The dibasic salt similarly was shown to decompose to potassium uranate on heating in accordance with the equation

$$K_2UO_5 \longrightarrow K_2UO_4 + {}^1/_2O_2 \qquad (2)$$

The formation of potassium pyrouranate and potassium uranate as thermal decomposition products was substantiated by X-ray diffraction patterns and chemical analyses.

Conclusions

The chemical reactions of the compound prepared by either the precipitation of uranium from uranyl nitrate solutions with hydrogen peroxide or the reaction of uranium trioxide with aqueous hydrogen peroxide can be suitably explained by the existence of a peroxyuranic acid structure. Of the two previously proposed acid structures (H_4UO_6 or $H_2UO_5 \cdot H_2O$), infrared spectral data, by establishing the presence of a hydrate water group, indicate that hydrated peroxyuranic acid ($H_2UO_5 \cdot H_2O$) most truly represents the chemical nature of the compound.

The uranium–oxygen–peroxyoxygen acid system shows a similarity to the known inorganic oxygen–peroxyoxygen acid systems. This similarity is based on the preparation of the oxygen acid and the peroxyoxygen acid from the acid anhydride by the addition of water and peroxide, respectively. A comparison of the sulfur and uranium acid systems suitably illustrates this similarity.

SO_3	Acid anhydride	UO_3
H_2SO_3	Primary oxygen acid	H_2UO_4
H_2SO_5	Peroxyoxygen acid	H_2UO_5
$H_2SO_4 \cdot H_2O$	Hydrated oxygen acid	$H_2UO_4 \cdot H_2O$
$H_2SO_5 \cdot H_2O$	Hydrated peroxyoxygen acid	$H_2UO_5 \cdot H_2O$
$H_2S_2O_7$	Pyro (oxygen) acid	$H_2U_2O_7$

The preceding data and discussion were primarily intended to establish the structure of hydrated uranium peroxide through reaction with strong bases. In light of the previously established amphoteric character of other hexavalent uranium oxide hydrates, peroxyuranic acid would be expected to react, as a base, with strong acids.

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[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING UNIVERSITY OF CALIFORNIA, BERKELEY]

The Low Temperature Heat Capacity and Entropy of Thallous Chloride[1]

BY I. R. BARTKY AND W. F. GIAUQUE

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The heat capacity of thallous chloride has been measured from 15 to 310°K. The entropy at 298.15°K. was found to be 26.59 cal. deg.$^{-1}$ mole^{-1}. The heat capacity, entropy, $(F^0 - H_0^0)/T$ and $(H^0 - H_0^0)/T$ functions for TlCl are tabulated from 15 to 300°K. The entropy change calculated from the third law of thermodynamics for the cell reaction $Tl + AgCl = TlCl + Ag$ was found to be in good agreement with the cell temperature coefficients of Gerke provided the entropy change for the step $Tl(s) = Tl(amalg)$ is calculated from $\Delta S = (\Delta H_{\text{calorimetric}} + \mathbf{FE})/T$ rather than from $d\mathbf{E}/dT$. It is evidently difficult to obtain reliable cell temperature coefficients involving a metal electrode even when it is as soft as thallium. Third law results have been used to calculate these heats of reaction at 298.15°K.: $Tl(cryst.) + AgCl = TlCl + Ag$, $\Delta H^0 = -18{,}430$ cal. mole^{-1}; $Tl + {}^1/_2Cl_2 = TlCl$, $\Delta H^0 = -48{,}800$ cal. mole^{-1}.

Gerke[2] studied a number of cells in order to test the validity of the third law of thermodynamics by comparing the entropy changes as calculated from the temperature coefficients of the cell voltages with those calculated from the available low temperature heat capacity data by means of the third law. He found a discrepancy of 2.0 cal. deg.$^{-1}$ mole^{-1} in the cell

$$Tl + AgCl = TlCl + Ag \qquad (1)$$

The heat capacity data available at that early date often were inaccurate since the techniques of low temperature calorimetry were in the first stages of their development. Thus Gerke considered that the discrepancy had its origin in the heat capacity data and particularly in that on thallous chloride. The present work provides accurate heat capacity data for thallous chloride.

Calorimetry and Material.—The low temperature heat capacity was measured in an apparatus similar to that described by Giauque and Egan.[3] The particular calorimeter was described by Kemp and Giauque[4] and its most recent modification by Papadopoulos and Giauque.[5] Briefly, the present calorimeter was of copper and the temperature was measured by a gold resistance thermometer-heater, for high precision, and Laboratory Standard Copper-Constantan Thermocouple No. 105 for simultaneous reference before and after every heat input. The thermocouple was compared with the triple (13.94°K.) and boiling points (20.36° K.) of hydrogen and the triple (63.15°K.) and boiling points (77.34°K.) of nitrogen, during the course of the present work.

0° was taken as 273.15°K. and 1 defined calorie was taken equal to 4.1840 absolute joules.

The thallous chloride was supplied 99.9+% pure by the Chemical Commerce Co. It was received in the form of a rather voluminous precipitated powder. This material was heated to the melting point (about 430°), in a Pyrex beaker so that a large reduction in volume occurred. This eliminated the possibility that particles with microscopic properties could remain in the sample used for the heat capacity measurements as could be the case with a fine powder. The well-crystallized solid was broken easily with a mortar and pestle and the crystals were passed through an 8 mesh in.$^{-1}$ screen so that they would pack well within the calorimeter. The use of this material, rather than the powder, at least doubled the amount of material which could be placed in the calorimeter and also improved the heat con-

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(1) This work was supported in part by the National Science Foundation. The U. S. Government may reproduce this article.

(2) R. H. Gerke, THIS JOURNAL, **44**, 1684 (1922).

(3) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(4) J. D. Kemp and W. F. Giauque, THIS JOURNAL, **59**, 79 (1937).

(5) M. N. Papadopoulos and W. F. Giauque, *ibid.*, **77**, 2740 (1955).

ductivity considerably; 569.550 g. of TlCl was taken for the measurements. Helium was used within the calorimeter to facilitate heat conduction.

The Heat Capacity Measurements and Derived Thermodynamic Properties.—The actual observations are given in Table I. The measurements were continuous in the sense that each one began where the previous one stopped so that there were no unobserved regions. The approximate temperature rises may be estimated from the average temperatures given in the table.

TABLE I

THE HEAT CAPACITY OF THALLOUS CHLORIDE, CAL. DEG.$^{-1}$ MOLE^{-1}

569.550 g. in the calorimeter; 0° C. = 273.15°K.; molecular weight = 239.847.

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series 1		81.09	10.20	216.03	12.06
13.55	2.035	86.58	10.35	223.87	12.08
14.39	2.248	92.78	10.54	232.10	12.06
15.91	2.609	99.09	10.72	239.66	12.10
18.02	3.096	105.01	10.87	247.10	12.10
21.07	3.731	110.60	11.02	254.83	12.11
24.51	4.437	116.33	11.09	262.53	12.14
27.30	4.948	122.28	11.20	270.52	12.18
30.48	5.478	128.74	11.30	277.98	12.20
33.99	6.068	135.66	11.42	285.32	12.13
37.86	6.596	142.49	11.49	292.73	12.19
41.97	7.105	149.80	11.55	300.31	12.17
45.62	7.594	158.17	11.63	Series 2	
49.53	8.042	167.36	11.69	164.32	11.66
54.26	8.545	175.78	11.75	172.54	11.72
59.11	8.984	183.80	11.93[a]	180.48	11.79
64.04	9.345	191.88	11.78[a]	188.16	11.84
70.04	9.686	200.22	11.91[a]	195.73	11.89
75.79	9.977	208.27	12.02	203.08	11.93

[a] Results given no weight because of heat transfer due to water vapor in insulating vacuum space.

The several measurements of series 2 were made to replace several measurements of series 1 near 200°K. which were of lesser accuracy due to water vapor which accidentally had entered the insulating vacuum space. The thermodynamic properties of thallous chloride are given in Table II.

A Debye extrapolation of 0.816 cal. deg.$^{-1}$ mole^{-1} was made below 13°K. A salt with the mass ratios of Tl and Cl should deviate somewhat from a Debye function at very low temperatures; however, the entropy effect due to such a deviation should be very small in the present case.

Comparison of the Entropy Differences from Cell Data with those Obtained from the Third Law of Thermodynamics.—Gerke[2] studied the cells

$$\text{Tl(2-phase amalg.)} + \text{AgCl} = \text{TlCl} + \text{Ag} \qquad (2)$$

and

$$\text{Tl(cryst.)} = \text{Tl(2-phase amalg.)} \qquad (3)$$

The values of dE/dT were (2), -0.0000794 and (3), $+0.000032$ volts deg.$^{-1}$. The combined value, -0.0000474 gives $\Delta S = -1.09$ cal. deg.$^{-1}$ mole^{-1} for reaction 1

$$\text{Tl(s)} + \text{AgCl} = \text{TlCl} + \text{Ag} \qquad (1)$$

TABLE II

THERMODYNAMIC FUNCTIONS FOR SOLID THALLOUS CHLORIDE, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	$C_p{}^0$	S^0	$-\frac{F^0 - H_0{}^0}{T}$	$\frac{H^0 - H_0{}^0}{T}$
15	2.394	(1.097)	(0.314)	(0.783)
20	3.524	$1.94\bar{5}$	0.614	1.331
25	4.527	2.840	0.969	1.871
30	5.432	3.747	1.357	2.390
35	6.209	$4.64\bar{5}$	1.763	2.882
40	6.892	5.519	2.178	3.341
45	7.522	6.368	2.596	3.772
50	8.092	7.190	$3.01\bar{5}$	4.175
60	9.050	8.755	3.843	4.912
70	9.685	10.202	4.649	5.553
80	10.13	11.526	5.427	6.099
90	10.47	12.740	6.173	6.567
100	10.75	13.858	6.887	6.971
110	10.98	14.894	7.568	7.326
120	11.16	15.857	8.219	7.638
130	11.31	16.756	8.842	7.914
140	11.46	17.599	9.437	8.162
150	11.56	18.394	10.008	8.386
160	11.64	19.142	10.556	8.586
170	11.71	$19.8\bar{5}0$	11.082	8.768
180	11.78	20.521	11.588	8.933
190	11.85	21.160	$12.07\bar{5}$	9.085
200	11.91	21.769	$12.54\bar{5}$	9.224
210	11.96	22.352	12.998	9.354
220	12.00	22.909	13.436	9.473
230	12.03	23.443	13.859	9.584
240	12.07	23.956	14.269	9.687
250	12.10	24.449	14.667	9.782
260	12.12	24.924	15.052	9.872
270	12.13	25.381	15.426	9.955
273.15	12.14	25.521	15.541	9.980
280	$12.1\bar{5}$	25.823	15.790	10.033
290	12.16	26.249	16.143	10.106
298.15	12.17	26.586	16.423	10.163
300	12.18	26.662	16.487	10.175

This result may be taken to apply to temperatures near 298°K. since there should be a trivial temperature coefficient of ΔS. These values of entropies at 298.15°K. were utilized

$$\text{Ag},^{6}\ S = 10.21 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\text{AgCl},^{7}\ S = 22.97$$

$$\text{Tl},^{8}\ S = 15.35$$

$$S(\text{TlCl}) = -1.09 + S(\text{Tl}) + S(\text{AgCl}) - S(\text{Ag}) = 27.02$$

which may be compared with the value 26.59 cal. deg.$^{-1}$ mole^{-1} observed in this research. The accuracy of the various heat capacity determinations is such that the discrepancy of (cell-third law) 0.43 cal. deg.$^{-1}$mole^{-1} is almost certainly due to the difficulty in measuring cell temperature coefficients.

Gerke's research was concerned with cell temperature coefficients, and it was reasonable that he should try to determine the entropy changes in the cells concerned entirely by means of the observed temperature coefficients of e.m.f. However, he proposed and calculated an alternative for the most difficult step, namely, cell 3, involving the solid thallium metal although he did not utilize the result. Especially when the free energy

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(6) P. F. Meads, W. R. Forsythe and W. F. Giauque, THIS JOURNAL, **63**, 1902 (1941).

(7) E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1**, 444 (1933).

(8) J. F. G. Hicks, Jr., THIS JOURNAL, **60**, 1000 (1938).

and heat of a reaction are small, the most reliable way to obtain the entropy change is to calculate $\Delta S = (\Delta H - \Delta F)/T$.

Richards and Daniels[9] measured the heat of solution of thallium in mercury over a range of composition. They also measured the e.m.f. of cells in which the only process was the transfer of thallium from the pure metal to certain amalgam concentrations. The e.m.f. of the reaction

$$\mathrm{Tl(s)} = \mathrm{Tl(2\text{-}phase\ amalgam)} \qquad (4)$$

with various conditions of the solid thallium has been measured by several observers whose data are given in Table III. Where necessary small corrections have been applied to adjust the data to 25°.

TABLE III

DATA FOR CELL $\mathrm{Tl(s)} = \mathrm{Tl}$(2-PHASE AMALGAM)

$T = 298.$°K., ΔS in cal. deg.$^{-1}$ mole^{-1}

Observer	Condition of Tl	E, v.	10^5 dE/dT	ΔS
Richards and Daniels[9]	Stick	0.0026	1.8	0.41
Jones and Schumb[10]	?	.0028	4	.9
Richards and Smyth[11]	Solid casting	.0021		
Richards and Smyth	Electrolytic crystals	.0027	(Decreased to lower values)	
Gerke[2]	Stick	.0027	2.0	.46
Gerke	Crystals	.0024	3.2	.74

The data in Table III indicate that an e.m.f. of 0.0024 volt is unlikely to be in error by as much as half a millivolt which is only 0.04 cal. deg.$^{-1}$, mole^{-1} in $\Delta S = (\Delta H - \Delta F)/T$, whereas the temperature coefficient data are uncertain to about half a unit.

There is no simple way of utilizing thermal data to calculate $\Delta S = (\Delta H - \Delta F)/T$ for the reaction in Table III because the process is rather involved as

$$\mathrm{Tl} + \frac{B}{A - B}\,\mathrm{Tl{\cdot}AHg(l)} = \frac{A}{A - B}\,\mathrm{Tl{\cdot}BHg(s)} \qquad (5)$$

where A and B represent the moles of Hg per mole of Tl in the liquid and solid phases, respectively. There are insufficient data to enable the calculation of the partial molal entropies of the Tl and Hg in the solid amalgam. Thus the data in Table III are useful only in displaying the variation which we assume to be due to microscopic surface effects on the solid electrode.

Gerke avoided the thermodynamic complexities of the 2-phase amalgam by considering the two steps

$$\mathrm{Tl(s)} = \mathrm{Tl}(N_2 = 0.336) \qquad (6)$$

where N_2 refers to the mole fraction of Tl; $t = 30°$; $\mathbf{E} = 0.01246$ v.; $\Delta F = -289$ cal. mole^{-1}; $\Delta H = +720$ cal. mole^{-1} from which $\Delta S = 3.34$ cal. deg.$^{-1}$ mole^{-1}, and the calculated value of $\mathrm{d}\mathbf{E}/\mathrm{d}T = 0.000145$ v. deg.$^{-1}$ and

$$\mathrm{Tl}(N_2 = 0.336) = \mathrm{Tl(2\text{-}phase\ amalgam)} \qquad (7)$$

$t = 30°$, $\mathrm{d}\mathbf{E}/\mathrm{d}T = -0.000126$ v. deg.$^{-1}$. Adding reactions 6 and 7, the resultant $\mathrm{d}\mathbf{E}/\mathrm{d}T = +0.000019$ v. deg.$^{-1}$, as compared to the directly observed value $+0.000032$ found by Gerke for reaction 3.

Combining the results for reactions 2, 6 and 7 the calculated $\mathrm{d}\mathbf{E}/\mathrm{d}T$ for reaction 1 is -0.0000604 v. deg.$^{-1}$ and $\Delta S = -1.39$ cal. deg.$^{-1}$ mole^{-1}, $S(\mathrm{TlCl}) = -1.39 + S(\mathrm{Tl}) + S(\mathrm{AgCl}) - S(\mathrm{Ag}) = 26.72$. Considering the various possible errors in the several data used in the calculation, the above value is in very satisfactory agreement with the result 26.59 cal. deg.$^{-1}$ mole^{-1} obtained by direct measurement in this research.

Gerke comments on the fact that the stick of thallium used for his measurements produced crystals during the measurements, that the e.m.f. dropped slightly and the $\mathrm{d}\mathbf{E}/\mathrm{d}T$ increased as might be expected of a more stable metal. One of us (W.F.G.) recalls seeing the very pronounced crystal growth of the thallium during Gerke's experiment and at that time it seemed justifiable to accept the temperature coefficient results after this occurrence. However, in view of the above results it seems necessary to conclude that crystallization probably still in process, was complicating the temperature coefficient measurements. The temperature coefficient, 0.000020 v. deg.$^{-1}$, obtained by Gerke for reaction 3, in the first measurements before the recrystallization started is essentially correct, and this is in accord with the fact that microcrystals such as might be expected on a surface should have a higher free energy but only a very small increase in entropy. This is due to the fact that most of the microcrystalline energy and free energy exist at the absolute zero. These properties have only modest temperature coefficients and only a small associated entropy change.

The heat of reaction for $\mathrm{Tl(cryst.)} + \mathrm{AgCl} = \mathrm{TlCl} + \mathrm{Ag}$ may be calculated from the cell e.m.f. and the entropy change. For such a purpose we consider that ΔS from the third law of thermodynamics will ordinarily be the more reliable.

Utilizing data from Gerke's[2] several cells and converting to absolute volts

$$\mathrm{Tl(cryst.)} + \mathrm{AgCl} = \mathrm{TlCl} + \mathrm{Ag}$$

$$\Delta F^0_{25°} = -\mathbf{FE} = -23062 \times 0.7795 = -17977 \text{ cal. mole}^{-1}$$

$$\Delta H^0_{25°} = \Delta F^0 + 298.15(-1.52) = -18430 \text{ cal. mole}^{-1}$$

$$\mathrm{Tl(cryst.)} + {}^1\!/_2\mathrm{Cl_2} = \mathrm{TlCl}$$

$$\Delta F^0_{25°} = -23062 \times 1.9161 = -44209 \text{ cal. mole}^{-1}$$

and utilizing the entropy of $\mathrm{Cl_2} = 53.290$ cal. deg.$^{-1}$ mole^{-1};[12]

$$\Delta H^0_{25°} = \Delta F^0 + 298.15(-15.40) = -48800 \text{ cal. mole}^{-1}$$

Gerke comments on the difficulty in measuring the temperature coefficient of the chlorine electrode and this is borne out by a comparison of his value -15.12 compared to the third law result -15.40 given above for the formation of TlCl from the elements. In obtaining the value -15.12 we have utilized the calorimetric correction for the electrode $\mathrm{Tl(cryst.)} = \mathrm{Tl}(N_2 = 0.336)$ discussed above. However, the agreement is close enough to indicate that the e.m.f. of the cell $\mathrm{Tl} + {}^1\!/_2\mathrm{Cl_2} = \mathrm{TlCl}$ should be quite accurate.

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[9] T. W. Richards and F. Daniels, THIS JOURNAL, **41**, 1732 (1919).

[10] G. Jones and W. C. Schumb, *Proc. Amer. Acad. Arts Sci.*, **56**, 217 (1919).

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[12] R. H. Sherman and W. F. Giauque, *ibid.*, **75**, 2007 (1953).