Energy Studies on α- and β-Thallium(I) Fluorides

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The cohesive energies of the α and β polymorphs of thallium(I) fluoride are presented and discussed, and the results interpreted in terms of probable structures for these compounds. Comparisons are drawn between the calculated and thermodynamic values for the cohesive energies. The agreement between the calculated and thermodynamic values for the cohesive energies is good, and indicative of an ionic structure.

THE cohesive energies of the thallium(I) halides have been reported on several occasions.[1-6] Alcock and Jenkins [7] published revised results for the crystal structure and cohesive energy of β-thallium(I) fluoride, and used them to postulate a highly distorted structure for Tl^+ in this compound. In this paper I comment on their results and show, in the light of further work, that their interpretation of the available information is not the most probable one.

CALCULATIONS

The cohesive energy (U) is best calculated by means of equations (1)—(3). The terms in these equations have their usual significances, as explained in the Tables. In studying TlF, certain approximations have to be made because of the paucity of physical data for this compound.

Madelung Constants.—α- and β-Thallium(I) fluorides have distorted octahedral structures, the α form being tetragonal and the β form orthorhombic. The Madelung constants have been evaluated by the method of Bertaut,[8] as extended

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by Templeton[9] and by Jones and Templeton.[10] A spherical charge distribution was assumed, and convergence to better than 0.01% was obtained with a summation limit of *ca.* 2 reciprocal space units. The calculations

$$U = -\{[A(L)e^2/L][1 - (\rho/L)]/(4\pi\varepsilon_0) + C[1 - (6\rho/L)]/L^6 + D[1 - (8\rho/L)]/L^8 + (3vT\beta/k)(\rho/L)\}N_A/10^3 \quad (1)$$

$$L/\rho = \{(9v\phi/k) + [2A(L)e^2/L] + (42C/L^6) + (72D/L^8)\}/\{[A(L)e^2/L] + (6C/L^6) + (8D/L^8) - (3vT\beta/k)\} \quad (2)$$

$$\phi = 1 + T\{[(\partial k/\partial T)_P/k] + [\beta(\partial k/\partial P)_T/k^2] + (2\beta/3)]\} \quad (3)$$

were made in terms of a standard distance, L. Ideally, L should be the shortest interatomic distance in the structure. From a practical point of view, however, some deviation from the ideal value is permissible since the important quantity is $A(L)/L$; this fact is often not appreciated.[7] The results are listed in Table 1.

TABLE 1

Madelung constants

	$10^{10}L$/m	$A(L)$	$[10^{-10}A(L)/L]$/ $\mathrm{m^{-1}}$	Summation limit/ RU[b]
α-TlF (373 K)	2.69[a]	1.687 517	0.627 330	1.9
β-TlF (298 K)	1.75	1.012 659	0.578 662	2.9
	2.00	1.171 512	0.585 756	2.5
	2.25[a]	1.317 951	0.585 756	2.2
	2.50	1.464 388	0.585 755	2.0
	2.75	1.610 742	0.585 724	1.8
	3.00	1.756 548	0.585 516	1.7

[a] These values were used in the further calculations reported herein. [b] RU = Reciprocal space unit.

Compressibilities and Expansivities.—Volume-decrement data for TlCl, TlBr, and TlI have been interpolated analytically[5] at a pressure of 101 325 N $\mathrm{m^{-2}}$, and the compressibility (k) for β-TlF has been derived from molar volume proportionalities.[11] From powder photographs of β-TlF at different temperatures,[12] an average linear expansivity (α) of *ca.* 4×10^{-5} $\mathrm{K^{-1}}$ has been derived, and the volume expansivity (β) has been equated to 3α. The compressibility for β-TlF was used to estimate that for α-TlF, but the volume expansivity for β-TlF was assumed to apply also to the α form. Since the temperature and pressure coefficients of compressibility are unknown for TlF, ϕ [equation (1)] was taken as unity. A study of the data on alkali-metal halides indicates that ϕ differs there from unity by *ca.* 1%; this deviation represents an uncertainty of *ca.* 0.5 kJ $\mathrm{mol^{-1}}$ in U.

Although the compressibility data so obtained may be questioned, their use in determining an effective repulsion energy is justifiable. Errors in U from this source are probably *ca.* 4 kJ $\mathrm{mol^{-1}}$. A Huggins-type potential[13] is much less satisfactory: not only does it require an assumed value for ρ, but the basic radii cannot be evaluated uniquely, and for good reason.[2,14] The results are listed in Table 2. The constancy of ρ/L is notable, as has been reported before for ionic compounds.[2]

TABLE 2

Pressure, volume, and temperature data

	$10^{11}k$/ $\mathrm{N^{-1}\,m^2}$	$10^4\beta$/ $\mathrm{K^{-1}}$	ϕ	$[10^{19}3vT\beta/k]$/ J	$10^{10}\rho$/ m	ρ/L
α-TlF	3.25	1.2	1.0	1.830	0.303	0.112 3
β-TlF	3.18	1.2	1.0	1.465	0.251	0.111 5

Lattice Sums and van der Waals Potentials.—The van der Waals potentials for ionic crystals may be calculated from equations (4)—(10). The lattice sums were obtained to

$$C = [S_{ij}c_{ij} + (S_{ii}c_{ii}/2) + (S_{jj}c_{jj}/2)]/16\pi^2\varepsilon_0^2 \quad (4)$$

$$c_{ij} = (3/2)\varepsilon_i\varepsilon_j\alpha_i\alpha_j/(\varepsilon_i + \varepsilon_j) \quad (5)$$

$$S_{ij} = L^6 \sum_{\substack{i \\ i \neq j}} \sum_{j} (1/r_{ij}^6) \quad (6)$$

$$D = [T_{ij}d_{ij} + (T_{ii}d_{ii}/2) + (T_{jj}d_{jj}/12)]/16\pi^2\varepsilon_0^2 \quad (7)$$

$$d_{ij} = (9/4)(c_{ij}/e^2)[(\alpha_i\varepsilon_i/p_i) + (\alpha_j\varepsilon_j/p_j)] \quad (8)$$

$$T_{ij} = L^8 \sum_{\substack{i \\ i \neq j}} \sum_{j} (1/r_{ij}^8) \quad (9)$$

$$p_i = 4\pi^2 m\varepsilon_i\alpha_i/h^2e^2 \quad (10)$$

better than 0.01% by direct space summation, in terms of the standard distances L; i refers to the cations and j to the anions in the structure. The polarizabilities, α_i and α_j, are taken from Ladd,[6,15] which allows ε_i and ε_j to be used as the ionization potentials of the positive and negative ions, without multiplication by the arbitrary factors[1,6,14-16] 0.75—0.90 and 2.6 respectively.

The electron numbers, p, were obtained, following Mayer,[17] as the geometric mean of the theoretical number of outermost electrons and that number given by equation (10), where m and e are, respectively, the mass and charge of an electron, and h is the Planck constant. The results are listed in Table 3.

TABLE 3

Lattice sums and van der Waals constants

	α-TlF	β-TlF
$10^{10}L$/m	2.69	2.25
S_{+-}	5.383 797	1.786 557
S_{++}	1.405 634	0.503 402
S_{--}	1.405 634	0.828 018
T_{+-}	4.817 927	1.141 003
T_{++}	0.576 669	0.147 232
T_{--}	0.576 669	0.349 710
10^{10}Summation limit/m	158	133
$10^{40}\alpha_+$/F $\mathrm{m^2}$	7.01	7.01
$10^{40}\alpha_-$/F $\mathrm{m^2}$	2.89	2.89
$10^{19}\varepsilon_+$/J	32.71	32.71
$10^{19}\varepsilon_-$/J	5.527	5.527
$10^{97}c_{+-}$/J $\mathrm{F^2\,m^4}$	1.437	1.437
$10^{97}c_{++}$/J $\mathrm{F^2\,m^4}$	12.06	12.06
$10^{97}c_{--}$/J $\mathrm{F^2\,m^4}$	0.346	0.346
$10^{117}d_{+-}$/J $\mathrm{F^2\,m^6}$	5.52	5.52
$10^{117}d_{++}$/J $\mathrm{F^2\,m^6}$	70.1	70.1
$10^{117}d_{--}$/J $\mathrm{F^2\,m^6}$	0.646	0.646
p_+/J F $\mathrm{C^{-2}}$	6.9	6.9
p_-/J F $\mathrm{C^{-2}}$	1.5	1.5
$10^{77}C$/J $\mathrm{m^6}$	13.30	4.64
$10^{97}D$/J $\mathrm{m^8}$	37.95	9.34

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[12] M. F. C. Ladd, unpublished work.

[13] M. L. Huggins, *J. Chem. Phys.*, 1937, **5**, 143.

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Cohesive Energies.—The cohesive energies of α- and β-TlF were calculated from equations (1)—(10) (Table 4). Two sets of results for the corresponding thermodynamic values (ΔU), calculated from a Born–Haber–Fajans cycle [equation (11)], with their components, are also presented, and an attempt was made to estimate the probable error in the results.

TABLE 4

Cohesive-energy data: α-TlF at 373 K, β-TlF at 298 K

$\Delta H_f(\text{TlF,s})/\text{kJ mol}^{-1}$	-324.7 [a]		-325.5 ± 4.2 [b]
$\Delta H_{\text{sub}}(\text{Tl,s})/\text{kJ mol}^{-1}$	182.2 [a]		179.9 (±2) [c,d]
$I(\text{Tl,g})/\text{kJ mol}^{-1}$	595.5 [a]		595.5 ± 0.0 [a]
$\frac{1}{2}D(\text{F}_2\text{,g})/\text{kJ mol}^{-1}$	79.0 [a]		78.9 ± 0.3 [e]
$E(\text{F,g})/\text{kJ mol}^{-1}$	-349.7 [a]		-327.9 ± 0.2 [f]
$2RT/\text{kJ mol}^{-1}$	5.0		5.0
$\int_{298}^{373} C_p(\text{g})\,\text{d}T/\text{kJ mol}^{-1}$	3.1		3.1
$\int_{298}^{373} C_p(\text{s})\,\text{d}T/\text{kJ mol}^{-1}$	4.4 [g]		4.4 [g]
$\Delta U(\alpha\text{-TlF,s})/\text{kJ mol}^{-1}$	-825.4		-845.6 ± 6.2
$\Delta U(\beta\text{-TlF,s})/\text{kJ mol}^{-1}$	-826.7		-846.9 ± 6.2
$U(\alpha\text{-TlF,s})/\text{kJ mol}^{-1}$		-863.5	
$U(\beta\text{-TlF,s})/\text{kJ mol}^{-1}$		-813.4	

[a] D. D. Wagman, W. H. Evans, V. B. Parker, I. Harlow, S. M. Bailey, and R. H. Schumm, Nat. Bur. Stand., Tech. Note 270–3, 1968. [b] D. Cubicciotti and G. L. Withers, *J. Phys. Chem.*, 1965, **69**, 4030. [c] Estimated error. [d] D. R. Stull and G. C. Sinke, *Adv. Chem.*, 1956, **18**, 1. [e] J. G. Stamper and R. F. Barrow, *Trans. Faraday Soc.*, 1958, **54**, 1592. [f] R. Berry and R. Stephen, *J. Chem. Phys.*, 1971, **55**, 4146. [g] W. G. Lyon, F. F. Westman, jun., and M. Chavret, *J. Chem. Thermodynamics*, 1971, **3**, 571 (result includes enthalpy of transition at 356 K).

$$\Delta U = \Delta H_f - \Delta H_{\text{sub}} - I(\text{Tl}) - \tfrac{1}{2}D(\text{F}_2) - E(\text{F}) + nRT \qquad (11)$$

DISCUSSION

The two sets of data used in calculating ΔU, listed in Table 4, differ principally in the value of $E(\text{F},g)$. A more recent determination of $D(\text{F}_2,g)$ by Stricker and Krauss[18] was rejected because of its relatively large error (138.9 ± 6.8 kJ mol^{-1}). The errors in U are more difficult to calculate, but a reasonable estimate is *ca.* ±7 kJ mol^{-1}. In the case of β-TlF, although the data from reference (*a*) in Table 4 give better agreement with U, the second set of data is preferred because the probable errors are known and the determination of $E(\text{F},g)$ is more recent. In view of the probable error, however, the differences in the results, for a given polymorph, are not statistically significant.

Although it is rarely possible to make positive conclusions about bonding on the basis of a model-dependent energy study, the agreements in Table 4 are good, and there seems to be little evidence to support the highly distorted Tl^+ model of Alcock and Jenkins.[7] Some distortion undoubtedly exists, but no more than is accounted for by the van der Waals polarization energy. X-Ray and neutron studies[7] of β-TlF have established its structure. However, in view of the hypothesis therein of the distorted ion, anisotropic refinement, at least for the species Tl^+, would seem to have been desirable. In fact, a constraint seems to have been applied, in that the isotropic temperature factors for the two crystallographically independent Tl^+ ions have the same value, 1.39 Å^2, among the preferred parameters. In α-TlF, the calculated value of U is too low, and probably reflects an error in the crystal structure, similar to that which existed in that of β-TlF before the work of Alcock and Jenkins.[7]

TABLE 5

Unit-cell dimensions

	α-TlF	β-TlF
$10^{10}a/\text{m}$	5.380	5.1848
$10^{10}b/\text{m}$	5.380	6.0980
$10^{10}c/\text{m}$	6.120	5.4916
$10^{30}V_c/\text{m}^3$	177.1	173.6

The entropy of the α–β transition at 356 K is less than 1 J K^{-1} mol^{-1}. From a consideration of the Boltzmann equation, this value is consistent with the similarity of the two polymorphs. Table 5 lists unit-cell dimensions for β-TlF, and for α-TlF referred to an F unit cell. It may be noted that a (and b) for α-TlF are very close to a and c for β-TlF, suggesting a simple structure relation; the volumes occupied per ion pair are 44.3×10^{-30} and 43.4×10^{-30} m^3 respectively.

The most important difference in the calculated values of U for α- and β-TlF arises in the Madelung term $A(L)/L$. If a structure is postulated for α-TlF in which $a_\alpha = b_\alpha \simeq (a_\beta c_\beta)^{\frac{1}{2}}$, and the relative co-ordinates of the α-TlF structure are inserted, the value of $A(L)/L$ becomes 0.59. This idea is speculative and will not be pursued further. It does, however, suggest how the apparent difference in U for α- and β-TlF might be removed in further structural studies.

The closest interatomic distance in α-TlF is 2.69×10^{-10} m, whereas the sum of the ionic radii is *ca.* 2.79×10^{-10} m. The range of values for the Tl–F distance in β-TlF leads to a minimum value[7] for $r(\text{Tl}^+)$ of 0.93×10^{-10} m. This value is improbably low, and difficult to reconcile with the value of *ca.* 1.5×10^{-10} m in the other thallium(I) halides. The postulated maximum[7] $r(\text{Tl}^+)$ is 2.59×10^{-10} m. Such anisotropy in the electron density cannot be modelled with a spherically symmetrical X-ray scattering factor. It is possible that the structure model for β-TlF is not yet sufficiently refined for precise measures of Tl–F distances to be known.

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[18] W. Stricker and L. Krauss, *Z. Naturforsch.*, 1968, **23**, 486.