as the reference state for elemental sulfur for temperatures other than 298.16°K. The computed values are presented in Table VIII.

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BARTLESVILLE, OKLAHOMA

[CONTRIBUTION NO. 28 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thermodynamic Properties of Furan

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A sample of furan was purified and used for calorimetric studies and for measurement of vapor pressure, density, refractive index, infrared spectrum (2–15μ) and mass spectrum. The heat of formation of liquid furan ($-\Delta H_f$ = 14.90 kcal. mole^{-1}) was derived from heat of combustion measurements. Low temperature thermal studies included measurement of the heat capacity of the solid, transition temperature (150.0°K.), heat of transition (489.2 cal. mole^{-1}), triple point (187.55° K.), heat of fusion (908.8 cal. mole^{-1}) and heat capacity of the liquid. The entropy of the liquid at 298.16°K., calculated from these data is 42.22 cal. deg.$^{-1}$ mole^{-1}. The observed vapor pressures between 2 and 62° are represented by the equation $\log_{10} p$ (mm.) = $6.97523 - 1060.851/(t + 227.740)$. The heat of vaporization at the normal boiling point (31.36°) is 6474 cal. mole^{-1}. The vapor heat capacity, measured at five temperatures between 317 and 488°K., is given by the equation $C_p^\circ = -7.55 + 9.352 \times 9.352 \times 10^{-2}T - 5.287 \times 10^{-5}\, T^2$ cal. deg.$^{-1}$ mole^{-1}. The equation $B = -279 - 22.6 \exp(950/T)$ cc. mole^{-1} was derived for the second virial coefficient from calorimetric data. A vibrational assignment which was partly empirical was made and used with molecular structure data to compute thermodynamic functions of the ideal gas to 1500°K. The heat, free energy and equilibrium constant of formation at temperatures to 1500° were calculated using appropriate calorimetric data and thermodynamic functions.

An investigation of the thermodynamic properties of furan was included in the research program of this Laboratory following a recent study of its sulfur analog, thiophene.[1] Derivatives of furan are used widely in the petroleum industry and are important items in the chemical trade. This investigation, in addition to supplying thermodynamic data for furan itself, has provided fundamental information which will be needed for future studies of the various derivatives of furan.

The several phases of this investigation, in the order of their presentation in this paper, were: (1) purification of the material and determination of the infrared spectrum of the liquid and of some of its physical properties including the triple point, density and refractive index; (2) measurement of the vapor pressure as a function of temperature; (3) determination of the heat of combustion and heat of formation; (4) measurement of the heat capacity of the solid and liquid and the heats of transition and fusion; (5) measurement of the heat of vaporization and the vapor heat capacity; (6) calculation of the entropy of the liquid and of the ideal gas from the appropriate experimental data; and (7) calculation of the thermodynamic functions and the heat, free energy and equilibrium constant of formation of the ideal gas at selected temperatures from molecular structure, spectroscopic and calorimetric data.

Units and Conversion Factors.—In this paper the defined calorie (1 cal. = 4.18 40 abs. j.) is used throughout for the unit of energy. Celsius temperatures are converted to Kelvin temperatures by adding 273.16°. The molecular weight of furan calculated from the 1949 atomic weights is 68.072.

The Material and Its Physical Properties

Purification and Purity.—About 1.2 l. of technical furan was distilled through a 70-plate column packed with steel helices. An atmosphere of nitrogen was maintained in the still at all times, and an inhibitor (hydroquinone) was added to each fraction when it was removed. Two 70-ml. heart cuts, samples A and B, were used for low-temperature and vapor pressure measurements, respectively, and portions of both samples were used for determining the heat of combustion. Later these two samples were combined for the determinations of the density, refractive index and infrared spectrum. Several other cuts, totaling about 300 ml., were combined into a third sample (C), which was used for the heat of vaporization and vapor heat capacity measurements. Each sample of furan was separated from the inhibitor and dried by a bulb-to-bulb distillation under its own vapor pressure in which the vapors passed over anhydrous magnesium perchlorate. The samples were stored in sealed ampoules under their own vapor pressure.

In the course of the low temperature thermal measurements, the purity of sample A was determined to be 99.98 ± 0.01 mole %.[2] The purity of sample B was not determined quantitatively. Since the boiling and condensation temperatures observed in the vapor pressure measurements differed by only 2 millidegrees at the normal boiling point, it is evident that sample B did not contain enough impurity of different volatility to have any significant effect on the vapor pressure measurements. The heat of combustion of this sample was indistinguishable from that of sample A. Since this measurement is sensitive to about 0.05 mole % of C_5-hydrocarbons (the most probable impurities), it is believed that sample B was more than 99.9 mole % pure. The mass spectra of samples A and C were determined.[3] Isopentane (0.01 mole %) and a trace of an unidentified impurity (peak at 85) were found in sample A. Sample C showed 0.04 mole % isopentane and a somewhat larger trace of the same unidentified impurity. This analysis sug-

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(1) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 797 (1949).

(2) This value was calculated with the assumptions of ideal solutions and liquid-soluble, solid-insoluble impurities and is somewhat arbitrary since there is evidence that some of the impurities were solid-soluble. See discussion of the melting point.

(3) A mass spectrum, obtained from this study and corrected for impurities, has been published in the "Catalog of Mass Spectra," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1951, No. 545.

gests that sample C contains about four times the impurity of sample A and is about 99.9 mole % pure.

Melting Point.—The triple point of furan was determined as part of the low temperature measurements. The equilibrium temperatures, observed as a function of the fraction melted, are given in Table I. The cryoscopic constant, $\Delta H_{\text{fus}}/RT^2_{\text{T.P.}}$ = 0.0130 deg.$^{-1}$, was calculated from the heat of fusion (see below). If the impurities are all liquid-soluble, solid-insoluble and form ideal solutions in furan, then

TABLE I

MELTING POINT OF FURAN

$N_2 = 0.0130\,\Delta T$; triple point = 187.55 ± 0.05°K.; impurity $N_2^* = 0.019 \pm 0.010$ mole %

Melted, %	1/*F*	$T_{\text{obsd.}}$, °K.	$T_{\text{calcd.}}$, °K.
12.94	7.731	187.4407	187.4360
25.16	3.974	.4913	.4915
49.81	2.008	.5205	.5206
70.01	1.428	.5282	.5291
90.21	1.109	.5348	.5339
100.00	1.000	....	.5355
Pure	0.000	....	.550

$$T_{\text{T.P.}} - T = \Delta T = N_2^*/0.0130F \qquad (1)$$

where N_2^* is the mole fraction of impurities in the entire sample and F is the fraction of furan melted.[4] If the equilibrium temperatures are plotted as a function of $1/F$, the impurity can be calculated from the slope, and the triple point can be obtained by extrapolation to $1/F = 0$. This analysis is not strictly applicable in the present case where T is not a linear function of $1/F$. The apparent impurity (corresponding to the slope) in different regions varies from 0.027 mole % (between 90 and 70% melted) through 0.019 mole % (between 50 and 25% melted) to 0.017 mole % estimated from premelting. This trend probably is due to the formation of solid solutions.

Density.—The density of furan was determined at three temperatures in a 25-cc. Bingham pycnometer. The values obtained were

t, °C.	10	15	20
d^t_4 g. cc.$^{-1}$	0.9514_4	0.9446_7	0.9378_1

These densities are believed to be accurate to $\pm 10^{-4}$ g. cc.$^{-1}$, while the internal precision is $\pm 5 \times 10^{-5}$ g. cc.$^{-1}$. The coefficient of expansion at 15° is $1.44 \pm 0.01 \times 10^{-3}$ deg.$^{-1}$.

Refractive Index.—The index of refraction of furan at 20° was measured at six wave lengths by the proposed ASTM method,[5] using a Bausch & Lomb precision refractometer. The errors of measurements should not exceed $\pm 6 \times 10^{-5}$. The values of the refractive index found are

λ, Å.	6562.8	5892.6	5460.7	5015.7	4861.3	4358.3
N_λ^{20}	1.41822	1.42140	1.42418	1.42791	1.42954	1.43619

These data are represented between 6562.8 and 4358.3 Å. within $\pm 2 \times 10^{-5}$ by the empirical equation

$$N_\lambda^{20} = 1.40501 + 0.0047922/(\lambda - 0.125601)^{1.6} \qquad (2)$$

derived by the method of Forziati.[6]

Infrared Spectrum.—The infrared spectrum of furan was determined for the liquid state between 2 and 15 μ. The spectrogram obtained in this study has been included in reference 7. The infrared data for liquid furan that are pertinent to the calculation of the thermodynamic functions are presented in a subsequent section (Table VII).

Vapor Pressure and Boiling Point

The vapor pressure of furan was measured from 2 to 62° by comparative ebulliometry. The method and apparatus have been described previously.[1] The results of the measurements are presented in Table II. An Antoine equation was fitted to the data, using the least squares treatment of Willingham, *et al.*,[8] and giving all points equal weight. The equation obtained is

TABLE II

VAPOR PRESSURE OF FURAN, EBULLIOMETRIC METHOD

Boiling point, °C.		Pressure, mm.	
Water	Furan	Obsd.	Calcd. (eq. 3)
70.000	2.552	233.72	233.71
75	7.267	289.13	289.13
80	12.018	355.22	355.27
85	16.797	433.56	433.54
90	21.614	525.86	525.81
95	26.469	633.99	634.00
100	31.357	760.00	760.00
105	36.279	906.06	906.02
110	41.241	1074.6	1074.7
115	46.232	1268.0	1268.0
120	51.265	1489.1	1489.2
125	56.329	1740.8	1740.8
130	61.430	2026.0	2025.9

$$\log_{10} p = 6.97523 - 1060.851/(t + 227.740) \qquad (3)$$

Values of the vapor pressure calculated from this equation are included in Table II for comparison with the observed data. The normal boiling point of furan calculated from this equation is 31.36°.

Heat of Combustion and Heat of Formation

The heat of combustion of furan at 25° was determined, using a bomb calorimeter of the "constant temperature environment" type. This datum has been used to calculate the standard heat of formation. The apparatus, conditions and techniques have been described previously.[9] The bomb used in these combustions was made of illium and sealed with a fine-gold gasket. The volume of the bomb was 0.374 l. When many of the experiments showed evidence of incomplete combustion, a platinum baffle was suspended in the crucible over the ampoule to prevent splattering and to localize the combustion zone.[10] This technique was used in two experiments and probably was beneficial.

Calibration.—The energy equivalent of the system, S_B, was determined from combustions of NBS standard sample 39f (benzoic acid), which has a certified value of 26.4338 abs. kj. per gram mass for its isothermal heat of combustion under standard conditions.[11] This value has been corrected to 26.4306 abs. kj. because the conditions of this investigation were not quite those of the standard bomb process. During the first part of this investigation, the energy equivalent was 3192.8[12] cal. deg.$^{-1}$. After making minor repairs the energy equivalent was redetermined and found to be 3193.7[13] cal. deg.$^{-1}$.

The results of the combustion experiments refer to the isothermal process at 25° and true mass.

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[4] S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

[5] ASTM proposed method of measurement of refractive index and refractive dispersion of hydrocarbon liquids. "ASTM Standards on Petroleum Products and Lubricants," American Society of Testing Materials, Philadelphia, Pa., 1950, Appendix IV, p. 685.

[6] A. F. Forziati, *J. Research Natl. Bur. Standards*, **44**, 373 (1950).

[7] "Catalog of Infrared Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1952, Serial No. 1277.

[8] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

[9] W. N. Hubbard, J. W. Knowlton and H. M. Huffman, THIS JOURNAL, **70**, 3259 (1948).

[10] This baffle is a modification of Sunner's "top" [S. Sunner, Dissertation, University of Lund, 1949, "Studies in Combustion Calorimetry Applied to Organo-Sulfur Compounds," Carl Bloms Boktryckeri, Lund, Sweden, 1949, pp. 45–49] and is used regularly in this Laboratory in the combustion of sulfur compounds. *Cf.* also, S. Kaarsemaker, Dissertation, Vrije Universiteit, 1951, D. B. Centen's Uitgevers-Mattschappij N. V., Amsterdam, 1951, pp. 31–32.

[11] (a) NBS certificate for standard sample 39f; (b) R. S. Jessup, *J. Research Natl. Bur. Standards*, **36**, 421 (1946); (c) *ibid.*, **29**, 247 (1942).

[12] Mean of six experiments, average deviation 0.007%, maximum spread 0.025%.

[13] Mean of six experiments, average deviation 0.009%, maximum spread 0.034%.

TABLE III

SUMMARY OF FURAN COMBUSTIONS

Combustion,[a] no.	Mass of furan, g.	Mass of oil,[b] g.	Mass of fuse,[c] g.	S_B,[d] cal. deg.$^{-1}$	S_1,[d] cal. deg.$^{-1}$	S_F,[d] cal. deg.$^{-1}$	Δt	q_{HNO_3},[e] cal.	$q_{ign.}$ cal.	$-\Delta U_B/M$,[d] cal. g.$^{-1}$	Deviation from mean, cal. g.$^{-1}$
2B	0.82150	0.02992	0.00392	3192.8	3.33	3.52	1.99095	1.2	1.28	7314.3	−0.7
4B	.83189	.04282	.00389	3192.8	3.35	3.53	2.06058	1.2	1.28	7315.9	+ .9
9A	.85437	.01538	.00408	3192.8	3.34	3.52	2.01531	1.2	1.28	7315.1	+ .1
16A	.88428	.01214	.00524	3193.7	3.75[f]	3.93[f]	2.07253	0.8	1.28	7314.1	− .9
17A	.90700	.00941	.00531	3193.7	3.76[f]	3.93[f]	2.11575	.6	2.56[g]	7315.5	+ .5

Average 7315.0 ± 0.6 = 0.01%

Maximum spread 1.8 cal. g.$^{-1}$ = 0.025%

[a] In combustions 2 and 4 sample B was burned. Sample A was used in the other three combustions. [b] In combustions 2 and 4 the heat of combustion of the oil was 11,265 cal. g.$^{-1}$. In the other combustions, 11,272 cal. g.$^{-1}$. [c] The heat of combustion of the filter paper fuse was 3902.5 cal. g.$^{-1}$. [d] S_B = energy equivalent of system minus contents; S_1 = energy equivalent of initial contents; S_F = energy equivalent of final contents; $\Delta U_B/M$ = energy of bomb process per g. [e] Correction for nitric acid formed: $1/2\ N_2 + 1/2\ H_2O + 5/4\ O_2 \rightarrow HNO_3(aq)$, $\Delta U = -13.82$ kcal. mole^{-1} [E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **33**, 264 (1944)]. [f] In combustions 16 and 17 the platinum baffle was used (see text). [g] Due to mechanical failure of the firing mechanism, twice the normal ignition energy was delivered in combustion 17.

Ampoule Technique.—The furan was enclosed in sealed, soft-glass ampoules selected so that the quantities of furan contained were nearly sufficient to produce a 2° temperature rise in the combustion experiments. The mass of each sample was determined from the difference between the weights of the empty and filled ampoules.

The technique used in this Laboratory for handling volatile materials has not been described previously and differs in several details from that employed by other workers. The ampoules used were about 80 mg. in weight, 12 mm. in diameter, and flattened on two sides. The stem of each ampoule was drawn down to a fine capillary, and a glass tube was slipped over each capillary for protection, as shown in Fig. 1B.

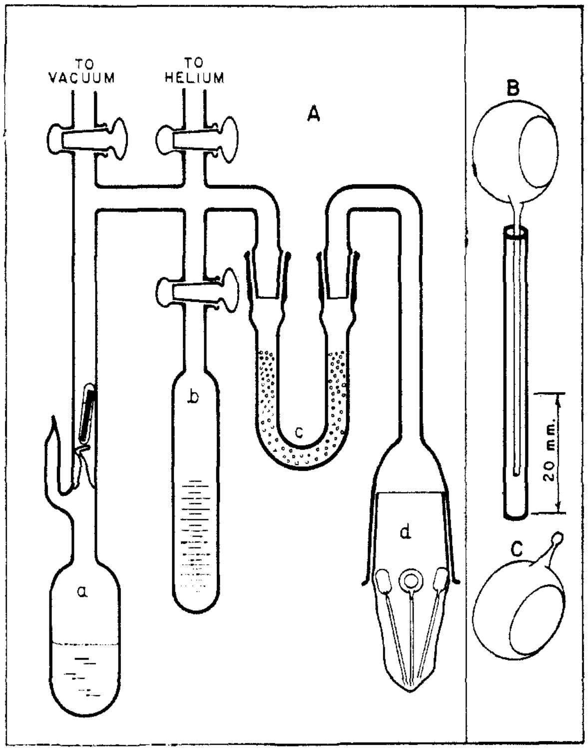

Fig. 1.—A, filling system; B, ampoule and supporting glass tube; C, sealed ampoule.

The all glass system used for filling the ampoules is illustrated schematically in Fig. 1A. A bulb with internal break-off tip (a) containing the furan was sealed to the system and the U-tube (c) was filled with a drying agent (magnesium perchlorate). Each of several weighed ampoules with its supporting tube was placed, capillary down, in the receiver (d). After the system was evacuated, the break-off tip was opened and the furan was distilled into the calibrated receiver (b). Then a slight excess over the amount needed to fill the ampoules was distilled into the second receiver (d). The distillation was stopped, and dry helium was cautiously admitted to the system, causing the ampoules to fill. After the system reached room temperature and pressure, the ampoules were removed. The ampoules were held in a special pair of forceps and sealed, using a very sharp oxyhydrogen flame.[14] The furan in the capillary stem at the time of sealing protected the sample from moisture in the air. The ampoules and their capillaries then were placed in a vacuum desiccator for removal of surface furan and for storage. Later, at the beginning of each combustion experiment, an ampoule and its stem were weighed together.

Experimental Results.—In all, 17 combustion experiments were performed with furan. The results of only 5 were included in the final average. The remaining 12 experiments showed evidence of incomplete combustion or explosion and were discarded.

In 2 of the 12 unsatisfactory combustions, the ampoule failed to fire, although the fuse burned. Six experiments were discarded because carbon was deposited on the bomb; in at least five of these experiments the reactions occurred explosively. In each of four other combustions (numbers 8, 10, 14 and 15) there were neither carbon deposits nor evidences of explosion. The values of $-\Delta U_B/M$ obtained in these experiments were 7239, 7166, 7247 and 7268 cal. g.$^{-1}$, respectively. These low and erratic results suggest incomplete reactions with products other than carbon dioxide and water. Unfortunately, carbon dioxide analyses of the bomb gases could not be made at the time of these experiments.

Table III gives the results of the five accepted combustion experiments and shows the correction terms. It is believed that these five combustions were complete, since it is highly improbable that the precision of a group of incomplete combustions would be comparable to that of benzoic acid. The presence of 0.01 mole % of isopentane would increase the heat of combustion of pure furan by 0.4 cal. g.$^{-1}$. No correction has been made for impurity.

The mean value of these five experiments has been used to calculate the following derived thermal data in kcal. mole^{-1} for furan at 25°:

$-\Delta U_R$	$-\Delta H_R$	$-\Delta H_f^\circ(l)$	$-\Delta H_f(g)^{15a}$	$-\Delta H_f^\circ(g)^{15b}$
497.67	497.97	14.90	8.34	8.29

ΔU_R was computed using the Washburn correction,[16] $\Delta U_R = (1 + r)\Delta U_B$, where $r = -0.0056$. The heat of combustion at constant pressure, $-\Delta H_R$, is given for liquid furan and for

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(14) The technique for sealing ampoules has since been improved by using a very small ($^1/_2 \times {}^1/_2$ mm.) flame obtained by burning H_2 at the end of a very fine capillary. This technique was demonstrated by Lars Bjellerup of the University of Lund, Sweden.

(15) (a) At saturation pressure (600 mm.); (b) at unit fugacity.

(16) E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

the real gases at 1 atm. The heat of formation of liquid furan was calculated using the values -68.3174[17a] and -94.0518[17b] kcal. mole^{-1} for the heats of formation of water and carbon dioxide from the elements in their respective standard states.[18] The heats of formation of furan at saturation pressure and at unit fugacity were obtained using the heat of vaporization and gas imperfection data reported elsewhere in this paper.

Discussion.—Landrieu, Baylocq and Johnson[19] have reported 7352 cal. g.$^{-1}$ for $-\Delta U_B/M$ for the combustion of liquid furan. The disagreement with the value found in the present research can be attributed principally to the absence of certain corrections in the earlier work and to difference between the purity of the two samples.

The resonance energy of furan has been calculated from the old value of the heat of combustion by Pauling, by Wheland and by Franklin.[20] Using the present value, the resonance energy calculated by the different methods of these authors will be raised about 1 kcal. mole^{-1} to 23.7, 24.6 and 25.6 kcal. mole^{-1}, respectively. In an alternative calculation using heat of hydrogenation data, Wheland[21] has obtained 17 kcal. mole^{-1} for the resonance energy of furan. The difference between this value and the value obtained from heat of combustion data is far greater than the experimental uncertainties of the two thermochemical measurements. This discrepancy probably arises from the different approximations used in the two methods of estimating the energy of non-resonating furan.

Low Temperature Thermal Data

The Apparatus.—The measurements were made in an adiabatic calorimetric system described by Ruehrwein and Huffman.[22] About 0.7 mole of furan was contained in a sealed, copper calorimeter, which was mounted in the calorimetric system. Measured amounts of electrical energy were supplied to the calorimeter, and the initial and final temperatures were determined with a platinum resistance thermometer. During measurements, the temperature of the environment was maintained equal to that of the calorimeter to prevent heat interchange. The precision of the measurements was, in general, better than 0.1%; and above 30°K. it is believed that the absolute uncertainty is not greater than 0.2%.

The Results.—Thermal measurements on furan between 12 and 300°K. show a small lambda point at 56°K., a transition at 150°K. and fusion at 187.55°K. The heat capacity, heat of fusion, melting point, heat of transition and transition temperature were determined. The experimental heat capacity data are given in Table IV. The temperatures listed are mean temperatures of the individual measurements. $C_{satd.}$ is the heat capacity of the condensed phase under its own vapor pressure.

The lambda point between 50 and 60°K., with a maximum at about 56°K., absorbed so little energy that its shape was not defined.

The large transition at 150°K. is practically isothermal, although it may be a narrow lambda point. This transition exhibited hysteresis and the heat-capacity measurements between 80 and 160°K. showed some dependence upon the thermal history of the sample. When the time of cooling through the transition was varied between a few hours and several days, it was observed in the series of measurements following the most rapid cooling that the heat capacity between 80 and 150°K. averaged about 0.25% (0.03 cal. deg.$^{-1}$ mole^{-1}) higher than the other measurements in this region and that the heat of transition was about 0.6% (3 cal. mole^{-1}) less than that of the other determinations. This corresponded to supercooling about 1% of the high temperature phase. The data obtained for the rapidly cooled material were discarded. The other series in this region which followed slower cooling (> one day) through the transition showed no further observable dependence on the thermal treatment of the sample, and it is believed that the measurements below 150° reported in Table IV are characteristic of the equilibrium phase.

TABLE IV

MOLAL HEAT CAPACITY OF FURAN, CAL. DEG.$^{-1}$

T, °K.	ΔT	$C_{satd.}$
	Crystals I	
11.72	0.704	0.919
12.64	1.151	1.096
12.73	1.520	1.125
13.97	1.517	1.416
14.58	2.204	1.546
15.67	1.895	1.795
16.90	2.443	2.073
17.74	2.232	2.267
19.38	2.512	2.657
20.04	2.373	2.814
22.04	2.793	3.287
22.45	2.437	3.384
24.82	2.302	3.922
25.03	3.184	3.974
27.55	3.151	4.523
28.15	3.054	4.649
30.50	2.727	5.140
31.32	3.280	5.314
33.37	3.009	5.723
34.50	3.094	5.939
37.88	3.666	6.552
41.76	4.091	7.194
46.10	4.588	7.824
50.49	4.184	8.404
53.53	1.882	8.765
53.56	1.902	8.769
54.02	4.915	8.809
54.80	3.879	8.890
55.00	4.836	8.915
55.44	1.847	8.956
55.68	2.427	8.988
57.26	1.801	9.100
58.36	2.935	9.168
58.78	4.600	9.201
59.03	4.584	9.224
59.20	2.074	9.221
61.52	3.381	9.422
63.91	5.173	9.623
68.43	4.931	9.945
69.97	6.962	10.059
73.63	5.471	10.290
78.98	5.226	10.619
84.10	5.019	10.927
89.03	4.853	11.181
93.82	4.723	11.382
95.54	6.716	11.452
103.50	9.206	11.789
112.51	8.816	12.192
119.44	6.776	12.545
121.16	8.474	12.604
125.55	6.774	12.851
126.11	6.570	12.857
129.48	8.165	13.033
129.72	6.670	13.038
132.22	6.563	13.224
132.58	6.374	13.219
136.72	6.317	13.468
142.18	4.612	13.849
	Crystals II	
153.27	5.231	17.169
153.38	5.336	17.188
154.41	5.201	17.278
155.47	4.458	17.345
156.75	5.226	17.392
158.66	5.236	17.496
158.88	5.987	17.503
159.57	5.118	17.547
160.77	6.135	17.624
163.85	5.145	17.792
166.84	6.005	18.008
169.36	5.878	18.176
172.78	5.870	18.448
175.18	5.747	18.627
178.58	5.727	18.961
183.75	4.612	20.488
	Liquid	
191.00	3.498	23.857
194.14	5.299	23.899
196.23	6.955	23.921
200.31	7.025	23.990
203.16	6.905	24.033
207.74	7.844	24.122
210.04	6.854	24.161
217.29	7.650	24.309
225.32	8.416	24.520
233.64	8.325	24.755
241.97	8.230	25.030
250.15	8.135	25.312
256.25	9.530	25.540
258.24	8.032	25.637
265.71	9.396	25.917
266.22	7.941	25.933
274.11	7.840	26.284
275.42	10.022	26.319
282.29	8.517	26.630
285.36	9.864	26.778
290.75	8.398	27.038
294.77	8.965	27.229
299.09	8.285	27.440

Between 150 and 160°K., also, the measured heat capacity varied with the thermal history. Three series of measurements which commenced below the transition temperature absorbed about 0.2 cal. mole^{-1} more energy than two other series which started above the transition. This phenomenon may be due either to superheating of a small fraction of the low temperature phase or to slight supercooling of the high-temperature phase when "backing into a lambda point." Since the energy involved is too small to

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[17] (a) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945); (b) E. J. Prosen, R. S. Jessup and F. D. Rossini, *ibid.*, **33**, 447 (1944).

[18] Carbon, graphite under 1 atm.; water, liquid under 1 atm.; and gases, unit fugacity.

[19] P. Landrieu, F. Baylocq and J. Johnson, *Bull. soc. chim.*, **45**, 36 (1929).

[20] (a) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 138; (b) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 70; (c) J. L. Franklin, THIS JOURNAL, **72**, 4278 (1950).

[21] Reference 20b, p. 61.

[22] R. A. Ruehrwein and H. M. Huffman, *ibid*, **65**, 1620 (1943).

have any significant effect on the calculation of the entropy, no choice was made between the alternatives, and all the measurements were included in Table IV.

Three determinations of the heat of transition were made; one of these that showed supercooling was discarded. The values obtained were 489.0 and 489.4 cal. mole^{-1} which average was 489.2 cal. mole^{-1}. The furan molecule is nearly a regular pentagon. It is quite likely that the high temperature crystal of furan is a so-called solid rotator crystal in which the molecules are randomly oriented in any of five positions. (The crystals are clear and ice-like, as is usually reported for such crystals.) If the molecules are regularly oriented in the low temperature crystal, the entropy associated with the order-disorder change would be $R \ln 5 = 3.20$ e.u. The observed entropy of transition is 3.26 e.u.

Hysteresis in the transition prevented precise determination of the transition temperature. About 12 hours were required to reach each apparent equilibrium. In one experiment the apparent equilibrium temperatures and the corresponding percentages of the high temperature form were 150.16° (12%), 150.02° (30%) and 150.00°K. (72%). In another pair of experiments, the transition temperature was approached by both slow cooling and slow heating. In the cooling experiment the apparent equilibrium temperature was 149.87°K. when 77.9% of the sample was in the high temperature form. In the heating experiment the temperature was 150.12°K. with 24.9% in the high temperature form. After consideration of these data, 150.0 ± 0.1°K. was selected for the transition temperature.

Two determinations of the heat of fusion were made, which gave the values 908.6 and 909.0 cal. mole^{-1} which average was 908.8 cal. mole^{-1}. The results of the melting point study have been reported elsewhere in this paper. The heat of fusion obtained in that experiment was 910.3 cal. mole^{-1}.

The heat capacity of liquid furan at saturation pressure is represented within ±0.05% by the empirical equation

$$C_{\text{satd.}}(\text{l}) = 35.17 - 0.14860T + 5.695 \times 10^{-4}T^2 - 5.322 \times 10^{-7}T^3 \text{ cal. mole}^{-1} \quad (4)$$

This equation was fitted to the experimental data by an approximate least-squares method.

Heat of Vaporization and Vapor Heat Capacity

Apparatus.—Apparatus and experimental procedure having been described in publications from this Laboratory,[23] only a brief account will be given here. Vapor was produced by electrical heating in a cycling vaporizer, and the proportionality between flow rate and electrical power was determined by condensing and weighing the vapor produced by a measured power input during a measured time interval. Heats of vaporization believed to be accurate to ±0.1% were derived from these measurements. The vapor was passed through a flow calorimeter; and the apparent heat capacity, $W/(F\Delta T)$, was calculated from the power input to the calorimeter, W; the flow rate, F; and the temperature rise, ΔT. These data were corrected (for heat losses from the calorimeter) to the true heat capacity, C_p, using the relation C_p (apparent) $= C_p + k/F$ and extrapolation to $1/F = 0$. The heat capacity data are believed to be accurate to ±0.2%. The effect of impurities in the sample was estimated to be less than 0.1% and was neglected.

Results.—The heat of vaporization was determined in replicate experiments at each of three temperatures. The mean values obtained were

T, °K.	279.16	293.16	304.52
ΔH_{vap}, cal. mole^{-1}	6810 ± 6	6628 ± 2	6474 ± 1

where the uncertainty given is the maximum deviation from the mean. For interpolation in this temperature range the following equation may be used

$$\Delta H_{\text{vap}} = 8854 - 1.882T - 0.01949T^2 \text{ cal. mole}^{-1} \quad (5)$$

The heat capacity of the vapor was determined at two or more pressures at each of five temperatures between 317 and 488°K. The results are given in Table V. The values of C_p° (obsd.) were obtained at each temperature by linear extrapolation to zero pressure. Over the temperature range of the experiments, the observed values of C_p° are represented to better than 0.05% by the empirical equation

$$C_p^\circ = -7.55 + 9.352 \times 10^{-2}T - 5.287 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (6)$$

obtained by the method of least squares.

Values of the second virial coefficient, B in the equation of state $PV = RT + BP$, were calculated from the heat of vaporization and vapor pressure data using the exact form of the Clapeyron equation; that is

$$B = [\Delta H_{\text{vap}}/T(\mathrm{d}P/\mathrm{d}T)] - RT/P + v_L$$

where v_L is the molal volume of the liquid. In addition, the relation $(\partial C_p/\partial P)_T = -T(\mathrm{d}^2B/\mathrm{d}T^2)$ was evaluated at five temperatures from the vapor heat capacity data. All these gas imperfection data were correlated by the empirical equation

TABLE V

MOLAL VAPOR HEAT CAPACITY OF FURAN, CAL. DEG.$^{-1}$

T, °K.	317.25	358.20	402.20	449.20	487.20
C_p (760 mm.)	17.317	19.441	21.638	23.875	25.515
C_p (493 mm.)	17.143	..	..	..	..
C_p (273 mm.)	16.985	19.255	21.555	23.826	25.475
C_p° (obsd.)	16.80	19.15	21.51	23.80	25.45
C_p° (calcd.)[a]	16.74	19.02	21.31	23.55	25.20
ΔC_p° (obsd. − calcd.)	0.06	0.13	0.20	0.25	0.25
	$(\partial C_p/\partial P)_T$ cal. deg.$^{-1}$ atm.$^{-1}$ mole^{-1}				
$(\partial C_p/\partial P)_T$ (obsd.)	0.51	0.29	0.13	0.08	0.06
$(\partial C_p/\partial P)_T$ (calcd.)[b]	0.51	0.27	0.15	0.09	0.06

[a] Harmonic oscillator, rigid rotator approximation. [b] Calcd. using Eq. 7

$$B = -279 - 22.6 \exp.(950/T) \text{ cc. mole}^{-1} \quad (7)$$

which constants were evaluated by methods described elsewhere.[24] The values of B derived from the experimental data and calculated from eq. (7) are

T, °K.	279.16	293.16	304.52
B (obsd.) cc. mole^{-1}	975	851	789
B (calcd.) cc. mole^{-1}	958	856	791

In Table V, the values of $(\partial C_p/\partial P)_T$ obtained from the experimental data may be compared with the values of $(\partial C_p/\partial P)_T$ calculated from eq. (7).

The Entropy

The calorimetric data obtained have been used to compute the entropy of furan in both the liquid and ideal gaseous states at 298.16°K. The entropy calculations are summarized in Table VI. The uncertainties given do not include any provision for the slight possibility that a fraction of the high temperature phase was supercooled through the transition at 150°K. The gas imperfection correction $P\mathrm{d}B/\mathrm{d}T$ was calculated from eq. (7).

TABLE VI

MOLAL ENTROPY OF FURAN, CAL. DEG.$^{-1}$

0–12°K.	Debye extrapolation, $\theta = 95.5$°K. 3.5 degrees of freedom	0.347
12–150.0	Crystals I, graphical $\int C_{\text{satd}}\, \mathrm{d} \ln T$	18.076
150.0	Transition 489.2/150.0	3.262
150.0–187.55	Crystals II, graphical $\int C_{\text{satd}}\, \mathrm{d} \ln T$	4.047
187.55	Fusion 908.8/187.55	4.846
187.55–298.16	Liquid, graphical $\int C_{\text{satd}}\, \mathrm{d} \ln T$	11.638
Entropy of liquid at 298.16°K.		42.22 ± 0.08
298.16	Vaporization 6561/298.16	22.005
298.16	Compression $R \ln(p/760)$	− 0.471
298.16	Gas imperfection	0.112
Entropy of ideal gas at 298.16°K.		63.86 ± 0.10

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[23] (a) G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); (b) G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

[24] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

Vibrational Assignment and Thermodynamic Functions

Vibrational Assignment.—The calorimetric data were extended to other thermodynamic functions and to higher temperatures by means of calculations based on spectroscopic and molecular structure information. For these calculations, it was necessary to use a set of vibrational frequencies of the furan molecule which was partly schematic. Since only 18 of the 21 fundamental frequencies could be obtained from the available spectroscopic data, the remaining three frequencies were selected empirically to give agreement between calculated and observed values of the vapor heat capacity and entropy.

The assignment from observed spectra was based primarily on the Raman data of Reitz,[25] the infrared data of Thompson and Temple[26] for the vapor and the infrared data of this investigation for the liquid. These data are given in part in Table VII. The results of earlier investigations of both spectra[27] were also considered.

TABLE VII

SPECTRA OF FURAN, 0–1600 cm.$^{-1}$ and 2900–3200 cm.$^{-1}$

Raman[a] (liquid) $\Delta\bar{\nu}$, cm.$^{-1}$	ρ	Infrared[b] (vapor) $\bar{\nu}$, cm.$^{-1}$	Infrared[c] (liquid) $\bar{\nu}$, cm.$^{-1}$	Assignment
500 (0)				1483 − 986 = 497 (A.)?
601 (4)	0.86	605		B_2
724 (3)	.63			A_1
		744	744	B_2
839 (3)	*dp*	837	843	B_1
871 (4)	.84	872	870	B_1
986 (4)	.27	994	991	A_1
1034 (4)	*dp*		1038	A_2
1061 (5)	.22	1067	1062	A_1
1138 (12)	.15			A_1
1171 (0)	*dp*	1180	1174	B_1
1200 (00)	*dp*		1203	2(601) (A_1)
1270 (0)		1270	1266	605 + 663 = 1268 (B_1)
1324 (1)			1330	2(663) = 1326 (A_1)
		1340		605 + 844 = 1349 (A_1)
1380 (8)	.42	1381	1381	A_1
1457 (2)		1458	1445	2(724) = 1448 (A_1)
1483 (12)	.12	1486	1486	A_1
		1558	1552	724 + 837 = 1561 (B_2)
		1579	1570	B_1
		1596	1592	724 + 872 = 1596 (B_2) 605 + 994 = 1599 (B_1)
		2900	2915	4(724) = 2896 (A_1) ?
		2960	2959	2(1486) = 2972 (A_1)
3089 (3)	*p*			A_1
3121 (5)	*p*(Hg)		3135	Fermi resonance: A_1 fundamental with 2(1570) = 3140 (A_1)
3154 (5)	.19	3185	3155	

[a] Reference 25. [b] Reference 26. [c] This research.

The complete set of vibrational frequencies used for thermodynamic calculations is given in Table VIII. These frequencies may be grouped according to the certainty of their assignment into four categories which will be discussed in the order of decreasing certainty.

TABLE VIII

VIBRATIONAL FREQUENCIES OF FURAN USED FOR THERMODYNAMIC CALCULATIONS

bold face = assignment definite, light face = probable fundamental, *italics* = unobserved

Symmetry, C_{2v}

Class A_1 Raman, polarized infrared, active $\bar{\nu}$, cm.$^{-1}$	Class B_1 Raman, depolarized infrared, active $\bar{\nu}$, cm.$^{-1}$	Class A_2 Raman, depolarized infrared, inactive ν, cm.$^{-1}$
724	838	*663*
994	**872**	..[b]
1067	..[b]	1034
1138	1180	Class B_2 Raman, depolarized infrared, active
1381	**1579**	
1486	*3089*[a]	**605**
3089	*3138*[a]	**744**
3138		..[b]

[a] Used twice. [b] Three frequencies 700, 1000 and 1300 cm.$^{-1}$ were selected to fit the calorimetric data. These have not been assigned to specific symmetry classes.

The first category, shown in "bold face," comprises the observed frequencies that are definitely fundamentals and whose assignment to symmetry classes is certain. Since arguments for these assignments have been given in detail by Thompson and Temple,[26] only a brief summary will be given here. All the frequencies placed in the A_1 class have strong, polarized Raman lines. (Fermi resonance between a C–H stretching fundamental and the second harmonic of 1579 gives the doublet, 3121–3154.) The frequencies 605, 744 and 872 cm.$^{-1}$ have strong infrared bands and can be assigned on the basis of the band contours in the infrared spectrum of the vapor. The infrared band at 1579 cm.$^{-1}$ is the only strong band found in the region where the C=C stretching vibration of the B_1 class would be expected. (The weak infrared band at 1270 cm.$^{-1}$ assigned by Thompson and Temple to be a B_1 fundamental has been omitted here; see below.)

The second category, shown in "light face," comprises the frequencies that appear as strong Raman lines or infrared bands and are almost certainly fundamentals, but whose assignment to particular symmetry classes is somewhat arbitrary. Thompson and Temple assigned the 838 cm.$^{-1}$ frequency to the B_2 class instead of to the B_1 class).

The third category, shown in "italics," comprises assigned frequencies which have not been observed directly. The two C–H stretching vibrations in the B_1 class are probably unresolved in the observed spectra from their counterparts in the A_1 class, and the same values were assigned to these B_1 frequencies as to the corresponding A_1 frequencies. The frequency 663 cm.$^{-1}$ in the A_2 class was assigned by interpreting the weak infrared band at 1270 cm.$^{-1}$ as the combination 605 + 663 = 1268 ($B_2 \times A_2 = B_1$) and the weak Raman line at 1324 cm.$^{-1}$ as the overtone 2(663) = 1326. The contour of the 1270 cm.$^{-1}$ band in the infrared spectrum of the vapor is consistent with this interpretation. No unobserved frequency other than 663 cm.$^{-1}$ could be located by means of overtones and combinations. Each of the observed frequencies (including those in the regions omitted from Table VII) could be interpreted as one of the 18 funda-

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[25] A. W. Reitz, *Z. physik. Chem.*, **B38**, 275 (1937); **B33**, 179 (1936).

[26] H. W. Thompson and R. B. Temple, *Trans. Faraday Soc.*, **41**, 27 (1945).

[27] Raman: (a) G. B. Bonino and R. Manzoni-Ansidei, *Ricerca sci.*, **7**, I, 315 (1936); *Z. physik. Chem.*, **B25**, 327 (1934); infrared: (b) J. Lecompte, *Bull. soc. chim.*, 415 (1946); (c) L. W. Pickett, *J. Chem. Phys.*, **10**, 660 (1942); (d) R. Manzoni-Ansidei and M. Rolla, *Atti. accad. Lincei, Classe sci. fis. mat. nat.*, **27**, 410 (1938).

mentals, their overtones, or their binary combinations (except one infrared band at 2590 cm.$^{-1}$).

The last category comprises three frequencies which could not be assigned from the spectroscopic data. Attempts to estimate these three unobserved frequencies by normal coördinate calculations did not give results consistent with the calorimetric data. Therefore, values of these frequencies (700, 1000, 1300 cm.$^{-1}$) were selected empirically to bring the calculated thermodynamic functions into agreement with the calorimetric data. It was not possible to use a single average value for these three frequencies, since such a choice gave calculated heat capacity values higher than those observed (*i.e.*, negative anharmonicity). The separation of the frequencies adopted here gives furan about the same anharmonicity as thiophene.[1] Little theoretical significance should be attached to the values selected.

Lord and Miller[28] have suggested that the weak Raman line at 500 cm.$^{-1}$ is the low A_2 frequency and that a second A_2 frequency is obscured by the strong Raman line at 724 cm.$^{-1}$. This interpretation of the spectra leads to a calculated entropy about 0.2 cal. deg.$^{-1}$ mole^{-1} larger than is observed. In fact, no group of frequencies including one below 600 cm.$^{-1}$ was found which gave reasonable agreement between calculated and observed thermodynamic properties. It is possible that the furan did not form thermodynamically perfect crystals under the experimental conditions used (note the hysteresis in the transition) and thus did not obey the third law of thermodynamics. This proposition was considered carefully. It was found that a vibrational assignment which *gives good agreement between the calculated and observed entropy* also gives *better agreement between the calculated and observed heat capacity than other assignments.* Therefore it seems likely that furan does not retain any residual entropy at temperatures approaching the absolute zero.

Thermodynamic Functions.—Values of thermodynamic functions of furan were calculated using a harmonic oscillator, rigid rotator model. The frequency assignment of Table VIII was used. Sirvetz[29] has determined the moments of inertia of furan by microwave spectroscopy. The values used in these calculations were $I_a = 88.840$, $I_b = 90.764$, $I_c = 179.684 \times 10^{-40}$ g. cm.^{2} and $I_aI_bI_c = 1448.88 \times 10^{-117}$ g.^{3} cm.^{6}. The symmetry number is 2. The fundamental constants of Wagman, *et al.*,[17a] were used.

The calculated values of C_p° are compared with the experimental results in Table VI. Values of the entropy were calculated at three temperatures and are in good agreement with the experimental values as shown in the following tabulation:

T, °K.	279.16	293.16	304.52
S° (calcd.) cal. deg.$^{-1}$ mole^{-1}	62.86	63.60	64.19
S° (obsd.) cal. deg.$^{-1}$ mole^{-1}	62.87	63.60	64.18

Values of the functions $(F_T^\circ - H_0^\circ)/T$, $(H_T^\circ - H_0^\circ)/T$, $H_T^\circ - H_0^\circ$, S° and C_p° at selected temperatures up to 1500°K. are given in Table IX. The values given in this table include more significant figures than is justified by their absolute accuracy, in order to retain the internal consistency of the thermodynamic functions, and also to retain the significance of the temperature increments of a given function.

TABLE IX

MOLAL THERMODYNAMIC FUNCTIONS OF FURAN

T, °K.	$-(F_T^\circ - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_T^\circ - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_T^\circ - H_0^\circ$, kcal.	S° cal. deg.$^{-1}$	C_p° cal. deg.$^{-1}$
273.16	53.10	9.44	2.5798	62.55	14.22
298.16	53.95	9.90	2.9530	63.86	15.64
300	54.01	9.94	2.982	63.95	15.75
400	57.16	12.09	4.835	69.25	21.20
500	60.10	14.38	7.190	74.48	25.73
600	62.92	16.59	9.95	79.51	29.31
700	65.63	18.61	13.03	84.24	32.13
800	68.24	20.45	16.36	88.68	34.41
900	70.75	22.11	19.90	92.85	36.30
1000	73.15	23.61	23.61	96.76	37.89
1100	75.47	24.97	27.46	100.44	39.23
1200	77.69	26.20	31.45	103.90	40.37
1300	79.84	27.33	35.53	107.17	41.36
1400	81.90	28.37	39.71	110.27	42.21
1500	83.89	29.31	43.97	113.20	42.94

These functions have been used in conjunction with the heat of combustion data and with the thermodynamic functions of graphite, hydrogen and oxygen given by Wagman[17a] to compute the heat, free energy and common logarithm of the equilibrium constant of formation of furan from its elements at various temperatures. Values computed for the liquid at 298.16°K. and for the ideal gas at unit fugacity at several temperatures are given in Table X.

TABLE X

HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT OF FORMATION OF FURAN[a]

T, °K.	$-\Delta H_f^\circ$, kcal. mole^{-1}	ΔF_f°, kcal. mole^{-1}	$-\log_{10} K_f$
4 C (graphite) + $2H_2(g)$ + 1/2 $O_2(g)$ $\longrightarrow$ C_4H_4O (liq.)			
298.16	14.903	+ 0.050	+0.037
4 C (graphite) + $2H_2(g)$ + 1/2 $O_2(g)$ $\longrightarrow$ C_4H_4O (g)			
0	5.157	− 5.157	$-\infty$
298.16	8.293	+ 0.208	+0.15
300	8.311	0.261	0.19
400	9.191	3.258	1.78
500	9.872	6.452	2.82
600	10.39	9.77	3.56
700	10.82	13.16	4.11
800	11.13	16.61	4.54
900	11.37	20.09	4.88
1000	11.53	23.60	5.16
1100	11.63	27.11	5.39
1200	11.68	30.64	5.58
1300	11.71	34.17	5.74
1400	11.72	37.69	5.88
1500	11.72	41.22	6.01

[a] For the formation of furan from the elements by the reactions shown with all products and reactants in their appropriate standard states at the temperature given. The standard reference state of gases is unit fugacity and of liquids and solids is the substance under one standard atmosphere.

Remarks.—In spite of the uncertainties in the vibrational assignment used to compute the thermodynamic functions of furan, the results obtained in

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(28) R. C. Lord, Jr., and F. A. Miller, *J. Chem. Phys.*, **10**, 328 (1942).

(29) M. H. Sirvetz, *ibid.*, **19**, 1609 (1951).

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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BARTLESVILLE, OKLA.

[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

RECEIVED APRIL 26, 1952

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).

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

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