0 ^a	0 ^b	0 ^c	0 ^d	0 ^e	0 ^f
	33.1	---	29	30.5	32	31.8
Levels	96.4	---	99	99	100	99.6
	130.2	155	152	145	139	---
	137.0	168	176	160	---	---
	199.1	235	230	(228)	---	---

^a Energy levels by absorption and/or fluorescence spectroscopic data for Pr^{3+} doped into LaCl_3 . (Sarup and Crozier).³⁷⁾

^b Levels deduced from heat-capacities by volumetric lattice contribution method.¹⁵⁾

^c Calculated from estimated crystal-field parameters.¹⁵⁾

^d Observed in electronic Raman scattering (Chirico, *et al.*)¹⁵⁾

^e Observed in electronic Raman scattering (Hougen and Singh).³⁸⁾

^f Observed in absorption spectra data (Dorman).³⁹⁾

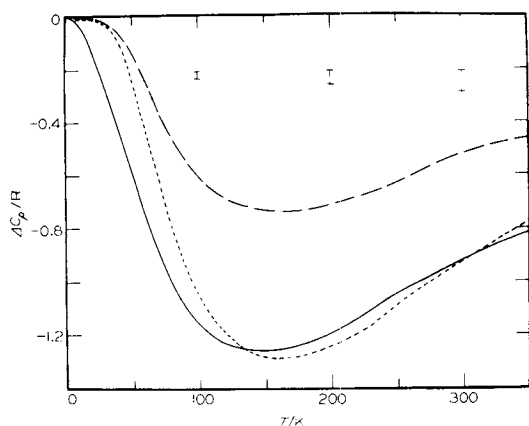


Fig. 7. Temperature dependence of $\Delta C_p/R$ for the trihydroxide pairs:

$[C_p\{\text{Gd}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$, (—);
 $[C_p\{\text{Y}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$, (---);
 and the estimated $[C_p\{\text{Lu}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ (· · · · ·).

The error bars represent 0.5 per cent of $C_p[\text{La}(\text{OH})_3]$.

ty deleted. The dotted curve is an estimate of the quantity $[C_p\{\text{Lu}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ derived by extrapolation of the experimentally observed lattice heat-capacity variation between $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$ (e.g. see reference 18). If the lattice heat-capacity contribution for the lanthanide trihydroxides were exclusively a linear function of the molar volume, then the $[C_p\{\text{Y}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ curve would lie almost exactly midway between the dashed and dotted curves from 5 to 350 K. In contrast, if the trend in the lattice contributions was determined principally by the molar-mass variation, it would lie entirely below the dotted curve instead of only for temperatures below about 120 K.

From the results obtained for $\text{Y}(\text{OH})_3$, a shift in the relative importance of the cationic mass and volume in determining the trend in the lattice contributions across the series occurs near 100 K. The experimental observations may be rationalized by considering the type and nature of the lattice vibrational modes being activated at each temperature.^{29,40} At very low temperatures, low-frequency modes — roughly characterized as unit-cell vibrations — are those primarily activated. The lanthanide contraction which is an intramolecular contraction, has little effect upon these vibrations. In essence the force constants between

the unit cells are unchanged, while the cell masses increase across the series. This occasions a decrease in the vibrational frequencies of the unit cells with increasing atomic number and, therefore, a corresponding increase in lattice contribution at a given temperature.

At higher temperatures an increasing proportion of the observed heat capacity is due to thermal activation of optical vibrational modes. The effect of the lanthanide contraction upon these modes is to increase their frequency by increasing the intramolecular force constants to such an extent that the counteracting effect of the increased cationic mass is largely overshadowed. [An analogous effect is routinely observed in temperature dependence of vibrational spectra. As the temperature is decreased (i.e., as the molecule contracts) the vibrational mode frequencies are generally seen to increase.] In the case of the lanthanide trihydroxides the molar-mass variation between the lanthanum and gadolinium iso-anionic compounds is small enough to be insignificant in determining the trend in lattice contribution across the series between 10 and 350 K. Even when considering $\text{Y}(\text{OH})_3$, which has a molar mass approximately 2/3 that of the lanthanide compounds, the effect of molar mass is clearly dominant only below 80 K. The difference between the heat capacities of lutetium and yttrium ethylsulfates^{41, 42} clearly exhibits the same type of behavior as that of the corresponding trihydroxides.

The apparent differences with temperature of the functional dependence of the lattice contribution upon molar mass and volume makes it imperative that lattice approximations (e.g., the method of “corresponding states”) which employ observations made at high temperatures to imply low-temperature properties or *vice versa* be applied with caution. Related problems have been discussed by Saxena,²⁷ by Cantor,²⁸ and by Kieffer.^{29–32}

Thus the trend in lattice heat capacities of iso-anionic series of lanthanide compounds may be rationalized in terms of two contributing factors: *molar mass* and *molar volume*. At low temperatures, the lattice contribution is due primarily to thermal activation of acoustic lattice modes and molar mass is the dominant factor. At higher temperatures increasing thermal activation of

optical lattice modes, which are strongly affected by the lanthanide contraction, results in lattice heat-capacities which are related predominantly to the trend in molar volume. For the light lanthanide trihydroxides the molar-mass variation is dominated by the molar-volume effect at least above 50 K. Only for much lighter $Y(OH)_3$ is the mass effect clearly visible and then only below 100 K.

Hence, in emphasizing the importance of volume, we do not mean to slight mass – especially not at lower temperatures. Data on $U(OH)_3$, which is isostructural with the $Ln(OH)_3$'s should help to clarify and to test the role of mass. Although we have demonstrated the great utility of the volumetric scheme as an interpolation device for $C_p(T)$ or $S^\circ(298\text{ K})$ for a system of isostructural compounds, what about the broader implications? How generally does it supplant the Latimer rule even when "augmented" to provide magnetic contributions, etc.?

We have examined isostructural series on which sufficient data exist to make a judgment. Many interesting trends are observed. For example, as seen in figure 8, extrapolation by the Latimer scheme from the entropies (298 K) of MoS_2 , WS_2 , PtS_2 to that of TiS_2 would lead to a Latimer-scheme value of $S^\circ/R = 7$; on the other hand the volumetric approach would lead to $S^\circ/R = 9.5$. Experiment ($S^\circ/R = 9.4$) confirms the latter! In other instances the general trend of cation mass with molar volume in iso-anionic series often tends to make choice between the two systems difficult inasmuch as molar mass and molar volume usually go hand in hand. Identification of key compounds

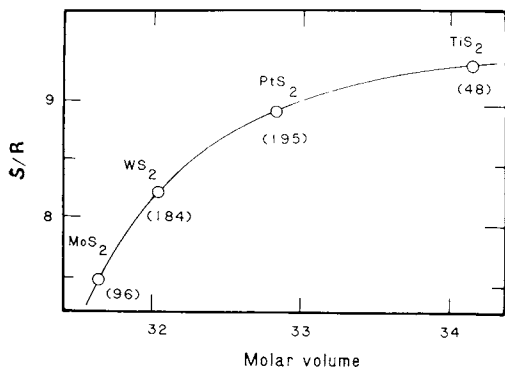


Fig. 8. Entropy versus molar volume for the MS_2 compounds at 298.15 K. The cation masses appear in parentheses below the points.

on which to test the scheme and to develop more reliable correlations is underway.

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【 会員の頁 】

★ IUPAC 化学熱力学会議

(IUPAC Conference on Chemical Thermodynamics)

標記の国際会議が、1982年9月6日から10日までロンドンに於て開催される。ちなみに本会議は第12回目に当る。

セカンドサーキュラーを希望する人は下記宛連絡されたい。

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★第2回チェコスロヴァキアカロリメトリー会議

(Second Czechoslovak Conference on Calorimetry)

上記の会議が1982年9月13日～17日の間、PragueとLibliceで開催される。

会議の主題：(i) 溶液カロリメトリー、(ii) 生化学および高分子系のカロリメトリー、(iii) 特殊なカロリメトリー。

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