NOMENCLATURE

C = "White factor" empirical
E = linear thermal expansion factor for stainless steel (length at test temperature relative to length at room temperature)
f = fluid friction factor
g = acceleration of gravity, cm./sec.^{2}
h_1 = head with reservoir full, cm.
h_2 = head with reservoir empty, cm.
h_m = log mean head, cm.
h_r = kinetic energy correction, cm.
h_γ = surface tension correction, cm.
H = corrected head, cm.
k = "White parameter," $= Re(r_t/r_c)^{0.5}$
L = capillary length, cm.
m = factor in kinetic energy correction = (1.12)
q_f = efflux volume, cm.^{3}
r_t = capillary radius, cm.
r_c = radius of curvature of coil, cm.
R = radius of reservoir, cm.
Re = Reynolds number in capillary
ρ = density, g./cc.
t_f = efflux time, sec.
T = absolute temperature, $^\circ$K.
γ = surface tension, dynes/cm.
μ = viscosity, centipoises

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Heat Contents and Thermodynamic Functions for Thallous Chloride Above Room Temperature

HAROLD EDING and DANIEL CUBICCIOTTI
Stanford Research Institute, Menlo Park, Calif.

Heat contents of solid and liquid TlCl were measured to 700° C. These were combined with literature data to calculate the absolute entropy and free energy functions of the condensed phases. Values of the same functions for gaseous TlCl were calculated from molecular constant data.

To COMPLEMENT a study of the thermodynamics of vaporization of thallous chloride (2), it was necessary to have the heat contents of the condensed phases above room temperature. Goodwin and Kalmus (3) have reported values; however, it seemed worthwhile to repeat their measurements.

Thallous chloride was prepared by dissolving pure Tl (99.95% from American Smelting and Refining) in dilute nitric acid and precipitating it with hydrochloric acid. The precipitate was collected on a sintered glass filter, then placed in a fused quartz bulb and distilled under pure, dry nitrogen. A sample of the material so prepared was analyzed for chloride and found to contain 14.78% Cl (theoretical 14.78%). About 10 grams were placed in a thin-walled platinum test tube and the end sealed with platinum solder. (The closure was tested by heating the sample above the

Table I. Thermodynamic Functions for Thallous Chloride

Temp., °K.	Condensed Phases			Gaseous TlCl		
	$H_T - H_{298}$ kcal./mole	S_T cal./mole deg.	$-\left(\dfrac{F_T - H_{298}}{T}\right)$ cal./mole deg.	$H_T - H_{298}$ kcal./mole	S_T cal./mole deg.	$-\left(\dfrac{F_T - H_{298}}{T}\right)$ cal./mole deg.
298	0	26.59	26.59	0	61.20	61.20
400	1.27	30.25	27.07	0.89	63.70	61.48
500	2.55	33.12	28.02	1.77	65.68	62.14
600	3.89	35.55	29.06	2.66	67.33	62.89
700	5.26	37.68	30.30	3.54	68.65	63.59
704	5.32(c)	37.78	30.20	...	...	...
704	9.04(l)	43.07	30.20	...	...	...
800	10.75	45.38	31.93	4.43	69.85	64.31
900	12.55	47.52	33.57	5.32	70.89	64.98
1000	14.35	49.38	35.03	6.22	71.85	65.63
1250	18.9	53.3	38.2	8.45	73.81	67.05

boiling point of thallous chloride and was considered satisfactory because the sample did not change weight.) A Pt-10% Rh thermocouple (calibrated vs. a similar NBS-calibrated thermocouple) was wired to the outside of the test tube, the system packed in insulation, and a cooling curve run. The freezing point was 430.8 ±0.5°C.

The heat content was determined with a drop calorimeter, which consisted of a tube furnace mounted above a Parr adiabatic calorimeter. A hole was placed in the lid of the calorimeter, and the calorimeter bucket was replaced with a 3-inch diameter can containing a 1-inch copper tube. The annular space in the can was filled with water, and the calorimetric thermometer was oscillated to provide stirring and to register the temperature rise of the unit. A lid for the copper tube closed automatically when the sample dropped into the tube. The calorimeter equivalent was determined using an NBS sample of sapphire (Al_2O_3) sealed in a platinum tube which matched the thallium chloride sample in heat content. A blank tube was also used to correct for the small amount of radiation loss. The furnace temperature was determined with a chromel-alumel thermocouple calibrated at the melting point of zinc.
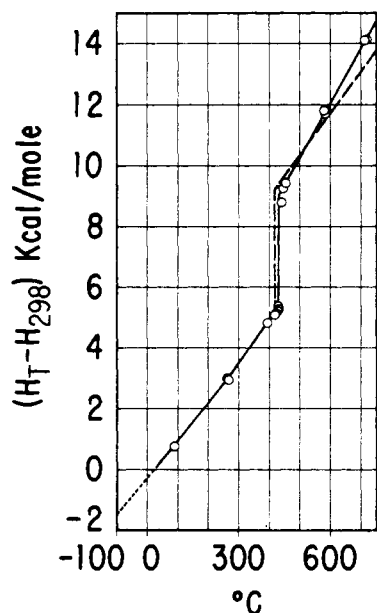

Figure 1. Heat content of thallous chloride above room temperature. Points and full line indicate present data; dashed line represents data of Goodwin and Kalmus reported by Kelley; dotted line indicates low temperature value of Bartky and Giauque.

RESULTS AND DISCUSSION

The results obtained, together with the other data available, are shown Figure 1. The heat contents of the solid above room temperature join smoothly with the data below room temperature reported by Bartky and Giauque (1). For the solid the present data were somewhat less than one percent lower than the values reported by Kelly (5) [calculated from the measurements of Goodwin and Kalmus (3)]. For the melting process and for the liquid our data are notably different from those of Kelley and Goodwin and Kalmus.

The heat contents can be represented by the following equations, from which the average deviation of the experimental points is about one per cent:

$(H_T - H_{298})$ solid, kcal./mole

$$= 10.8 \times 10^{-3}\,(T - 298) + 2.30 \times 10^{-6}\,(T^2 - 298^2)$$

$(H_T - H_{298})$ liquid, kcal./mole $= 17.9 \times 10^{-3}\,T - 3.54$

From these the following values are derived:

C_p, solid, cal./mole deg. $= 10.8 + 4.6 \times 10^{-3}\,T$.

C_p, liquid, cal./mole deg. $= 17.9$

ΔH_{fusion}. kcal./mole $= 3.72$.

From these data, values for the heat content, entropy, and free energy functions were calculated for the condensed phases and are reported in Table I. Values for the same functions were calculated for gaseous TlCl using the internuclear distance given by Mandel and Barrett (6) and the vibration frequency by Herzberg (4). The values for the gas differ slightly from those of Kelley (5) because he used a larger internuclear distance (derived from rotation-vibration spectra.)

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