this research are adequate for most thermodynamic calculations. However, the study of the thermodynamic properties of furan will not be finished until the vibrational assignment is completed by spectroscopists who reinvestigate the Raman spectra and study deuterated furans.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low Temperature Heat Capacities and Entropies at 298.16°K. of Magnesium Orthotitanate and Magnesium Dititanate

BY S. S. TODD

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Low temperature heat capacity measurements of magnesium orthotitanate and magnesium dititanate were conducted throughout the temperature range from 50 to 298°K. The entropies at 298.16°K. were found to be 24.76 ± 0.15 and 30.4 ± 0.2 cal./deg. mole.

In recent papers,[1] low temperature heat capacity data and entropies at 298.16°K. were reported for the meta- and orthotitanates of barium and strontium. This paper gives similar results for crystalline magnesium orthotitanate and magnesium dititanate, neither of which has been studied previously. Measurements of magnesium metatitanate were made by Shomate[2]; so results now are available for all the known compounds in the $MgO-TiO_2$ system.

Materials and Method.—The titanates employed in this work are the same as those described by Orr and Coughlin[3] for use in their high temperature heat content measurements. Analytical and X-ray diffraction data indicate the purities are 99.5% or better.

The heat capacity measurements were made with previously described[4] apparatus. The sample masses were 215.57 g. of magnesium orthotitanate and 197.05 g. of magnesium dititanate.

Heat Capacities.—The heat capacity results, expressed in defined calories (1 cal. = 4.1833 int. joules), are in Table I. The trend of heat capacity with temperature appears entirely normal in both instances, and no anomalous behavior of any sort was found.

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
		Mg_2TiO_4 (mol. wt. 160.54)			
52.38	1.938	114.62	10.61	216.25	24.30
56.39	2.310	123.59	12.21	226.20	25.27
60.68	2.778	135.97	13.98	236.18	26.18
65.25	3.330	145.99	15.51	245.89	27.01
69.87	3.912	155.92	16.94	256.26	27.82
74.58	4.519	165.97	18.35	266.13	28.62
80.11	5.296	175.89	19.66	276.19	29.33
84.57	5.940	185.88	20.91	286.40	30.03
94.77	7.476	195.90	22.08	296.53	30.62
104.37	8.959	206.30	23.21	(298.16)	(30.76)
		$MgTi_2O_5$ (mol. wt. 200.12)			
52.53	2.951	115.60	13.85	216.08	28.23
56.62	3.504	124.70	15.46	226.07	29.24
60.88	4.163	136.13	17.40	236.00	30.23
65.31	4.896	146.12	19.04	245.75	31.11
69.91	5.666	155.90	20.52	256.06	31.95
74.59	6.454	165.85	22.00	266.21	32.81
80.36	7.474	175.89	23.37	276.15	33.60
85.12	8.330	185.83	24.71	286.40	34.35
94.89	10.10	195.87	25.94	296.40	35.03
104.56	11.85	206.20	27.10	(298.16)	(35.15)

Entropies.—The measured portions of the entropies at 298.16°K. were obtained by Simpson-rule integrations of plots of C_p against $\log T$. The portions below 51°K. were obtained by extrapolation, using the following empirical Debye and Einstein function sums which fit the data over the entire measured range, with a maximum deviation of 1.4%

$$Mg_2TiO_4,\ D\left(\frac{305}{T}\right) + 3E\left(\frac{447}{T}\right) + 3E\left(\frac{823}{T}\right)$$

$$MgTi_2O_5,\ D\left(\frac{246}{T}\right) + 4E\left(\frac{420}{T}\right) + 3E\left(\frac{906}{T}\right)$$

The extrapolated portions are only 2.7 and 3.7% of the totals for 298.16°K. The entropy results appear in Table II.

TABLE II

ENTROPIES (CAL./DEG. MOLE)

	Mg_2TiO_4	$MgTi_2O_5$
0-51.00°K. (extrap.)	0.66	1.11
51.00-298.16°K. (meas.)	24.10	29.30
$S°_{298.16}$	24.76 ± 0.15	30.4 ± 0.2

Employing the entropies of magnesium oxide and titanium dioxide (rutile) from Kelley's[5] compilation, the entropies of formation at 298.16°K.

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[1] S. S. Todd and R. E. Lorenson, THIS JOURNAL, **74**, 2043 (1952).

[2] C. H. Shomate, *ibid.*, **68**, 964 (1946).

[3] R. L. Orr and J. P. Coughlin, *ibid.*, **74**, 3186 (1952).

[4] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

[5] K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

of magnesium ortho- and dititanates from their constituent oxides are −0.4 and −0.2 cal./deg. mole, as compared with −0.7 for magnesium metatitanate. Thus, the entropies of the compounds in this system do not deviate markedly from the sums of the entropies of the oxides. Similar behavior for magnesium meta- and orthosilicates was noted by Kelley.[6]

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[6] K. K. Kelley, THIS JOURNAL, **65**, 339 (1943).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Heats of Solution and Formation of Some Iron Halides

BY JAMES C. M. LI AND N. W. GREGORY

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Heats of solution have been determined for $FeCl_2$, $FeCl_3$, $FeBr_2$, $FeBr_3$ and $FeBrCl_2$ at concentrations of the order 10^{-3} molal. Heats of formation calculated from these data agree with quantities measured by independent methods when corrections are applied for hydrolysis and complex ion formation in the iron(III) solutions.

The complex nature of the ionic species in aqueous iron halide solutions makes interpretation of heats of solution of these compounds difficult. A question arises concerning the reported value for the heat of formation of iron(III) chloride based on determination of its heat of solution.[1,2] A correction for complex ion formation and hydrolysis does not appear to have been included in the interpretation of data and the value obtained is not in good agreement with that determined from equilibrium studies in anhydrous systems.[3] We have reinvestigated the heats of solution of $FeCl_2$ and $FeCl_3$ at low concentrations and have obtained similar results for $FeBr_2$, $FeBr_3$ and $FeBrCl_2$. Taken in conjunction with the reported characteristics of iron(III) solutions,[2] these data lead to heats of formation which are in good agreement with quantities observed in equilibrium studies.

Experimental Part

Thermal measurements were made in a simple adiabatic calorimeter, consisting of a dewar flask equipped with stirrer and sample-holding and breaking device. 750 ml. of water, carefully saturated with and maintained under a nitrogen atmosphere to minimize oxidation of iron(II), served as the solvent. The calorimeter thermometer was constructed from 6-mm. Pyrex glass tubing in the form of a spiral of 17 turns, 2 inches in diameter and 5.5 inches long, filled with toluene and a small amount of mercury. The lower end was connected to a capillary of 0.4 mm. diameter which turned upward and served as the thermometer stem. The sensitivity, as measured with a cathetometer read to 0.1 mm., corresponded to 0.0004 degree, or 0.36 calorie.

The entire device was placed in an air-bath controlled to ±0.01° at 25° with only the stirring rod, breaking rod and thermometer stem extending out of the thermostat. In tests for temperature drift the thermometer reading was observed to stay within the error of the cathetometer for periods of more than two hours during blank runs under normal operating conditions.

Samples were carefully prepared, purified by vacuum sublimation where possible, analyzed, and transferred to small Pyrex capsules in a dry-box. The capsules were evacuated and sealed and the quantity of material present determined by subsequent analysis of the solution. The calorimeter was calibrated by measuring heats of solution of LiCl, NaCl, KCl, KBr and KI.[2] For each compound various amounts were used to give approximately 36, 72, 108, 144 and 180 calories. Deviation of results for the various substances was within ±0.3 calorie.

The heat conductivity of toluene is much lower than that of mercury which offsets some of the advantage gained by its greater coefficient of thermal expansion. However, our experience confirms an approximate calculation of the time required (somewhat less than two minutes with efficient stirring) to reduce the temperature differential between the center of the liquid column and the outer edge of the glass tube to 0.001 of the original value produced on dissolving the sample. Stirring appears to be the major factor in the problem of heat transfer; in the absence of stirring in the calorimeter, more than 30 minutes was required for the system to reach uniform temperature. Thermal equilibrium in times of the order of two minutes was considered satisfactory for the purpose of the present work.

It should also be noted that the compressibility of toluene is sufficiently large to require a correction in the temperature reading if barometric pressure varies appreciably. The error becomes significant for variations of the order of 2 cm.

The heat of stirring at the rate employed was of the order of 0.2 calorie per minute. Allowance for this was included in the calibration by adjusting the temperature of the air-bath so that the heat leaking out of the calorimeter matched the input from stirring (*i.e.*, the calorimeter remained at constant temperature with a constant rate of stirring). This steady state was maintained for a period of 15 minutes or more before breaking the sample holder. After solution of the sample the temperature would again stay constant at its maximum value and was observed for a period of 10 minutes or more. Hence it was assumed that the heat of stirring was exactly compensated by heat leakage during the run and no correction applied for either. The change of heat of stirring while the sample was dissolving was neglected inasmuch as these compounds dissolved almost immediately in water.

As an illustration of the temperature behavior during a run, the following examples are observations made with $FeBr_3$ samples.

Time, minutes	Cathetometer reading	Time, minutes	Cathetometer reading
0 to 19	94.665	0 to 8	94.720
Capsule broken		Capsule broken	
20	95.855	9	95.925
21 to 28	95.865	10 to 20	95.940

Results and Discussion

Iron(II) Chloride.—Samples were prepared by thermal decomposition of the hydrate with subsequent sublimation of anhydrous $FeCl_2$ in high vacuum at 550°. After the thermal measurements, solutions were tested for Fe^{+++} ion with negative results in all cases. Data are shown in Table I. An average value for the heat of solution

$$FeCl_2(s) = Fe^{++}(aq) + 2Cl^-(aq)$$

has been taken as −19.5 ± 0.2 kcal./mole, neglecting the small contribution accompanying fur-

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[1] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

[2] F. D. Rossini, *et al.*, Natl. Bur. Stds. Circ. 500, U. S. Govt. Printing Office, Washington, D. C., 1950.

[3] W. Kangro and E. Petersen, *Z. anorg. Chem.*, **261**, 157 (1950).