unexpected that the mole fraction becomes increasingly less suitable as the concentration variable as the difference in molal volumes increases.

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NOMENCLATURE

A_{ij} = function defined in Equation 2
A_{ijk} = function defined in Equation 4
B_{ij}, C_{ij}, D_{ij} = constants in Equation 2
B_{ijk}, C_{ijk}, D_{ijk}, E_{ijk}, F_{ijk}, G_{ijk} = constants in Equation 4
n = refractive index
n_i = refractive index of pure component i
x_i = mole fraction of component i

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Enthalpies, Entropies, and Free Energy Functions of TlF, TlBr, and TlI Above Room Temperature

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The enthalpy increments above 298° K. for solid and liquid thallous fluoride, bromide, and iodide were measured with a drop calorimeter. These data together with literature values for the absolute entropies were used to calculate the enthalpy, entropy, and free energy for these compounds. The thermodynamic functions for the gaseous phases of these compounds were calculated from molecular constant data.

AS A PART of our studies of the thermodynamics of evaporation of thallous fluoride (*5*), bromide (*3*), and iodide (*4*), it was necessary to determine the enthalpies of these salts in their condensed phases from room temperature to their boiling points. These results can be combined with the absolute entropies of the crystals at room temperature to yield the free energy function for the condensed phases. In addition, there is sufficient molecular constant data available to calculate the thermodynamic functions (entropy, enthalpy, and free energy function) for the gas phases. Results of this type for thallous chloride have already been reported (*6*).

EXPERIMENTAL

Enthalpy Measurements. The calorimeter was essentially the same as that used for thallous chloride (*6*) except that the calorimeter bucket of the original Parr equipment was replaced by a metal block containing two cavities. The samples dropped into one cavity, while the other cavity contained a small amount of silicone oil in which the calorimetric thermometer was oscillated and registered the temperature rise of the unit.

Preparation of Samples. The halides were prepared by the methods described in the respective papers (*3–5*) on vapor pressures. The purities are also reported there. Samples of approximately 20 grams of each of the halides were sealed into platinum–10% rhodium containers (5/16 inch O.D. × 3 inches long). Proper taring resulted in information on the weights of the containers and contents. Their closures were tested for leaks by heating the containers to the boiling points of their contents and finding no weight loss.

The melting and any transition points were determined by cooling curves. A platinum–10% rhodium thermocouple, checked against one calibrated by the NBS was tightly wired to the outside middle of the capsule. Cooling and heating curves made on these gave sharp breaks for freezing and melting and somewhat less sharp ones at transition points. The values obtained are given in Table I.

ENTHALPIES FOR CONDENSED PHASES

The measured enthalpy increments above 298° K. are shown as data points in Figure 1. To the authors' knowledge, there have been no other measurements on the fluoride and iodide. For the bromide, Goodwin and Kalmus (*7*) have given values to temperature somewhat above the melting point. Their results are shown for comparison. They agree, in general, with the authors' data, but the derived heat capacities, especially of the liquid, differ appreciably.

The enthalpies were fitted to analytical expressions that were first and second order in temperature. These expressions fit the experimental points to somewhat better than

Table I. Analytical Expressions of Enthalpy Data and Transition Parameters

TlF

Solid I (up to 355° K.):
$(H_T - H_{298})$ cal./mole = $12.31\,T + 1.31 \cdot 10^{-3}\,T^2 - 3787$
C_p cal./(mole deg.) = $12.31 + 2.62 \cdot 10^{-3}\,T$
Transition: T = 355 ± 1° K.
ΔH_{tr} = 92 cal./mole; $\Delta S_{tr} = 0.26$ e.u.

Solid II (355° to 595.4° K.):
$(H_T - H_{296})$ cal./mole = $5.29\,T + 8.89 \cdot 10^{-3}\,T^2 - 2159$
C_p cal./(mole deg.) = $5.29 + 17.78 \cdot 10^{-3}\,T$
Fusion: T = 595.4 ± 0.5° K.
ΔH_{fusion} = 3315 cal./mole; $\Delta S_{\text{fusion}} = 5.57$ e.u.

Liquid (measured up to 850° K.):
$(H_T - H_{298})$ cal./mole = $16.08\,T - 2116$
C_p cal./(mole deg.) = 16.08

TlBr

Solid (up to 733.2° K.):
$(H_T - H_{298})$ cal./mole = $9.95\,T + 3.55 \cdot 10^{-3}\,T^2 - 3280$
C_p cal./(mole deg.) = $9.95 + 7.10 \cdot 10^{-3}\,T$
Fusion: T = 733.2 ± 0.5° K.
ΔS_{fusion} = 3920 cal./mole; $\Delta S_{\text{fusion}} = 5.35$ e.u.

TlBr (continued)

Liquid (measured up to 950° K.):
$(H_T - H_{298})$ cal./mole = $25.25\,T - 4.52 \cdot 11^{-3}\,T^2 - 6238$
C_p cal./(mole deg.) = $25.25 - 9.04 \cdot 10^{-3}\,T$

TlI

Solid I (up to 451° K.):
$(H_T - H_{298})$ cal./mole = $11.56\,T + 1.66 \cdot 10^{-3}\,T^2 - 3595$
C_p cal./(mole deg.) = $11.56 + 3.32 \cdot 10^{-3}\,T$
Transition: T = 451 ± 1° K.
ΔH_{tr} = 218 cal./mole; $\Delta S_{tr} = 0.48$ e.u.

Solid II (451° to 714.8° K.):
$(H_T - H_{298})$ cal./mole = $7.72\,T + 5.63 \cdot 10^{-3}\,T^2 - 2451$
C_p cal./(mole deg.) = $7.72 + 11.26 \cdot 10^{-3}\,T$
Fusion: T = 714.8 ± 0.5° K.
ΔH_{fusion} = 3520 cal./mole; $\Delta S_{\text{fusion}} = 4.93$ e.u.

Liquid (measured up to 950° K.):
$(H_T - H_{298})$ cal./mole = $17.2\,T - 2833$
C_p cal./(mole deg.) = 17.2

Table II. Thermodynamic Functions for Condensed Phases

T, ° K.	$H^\circ_T - H^\circ_{298}$, Cal./Mole	$S^\circ_T - S^\circ_{298}$, E.U.	$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$, E.U.
	TlF		
298	0	0	25.9
355	748	2.30	26.1
355	840	2.56	26.1
400	1,390	4.00	26.5
500	2,710	6.96	27.5
595.4(c)	4,140	9.57	28.5
595.4(l)	7,455	15.14	28.5
700	9,140	17.75	30.6
800	10,750	19.89	32.4
900	12,355	21.79	34.0
1,000	13,965	23.48	35.5
1,250	17,985	27.07	38.6
	TlBr		
298	0	0	29.30
400	1,270	3.66	29.78
500	2,585	6.59	30.72
600	3,970	9.11	31.79
700	5,425	11.36	32.91
733.2(c)	5,920	12.05	33.28
733.2(l)	9,840	17.40	33.28
800	11,070	19.00	34.47
900	12,825	21.06	36.08
1,000	14,490	22.83	37.64
1,250	18,260	26.27	40.97
	TlI		
298	0	0	30.52
400	1,295	3.74	31.02
451	1,957	5.30	31.48
451	2,175	5.78	31.48
500	2,820	7.13	32.02
600	4,210	9.67	33.18
700	5,710	11.98	34.34
714.8(c)	5,945	12.31	34.51
714.8(l)	9,465	17.24	34.51
800	10,925	19.17	36.03
900	12,645	21.20	37.67
1,000	14,365	23.01	39.16
1,250	18,665	26.84	42.43

Table III. Molecular Constants Used in Calculations

	Internuclear Distance, A.	Ref.	Fundamental Vibration Frequency, Cm.$^{-1}$	Anharmonicity Constant, $\omega_e x_e$ Cm.$^{-1}$	Ref.
TlF	2.084	*(1)*	477	2.3	*(2)*
TlBr	2.618	*(1)*	192	0.39	*(8)*
TlI	2.814	*(1)*	123	0.088	*(11)*

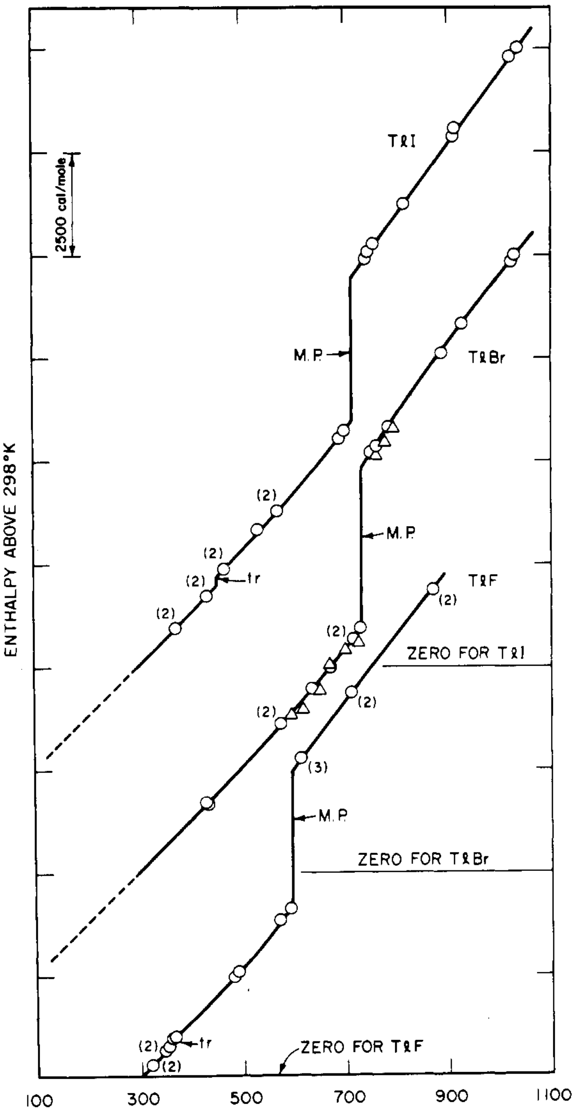

Figure 1. Enthalpy increments above 298° K. for thallous iodide, bromide, and fluoride

Circled points, present measurements; small numbers in parentheses, number of indistinguishable data points; triangles, for bromide (7); m.p. and tr, melting and transition points; full curves, derived analytical expressions; dashed portions of TlI and TlBr, lower temperature data (12)

Table IV. Thermodynamic Functions for Gas Phases

	TlF			TlBr			TlI		
T, ° K.	$H^\circ_T - H^\circ_{298}$, Cal./Mole	$S^\circ_T - S^\circ_{298}$, E.U.	$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$, E.U.	$H^\circ_T - H^\circ_{298}$, Cal./Mole	$S^\circ_T - S^\circ_{298}$, E.U.	$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$, E.U.	$H^\circ_T - H^\circ_{298}$, Cal./Mole	$S^\circ_T - S^\circ_{298}$, E.U.	$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$, E.U.
298	0	0	58.41	0	0	63.93	0	0	66.06
400	861	2.48	58.74	905	2.62	64.29	910	2.63	66.41
500	1725	4.41	59.37	1795	4.61	64.94	1810	4.62	67.06
600	2602	6.01	60.19	2690	6.23	65.66	2700	6.29	67.85
700	3486	7.37	60.80	3590	7.61	66.42	3605	7.71	68.62
800	4374	8.56	61.60	4485	8.83	67.14	4500	8.86	69.29
900	5269	9.55	62.21	5385	9.86	67.81	5395	9.90	69.97
1000	6164	10.55	62.90	6285	10.82	68.46	6300	10.86	70.62
1250	8419	12.57	64.24	8545	12.84	69.94	8555	12.85	72.07
$H_{298} - H_0$, Cal./Mole	2226			2435			2508		

1%. The analytical expressions for enthalpies above 298° K. are given in Table I. They were used to calculate the curves drawn in Figure 1, and an indication of the fidelity of the equations is so presented.

THERMODYNAMIC FUNCTIONS FOR CONDENSED PHASES

From these equations, the enthalpy and entropy increments above room temperature were calculated for the condensed phases. These are presented in Table II. The free energy function

$$\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right) = -S^\circ_T + \left(\frac{H^\circ_T - H^\circ_{298}}{T}\right)$$

can be calculated from these data if the absolute entropy at 298 ° K. is known for the solid. For TlBr and TlI, these entropies have been determined by Takahashi and Westrum (*12*) from low temperature heat capacity measurements. The values for $S^\circ_{298.15}$ are 29.30 and 30.52 e.u., respectively, for TlBr and TlI. The absolute entropy for TlF was established from the vapor pressure data (*5*) to be 25.9 e.u. The free energy functions for the condensed phases are given in Table II.

THERMODYNAMIC FUNCTIONS FOR GASEOUS PHASES

The thermodynamic functions for the gases in their ideal standard states were calculated from molecular constant data (*10*). The molecular constants used are given in Table III. No contribution from excited electronic states was included because the lowest excited state is too far above ground. [For TlF, Barrow and coworkers (*2*) give 35,164 cm.$^{-1}$ as the lowest electronic state and those of the other halides were presumed to be equally far above ground.] The anharmonicity correction was small, amounting to less than 1% in all cases. The thermodynamic functions for the gas phases are given in Table IV.

The small differences between the authors' values and those of Kelley (*9*) for the fluoride and bromide are due to the anharmonicity correction applied. For the iodide, a more recent and lower value for the vibration frequency was used.

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