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Thermodynamic Properties of Key Organic Oxygen Compounds in the Carbon Range C_1 to C_4

Part 1. Properties of Condensed Phases

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A survey of the published values of heat capacity and enthalpy obtained from calorimetric measurements on the crystal, glass, and liquid phases of the first few members of homologous series of organic oxygen compounds is presented. Equations for the heat capacities expressed as polynomial functions of temperature were fit to selected data by a least squares procedure. Tables of smoothed values of thermodynamic properties, derived from these functions, are presented for 38 compounds.

Key words: condensed-phase organic oxygen compounds; critically evaluated data; enthalpy; entropy; heat capacity; thermodynamic properties.

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1. Introduction

1.1. Scope and Objectives

The general objective of this series is to collect and tabulate the "best" values of the equilibrium thermodynamic and thermochemical properties of pure organic compounds which have from one to four carbon atoms per molecule. The thermodynamic properties of organic oxygen compounds have been studied more extensively than those of any other element except hydrogen and carbon. The group which contains up to four carbon atoms includes the initial members of homologous series of aliphatic compounds and their properties can serve as the starting point for the estimation of a much larger class of compounds. It also includes most of the organic compounds produced in high volume for industrial use.

For the most part the selections result either directly from measured properties or, as for perfect gas properties, from calculations using experimental values of molecular properties. All the data have been analyzed in a consistent manner and the final selections appear in the form of tables of smoothed properties.

This first part surveys the properties of condensed (solid and liquid) phases which are related to enthalpy as a function of temperature. Such properties are heat capacity, entropy, and Gibbs energy. Most of the data are obtained from calorimetric measurements, although some phase transition temperatures and enthalpy changes are based on other techniques. The range of temperatures encompassed in the tables reflects the range of experimental data except that an extrapolation to 0 K is made wherever feasible.

Tables of selected properties are reported for 42 species (including hydrates and racemic and resolved forms of optically active compounds). The second part of the series tabulates thermodynamic properties of *perfect* gases for 27 compounds, 21 of which are common to the compounds in the first part.

1.2. Review of Condensed Phase Thermodynamic Properties

1.2.a. Low Temperature Limit for C_s and S

The second and third laws of thermodynamics imply that absolute zero is an unattainable temperature. They also imply that C_s/T and the entropy of a crystal in its equilibrium state approach zero as the temperature approaches absolute zero. Thus the entropy of a crystal at temperature T_f can be calculated by,

$$S_{T_f}(c) = \int_0^{T_f} \frac{C_s(c)}{T}\, dT. \qquad (1)$$

The entropy calculated in this way from measured values of heat capacity is the "third law" entropy of a crystal. The motivation behind much of the low temperature studies in the past has been the testing of the third law of thermodynamics and the measurement of third law entropies.

There have been two kinds of tests. One test compares the change in entropy observed when a system undergoes a reversible physical or chemical transition to the difference in third law entropies of the initial and final states measured independently. The other kind compares the third law entropy of a perfect gas with that calculated from the molecular partition function derived from spectroscopic and molecular structure data. The final consensus is that the third law of thermodynamics is valid when properly applied. However, the substitution of measured heat capacity values into equation (1) may not always yield the correct third law entropy. In some cases some amount of randomness which exists at equilibrium at higher temperatures becomes frozen in as the temperature is lowered and persists down to the lowest observed temperature. In such cases the entropy calculated from equation (1) will be too low.

The use of equation (1) requires an interpolation of C_s/T between the lowest measured temperature and 0 K. The uncertainty inherent in this interpolation is strongly dependent on the value of the lowest experimental temperature. This is limited by the refrigerant used to cool the calorimeter. Liquid air was used for many studies before 1940. The lowest temperature practically obtainable with liquid air is about 90 K. Although interpolation of C_s from these temperatures to 0 K have been made, they cannot be considered reliable.

The use of liquid hydrogen permits measurements to be made down to around 11 K. Data for 20 compounds in this survey have been obtained in this way. Lower temperatures require either the use of liquid helium or of some other cooling technique. Measurements extend to 3 - 5 K for three of the compounds reviewed here.

The modern theories of the thermodynamic properties of crystals began with the concepts introduced by Einstein in 1907, and more especially by Debye in 1912. Debye calculated crystal properties in terms of the acoustic vibrations present in a continuous elastic solid. The constant volume heat capacity is then given by,

$$C_v = 9rR\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^4\,e^x}{(e^x-1)^2}\,dx\,. \qquad (2)$$

In equation (2) r is the number of atoms per molecule and Θ is a characteristic parameter now called the Debye temperature.

Equation (2) fits the heat capacities, within experimental error, measured for many solids during the early years of this century. At temperatures less than about $\Theta/10$ the integral in (2) is nearly equal to the constant $4\pi^4/15$. In this range equation (2) is closely approximated by

$$C_v = \frac{12rR\pi^4}{5}\left(\frac{T}{\Theta}\right)^3. \qquad (3)$$

Equation (3) predicts that C_v is proportional to T^3. This is the usual justification for interpolating C_{sT} from the lowest measurement to 0 K, when measurements extend at least down to 20 K. In this procedure Θ is adjusted to fit several heat capacity measurements at the low end and is then used to calculate C_s down to 0 K. Differences among C_v, C_p, and C_s are negligible at these temperatures.

Debye's model represents the lattice contributions to the thermodynamic properties of elements and simple compounds, that exist as regular atomic or ionic lattices. Many features are present in real crystals which are not included in the Debye model. For example loosely bound electrons in metals also contribute to observed properties. The effect on heat capacity is negligible at high temperatures but dominates the contributions below 1 K. The electronic contribution is proportional to temperature. Many other sources of deviations from the Debye model now have been identified. At the accuracy possible in the measurement of heat capacity and other properties today, significant deviations from the predictions of the Debye model can be seen for most crystals and temperatures. The assumptions in the Debye model and its derivations, as well as more modern comprehensive theories of crystals, are described by Gopal [1], Wallace [2], and Swalin [3].

The Debye model is not appropriate for molecular crystals formed from complicated organic compounds. Nevertheless, heat capacities of these compounds have sometimes been represented in terms of Einstein or Debye functions. It is also frequently assumed that the heat capacity is proportional to T^3 below 15 or 20 K, although this has not been firmly established for organic crystals in general. However, it is unlikely that this assumption gives rise to appreciable errors in the third law entropy when used with data down to 20 K or lower. Bondi [4] reviewed some empirical procedures for estimating the heat capacity of crystals, but no theoretical model suitable for organic crystals, which is simple enough for practical calculations is yet available. Stull, Westrum, and Sinke [5] have reviewed methods of extrapolating heat capacities of organic crystals using Einstein and Debye functions.

1.2.b. The Estimation of Entropy and Enthalpy at 90 K

In papers published before 1930 it was a common practice to calculate the third law entropy from heat capacity measurements down to liquid air temperatures by the use of graphical interpolation between the lowest measured value and 0 K. This is not a well defined procedure, however, and the results are quite uncertain.

By 1929 reliable low temperature measurements had been made for 25 organic compounds. For 12 of these, measurements extended down to around 20 K. At this time, Parks, Kelley and Huffman [6] and Kelley, Parks and Huffman [7] published an empirical procedure for estimating S_{90} which they used to revise the entropies of 13 compounds for which measurements had been made only to 90 K. For several years thereafter, this procedure was used by them and by other investigators to calculate S_{90} for other compounds.

Measurements now include 20 K or below for many more compounds. An examination of these data reveals a rough correlation between the heat capacity at 90 K and the entropy and enthalpy. For the 28 compounds listed in table 1 plus 2-methyl-2-propanol, dimethoxymethane, and 3-methyl-2-butanone we find that

$$S_{90}(c) = 0.8722\ C_{s90}(c) \qquad (\pm 3.59)\ \mathrm{J\ K^{-1}} \qquad (4)$$

$$H_{90}(c) - H_0 = 45.84\ C_{s90}(c) \qquad (\pm 134)\ \mathrm{J\ mol^{-1}}. \qquad (5)$$

The values in parentheses are root mean square deviations. The maximum deviations are 9.6 J K^{-1} mol^{-1} and 345 J mol^{-1}, respectively.

The method of Parks, Kelley and Huffman assumes that the heat capacity of an organic compound at any temperature, C_{sT}, can be related to the heat capacity of a hypothetical standard substance, C_s°, by

$$C_{sT} = (A + BT) C_{sT}^0. \qquad (6)$$

The values of A and B for a particular compound are evaluated by comparing experimental values of C_s for a compound at two temperatures with those of the standard. Then the entropy of the compound at 90 K can be calculated by

$$S_{90} = A S_{90}^\circ + B(H_{90}^\circ - H_0^\circ)\ . \qquad (7)$$

They chose two standards, one for aliphatic compounds and one for cyclic compounds, to represent S_{90} for the twelve compounds for which values were known at that time.

If we retain the two fixed temperatures, T_1 and T_2, for the comparison, their procedure is mathematically equivalent to the following equation.

$$S_{T_1} = a C_{sT_1} + b\,(C_{sT_2} - C_{sT_1}), \qquad (8)$$

in which a and b are empirical "universal" constants for a particular class of compounds. The root mean square deviation between the observed S_{90} and the S_{90} calculated by the Parks, Kelley and Huffman method using their parameters is 4.49 J K^{-1} mol^{-1} and the maximum deviation is 10.0 J K^{-1} mol^{-1} for the same group of compounds used to establish equations (4) and (5). The agreement can be improved by using optimum values of a and b in equation (8), but it is not significantly better than the simple equation (4).

In 1926 Parks and Anderson [8] tested a group additivity approach to estimate the entropy of a series of aliphatic acids and hydroxy compounds at 298.15 K. They concluded that the procedure was "approximately valid". However, at that time they had entropy data for only eleven compounds and these were based on heat capacity measurements down to only about 80 K. Using

TABLE 1. Observed and Observed-Calculated Values of Properties of Crystals at 90 K

Compound Name	Heat Capacity, C_s J K^{-1} mol^{-1} observed	obs.-calc.	Entropy, S J K^{-1} mol^{-1} observed	obs.-calc.	Enthalpy, $H - H_0$ J mol^{-1} observed	obs-calc.	Reference
Pentane	68.98	1.09	58.42	0.17	3100.	23.	[10]
Hexane	76.72	1.62	63.58	-0.03	3403.	45.	[11]
2-Methylpentane	75.48	1.92	65.41	0.63	3422.	87.	[11]
2,3-Dimethylbutane	71.70	-0.32	66.05	0.10	3290.	-21.	[11]
Methanol	40.75	2.23	32.89	0.81	1787.	15.	*
Ethanol	43.99	-1.68	39.42	0.45	2072.	-40.	*
1-Propanol	51.95	-0.93	44.27	-0.12	2345.	-48.	*
2-Propanol	50.40	-1.31	43.41	-1.56	2294.	-43.	*
1-Butanol	59.65	-0.45	48.10	-1.59	2595.	-79.	*
L-2-Butanol	57.64	-1.29	49.93	-0.40	2605.	-13.	*
2-Methyl-1-propanol	57.26	-1.29	50.03	-0.83	2605.	-45.	*
1-Pentanol	69.02	1.71	58.85	3.81	3118.	163.	[12]
1,2,3-Propanetriol	51.55	1.00	38.36	-0.19	2123.	30.	*
Dimethyl Ether	52.26	-0.64	45.38	-0.15	2386.	-17.	*
Diethyl Ether	68.80	1.59	59.96	0.66	3079.	-3.	*
Methyl Propyl Ether	66.10	-1.17	55.99	-1.79	2938.	-85.	*
Methyl Isopropyl Ether	66.33	0.23	59.70	1.28	3073	106.	*
Propanone	61.11	0.99	53.8	0.5	3146.	143.	*
2-Butanone	66.45	-0.88	61.69	1.59	3183.	-102.	*
2-Pentanone	75.63	-0.23	65.39	-1.28	3452.	-82.	[13]
3-Pentanone	77.30	0.12	68.51	0.64	3544.	41.	[13]
Pentanoic Acid	70.75	-4.63	57.88	-2.51	3110.	-148.	[14]
Butanedioic Acid	63.55	2.32	47.70	1.25	2670.	-243.	*
1,2-Epoxyethane	45.03	0.04	39.02	-3.61	2290.	53.	*
1,2-Epoxypropane	50.43	-0.60	52.62	3.99	2389.	77.	*
1,2-Epoxybutane	58.80	0.56	53.62	-0.37	2764.	21.	*
Furan	46.91	-1.41	50.49	2.74	2484.	27.	*
2-Methylfuran	55.77	1.41	51.00	-2.75	2655.	-27.	[15]
Tetrahydrofuran	54.21	5.91	47.76	-1.58	2791.	-298.	*

*Selected, this work.

a much larger set of data as a basis we have now investigated a group additivity procedure for estimating the values of S_{90} and $H_{90}- H_0$ for the type of compounds covered in this survey. This consists of

$$S_{90} = \Sigma\, g_i\, s_i \tag{9}$$

$$C_{s90} = \Sigma g_i\, c_i \tag{10}$$

$$H_{90} - H_0 = \Sigma\, g_i\, h_i\ . \tag{11}$$

In these equations g_i are the numbers of atomic groups of various types which are present in the molecule. Each group consists of a central polyvalent atom and its immediately bonded neighbors. These are the types of groups used by Benson [9] and co-workers to estimate various thermodynamic properties of fluids. The s_i, c_i, and h_i are the contributions of each type of group to the entropy, heat capacity, and enthalpy, respectively. Table 1 lists the experimental values of C_{s90}, S_{90}, and $H_{90} - H_0$ and the differences between values calculated from equations (9–11) and the experimental values for 29 organic oxygen compounds.

Table 2 lists the values of the parameters s_i, c_i and h_i obtained by a least squares fit of equations (9–11) to the data of table 1. These also include corrections for 3-, 5-, and 6-membered rings. The uncertainty intervals shown are the standard deviations in the parameters obtained from the least squares calculation.

Values in parentheses are contributions from groups present in only a single compound. These were calculated by subtracting the sum of the contributions from the other groups from the experimental values for the eight additional compounds listed at the end of the table.

Thus, for example, the entropy of 2-methyl-1-propanol at 90 K is calculated from the data in table 2 by

$C(H)_3C$	2×21.09	$= 42.18$
$C(H)_2(C)(O)$		6.89
$C(H)(C)_2(O)$		-8.20
$O(H)(C)$		10.99
Total		51.86 J K^{-1} mol^{-1}.

Values enclosed in brackets in table 2 were estimated by exploiting certain regularities and trends in the experimentally based values. For example, the replacement of one bonded atom by another has about the same effect in different groups having the same central atom. This is illustrated in the following series of substitutions.

TABLE 2. Group Contributions to Thermodynamic Properties of Crystals at 90 K

Group	Heat Capacity, c_i	Entropy, s_i	Enthalpy, h_i
	J K^{-1} mol^{-1}		J mol^{-1}
$C(H)_3(P)$*	23.12 ± 0.83	21.09 ± 0.96	$1117. \pm 40.$
$C(H)_2(C)_2$	7.21 ± 0.48	5.36 ± 0.55	$281. \pm 23.$
$C(H)(C)_3$	-10.24 ± 1.85	-9.20 ± 2.14	$-578. \pm 90.$
$C(H)_2(C)(O)$	7.15 ± 1.16	6.89 ± 1.35	$339. \pm 56.$
$C(H)(C)_2(O)$	-9.93 ± 1.60	-8.20 ± 1.85	$-553. \pm 78.$
$C(C)_3(O)$	(−29.67)[1]	(−25.36)[1]	(−1475.)[1]
$C(H)_2(O)_2$	(9.50)[2]	(7.72)[2]	(490.)[1]
$C(H)_2(C)(CO)$	8.53 ± 1.17	6.56 ± 1.5	$250. \pm 56.$
$C(H)(C)_2(CO)$	(−9.66)[3]	(−13.96)[3]	(−858.)[3]
$C(H)_3(COOH)$	(47.86)[4]	[38.90]	[2154.]
$C(H)_2(C)(COOH)$	30.62 ± 0.88	23.22 ± 1.2	$1298. \pm 43.$
$C(H)(C)(O)(COOH)$	(14.19)[5]	[9.1]	[463.]
$CO(C)_2$	13.86 ± 1.93	12.57 ± 2.3	$770. \pm 93.$
$CO(H)(C)$	(22.54)[6]	[18.0]	[1008.]
$O(H)(C)$	15.39 ± 1.21	10.99 ± 1.40	$656. \pm 59.$
$O(C)_2$	6.65 ± 2.35	3.36 ± 2.72	$162. \pm 114.$
$C(H)_3(COOC_2H_5)$	(72.2)[7]	[60.4]	[3312.]
3-member ring	24.03 ± 2.38	25.50 ± 2.74	$1389. \pm 115.$
5-member ring	12.93 ± 2.94	19.90 ± 2.40	$1047. \pm 143.$
6-member ring	(7.55)[8]		

*P represents C, O, or CO.

Values in parentheses ( ) were calculated from a single compound.

[1]2-methyl-2-propanol, [2]Dimethoxymethane, [3]3-Methyl-2-pentanone
[4]Ethanoic acid, [5]D-2-Hydroxypropanoic acid, [6]Butanal
[7]Ethyl ethanoate, [8]Dioxane

Values in brackets [ ] were estimated.

Replace (H) by (C)	change in c_i	s_i	h_i
$C(H)_3(C) \rightleftharpoons C(H)_2(C)_2$	-15.91	-15.73	-836
$C(H)_2(C)_2 \rightleftharpoons C(H)(C)_3$	-17.45	-14.56	-859
$C(H)_2(C)(O) \rightleftharpoons C(H)(C)_2(O)$	-17.08	-15.09	-892
$C(H)_3(COOH) \rightleftharpoons C(H)_2(C)(COOH)$	-17.24		

Replace (C) by (O)	c_i	s_i	h_i
$C(H)_2(C)_2 \rightleftharpoons C(H)_2(C)(O)$	-0.06	1.53	58
$C(H)(C)_3 \rightleftharpoons C(H)(C)_2(O)$	0.31	1.00	25
$C(H)_2(C)(O) \rightleftharpoons C(H)_2(O)_2$	2.05	0.83	151
$C(H)_2(C)(COOH) \rightleftharpoons C(H)_2(O)(COOH)$	6.70		

The change in c_i for the last substitution is a marked exception to the general trend. The estimates for the groups $C(H)_3(COOH)$, $C(H)_2(O)(COOH)$ and $C(H)_3(COOC_2H_5)$ in table 2 were based on substitution effects.

The ratios among contributions of a particular group to different properties also show some regularity. Thus the values of s_i/c_i for the same group all fall in the range of 0.70 to 0.90, except for $O(C)_2$, $C(H)(C)_2(CO)$ and the ring contributions. Similarly the values of h_i/c_i are in the range of 34 to 56. The entropy and enthalpy contributions for CO(H)(C) were estimated by multiplying the heat capacity contribution by 0.8 and 45, respectively.

Properties of the compounds 1,2–ethanediol, 1,2,3,4–butanetetrol, ethanoic acid, n–butanoic acid, D–2–hydroxypropanoic acid, butanal, and ethyl ethanoate at 90 K that were used as the basis for calculating the entropy and enthalpy at higher temperature were estimated in the following manner. Enthalpies were calculated by means of equations (5) and (11), using the group parameters from table 2. Likewise the entropy was calculated from equations (4), (8), and (9). The values of $H_{90} - H_0$ and S_0 that were used in the Tables of Thermodynamic Functions were obtained by averaging the values obtained from the different procedures. The group contribution values were given the highest weight. However, the weighting was determined by the basis of the group contribution values and by comparison of the heat capacity calculated from equation (10) with the observed value at 90 K.

Complete sets of group contribution values were not available for ethanedioic acid, cis– and trans–butenedioic acids, and 1,4–dioxane. Values of $H_{90} - H_0$ were calculated from equation (5) and values of S_{90} were calculated by averaging equations (4) and (8). Equations (4) and (8) did not differ by more than 3 J K^{-1} mol^{-1} for these compounds.

1.2.c. Estimation of Liquid Heat Capacity

Schiff [16] found that the product of the specific heat and the density at a fixed reduced temperature was nearly constant for a series of esters. Williams and Daniels [17] observed that the heat capacity per unit volume was approximately constant for many non-associated organic liquids when compared at the same temperature. The value of this property increased for liquids as the amount of intermolecular association increased.

A survey of modern data for about 50 organic liquids reveals that the heat capacity per unit volume for many hydrocarbons, chloro- and nitro- derivatives of hydrocarbons, and ethers is in the range of 1.41 to 1.64 J K^{-1} cm^{-3} at 25 °C. In most cases an increase in branching of the carbon skeleton decreases the heat capacity per unit volume. The formula,

$$C_s = 1.52 + 0.6A - 0.25K - 0.15E \text{ J K}^{-1}\text{ cm}^{-3}, \qquad (12)$$

reproduces the heat capacity of liquid organic oxygen compounds having one to six carbon atoms per molecule within about 0.1 J K^{-1} cm^{-3} at 25 °C. The symbols in equation (12) are the number of certain groups per molecule as shown below.

A	-OH groups
K	-CO- or -CHO groups
E	epoxy groups

The effect of a carboxyl group depends on the number of carbon atoms in the molecule. It ranges from about 1.1 J K^{-1} cm^{-3} for methanoic acid to about 0.4 J K^{-1} cm^{-3} for butanoic acid.

1.2.d. Transitions in Condensed Phases

The existence of a substance in more than one crystalline form is called polymorphism. It is common among organic compounds. The thermodynamically stable form at any given temperature and pressure is the one that has the lowest (most negative) Gibbs energy. When each of the crystalline modifications is stable over a certain range of temperature at crystal-gas equilibrium, they are said to be enantiotropic. The enantiotropic form which exists in equilibrium with the liquid is labeled c,I and those which exist at successively lower temperatures are labeled c,II, c,III, etc. Two adjacent enantiomers are in mutual equilibrium at a certain transition temperature.

If one crystalline form is stable while another is metastable at all temperatures, they are called monotropic forms. A metastable form is labeled c,m in the following tables. Figure 1 is a schematic diagram of the Gibbs energies of various condensed phase forms plotted as a function of temperature. The thermodynamically stable phases are identified by a continuous line, while the metastable forms are shown as dotted lines. Temperatures at the intersections of lines are transition temperatures. If the plot represents equilibrium between the condensed phases and the gas phase, the transition temperatures are triple points. T_{tp} is the c,I–liq–g triple point and T_{tt} is the c,II–c,I–g triple point. T_x in Figure 1 is the c–liq–g triple point of the

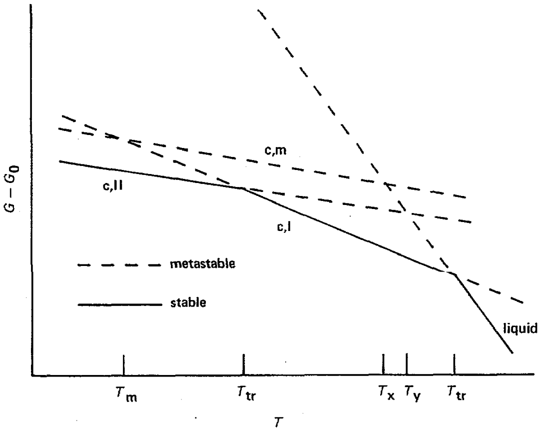

FIG. 1. Schematic diagram of Gibbs energy of several types of phases.

metastable form c,m and T_y is the c–liq–g triple point of c,II which is metastable at that temperature.

All the properties tabulated here refer to the condensed phase in equilibrium with the vapor. However, the differences between these properties and the values under a pressure of one atmosphere are negligible except for liquids at a temperature sufficiently high that the vapor pressure is greater than about two atmospheres.

When measured in a sealed calorimeter, as is normally done, the temperature of equilibrium between the crystal and liquid phases is the c–l–g triple point. Triple points are often measured with high accuracy during the course of determining sample purity in modern adiabatic calorimetry. See section 1.6.d for this procedure. A small amount of heat exchange gas, such as helium, may also be present in the calorimeter. This has a negligible effect on the triple point, however.

When measured in a container open to the air, the crystal-liquid equilibrium temperature is called the melting point (or freezing point). The melting point differs from the triple point because of the difference in pressure and because of the presence of dissolved air. If the vapor pressure of the sample is less than one atmosphere, the effect of pressure alone would raise the melting point by about 0.01 K above the triple point. However, the presence of air dissolved in the liquid phase lowers the melting point. The net effect is that the melting point is 0.01 to 0.05 K lower than the triple point. In tables headed "Reported Phase Transition Data for ..." melting points are identified by "mp" and c–l–g triple points by "tp". Selected values of c–l equilibrium temperatures are triple points. The presence of air has a negligible effect on solid-solid transition temperatures.

Isothermal transitions between distinct phases are accompanied by discontinuous changes in thermodynamic properties such as volume, enthalpy and entropy. These are first order transitions. Second order transitions are those in which volume, enthalpy, entropy and related quantities are continuous, but in which temperature derivatives such as coefficient of expansion and heat capacity are discontinuous. See Ubbelohde [18]. Glass transitions are of this type. Second order transitions also occur in crystals. In organic compounds they usually signal the onset of additional modes of molecular motion. Westrum and McCullough [19] give a detailed phenomenological classification of second order transitions.

It has been often observed that the heat capacity of a crystal starts increasing rapidly a few degrees below the triple point. In most cases this increase is caused by impurities or other artifacts of the measurement. An impurity will cause the sample to start melting below the triple point of the pure substance. Since a large absorption of heat accompanies fusion, even a small amount of melting has a large effect on the apparent heat capacity. Anomalies are sometimes observed in other properties just below the triple point. In some cases the pre–melting phenomena are characteristic of the pure substance. Partington [20], Sturtevant [21] and Ubbelohde [18] (Chap.12) have reviewed pre–melting phenomena.

In general we have not included large increases in heat capacity values obtained just below the triple point in the least squares calculation of parameters in the heat capacity equation. The extra heat absorption that they represent is usually included with the enthalpy of fusion (see section 1.6.c).

Some indications of anomalous properties of liquids just above the triple point have also been observed. These "pre–freezing" phenomena are associated with the formation of molecular clusters in the liquid [18]. Viscosity is the property which is most sensitive to such changes, but the occurrence of heat capacity minima has also been attributed to cluster formation. The following heat capacity minima were observed in the liquid phase among the compounds in this survey.

Compound	$T_{min} - T_{tp}$	100× $(C_{stp} - C_s(min))/C_{stp}$
Methanol	12.22	0.18
Propanone	21.2	1.63
Ethyl ethanoate	18.98	0.22
1,2–Epoxyethane	32.07	0.87
Tetrahydrofuran	14.40	0.47
1,4–Dioxane	4.03	0.10

Certain organic compounds form a special kind of crystal called a "plastic crystal". These were first recognized by Timmermans [22]. They have a glass-like appearance and are usually soft and tacky. Furthermore they have a high triple point and low entropy of fusion compared to normal crystals of similar compounds. An entropy of fusion equal to or less than 20 J K^{-1} mol^{-1} is considered indicative of a plastic crystal. Nearly all plastic crystals are formed by an enantiomorphic transition a few degrees below the melting point.

Plastic crystals are formed from substances whose molecules have tetrahedral, or other high order, symmetry. Timmermans called such molecules "globular". The lattice structure is usually cubic or hexagonal.

It is now generally accepted that the onset of relatively free rotation of molecules about their equilibrium lattice positions accounts for the transition which produces a plastic crystal. More accurately, the molecules readily switch back and forth among several equivalent, or nearly equivalent, orientations. The rotational disorder in the crystal explains the low entropy of fusion. Aston [23] and Ubbelohde [18] (p.136–143) reviewed properties of plastic crystals.

About 50 organic compounds have been suspected of forming plastic crystals. Four of these; methanol, 2–methyl–2–propanol, furan and tetrahydrofuran; are among the C_1 - C_4 organic oxygen compounds. Methanol is not completely typical of a plastic crystal, and Westrum and McCullough [19] have suggested that it may not belong to this class. Although tetrahydrofuran has the appropriate molecular symmetry, it does not exhibit the phase transition or low entropy of fusion characteristic of plastic crystals.

1.2.e. Properties of Optical Isomers

The following compounds have an asymmetric carbon atom and exist in optically active D- and L- forms: 2–butanol, 2–hydroxypropanoic acid, 1,2–epoxypropane and 1,2–epoxybutane. 1,2,3,4–butanetetrol and 2,3–dihydroxybutanoic acid have two like asymmetric carbon atoms and thus exist in the form of two diastereoisomers, an inactive meso isomer and optically active forms with D- and L- isomers.

The properties of a pair of enantiomers (D- and L- forms) differ only in the direction of rotation of polarized light. A racemic combination contains equal portions of both enantiomers and is not optically active. In the fluid states a racemic mixture is an ideal solution. Therefore the entropy of a racemic mixture in the fluid states is larger than that of either pure enantiomer by the amount R ln 2.

The physical properties of crystalline D–L mixtures differ from those of the pure enantiomers in several respects. Three types of D–L combinations are known (Eliel [24]).

Racemic Mixture. The enantiomers exist in two distinct crystalline phases. Their shapes are mirror images of each other and, in principle, they can be separated by examination. A racemic mixture melts lower than either pure isomer. Since the molecules are present in ordered lattices the entropy approaches zero at 0 K in accordance with the third law.

Racemic Solid Solution. Both isomers are mixed in the same crystal in a random or semi–random arrangement. The melting point and most other properties differ only slightly from those of the pure isomers. If the mixing is random the entropy is R ln 2 greater than that of either isomer. Racemic solid solutions often form glasses. The entropy does not approach zero at 0 K.

Racemic Compound. The two enantiomers exist in the same crystal in some ordered pattern. The melting point is generally higher than that of the pure enantiomers.The crystal meets the requirements of the third law.

Intermediate cases are known, and some racemic combinations may change from one type to another in different temperature ranges.

If sufficient thermal data exist to apply equation (25) to a DL combination and to either of the pure isomers then a racemic solid solution can be readily distinguished from either of the ordered DL forms. The entropy of the racemic liquid, calculated from (25) will be R ln 2 bigger than that of either pure isomer if the racemic solid is either a mixture or a racemic compound.

1.2.f. Properties of the Glass Phase

Several compounds included in this survey form a glass phase. The thermodynamic properties of glass phases are also given in the tables. When cooled sufficiently DL–2–butanol, 2–methyl–1–propanol, 1,2–propanediol, 1,2,3–propanetriol, and DL–hydroxybutanoic acid normally form a glass. In fact special techniques are required to crystallize these compounds. Methanol, 1–butanol, 1,2–ethanediol propanone, diethyl ether, and ethyl ethanoate normally crystallize at the melting point. However, a glass can be formed either by very rapid cooling of the liquid or by condensing the gas at low temperatures. Both crystal and glass forms of ethanol and 1–propanol can be produced.

As the temperature of a liquid is reduced below the melting point, a temperature is reached at which many physical properties undergo characteristic changes within a narrow range. Below this temperature the

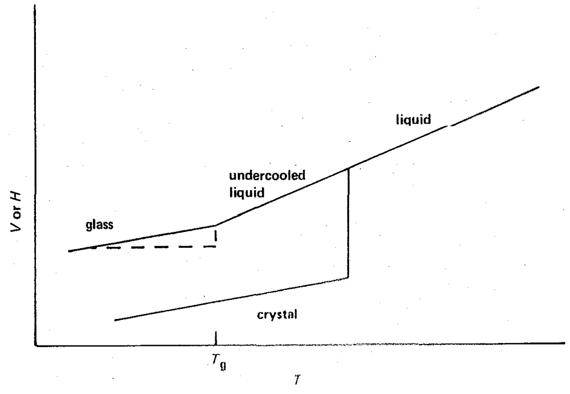

FIG. 2. Schematic diagram of enthalpy and volume in the vicinity of a glass transition.

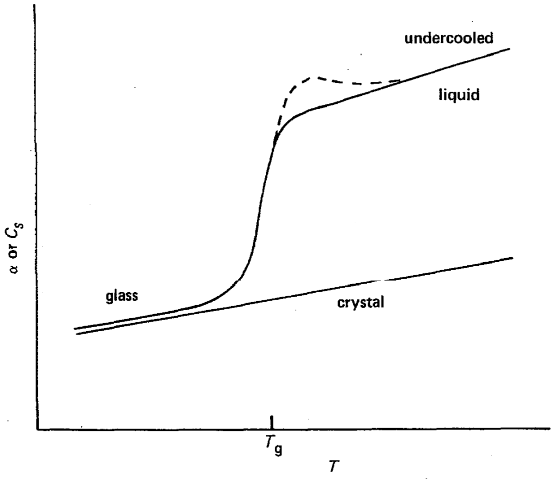

FIG. 3. Schematic diagram of heat capacity and coefficient of expansion in the vicinity of a glass transition.

substance exhibits typical glass-like behavior. This kind of glass transition has been observed in a wide variety of pure compounds and mixtures. These include oxides of elements of intermediate metallic properties, compounds containing oxy-anions of these elements, many kinds of organic compounds, and both inorganic and organic polymers.

The glass transition is a second order transition. Figure 2 shows the trends in H and V in the vicinity of this temperature and their relationship to the melting point. Under some conditions of measurement a small discontinuity may be observed in these properties, as shown by the dotted line. Figure 3 is the corresponding plot of α or C_s. Other equilibrium properties such as dielectric constant, refractive index, compressibility, bulk modulus and elastic modulus also change rapidly near the glass transition temperature. Ubbelohde [18] (Chap.16) has plotted observed values of a number of properties of 1,2,3-propanetriol in the vicinity of its glass transition temperature.

Transport properties also change rapidly at this temperature. Thermal conductivity decreases rapidly and both shear and bulk viscosity increase rapidly as the temperature is lowered through the glass transition region. Whereas the volume, coefficient of expansion, and heat capacity of a glass below T_g are similar to that of the crystal at the same temperature, the thermal conductivity of the glass is much less than that of the crystal. Relaxation properties such as dielectric relaxation, rotational diffusion, and mechanical energy loss change rapidly but in a complicated manner near T_g.

The characteristic changes of the glass transition occur over a range of temperature which may vary from around one to 20 degrees. Furthermore the range of rapid change is somewhat different for different properties. Even for the same property the transition region, as well as the functional dependence on temperature, depends somewhat on the heating or cooling rate, the time required to make a measurement, and the thermal history of the sample. Thermal history is especially important when heating a glass through the transition region. In general increasing the speed of a measurement increases the glass transition temperature.

The region from the glass transition to the c–l–g triple point is a region of instability. Spontaneous crystallization often occurs. It is difficult, or impossible, to maintain some compounds in the liquid state throughout this region. However, crystallization seldom, if ever, takes place below the glass transition temperature.

In recent years, the glass transition temperature is often measured by a differential thermal analysis (DTA) technique. This consists of recording the temperature of a sample, or of the difference between the sample and a reference substance, as the sample (or sample and reference) is heated or cooled at a steady rate through the transition region. The shape of the DTA curve is determined by the effective heat capacity of the sample and shows a characteristic break at T_g, although equilibrium usually is not attained in such experiments.

The average positions of the molecules in a liquid at equilibrium show some regularity. The regularity is most apparent in regions of the size of a few molecular diameters. The nature and extent of molecular distributions is a function of temperature. As a liquid cools below its freezing point there is no special change in the molecular distribution as long as no crystallization takes place. Even though the undercooled liquid is metastable relative to the crystal, it still achieves an internal equilibrium. As the temperature is lowered the time required to reach equilibrium increases. At some temperature this equals and then exceeds the time taken to measure a property. This is the glass transition temperature as observed for the property being measured. At lower temperatures the randomness at the glass transition becomes frozen in, and the molecular distribution no longer is characteristic of internal equilibrium. Below T_g the properties of a glass are primarily determined by short range molecular and atomic interactions (sometimes called kinetic contributions), but not the long range molecular orientations and distributions (sometimes called configurational contributions). Some investigators believe that if sufficient time were allowed to establish equilibrium no glass transition would be observed.

Older experimental evidence for the glass transition and theoretical interpretations of it were reviewed by Kauzman [25] and Davies and Jones [26]. These satisfactorily explain the qualitative aspects of the behavior of undercooled liquids. More recent studies have not significantly altered the basic concept of the glass transition (Ubbelohde[18]), but have been concerned with the quantitative explanation of the kinetics of processes that take place near T_g. Bondi [4] has described some of the newer correlations.

The purpose of the earlier measurements of the heat capacity of glasses at low temperatures was to determine if the third law of thermodynamics applied to glasses. It does appear that the heat capacity approaches zero at 0 K. This holds for the glass state of 1,2,3-propanetriol down to 1.5 K at least. However, some molecular disorder remains and the entropy does not become zero. The entropy of a glass at 0 K is the residual entropy. If the heat capacity of the liquid and of both glass and crystal are available to sufficiently low temperatures, the residual entropy can be calculated by

$$\begin{aligned}\Delta S_r &= S_0(\mathrm{gl}) - S_0(\mathrm{c}) \\ &= S_T(\mathrm{l}) - \int_0^T \frac{C_s(\mathrm{gl})}{T}\,\mathrm{d}T \ , \qquad (13)\end{aligned}$$

where the entropy of the liquid at some temperature, T, has been obtained by the usual third law procedure (equation(25)). In the tables of thermodynamic properties of glasses reported here, the entropy, enthalpy and Gibbs energy are given relative to the crystal at 0 K.

Goldstein [27, 28] has analyzed heat capacity data for several organic compounds in order to identify in detail the molecular phenomena responsible for the rapid increase in heat capacity, entropy, and other properties seen on heating a glass through the glass transition region. He considered four kinds of contributions to the observed changes. They are (1) the larger number of molecular configurations available to the undercooled liquid than to the glass (configurational effect), (2) secondary relaxational contributions (modes of internal molcular freedom which are not completely frozen in below T_g), (3) differences in vibrational frequencies between molecules in the undercooled and glass states, and (4) differences in anharmonicities between the two states. Very accurate heat capacity data are required for the liquid and for the glass phases which have been subjected to different thermal histories in order to resolve these contributions. The relative contributions vary among the six substances that he considered, but it appears probable that all four effects are significant.

Otsubo, Haseda, and Kanda [29] studied the effect of time required for a measurement on the apparent heat capacity of organic glasses. They concluded that the observed heat capacity is a sum of two contributions — the potential (configurational) energy and the kinetic energy contributions. The kinetic energy part attains equilibrium very quickly, but the potential energy part requires an increasing amount of time for equilibrium as the temperature is decreased below the glass transition temperature. Thus the rapid decrease in C_s below T_g, as well as the slight maximum sometimes seen above T_g are artifacts introduced by lack of equilibrium. Values of heat capacity measured below T_g reflect the kinetic contributions only. Thus there is little or no thermodynamic significance to the residual entropy calculated from such data. They predict that if the true equilibrium heat capacity was used the residual entropy of the glass would be zero, or very small, at 0 K.

1.3. Glossary of Symbols and Thermodynamic Formulae

Symbols for thermodynamic properties written without a superscript pertain to a condensed phase at a given temperature in a state of equilibrium with the gas. The superscript ° indicates a property in the standard state. The standard state of a condensed phase is the thermodynamically stable phase at a pressure of 101325.0 Pa (1 atm.). The difference in properties in the standard state and at equilibrium vapor pressure is generally negligible when the vapor pressure is below one atmosphere. When the vapor pressure is above one atmosphere, the standard state is a hypothetical state. A particular phase is identified by one of the following symbols written in parentheses after the property symbol.

c	crystal (different enantiomorphic forms are designated by I, II, etc.)
c,m	a metastable crystal
gl	glass
l	liquid
g	gas

Glossary of Symbols

Symbol	Name	Definition	S.I.Units
C_p	Heat capacity at constant pressure	$\left(\frac{\partial H}{\partial T}\right)_p$	J K^{-1} mol^{-1}
C_v	Heat capacity at constant volume	$\left(\frac{\partial U}{\partial T}\right)_p$	J K^{-1} mol^{-1}
C_s	Heat capacity at equilibrium vapor pressure	$T\frac{\mathrm{d}S}{\mathrm{d}T}$	J K^{-1} mol^{-1}
ΔC_s	Heat capacity change for melting	$C_s(\mathrm{l}) - C_s(\mathrm{c})$	J K^{-1} mol^{-1}
G	Gibbs energy (or Gibbs function)	$H - TS$	J mol^{-1}
$\frac{G - H_0}{T}$	no approved name		J K^{-1} mol^{-1}
I	Number of independent adjustable parameters in a least squares calculation		
H	Enthalpy	$U + PV$	J mol^{-1}
$H - H_0$	Enthalpy	$U + PV$	J mol^{-1}
ΔH_{tr}	Enthalpy (heat) of transition at T_{tr}	$H(\mathrm{c,I}) - H(\mathrm{c,II})$	J mol^{-1}
ΔH_{tp}	Enthalpy (heat) of fusion at T_{tp}	$H(\mathrm{l}) - H(\mathrm{c,I})$	J mol^{-1}

Glossary of Symbols, cont.

Symbol	Name	Definition	S.I.Units
ΔH_v	Enthalpy (heat) of vaporization	H(g) - H(l)	J mol^{-1}
M	Molecular weight		
N	Total number of data points used in a least squares calculation		
N_i	Number of data points in the i-th region		
P	Equilibrium vapor pressure		Pa
R	Gas constant	8.31441	J K^{-1} mol^{-1}
S	Entropy	Second law of thermodynamics	J K^{-1} mol^{-1}
ΔS_{tr}	Entropy of transition at T_{tr}	$\frac{\Delta H_{tr}}{T_{tr}}$	J K^{-1} mol^{-1}
T	Temperature	IPTS-68	K
T_{tr}	Transition temperature	Temperature of equilibrium between 2 phases	K
T_{tp}	Triple point	Temperature of equilibrium between c, l, and g	K
T_m	Melting point	Temperature of equilibrium between c and l in air at 1 atm.	K
U	Internal energy	First law of thermodynamics	J mol^{-1}
V	Volume		m^3
ΔV_v	Volume of vaporization	V(g) - V(l)	m^3
x_i	mole fraction of component i	$n_i / \Sigma n_i$	
α	Coefficient of expansion	$\left(\frac{\partial V}{\partial T}\right)_P$	K^{-1}
κ	Isothermal compressibility	$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$	pa^{-1}
w_i	Weighting factor for the i-th data point		

Relations among heat capacities

$$C_p - C_s + \alpha VT\frac{dP}{dT} = C_s + \alpha V\frac{\Delta H_v}{\Delta V_v} \tag{14}$$

$$\alpha V = \frac{dV}{dT} + \kappa V\frac{dP}{dT} \tag{15}$$

$$C_v = C_p - \frac{\alpha^2 VT}{\kappa} \tag{16}$$

$$C_p^\circ \simeq C_p + \alpha^2 TV(P - P^\circ) \tag{17}$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_P\right]TV. \tag{18}$$

Calculation of enthalpy

$$\frac{dH}{dT} = \left(\frac{\partial H}{\partial P}\right)_T \frac{dP}{dT} + \left(\frac{\partial H}{\partial T}\right) = C_s + V\frac{dP}{dT} \tag{19}$$

$$H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_s dT + \int_{P_1}^{P_2} V dP. \tag{20}$$

The term $V dP$ is negligible at pressure below about one atmosphere. For higher pressures, in the range covered by this report, the approximation $\int V dP \simeq VP$ is valid.

$$\begin{aligned} H_{T_2}(l) - H_0(c) = &\int_0^{T_{tr}} C_s(c, II)dT + \Delta H_{tr} \\ &+ \int_{T_{tr}}^{T_{tp}} C_s(c,I)dT + \Delta H_{tp} \\ &+ \int_{T_{tp}}^{T_2} C_s(l)dT + V(l)P \end{aligned} \tag{21}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V(1 - \alpha T) \tag{22}$$

$$H^\circ \simeq H + V(1 - \alpha T)(P^\circ - P). \tag{23}$$

Calculation of entropy

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} (C_s/T)dT \tag{24}$$

$$\begin{aligned} S_T = &\int_0^{T_{tr}} \frac{C_s(c,II)}{T} dT + \frac{\Delta H_{tr}}{T_{tr}} \\ &+ \int_{T_{tr}}^{T_{tp}} \frac{C_s(c,I)}{T} dT + \frac{\Delta H_{tp}}{T_{tp}} \\ &+ \int_{T_{tp}}^{T_T} \frac{C_s(l)}{T} dT \end{aligned} \tag{25}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\alpha \tag{26}$$

$$S^\circ \simeq S + V\alpha(P - P^\circ) \tag{27}$$

Calculation of Gibbs energy

$$\frac{G - H_0}{T} = \frac{H - H_0}{T} - S \tag{28}$$

$$\left(\frac{\partial\left(\frac{G - H_0}{T}\right)}{\partial P}\right)_T = \frac{V}{T} \tag{29}$$

$$\frac{G^\circ - H_0^\circ}{T} \simeq \frac{G - H_0^\circ}{T} + \frac{V(P^\circ - P)}{T}\ . \tag{30}$$

1.4. Units and Conversion Factors

Molecular weights were calculated from the following atomic weights as recommended by the IUPAC Commission on Atomic Weights [30].

C	12.011
H	1.0079
O	15.9994

TABLE 3. Units of Energy

to convert from	J	cal	to I.T. cal multiply by	cal_{15}	I.T. Btu
J	1	0.239006	0.238846	0.23892	0.00094782
cal	4.184	1	0.999331	0.99960	0.0039657
I.T.cal	4.1868	1.000669	1	1.00030	0.0039683
cal_{15}	4.1855	1.0004	0.9997	1	0.003967
I.T.Btu	1055.056	252.1644	251.9958	252.07	1

All numerical data reported in the tables are given in SI units. The pertinent ones are:

energy — joules; temperature — kelvins, International Practical Temperature Scale of 1968; and amount of substance — mole.

Factors for converting the values from the units given in the primary literature to SI units were taken from Tables 3 and 4.

Temperatures and thermodynamic properties reported in the tables are based on the International Practical Temperature Scale of 1968 (IPTS-68) [31]. The ice point, T_0, is taken to be 273.15 K. Whenever the original data were sufficiently accurate and the temperature scale sufficiently well defined, temperatures and heat capacities were converted to IPTS-68 before the least squares calculation of parameters in the smoothing equations. When the original data were based on IPTS-48 the conversion described by Douglas [32] was followed. In other cases the method of conversion was based on the author's description of his temperature scale. The data which were corrected to the new temperature scale are identified in tables headed "Sources of Heat Capacity Data."

TABLE 4. Units of Specific Energy

to convert from	$\mathrm{J\,kg^{-1}K^{-1}}$	$\mathrm{J\,g^{-1}K^{-1}}$	to $\mathrm{cal\,g^{-1}\,K^{-1}}$ multiply by	$\mathrm{I.T.cal\,g^{-1}K^{-1}}$	$\mathrm{I.T.Btu\,lb^{-1}R^{-1}}$
$\mathrm{J\,kg^{-1}\,K^{-1}}$	1	0.001	0.000239006	0.00023885	0.00023885
$\mathrm{J\,g^{-1}\,K^{-1}}$	1000.	1	0.239006	0.23885	0.23885
$\mathrm{cal\,g^{-1}\,K^{-1}}$	4184.	4.184	1	0.99933	0.99933
$\mathrm{I.T.cal\,g^{-1}\,K^{-1}}$	4186.8	4.1868	1.00067	1	1
$\mathrm{I.T.Btu\,lb^{-1}R^{-1}}$	4186.8	4.1868	1.00067	1	1

1.5 Correlation and Smoothing of Data

The recommended values of the thermodynamic properties reported in this survey were calculated from equations for the heat capacity as a function of temperature and certain auxiliary data, using the formulae of section 1.3. The parameters in the heat capacity equations were obtained by least squares fit of directly measured values. Smoothed data were used only when the raw data were not available. All values were converted to units of cal K^{-1} mol^{-1} for the calculation. Estimated values of entropy and enthalpy at 90 K (section 1.2.b) were used for those compounds for which measurements did not extend to lower temperatures.

Theory gives little practical guidance to the selection of a suitable function for heat capacity. Workers at the National Physical Laboratory in England have calculated smoothed values of heat capacity and derived functions by fitting the raw data to a series of Chebyshev polynomials. This procedure is described by Counsell, Lees, and Martin [12]. Westrum, Furukawa, and McCullough [33] have also discussed this problem. Although the use of orthogonal functions has certain computational advantages in a least squares calculation, values calculated from a series of Chebyshev polynomials should be the same as those calculated from a single polynomial of equivalent order which is obtained by a least squares fit to the same set of data. Because of its convenience for computation, flexibility, and simplicity we chose the direct polynomial in temperature as the smoothing function for heat capacity.

In a set of tables recently issued by the Engineering Sciences Data Unit [34] the heat capacities of liquid aliphatic alcohols in the range of C_1 to C_{16} were fit to the function,

$$C_s = b_1[1 + b_2(1 - T_r)^{-2/3} + b_3(1 - T_r)^{-1/3} + b_4(1 - T_r)^{1/3}]. \tag{31}$$

$$T_r = T/T_c$$

It was also stated that the parameters in this equation were correlated in terms of the molecular structures of the compounds. This relationship was not described, however.

In many cases an impractically large number of terms would be needed to fit the observed heat capacity data over the entire range of existence of a single phase, especially if the phase is a crystal or glass. Therefore the parameters were calculated for subsets of data, each covering a limited temperature range. Thus for the *i*–th region we have

$$C_s = a_i + b_iT + c_iT^2 + d_iT^3 + e_iT^4. \tag{32}$$

At boundaries between adjacent regions of the same phase, the calculation was constrained to attain continuity of C_s and dC_s/dT. The polynomial,

$$C_s = d_0T^3 + e_0T^4, \tag{33}$$

was used to fit data in the lowest temperature region when it extended down to 20 K or below. This makes the limiting value of C_s proportional to T^3 as it approaches zero. The T^4 term permits some deviation from this dependence at the high end of the region and helps achieve continuity with the next region. It was necessary to include a T^2 term only for the glass phase of 1,2,3-propanetriol. In some cases this procedure gave a systematic deviation between observed and calculated heat capacities in the temperature range of 10 to 40 K. This was especially pronounced for the glass phase of certain alcohols. See 1-propanol (Fig. 19), dl-2-butanol (Fig. 31), and 2-methyl-1-propanol (Fig. 40) for example.

According to equation (3) the parameter, d_0, in equation (33) equals $12rR\pi^4/5\Theta^3$. The Debye temperatures, Θ, calculated from most of the 23 compounds in this review which have sufficient low temperature data, lie in the range of about 200 to 260 K. The ratio, e_0/d_0, falls in the range of -0.020 to -0.029 for most of them. However, the values of Θ for methanol, 2-propanol, and 1,2,3-propanetriol and butanedioic acid range from 311 to 388 K. Data extend down to 3-5 K for three of these compounds. The value of e_0/d_0 is 0.25 for methanol and ranges from –0.09 to +0.07 for six others. It is not clear whether the values of d_0 and e_0 are related to the type of compound or whether they depend primarily on the accuracy and distribution of heat capacity data at the low temperature end.

A calorimeter measures the amount of heat absorbed by the sample when the temperature and pressure change from a initial state at T_1 and P_1 to a final state at T_2 and P_2. In a sealed calorimeter the sample consists of a condensed phase in equilibrium with a gas phase. An increase in temperature is accompanied by an increase in pressure and a consequent vaporization of some of the sample. Usually the vapor pressure is sufficiently low and the vapor volume sufficiently small that the heat absorbed by the vaporization of the sample can be ignored. If not, a correction for vaporization must be applied. If the temperature change is no more than a few degrees, the ratio $q/\Delta T$ is taken as the heat capacity, C_s. More rigorously, this quantity is the average heat capacity over the range of temperatures between T_1 and T_2.

$$\frac{q}{\Delta T} = \bar{C}_s = \frac{\int TdS}{\Delta T} = \frac{\int C_s dT}{\Delta T}. \tag{34}$$

The integrations are carried along the equilibrium P T path. If the gas phase pressure is too low to have an appreciable effect, then $TdS = dH$ and

$$\frac{q}{\Delta T} \simeq \frac{\int dH}{\Delta T} = \frac{\Delta H}{\Delta T} = \bar{C}_p. \tag{35}$$

If equation (32) represents the heat capacity from T_1

to T_2 then

$$\bar{C}_s = a_i + \frac{b_i(T_2 - T_1)}{2} + \frac{c_i\Delta^3 T}{3\Delta T} + \frac{d_i\Delta^4 T}{4\Delta T} + \frac{e_i\Delta^5 T}{5\Delta T}, \tag{36}$$

where $\Delta^n T = T_2^n - T_1^n$.

The difference between $\bar{C}_s$ and C_s is the curvature correction. If C_s is a linear function of temperature, $\bar{C}_s$ and C_s are identical. When T_1 and T_2 differ by no more than 3–4 degrees, the curvature correction is usually negligible.

In a measurement with a drop calorimeter the initial and final temperatures of the sample differ by 20 degrees or more. In this case the parameters in equation (32) must be calculated in a least squares fit of equation (36). Both C_s and $\bar{C}_s$ can be accommodated in the same calculation provided each type of heat capacity is associated with the appropriate set of independent variables.

The continuity constraints were introduced into the least squares calculations in the following way. Consider the following sets of parameters, each corresponding to a particular range of temperatures.

Temperature Range	*Equation*	
0 to T_0	$C_{s0} = d_0T^3 + e_0T^4$	(37)
T_0 to T_1	$C_{s1} = a_1 + b_1T + c_1T^2 + d_1T^3 + e_1T^4$	(38)
T_1 to T_2	$C_{s2} = a_2 + b_2T + c_2T^2 + d_2T^3 + e_2T^4$	(39)
T_2 to T_3	$C_{s3} = a_3 + b_3T + c_3T^2 + d_3T^3 + e_3T^4$	(40)

Equations (37–40) contain 17 independent parameters. However, if we impose the auxiliary conditions, $C_{si} = C_{sj}$ and $\mathrm{d}C_{si}/\mathrm{d}T = \mathrm{d}C_{sj}/\mathrm{d}T$ at each boundary, only 11 independent parameters remain. Each such auxiliary condition allows the calculation of one parameter from the others. If we eliminate d_0, e_0, d_2, e_2, d_3 and e_3 we have

$$d_0 = d_1 + 4a_1/T_0^3 + 3b_1/T_0^2 + 2c_1/T_0 \tag{41}$$

$$e_0 = e_1 - 3a_1/T_0^4 - 2b_1/T_0^3 - c_1T_0^2 \tag{42}$$

$$d_2 = d_1 + 4(a_1 - a_2)/T_1^3 + 3(b_1 - b_2)/T_1^2 + 2(c - c_2)/T_1 \tag{43}$$

$$e_2 = e_1 - 3(a_1 - a_2)/T_1^4 - 2(b_1 - b_2)/T_1^3 - (c - c_2)/T_1^2 \tag{44}$$

$$d_3 = d_2 + 4(a_2 - a_3)/T_2^3 + 3(b_2 - b_3)/T_2^2 + 2(c_2 - c_3)/T_2^2 \tag{45}$$

$$e_3 = e_2 - 3(a_2 - a_3)/T_2^4 - 2(b_2 - b_3)/T_2^3 - (c_2 - c_3)/T_2^2. \tag{46}$$

The substitution of (41–46) into (37–40) gives an equation for the heat capacity in terms of the remaining independent parameters.

$$C_s = a_1Z_1 + b_1Z_2 + c_1Z_3 + d_1Z_4 + e_1Z_5 + a_2Z_6 + b_2Z_7 + c_2Z_8 + a_3Z_9 + b_3Z_{10} + c_3Z_{11}. \tag{47}$$

In general the number of independent parameters, I, in equation (47) equals the total number of parameters in the set (37–40) minus two times the number of boundaries between regions. The values of Z_i are functions of T and are given, according to the temperature region, in table 5.

TABLE 5. Temperature Functions for the Z_i

	$T < T_0$	T_0 to T_1	T_1 to T_2	$T > T_2$
$Z_1 =$	$\mathrm{F}_4(T_{\mathrm{r}0})$	1	$\mathrm{F}_4(T_{\mathrm{r}1})$	$\mathrm{F}_4(T_{\mathrm{r}1})$
$Z_2 =$	$\mathrm{F}_1(T_{\mathrm{r}0})T$	T	$\mathrm{F}_1(T_{\mathrm{r}1})T$	$\mathrm{F}_1(T_{\mathrm{r}1})T$
$Z_3 =$	$\mathrm{F}_3(T_{\mathrm{r}0})T^2$	T^2	$\mathrm{F}_3(T_{\mathrm{r}1})T^2$	$\mathrm{F}_3(T_{\mathrm{r}1})\mathrm{T}^2$
$Z_4 =$	T^3	T^3	T^3	T^3
$Z_5 =$	T^4	T^4	T^4	T^4
$Z_6 =$	0	0	$[1 - \mathrm{F}_2(T_{\mathrm{r}1})]$	$[\mathrm{F}_2(T_{\mathrm{r}2}) - \mathrm{F}_2(T_{\mathrm{r}1})]$
$Z_7 =$	0	0	$[1 - \mathrm{F}_1(T_{\mathrm{r}1})]T$	$[\mathrm{F}_1(T_{\mathrm{r}2}) - \mathrm{F}_1(T_{\mathrm{r}1})]T$
$Z_8 =$	0	0	$[1 - \mathrm{F}_3T(_{\mathrm{r}1})]T^2$	$[\mathrm{F}_3T(_{\mathrm{r}2}) - \mathrm{F}_3(T(_{\mathrm{r}1})]T^2$
$Z_9 =$	0	0	0	$[1 - \mathrm{F}_2(T_{\mathrm{r}2})]$
$Z_{10} =$	0	0	0	$[1 - \mathrm{F}_1(T_{\mathrm{r}2})]T$
$Z_{11} =$	0	0	0	$[1 - \mathrm{F}_3(T_{\mathrm{r}2})]T^2$

where,

$$T_{\mathrm{r}0} = T/T_0,\ T_{\mathrm{r}1} = T/T_1,\ T_{\mathrm{r}2} = T/T_2$$

and,

$$\mathrm{F}_1(x) = (3 - 2x)x^2,\ \mathrm{F}_2(x) = (4 - 3x)x^3,\ \mathrm{F}_3(x) = (2 - x)x.$$

Similar functions can be written in terms of the variables of equation (36).

A weighting factor was assigned to each observed value of heat capacity used in the least squares calculation. Ideally these should be inversely proportional to the squares of the standard deviations for each point. Such data are not available, however, and the weighting factors were based on estimated uncertainties.

Special computer programs were written to convert the temperatures for the data points to the variables, Z_i, by means of the functions in table 5 and to carry out the multi-variable least squares calculation. These were run on an AMDAHL 470 V/6 computer. Some data sets were processed by a program written in FORTRAN IV and some by a program written in APL. Both programs used double precision arithmetic (1 byte exponent and 7 byte mantissa). The FORTRAN program used the Gauss elimination technique with pivoting of columns to solve the set of normal equations and the APL program used the primitive matrix division operator supplied by the IBM APL shared variable system.

In general the following procedure was used to calculate the parameters in equations (37–40) for a particular phase.

1) Select an initial set of heat capacity data, weighting factors, and boundary temperatures. The initial boundary temperatures were obtained by an examination of the heat capacity curve. The number of boundaries was determined by the range of temperature covered and by the general appearance of the curve.

2) Regress the data in terms of the variables of equation (47), and, if the data contains $\bar{C}_s$ values, the corresponding variables derived from equation (36).

The regression minimizes the sum

$$S = \sum_{j=1}^{N} w_j d_j^2 , \tag{48}$$

where

$$d_j = C_{sj}(\text{obs.}) - C_{sj}(\text{calc.}) \tag{49}$$

for the j-th data point. The weighting factors, w_j, were normalized so that

$$\sum_{j=1}^{N} w_j = N. \tag{50}$$

Initially, except for the 0-th region, only powers of T up to the third were used.

3) Repeat the regression calculation with revised boundary temperatures and weighting factors until the value of S in equation (48) appears to be minimized, and the deviations appear to be random. If a satisfactory fit is not obtained in this way either add more regions, or terms in T^4, or both. In a few cases it was also necessary to remove the constraint for dC_s/dT at a boundary near a glass transition temperature.

4) When a satisfactory fit is obtained calculate the dependent parameters from the independent ones by means of equations (41–46).

A combined calculation including one or more regions can only be applied to data for a single phase. Data for different phases are treated independently.

The results of the least squares calculation are summarized in tables headed "Parameters for Heat Capacity of ....".

Wherever heat capacity data are available for liquids at temperatures sufficiently high to make a distinction between C_s and C_p noticeable, values of C_p were calculated by means of equation (14). A separate least squares calculation was then made to fit these values. This calculation generally included the entire liquid region in order to attain continuity for the C_p values, even when C_p did not differ significantly from C_s except at the high end.

The values of heat capacities, C_s and C_p, in the final Tables of Thermodynamic Functions were calculated directly from the least squares parameters for each region using equations (37–40). The calculation of the other properties includes an integration from 0 (or the lowest available temperature) up to each tabulated temperature. Thus the result for any particular region depends on the parameters for the lower regions. The enthalpy for the i-th region is calculated by

$$H_{iT} - H_0 = h_i + a_i T + (1/2) b_i T^2 + (1/3) c_i T^3 + (1/4) d_i T^4 + (1/5) e_i T^5 + VP. \tag{51}$$

h_i is a constant for each region and is calculated from the parameters for the i-th region by

$$h_i = h_{i-1} + (a_{i-1} - a_i)T_i + (1/2)(b_{i-1} - b_i)T_i^2 + (1/3)(c_{i-1} - c_i)T_i^3 + (1/4)(d_{i-1} - d_i)T_i^4 + (1/5)(e_{i-1} - e_i)T_i^5 + \Delta H_t , \tag{52}$$

where T_i is the lower boundary for the i-th region and ΔH_t is the enthalpy of transition, if any, at T_i. For the lowest region, which extends to 0 K, $h_i = a_i = b_i = c_i = 0$. In a similar manner, the entropy of the compound in the i-th region is

$$S_i = s_i + a_i \ln T + b_i T + (1/2) c_i T^2 + (1/3) d_i T^3 + (1/4) e_i T^4 \tag{53}$$

in which

$$s_i = s_{i-1} + (a_{i-1} - a_i) \ln T_i + (b_{i-1} - b_i) T_i + (1/2)(c_{i-1} - c_i)T_i^2 + (1/3)(d_{i-1} - d_i)T_i^3 + (1/4)(e_{i-1} - e_i)T_i^4 + \Delta H_t/T_i \tag{54}$$

and $s_0 = 0$. Finally Gibbs energy is calculated by

$$\frac{G_{iT} - H_0}{T} = \frac{H_{iT} - H_0}{T} - S_{iT} . \tag{55}$$

1.6. Measurement of Properties

1.6.a. Sources of Low Temperature Heat Capacity Data

Techniques for measuring heat capacity at low temperature and the observations which led to the third law of thermodynamics were developed by Nernst during the period 1908 – 1912. These investigations were continued by Dewar in England, and at the Chemical Laboratory of the University of California during subsequent years.

The construction and operation of a low temperature calorimeter is a major project. Therefore most low temperature heat capacity data have been obtained at a few laboratories which have developed this capability. The primary sources of such data for the $C_1 - C_4$ organic oxygen compounds are listed in Table A. Studies published by Japanese investigators have been primarily concerned with glass phases. Those from USSR have been undertaken to determine the effect of isotope substitution on various physical properties.

The most prolific source of high quality thermodynamic data for organic oxygen compounds in recent decades has been the Division of Chemical Standards of the National Physical Laboratory in

TABLE A

Institution	Range of Publication Dates	Principal Investigators	References
Physical Chem. Inst. Univ. of Berlin	1910–1926	Nernst, Eucken, Simon, Lange	[35–37], [38], [39]
Univ. of California, Berkeley	1920–1949	Giauque, Latimer, Gibson, Parks, Kelley	[40], [41–43], [44–46]
Stanford University	1925–1956	Parks, Anderson, Huffman, Kelley	[47], [48–56]
Tohoku University	1926–1950	Kanda, Haseda, Mitsukuri, Hara	[57], [58], [59–61]
Dow Chemical Co., Midland Michigan	1963–1964	Oetting, Sinke	[62], [63], [64]
N. I. Labochevski Gorki State University	1962–1967	Rabinovich, Nikolaev	[65], [66], [127]
Osaka University	1967–1977	Haida, Suga, Seki Sugisaki	[92], [68], [69]
University of Michigan	1970–1971	Westrum, Carlson Vanderzee	[15], [70], [71]
National Physical Lab., Teddington, England	1963–1975	Andon, Counsell Martin	[12], [13], [72–74], [75], [76]

Teddington, England. During the period 1960–1979 they published a series of 49 papers on the "Thermodynamic Properties of Organic Oxygen Compounds". An additional 13 papers on the thermodynamic properties of this class of compounds brought the total to 62. They report data for 86 compounds, 22 of which are in the C_1 to C_4 carbon range. The properties include vapor pressure, heat of vaporization, vapor phase heat capacity, *PVT* relations in the gas phase, heats of combustion, and perfect gas properties, in addition to the low temperature thermal data. A bibliography of all their publications on the thermodynamic properties of organic compounds was issued in 1977 [77].

Several additional laboratories, listed below, have also supplied much low temperature heat capacity data for organic compounds. Only a few fall into the class covered by this summary, however. They are Pennsylvania State University [78, 79],The University of Chicago [80], Bartlesville Energy Technology Center (formerly U. S. Bureau of Mines) [81, 82], Rice University [83], and Johns Hopkins University [84]. At present few or no studies are in progress on organic oxygen compounds.

1.6.b. Types of Calorimeters

Sturtevant [21], Wilhoit [85], Ginnings [86], and Gmelin [87] have reviewed various types of calorimeters. Most measurements collected in this survey have been obtained with one of the following three general types of calorimeters.

Drop. The sample, usually contained in a sealed capsule, is equilibrated at some known initial temperature. It is then dropped into the calorimeter, which is initially at a temperature lower or higher than the sample. The sample plus calorimeter then reach a final equilibrium temperature. The heat added to or removed from the sample can then be calculated from a knowledge of the initial and final calorimeter temperatures and the effective heat capacity of the calorimeter. The calorimeter may consist of a solid block of material (usually copper or silver) and may have either the isoperibol or adiabatic type of jacket. This procedure is also called the method of mixtures. However, the designation, mixture calorimeter, will indicate that the sample is mixed directly with the water in the calorimeter. This type of calorimeter nearly always gives an average heat capacity over a considerable range of temperature. See section 1.5.

The Bunsen ice calorimeter is a special type of drop calorimeter in which the receptacle for the sample is surrounded by a mantle of ice in equilibrium with liquid water. If the initial temperature of the sample is above 0 °C the heat removed from the sample when it is placed in the calorimeter melts some of the ice. The amount melted is measured by observing the change in volume of the solid-liquid water system. The volume change is proportional to the heat evolved from the sample.

Essentially all measurements made before 1910, and many measurements made above room temperature after that time, used drop calorimeters. Nernst and Dewar also made some low temperature measurements with drop calorimeters in the period 1910–1913.

Isoperibol. The calorimeter, which contains the sample, an electric heater, and a thermometer, is surrounded by a jacket with its temperature held constant during the course of a given heat capacity measurement. A measured amount of heat is generated by the heater, and the corresponding rise in temperature of the calorimeter plus sample is measured. Corrections for exchange of thermal energy between calorimeter and jacket are applied. The effective thermal conductivity between calorimeter and jacket are determined in separate experiments. See Stout [88] for a detailed review of this technique.

Nernst introduced this type of calorimeter for low temperature heat capacity measurements in 1910. Originally the calorimeter was surrounded by a jacket filled with a refrigerant such as liquid air, but separated from it by an evacuated space. The heat leak correction was relatively large. Later improvements incorporated a thermal shield between calorimeter and jacket to reduce the rate of heat exchange. This type of calorimeter was also used by Parks and others at the University of California during the period 1920–1925. Additional refinements introduced by Giauque reduced the heat exchange still further.

Adiabatic. The calorimeter itself, and the method of measuring heat capacity is similar to that used for the isoperibol type. However, the temperature of the jacket is controlled to match the temperature of the calorimeter at all times. Ideally, no heat exchange occurs under these conditions. Westrum, Furukawa, and McCullough [33] and Stull, Westrum, and Sinke [5] have described this technique.

Williams and Daniels [17] described an early use of the adiabatic calorimeter to measure the specific heat of organic liquids at room temperature and above. They reported data for fifteen compounds, including several hydrocarbons and alcohols, along with a few miscellaneous types, at temperatures from around 30 to 80 °C. Later they published data[89] for three additional pure compounds and several concentrations each of ten mixtures. They kept the effect of vaporization of the sample small by allowing only a small vapor space. This technique represents a significant advance over measurements of this kind made in previous years. Unfortunately they reported their results for the pure liquids only in the form of graphs and linear or quadratic functions of temperature — not as directly measured values. They did list the observed heat capacities of the mixtures, however.

Both isoperibol and adiabatic type calorimeters are still used for low temperature measurements and both can produce data of high accuracy. The adiabatic type is superior for measuring enthalpy changes associated with slow transitions, for measuring sample purity, and for thermal conditioning of samples. The adiabatic type has been perfected and used extensively by Westrum (University of Michigan), Oetting and Stull (Dow Chemical Co.), Bartlesville Energy Technology Center, and the National Physical Laboratory.

1.6.c. Measurement of Enthalpies of Fusion

The procedure for the calorimetric measurement of enthalpy(heat) of fusion is very similar to the measurement of a heat capacity. If the initial temperature in such a measurement, T_1, is below the triple point and the final temperature, T_2, is above, then the total heat energy transferred to the sample is

$$q = \int_{T_1}^{T_{tp}} C_s(\mathrm{c})\mathrm{d}T + \Delta H_{tp} + \int_{T_{tp}}^{T_2} C_s(\mathrm{l})\mathrm{d}T . \tag{56}$$

The heat capacity of crystal and liquid are measured in separate experiments. The value of ΔH_{tp} calculated from equation (56) depends on the manner in which $C_s(\mathrm{c})$ and $C_s(\mathrm{l})$ are extrapolated to the triple point. If a large pre-melting effect is present, the value of ΔH_{tp} is very sensitive to the method of extrapolation. Berthelot and others at the end of the nineteenth century obtained enthalpies of fusion of some compounds from the difference between enthalpies of solution of the crystal and liquid phases in water.

The depression of the freezing point, $\Delta T = T_{\mathrm{m}} - T_{\mathrm{x}}$, which results from the addition of a second component to a pure substance is, for an ideal solution,

$$-\ln X_1 = A\Delta T\,(1 + B\Delta T + \ldots) , \tag{57}$$

where X_1 is the mole fraction of the compound whose melting point (or triple point) is T_{m}. T_{x} is the melting point of the mixture, and A and B are cryoscopic constants, given by

$$A = \Delta H_{tp}/RT_{\mathrm{m}}^2 \tag{58}$$

$$B = 1/T_{\mathrm{m}} - \Delta C_{tp}/2\Delta H_{tp} . \tag{59}$$

The derivation of equations (57–61) also assumes that the two components crystallize in separate phases.

For dilute solutions the term $B\Delta T$ is negligible compared to 1. For this condition, equation (57) can be converted to

$$\Delta T = K_{\mathrm{f}}\, m , \tag{60}$$

where m is the molality of the second component and

$$K_{\mathrm{f}} = M_1RT_m^{\,2}/1000\Delta H_{tp} . \tag{61}$$

Thus the enthalpy of fusion of a compound can also be obtained by measuring the freezing point depression as a function of the amount of a second substance added to the compound. This is the basis of the cryoscopic method. Substantial errors in the enthalpy of fusion measured in this way can be caused by small errors in measurement of freezing points, the presence of unknown amounts of additional impurities, deviations from the ideal solution, or formation of a compound or a solution in the solid phase.

1.6.d. Purity of Samples

In a sample which contains only a small amount of impurity, $-\ln X_1$ in equation (56) can be approximated by X_2. Furthermore if we assume that, during the melting of the sample, the impurity remains in the liquid phase, then its mole fraction, X_2, is X_2^*/F. X_2^* is the mole fraction in the total sample and F is the fraction of the sample in the liquid state. Equation (57) can then be approximated by

$$T_x = T_m - X_2^*/AF\,. \qquad (62)$$

Thus a plot of T_x versus 1/F gives a straight line whose slope is X_2^*/A and intercept is T_m (or T_{tp}) for the pure sample. Equation (62) is the basis for the calorimetric measurement of sample purity. A is calculated from the measured enthalpy of fusion and F is calculated from the amount of heat energy added during each stage of the melting process. This procedure also gives the triple point of the pure sample. Special calorimeters have been designed for purity determinations. The method gives the mole fraction of all impurities, provided the system conforms to the assumptions made in deriving equation (57), but does not identify the impurities.

The rapid increase in heat capacity often observed in crystals a few degrees below the triple point was discussed in section 1.2.c. Some authors have calculated the amount of impurity in their sample from this excess heat capacity. However, it requires the careful measurement of heat capacity in this region, and the calculation is based on the assumption that it is due to a partial melting of the crystal and is not an inherent property of the pure substance.

In recent years the sample purity has also been determined by gas chromatography. This method detects only certain kinds of impurities, depending on the experimental conditions. Great care is required to obtain quantitatively meaningful results from this method.

Water is an ubiquitous impurity in organic compounds. If an appreciable amount is present in a solid sample as ice at low temperatures its presence is revealed by an apparent hump in the heat capacity curve near 273 K.

1.6.e. Estimation of Errors

Errors in the tabulated values of heat capacity are introduced by experimental errors and by deficiencies in the calculation and smoothing procedure. The assumption that an observed value of $q/\Delta T$ equals the true heat capacity produces an error which, for a given δT, increases as the curvature of the heat capacity function increases. Failure of the polynomial function to represent adequately the true heat capacity also introduces an error into the calculated value. The magnitude of this effect depends not only on the limitation of the polynomial itself but also on the choice of data points used in the calculation, the choice of weighting factors, the choice of boundaries between regions, the distribution of data points with respect to temperature, and the details of the computational procedure. An attempt to control these factors in a manner which caused the deviations between observed and calculated values to be a random function of temperature was made. The goal was not achieved in every case, however.

Errors of measurement may be classified either as calorimetric errors or as sample definition errors. Sample definition errors are caused by errors in measurement in the quantity of sample in the calorimeter, impurities in the sample, evaporation of the sample during a measurement, and lack of equilibrium in the state of the sample. The effect of sample evaporation is roughly proportional to P/T^2. Departure from equilibrium is usually greatest near a glass transition. Pre-melting phenomena cause errors in heat capacity over a range of temperatures extending several degrees below the melting point. Sample definition errors, other than lack of equilibrium, are primarily systematic in nature.

Calorimetric errors result from errors in the measurement of temperature and energy. Systematic effects are caused by errors in the calibration of the thermometer, electrical measuring instruments, and the timer, and by errors in establishing the energy equivalent of the calorimeter. Errors in the measurement of the difference between initial and final temperatures are much more significant for calorimetry than are errors in the measurement of the absolute temperature alone. Lack of control of, or proper evaluation of, the heat exchange between the calorimeter and its surroundings gives rise to both systematic and random errors. All these factors are functions of temperature. In most instances the principal source of calorimetric error at low temperatures (especially below 80 K) is in measurement of temperature changes. As the temperature increases the error in heat exchange correction becomes larger and eventually dominates.

Errors may also arise in converting data as reported to the units and conditions adopted for a tabulation. Conversion of temperature scales is troublesome, especially for older data. Errors in auxiliary data may affect the conversion of C_s to C_p.

Errors in the tabulated values of heat capacity are propagated to values of enthalpy, entropy and Gibbs energy. Since these properties are calculated by integrating the heat capacity, some cancellation will occur if the heat capacity contains both positive and negative errors. In fact the integration usually eliminates a large portion of the random component of error, but only a small portion of the systematic component. Values of enthalpy and entropy are also subject to the accuracy of estimation of S and $H - H_0$ at the lowest observed temperature and to errors in the measurement of enthalpy changes and temperatures of phase transitions.

The root mean square deviation for heat capacity, as defined by equation (65), is given for each temperature region for each compound in tables titled "Parameters for Heat Capacity of ..." Both the root mean square deviation and the standard deviation, defined by equation (66), are also given for the combined calculation consisting of several regions. The algebraic average deviation, defined by equation (64), is also given for each region. This indicates the bias in the calculated values relative to the observed values for the region.

The root mean square deviation and standard deviation are often taken as a measure of random errors in a set of experimental data. However, when the quantity measured is a function of some independent variable these deviations are also affected by the fidelity with which the smoothing function fits to true values. Some indication of the size of the systematic errors may be gained by comparison of data from different investigators in the same temperature range. Generally, however, the best that can be done is to set an upper limit to the size of the systematic errors based upon a knowledge of those factors which could cause a systematic error.

In spite of the difficulty in assessing errors in measured data, it is obvious that some data are more accurate than others. To impart some indication of these differences, estimated uncertainties are given for the tabulated values in tables titled "Parameters for the Heat Capacity of ..." It is intended that these estimates reflect the combined effect of all sources of error in the values reported in tables titled "Thermodynamic Functions of ..." The uncertainties in heat capacity result from a consideration of experimental uncertainties reported by the investigator (if any), a general assessment of the accuracy of measurement and state of the art at the time of publication, the extent of agreement among different sources, the statistical results from the least squares calculation, the manner in which the data are distributed with respect to temperature, and the existence of special conditions such as glass transitions, pre-melting, and time dependent phenomena. An average, or representative, uncertainty is assigned to the heat capacity for each temperature region listed in the tables. It should be noted that, in some cases, the uncertainties may fluctuate appreciably even within a single region.

The assumption is made that the uncertainty in the change in enthalpy over a single region is given by $\delta C_i \Delta T_i$, where δC_i is the assigned uncertainty in heat capacity for that region, and ΔT_i is the corresponding temperature change. The total uncertainty in $H - H_0$ at the upper limit for a given region is then

$$(\delta H)^2 = \sum_i (\delta H_i)^2 . \qquad (63)$$

The terms in the summation include the uncertainties for each of the lower temperature regions and the uncertainties in the enthalpies of lower temperature phase transitions. Uncertainties in entropy were calculated in a similar manner, except that, for a single region, $\delta S_i = \delta C_i \ln(T_2/T_1)$. The uncertainty in Gibbs energy for a region is obtained by $(\delta H_i/\mathrm{T}) - \delta S_i$, and no uncertainty is attributed to the change in Gibbs energy for a phase transition.

The number of significant figures used for property values in tables titled "Thermodynamic Functions of ..." reflect these uncertainties. Roughly speaking one sigificant digit beyond position of last uncertainty is retained, except that two additional figures are retained for enthalpy. The exact cut-off point for enthalpy and entropy depends to some extent on temperature.

The number of significant digits retained for the values of the parameters in the heat capacity equations is also determined by the estimated uncertainties. The rule used is that one unit in the last digit retained times T_2^n (T_2 is the upper temperature for the region and n is the corresponding exponent for the terms in equations (37–40)) is less than (approximately 0.1 of) the estimated uncertainty in heat capacity for that region.

1.7. Other Compilations

Table 6 identifies those major compilations which contain heat capacity data for liquid and solid organic compounds of the type covered in this review. The first edition of the Landolt-Bornstein tables and their various supplements [90–93] tabulate the direct experimental results published in the earlier literature. The data in the International Critical Tables [94] are based on about the same sources of data as the Landolt-Bornstein tables and its first two supplements. They list the observed heat capacity values at various temperatures, or the average values over a range of temperatures. For some compounds the constants in a linear function of temperature are given.

In the more recent Landolt-Bornstein tables [95] smoothed values of heat capacity for liquid and solid phases are tabulated at nine standard temperatures from 20 to 298.15 K. Volume 6 of the Thermophysical Properties Research Center compilation [96] tabulates heat capacity for the liquid and gas phases. They are presented in the form of parameters in the polynomial function (similar to equation 31) obtained by a least squares fit. Tables of smoothed heat capacity values calculated from the polynomials (in units of Btu F^{-1} lb^{-1}) are given for the saturated liquid and the perfect gas. It also includes deviation plots which compare observed and calculated values. The supplement to this volume [97] lists the directly measured values of heat capacity converted to units of $\mathrm{kJ\ K^{-1}\ kg^{-1}}$.

The handbook by Raznjevic [98] lists heat capacity values for liquids at multiples of 10° on the Celsius scale. Evidently these have been smoothed or interpolated from the reported values, but no explanation of this procedure is given.

TABLE 6. Compilations which Report Heat Capacity Data for Organic Compounds

Abbreviated Name	Date of Publication	Reference
Landolt-Bornstein Tables	1923	[90]
Landolt-Bornstein Tables, first supplement	1927	[91]
International Critical Tables	1929	[94]
Landolt-Bornstein Tables, second suppl.	1931	[92]
Landolt-Bornstein Tables, third suppl.	1936	[93]
Landolt-Bornstein Tables, sixth edition	1961	[95]
N.B.S. Technical Note 270-3	1968	[327]
Thermophys. Prop. Research Center, vol 6.	1970	[96]
Thermophys. Prop. Research Center, suppl.	1976	[97]
Raznjevic, Handbook	1976	[98]
ESDU, Data Item No. 76012	1976	[99]
ESDU, Data Item No. 79028	1979	[34]

The Engineering Sciences Data Unit in England has issued an extensive set of tables on the thermodynamic properties of 2-propanol in the liquid and real gas phases [99]. They cover the range from room temperature to the critical point and include properties along the liquid-gas saturation line as well as in the single phase regions at various temperatures and pressures. Recently ESDU has published a collection of tables of heat capacity and enthalpy of liquid aliphatic alcohols in the carbon range of C_1 to C_{26}. The tabulated values were calculated by means of equation (31).

All these compilations except [98] and [327] cite the original sources of data used in the tables.

Table 7 identifies those compounds, from the present

TABLE 7. Substance Guide to Tables of Compiled Heat Capacity Values

Methanol	(273–334)[90], (89–293)[91], (273–313)[94], (157–331)[92], (283–403)[93], (20–298)[95] (298)[327], (273–323)[98], (177–389)[96], (180–390)[34]
Ethanol	(183–433)[90], (87–303)[91], (83–423)[94], (18–298)[92], (86–403)[93], (20–298)[95] (298)[327], (173–433)[98], (166–400)[96], (160–390)[34]
1–Propanol	(252–363)[90], (73–323)[94], (88–275)[92], (77–275)[93], (20–298)[95], (293)[98] (152–274)[97], (150–370)[34]
2–Propanol	(71–303)[91], (73–323)[94], (20–293)[92], (298)[93], (298)[95], (188–303)[97], (270–508)[99] (190–330)[34]
1–Butanol	(293–387)[90], (183–303)[91], (197–382)[94], (298)[93], (100–298),[95], (195–387)[98] (195–303)[97], (190–350)[34]
2–Butanol	(160–320)[34]
2–Methyl–1–propanol	(253–358)[90], (173–273)[94], (298)[95], (283–358)[98], (278–319)[97], (170–330)[34]
2–Methyl–2–propanol	(252–298)[90], (87–295)[91], (269)[94], (100–250)[95], (300–340)[34]
1,2–Ethanediol	(88–293)[91], (83–293)[94], (289–251)[93], (100–200)[95], (293–373)[98], (266–466)[96] (298)[327]
1,2–Propanediol	(250–412)[90], (91–276)[92], (253–453)[97]
1,2,3–Propanetriol	(19–323)[90], (11–299)[91], (12–373)[94], (70–299)[92], (273–293)[98], (283–510)[96]
1,2,3,4–Butanetetrol	(293–373)[90], (87–373)[91], (333)[94], (279–284)[92], (303–423)[93], (100–298)[95]
Dimethyl ether	(20–298)[95], (153–293)[97]
Diethyl ether	(183–453)[90], (294–286)[91], (303–453)[94], (76–320)[92], (80–255)[93], (298)[95] (173–293)[98], (166–300)[96]
Propanone	(293–322)[90], (70–313)[91], (63–353)[94], (18–297)[92], (273–319)[93], (20–298)[95] (223–323)[98], (177–322)[96]
Butanone	(293–351)[94], (297)[93], (80–298)[95], (193–373)[97]
Butanal	(80–298)[95]
Methanoic acid	(276–423)[90], (251–373)[94], (71–288)[93], (20–298)[95], (298)[327], (293)[98]
Ethanoic acid	(274–384)[90], (88–293)[91], (273–353)[94], (287–353)[93], (20–298)[95], (298)[327] (295–402)[97], (298)[98]
Propanoic acid	(299–409)[90], (240–410),[94], (289–373)[93], (298)[95], (293)[98]
Butanoic acid	(297–370)[90], (89–370)[91], (273–373)[94], (100–298)[95]
Ethanedioic acid anhydrous	(88–320)[90], (73–373)[94], (100–298)[95], (298)[327]
Ethanedioic acid,hydrate	(88–323)[90]
Butanedioic acid	(273–433)[94], (93–290)[92], (100–298)[95]
trans–Butenedioic acid	(91–297)[92], (100–298)[95]
cis–Butenedioic acid	(91–294)[92], (100–298)[95]
2–Hydroxypropanoic acid	(273–293)[90], (80–298)[95]
2,3–Dihydroxybutanedioic acid, hydrate	(138–323)[90], (123–323)[94]
2,3–Dihydroxybutandioic acid, anhydrous	(294–323)[90]
Ethyl ethanoate	(293)[90], (293)[94], (92–293)[93], (100–298)[95], (298–303)[97]
1,2–Epoxyethane	(20–298)[95], (298)[327]
Furan	(20–298)[95]
1,4–Dioxane	(296)[92], (92–257)[93], (100–298)[95]

review, whose heat capacity is given in the compilations from table 6. The numbers in parenthesis give the temperature range in K covered by the published table and the numbers in brackets are the identification numbers of the references in the bibliography.

1.8. Explanation of Figures and Tables

In the remaining sections data for each compound are presented in four types of tables. Their titles and contents are listed below. Sources of Heat Capacity Data for ....

Col. 1. Names of authors of the original report
Col. 2. Year of publication
Col. 3. Temperature range (in K) of measurement for each physical state (see sect. 1.3 for symbols)
Col. 4. Type of calorimeter used for the measurement (see sect. 1.6.b)
Col. 5. Type of measurement
  C - heat capacity (small temperature interval)
  H - enthalpy change (large temperature interval)
Col. 6. A brief description of the source and/or method of purification and purity of sample if reported.
  Superscript c - purity determined by thermal analysis (see sect. 1.6.d)
  Superscript g - purity determined by gas chromatography
Col. 7. Number of Points. The number of data points used in the least squares calculation of the parameters
Col. 8. Temp. Scale.
  "no" - no temperature scale corrections were applied to the data before being used in the least squares fit
  "corr" - data were converted to IPTS-68 before use (see sect. 1.4)
  "IPTS-68" - data reported in original sources in terms of IPTS-68
Col. 9. References. Identification numbers of sources in Reference List

Reported Phase Transition Data for ...

Col. 1. Names of authors in the original report
Col. 2. Date of publication
Col. 3. Initial and final states for the transition (see sect. 1.3 for definition of symbols), "glass" means a glass transition as described in section 1.2.f.
Col. 4. Reported transition temperature (in K), corrected to IPTS-68
Col. 5. For a phase transition (see sect. 1.2.d)
  mp - melting point
  tp - g-l-c or g-c-c triple point

  For a glass transition the method of measurement is identified by
  hc - heat capacity
  ce - coefficient of expansion
  vc - viscosity
  sp - softening point
  ml - mechanical loss
  dt - DTA curve
Col. 6. Enthalpy change for the reported transition
  c - measured by a calorimeter
  t - calculated from a measured cryoscopic constant (see sect. 1.6.c)
Col. 7. References. Identification numbers in List of References

Parameters for Heat Capacity of ...

The method of calculation is described in section 1.5. Each vertical column in these tables gives the data for one temperature region. When more than one region is included in a single least squares calculation, certain additional data for the combined calculation is given in a column following those for the individual regions. The information given in each row of this table is described below. Phase: Identifies the phase existing in each region

Data Points

Number: The number of data points used in the least squares calculation for each region. The total number of data points is given in the summary column, and, in parentheses, the number of independent parameters.

Temp./K: The range of temperature included by the data points for each region, and, in the summary column, for the combined set.

Parameters for: Identifies fit to C_s or C_p data Temp./K. The range of temperature for each region, and, in the summary column, the range of validity for the combined parameters.

$a_i,\ldots,e_i$: The values of the parameters in equations (37–40). The units are J $K^{(n+1)}$ mol^{-1}, $n = 0-4$.

Deviations

Average, *d*: The average deviation of observed from calculated heat capacities for each region separately,

$$\bar{d}_i = \frac{\Sigma\, w_j d_j}{N_i} \qquad (64)$$

and, in the summary column, for the combined data set.

R.M.S.,r(σ): The root mean square deviation for each region separately

$$\bar{r}_i = \sqrt{\frac{\Sigma w_j d_j^2}{N_i}} \qquad (65)$$

and, in the summary column, the combined root mean square deviation, and, in parentheses, the standard deviation for the combined calculation.

$$\sigma_i = \sqrt{\frac{\Sigma w_j d_j^2}{N-I}} \qquad (66)$$

is number of independent parameters.

Estimated Uncertainty in the Tabulated Values (same units as tabulated values)

$\delta(C)$: Estimated uncertainty in C_s for each region

$\delta(H\text{–}H_0)$: Estimated uncertainty in $H - H_0$ for each region

$\delta(S)$: Estimated uncertainty in S for each region

$\delta(G\text{–}H_0)/T$: Estimated uncertainty in $(G - H_0)/T$ for each region

Thermodynamic Functions of...

These tables list the smoothed values of properties calculated from the parameters in the previous types of tables using equations (50) - (54) of section 1.5. Symbols for column headings are defined in section 1.3. H_0 refers to the crystal at 0 K. The entropy of the crystal at 0 K is taken to be 0.

The figures given for each individual compound are deviation plots showing values of the observed minus the calculated heat capacities (in units of cal K^{-1} mol^{-1}) for all the points used in the least squares calculations. Some representative points not used in the least squares fit are also included in many of the figures. Values of $\bar{C}_s$ obtained from drop calorimeters are also plotted at a position corresponding to the average temperature of the measurement. In such cases a horizontal line whose limits correspond to the lower and upper temperatures of the measurement is drawn through the point. Some points which lie outside the range of the plot are also shown accompanied by an arrow and the numerical value of C_s(obs.) - C_s(calc.). Different symbols are used for data from different sources of data. These are identified by a list of reference numbers on each figure.

TABLE 8. Sources of Heat Capacity Data for Methanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Andrews	1848	l(298)	drop	H	dist.,dried over $CaCl_2$			[104]
von Reis	1881	l(289–336)	drop	H	not stated			[105]
Bose & Mueller	1907	l(276–315)	drop	H	not stated			[106]
Walden	1907	l(291–293)	mixture	C	not stated			[107]
Doroshevskii	1909	l(291–373)	drop	H				[108]
Parks	1925	c(89–152), l(188–290)	isoperibol	C	reagent sample,dist.over CaO and Na			[48]
Maass & Waldbauer	1925	c(90–169), l(183–195)	drop	H	free from HCHO and CH_3COCH_3			[109]
Drucker & Weissbach	1925	l(293)	isoperibol	C	not stated			[110]
Kelley	1929	c(19–168), l(181–292)	isoperibol	H	reagent sample,stand over CaO 2 weeks,fract.dist.several times			[44]
Mitsukuri & Hara	1929	l(190–265)	isoperibol	H	not stated			[61]
Fiock,Ginnings & Holton	1931	l(313–383)	isoperibol	C	$CHCl_3$ free,dist.in CO_2 atm. de-gas by boiling in vac.	8	corr	[111]
Ahlberg,Blanchard & Lundberg	1937	c(4–28)	isoperibol	C	E.I.DuPont de Nemours sample 99.7 mol% est.			[84]
Philip	1939	l(298)	not stated	C	commercial sample,dist.			[112]
Staveley & Gupta	1949	c(90–150), l(180–279)	adiabatic	C	analytical grade sample, dried and dist.			[100]
Hough, Mason & Sage	1950	l(313–363)	isoperibol	C	not stated			[113]
Swietoslawski & Zielenkiewicz	1960	l(293–329)	drop	H	not stated			[114]
Katayama	1962	l						[115]
Sugisaki, Suga & Seki	1967	c(20–120), gl(20–120)	adiabatic	C	not stated			[68]
Sugisaki, Suga & Seki	1968	c(22–112), gl(22–106)	adiabatic	C	dried,dist.in vac.	34	corr	[69]
Paz Andrade, Paz Fernandez & Rechacho	1970	l(313)	Calvet	C				[116]
Carlson & Westrum	1971	c(5–175), l(180–325)	adiabatic	C	specially purified sample from E.I.duPont de Nemours,then redistilled. sample I 99.98^c mol% sample II 99.88^c mol%	111	corr	[70]
Deshpande & Bhatgadde	1971	l(295–315)	adiabatic	C	purified by distillation			[117]

TABLE 9. Reported Phase Transition Data for Methanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Keyes, Townshend & Young	1922	c,I$\rightleftharpoons$l	174.63	mp			[118]
Parks	1925	c,II$\rightleftharpoons$c,I	161.06	tp	590.	c	[48]
		c,I$\rightleftharpoons$l	175.27	tp	3175.	c	
Maass & Waldbauer	1925	c,I$\rightleftharpoons$l	176.2	mp	2201.	t	[109]
Mitsukuri & Hara	1926	c,I$\rightleftharpoons$l	177.40	mp	2510.	t	[59]
Kelley	1929	c,II$\rightleftharpoons$c,I	157.36	tp	645.6	c	[44]
		c,I$\rightleftharpoons$l	175.23	tp	3163.	c	
Timmermans & Hennaut-Roland	1930	c,I$\rightleftharpoons$l	176.17	mp			[119]
Smyth & McNeight	1936	c,II$\rightleftharpoons$c,I	159.9	mp			[101]
		c,I$\rightleftharpoons$l	175.4	mp			
Roper	1938	c,I$\rightleftharpoons$l	175.49	mp			[120]
McKenna, Tartar & Lingafelter	1949	c,I$\rightleftharpoons$l	175.15	mp			[121]
Staveley & Gupta	1949	c,II$\rightleftharpoons$c,I	157.76	mp	711.	c	[100]
		c,I$\rightleftharpoons$l	175.38	mp	3160.	c	
Davidson	1957	c,II$\rightleftharpoons$c,I	169.56	mp			[102]
Faucher & Kolske	1966	glass	110.	ml			[124]
Sugisaki, Suga & Seki	1967	glass	102.	hc			[68]
Sugisaki, Suga & Seki	1968	glass	203.	hc			[69]
Carlson & Westrum	1971	c,II$\rightleftharpoons$c,I	157.35	tp	636.0	c	[70]
		c,I$\rightleftharpoons$l	175.61	tp	3215.	c	
Lesikar	1975	glass	102.6	dt			[123]
Lesikar	1975	glass	104.2	dt			[124]
Angell, Sare & Sare	1978	glass	103.	dt			[125]
SELECTED VALUES		c,II$\rightleftharpoons$c,I	157.35 ± 0.05		636.0 ± 4		
		c,I$\rightleftharpoons$l	175.61 ± 0.05		3215. ± 8		

2. Methanol (Methyl Alcohol)

Published values of heat capacity and transition data for methanol are summarized in Tables 8 and 9. Although a fairly extensive literature, starting in 1848, exists for the thermodynamic properties of methanol, the selected values for the crystal and liquid phases up to about 320 K were taken from Carlson and Westrum [70]. The existence of a crystal phase transition near 157 K has been recognized for some time [44, 48, 70, 100–103]. The transition was poorly characterized in earlier studies and sometimes was considered to be a second-order type transition. Tauer and Lipscombe [103] determined the crystal structures of the two forms by X-ray diffraction and concluded that the low temperature form (monoclinic) had a regular lattice structure and that the entropy should be zero at 0 K. The high temperature form is orthorhombic.

The careful measurements of Carlson and Westrum clearly show that the transition is first order and that the two forms are enantiotropic. The phase change is sluggish in both directions, and considerable thermal conditioning is required to obtain reproducible equilibrium data. This is possible only in an adiabatic type calorimeter. Crystal I shows a large premelting effect, and the extent is highly sensitive to impurities. They also applied vaporization and curvature corrections to their data.

Although it has been said that methanol forms a plastic crystal (see section 1.2.c), Carlson and Westrum [70] and Westrum and McCullough [19] point out that many properties of methanol are not consistent with the presence of molecular rotation in the crystal. The low entropy of fusion may be the result of the low entropy of the liquid caused by extensive intermolecular hydrogen bonding rather than a high entropy of the solid.

Carlson and Westrum calculate the third law entropy of the liquid at 298.15 K to be 127.111 ± 0.12 J K^{-1} mol^{-1}. NBS Technical note 270-3 [327] reports the entropy and heat capacity of the liquid at 298.15 K to be 126.8 J K^{-1} mol^{-1} and 81.6 J K^{-1} mol^{-1}, respectively. Table 11 reports the corresponding values of 127.27 ± 0.17 J K^{-1} mol^{-1} and 81.08 ± 0.20 J K^{-1} mol^{-1} that are calculated from the parameters in table 10.

The heat capacity of the liquid at higher temperatures was based on the measurements of Fiock, Ginnings and Holtan [111]. These were made in a special calorimeter used to determine the properties of steam. The methanol in the calorimeter consisted of the two phase system of liquid and gas in equilibrium. Their procedure gave directly the difference between the quantity α for the initial and final temperatures in each measurement. α is defined as

$$\alpha = H(\mathrm{l}) - \beta \tag{67}$$

$$\beta = V(\mathrm{l})T\,(\mathrm{d}P/\mathrm{d}T)\,. \tag{68}$$

These differences can be related to the integral of C_s between initial and final temperatures by

$$\int C_s(\mathrm{l})\mathrm{d}T = (\alpha_2 - \alpha_1) + (\beta_2 - \beta_1) - \int V(\mathrm{l})\mathrm{d}P \,. \qquad (69)$$

The division of this integral by $T_2 - T_1$ gives $\bar{C}_s$ which was used in the least squares calculation. The auxiliary data needed to calculate β and $\int V\mathrm{d}P$, as well as to calculate $\bar{C}_p$ was taken from Wilhoit and Zwolinski [126].

Properties of the glass phase were based on the data reported by Sugisaki, Suga and Seki [69]. They obtained the amorphous form by condensing it directly from the vapor phase at low temperatures (94–97 K). They prepared two samples, one of which they assumed to be completely amorphous and the other a mixture of glass and crystals. Both samples crystallized completely when heated slightly above the glass transition temperature, about 103 K. They calculated the fraction of amorphous material in the second sample (0.374) by comparing the heat evolved on crystallization of the two samples. They measured the heat capacity of the completely amorphous sample from 83 to 105 K and of the amorphous–crystal mixture from 22 to 106 K. They also measured the heat capacity of a crystalline sample from 21.6 to 112 K. The heat capacity of methanol glass below 83 K was calculated by subtracting the contribution of the crystalline portion from the measured data for the mixture. The parameters in table 10 and the smoothed data in table 11 were based on the combined data from the two samples up to 101 K. The data suggest the possibility of a sharp maximum in heat capacity between 101 and 105 K.

No measurements are available for the glass phase between 105 and the triple point, 175.61 K. Therefore, a calculation of the residual entropy of the glass, based entirely on experimental data, is not possible. An estimate of the entropy of the glass can be obtained by extrapolating the observed liquid heat capacity through this region. If the parameters from the lowest temperature region for the liquid from Table 10 are used for this extrapolation, along with a graphical estimate of the entropy change between 101 and 105 K, the residual entropy for the glass at 0 K is found to be $6.2 \pm 0.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The corresponding enthalpy is 2050 $\mathrm{J\,mol^{-1}}$. Sugisaki, Suga and Seki carried out a similar calculation and obtained a residual entropy of 7.07 $\mathrm{J\,K^{-1}\,mol^{-1}}$. However, because of the uncertainties in these calculations the reference state for the entropy, enthalpy and Gibbs energy in table 12 is the glass phase, rather than the crystal, at 0 K.

TABLE 10. Parameters for Heat Capacity of Methanol

Phase	c,II	c,II	c,II	c,II	c,II	c,I	l
Data Points							
Number	14	19	14	32	79(8)	15(3)	14
Temp./K	5.1 - 9.4	10.4 - 37.5	41.6 - 89.7	97.0 - 156.9	5.1 - 156.9	157.8 - 175.0	180.4 - 297.4
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 10.0	10.0 - 40.0	40.0 - 95.0	95.0 - 157.35	0 - 157.35	157.35 - 175.61	175.61 - 300.0
a_i		0.596	-12.391	-22.122		333.75	100.93
b_i x 10		-2.7324	9.5844	11.9676		-37.433	-3.2188
c_i x 10^3		31.816	-5.4176	-7.2007		12.196	0.8660
d_i x 10^5	19.9	-34.919	1.4773	1.8483			-0.00325
e_i x 10^7	496.7						
Deviations							
Average, d	0.004	-0.004	-0.008	0.008	0.000	0.016	0.004
R.M.S., $r(\sigma)$	0.012	0.048	0.121	0.435	0.151(0.159)	0.142(0.159)	0.055
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.02	0.04	0.08	0.15		0.3	0.20
$\delta(H-H_0)$	0.10	1.2	4.6	10.		12.	29.
$\delta(S)$	0.016	0.06	0.09	0.12		0.12	0.17
$\delta(G-H_0)/T$	0.006	0.026	0.03	0.04		0.04	0.05

Phase	l	l	l	l	l	gl	gl
Data Points							
Number	11	25(6)	14	11	25(6)	5	13
Temp./K	306.8 - 383.2	180.4 - 383.2	180.4 - 297.4	306.8 - 383.2	180.4 - 383.2	21.9 - 27.9	30.0 - 66.7
Parameters for	C_s	C_s	C_p	C_p	C_p	C_s	C_s
Temp./K	300.0 390.0	175.61 - 390.0	176.61 - 300.0	300.0 - 390.0	175.61 - 390.0	0 - 28.0	28.0 - 70.0
a_i	123.23		100.73	109.25			-25.936
b_i x 10	-4.7217		-3.1919	-3.2929			20.422
c_i x 10^3	1.1245		0.8542	0.6376			-28.118
d_i x 10^5	-0.00503		-0.00154	0.05033		124.01	15.964
e_i x 10^7						-236.15	
Deviations							
Average, d	-0.009	0.000	0.004	-0.009	0.000	0.117	-0.071
R.M.S., $r(\sigma)$	0.293	0.171(0.207)	0.055	0.293	0.171(0.207)	0.545	0.585
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.5		0.2	0.5		0.2	0.3
$\delta(H-H_0)$	53.					1.3	13.
$\delta(S)$	0.21					0.08	0.29
$\delta(G-H_0)/T$	0.05					0.04	0.10

Phase	gl	gl	gl
Data Points			
Number	10	6	34(8)
Temp./K	70.0 - 96.3	97.0 - 101.1	21.9 - 101.1
Parameters for	C_s	C_s	C_s
Temp./K	70.0 - 97.0	97.0 - 101.0	0 - 101.0
a_i	-84.36	-888616.12	
b_i x 10	37.683	272888.51	
c_i x 10^3	-41.665	-279317.98	
d_i x 10^5	17.124	95296.54	
Deviations			
Average, d	-0.069	0.092	0.000
R.M.S., $r(\sigma)$	0.506	0.961	0.754(0.862)
Estimated Uncertainty in Tabulated Values			
$\delta(C)$	0.4	0.8	
$\delta(H-H_0)$	17.	17.	
$\delta(S)$	0.3	0.3	
$\delta(G-H_0)/T$	0.11	0.11	

TABLE 11. Thermodynamic Functions of Methanol

CH_4O $M = 32.042$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}		J K^{-1} mol^{-1}	
			Crystal II			
0	0.000	0.000	0.00	0.000	0.000	0.000
4	-0.002	0.006	0.02	0.007	0.025	0.025
5	-0.004	0.012	0.06	0.016	0.056	0.056
6	-0.007	0.024	0.14	0.030	0.107	0.107
10	-0.041	0.149	1.49	0.191	0.696	0.696
15	-0.176	0.602	9.03	0.778	2.477	2.477
20	-0.448	1.380	27.61	1.829	5.064	5.064
25	-0.864	2.423	60.58	3.287	8.194	8.194
30	-1.413	3.667	110.02	5.081	11.605	11.605
35	-2.081	5.048	176.66	7.129	15.036	15.036
40	-2.849	6.499	259.97	9.349	18.224	18.224
50	-4.614	9.417	470.83	14.030	23.834	23.834
60	-6.582	12.242	734.5	18.824	28.803	28.803
70	-8.673	14.93	1045.0	23.602	33.221	33.221
80	-10.834	17.47	1397.4	28.301	37.18	37.18
90	-13.031	19.86	1787.3	32.890	40.76	40.76
100	-15.241	22.11	2211.5	37.36	44.03	44.03
110	-17.450	24.24	2666.8	41.69	46.99	46.99
120	-19.65	26.26	3150.6	45.90	49.74	49.74
130	-21.82	28.16	3661.2	49.99	52.37	52.37
140	-23.98	29.99	4198.1	53.96	55.01	55.01
150	-26.11	31.75	4761.8	57.85	57.76	57.76
157.35	-27.66	33.01	5194.1	60.67	59.91	59.91
			Crystal I			
157.35	-27.66	37.05	5830.1	64.71	46.70	46.70
160	-28.28	37.21	5954.	65.49	47.04	47.04
170	-30.55	37.86	6437.	68.41	49.85	49.85
175.61	-31.79	38.29	6723.	70.07	52.50	52.50
			Liquid			
175.61	-31.79	56.59	9938.	88.38	70.94	70.94
180	-33.19	56.94	10250.	90.13	70.86	70.86
190	-36.29	57.67	10958.	93.96	70.81	70.81
200	-39.26	58.33	11667.	97.60	70.93	70.94
210	-42.12	58.94	12377.	101.06	71.22	71.23
220	-44.88	59.51	13092.	104.39	71.68	71.69
230	-47.54	60.05	13811.	107.59	72.31	72.32
240	-50.10	60.58	14538.	110.68	73.11	73.11
250	-52.59	61.10	15274.	113.68	74.08	74.08
260	-54.99	61.62	16021.	116.61	75.21	75.21
270	-57.33	62.14	16779.	119.47	76.51	76.52
280	-59.60	62.68	17552.	122.28	77.98	77.99
290	-61.81	63.24	18340.	125.05	79.62	79.63
298.15	-63.56	63.71	18995.	127.27	81.08	81.08
300	-63.96	63.82	19145.	127.78	81.43	81.44
310	-66.06	64.42	19970.	130.48	83.42	83.44
320	-68.11	65.05	20816.	133.16	85.64	85.66
330	-70.12	65.71	21685.	135.83	88.06	88.11
340	-72.09	66.41	22580.	138.50	90.71	90.78
350	-74.02	67.15	23504.	141.2	93.57	93.68
360	-75.91	67.94	24458.	143.8	96.64	96.82
370	-77.77	68.77	25444.	146.5	99.9	100.2
380	-79.60	69.65	26466.	149.3	103.4	103.8
390	-81.40	70.58	27526.	152.0	107.1	107.7

TABLE 12. Thermodynamic Functions of Methanol
CH_4O $M = 32.042$

T/K	$(G\text{-}H_0)/T$ J K^{-1} mol^{-1}	$(H\text{-}H_0)/T$ J K^{-1} mol^{-1}	$H\text{-}H_0$ J mol^{-1}	$S\text{-}S_0$ J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Glass			
0	0.00	0.00	0.0	0.00	0.00
10	-0.09	0.26	2.6	0.35	1.00
15	-0.29	0.81	12.1	1.10	2.99
20	-0.64	1.72	34.5	2.36	6.14
25	-1.14	2.89	72.3	4.03	10.04
30	-1.80	4.45	133.5	6.25	14.33
40	-3.54	7.80	312.0	11.3	20.98
50	-5.62	10.94	547.2	16.6	25.83
60	-7.87	13.77	825.9	21.6	29.85
70	-10.19	16.35	1144.7	26.5	34.00
80	-12.54	18.82	1505.6	31.4	38.10
90	-14.9	21.2	1906.	36.1	42.1
95	-16.1	22.3	2122.	38.4	44.4
100	-17.2	23.5	2352.	40.8	54.6
101	-17.5	23.9	2416.	41.4	76.

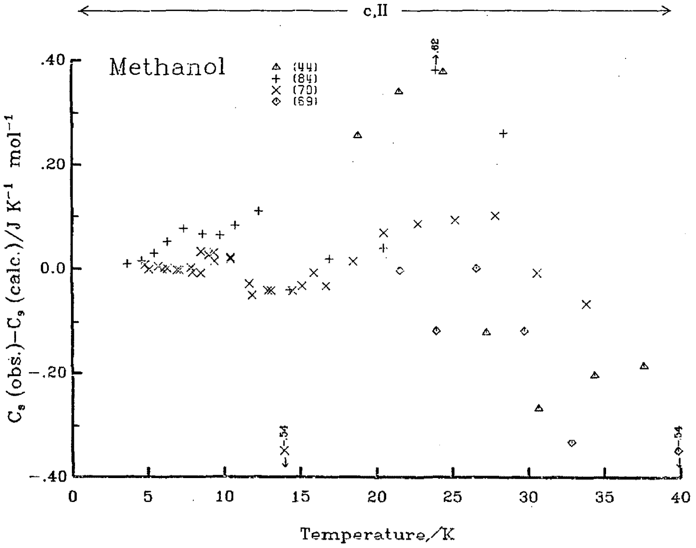

FIG. 4. Deviation plot for methanol, c,I, 0–40 K.

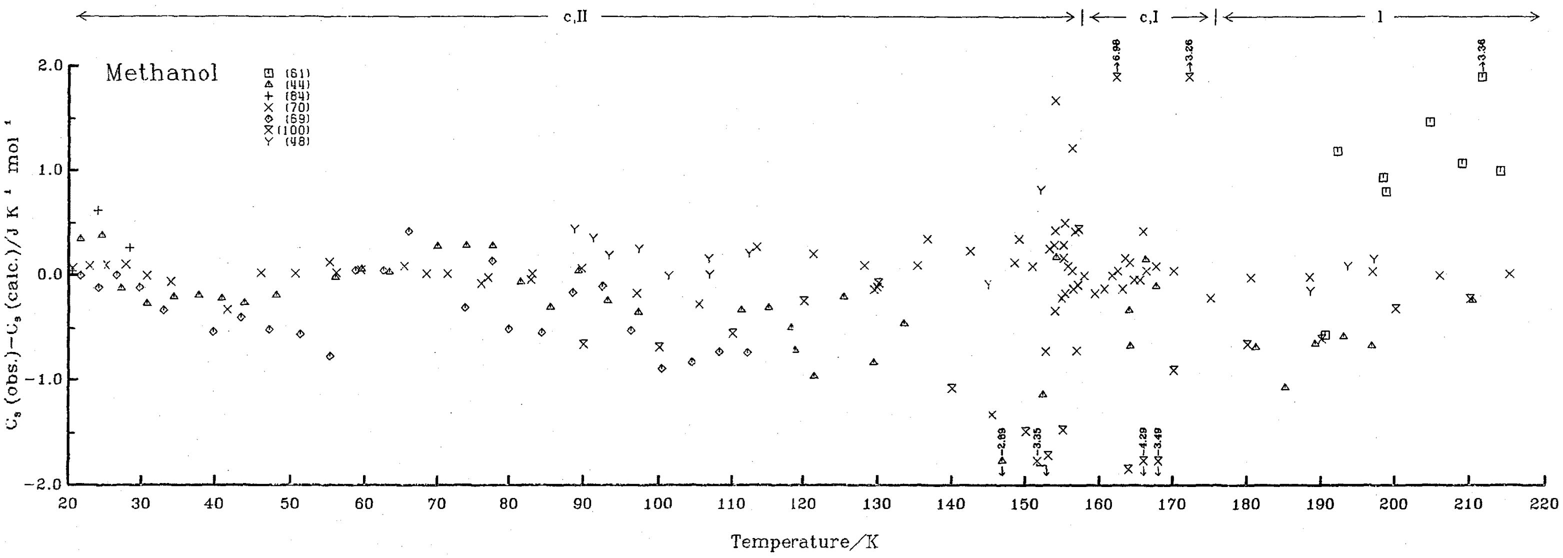

FIG. 5. Deviation plot for methanol c,I c,II,l, 20–220 K.

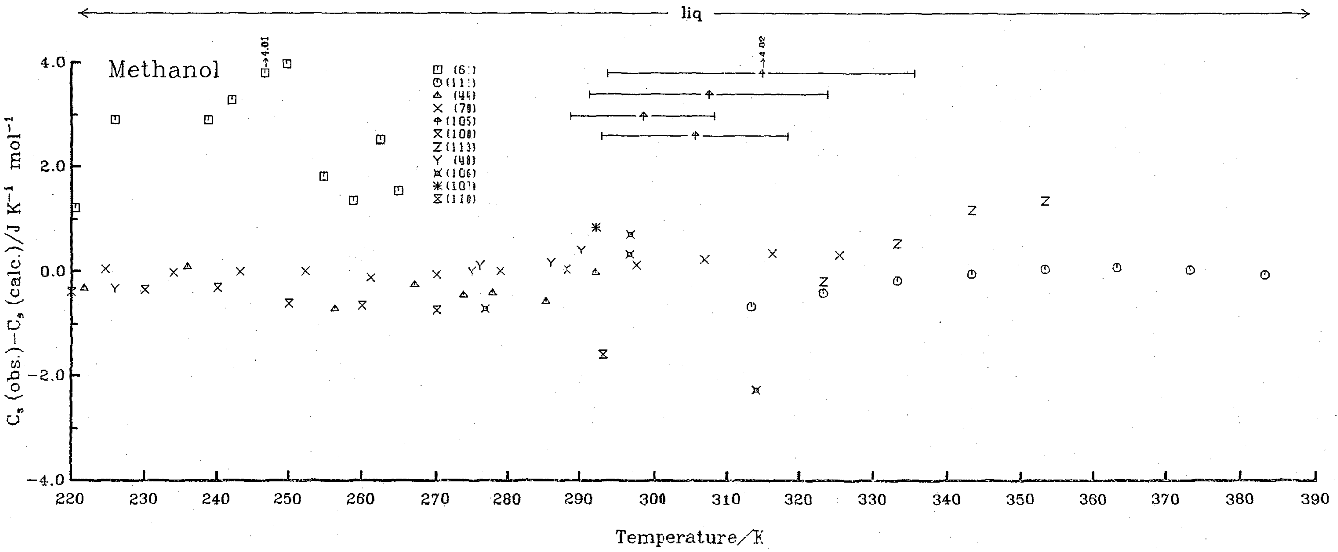

FIG. 6. Deviation plot for methanol 220–390 K.

FIG. 6. Deviation plot for methanol 220–390 K.

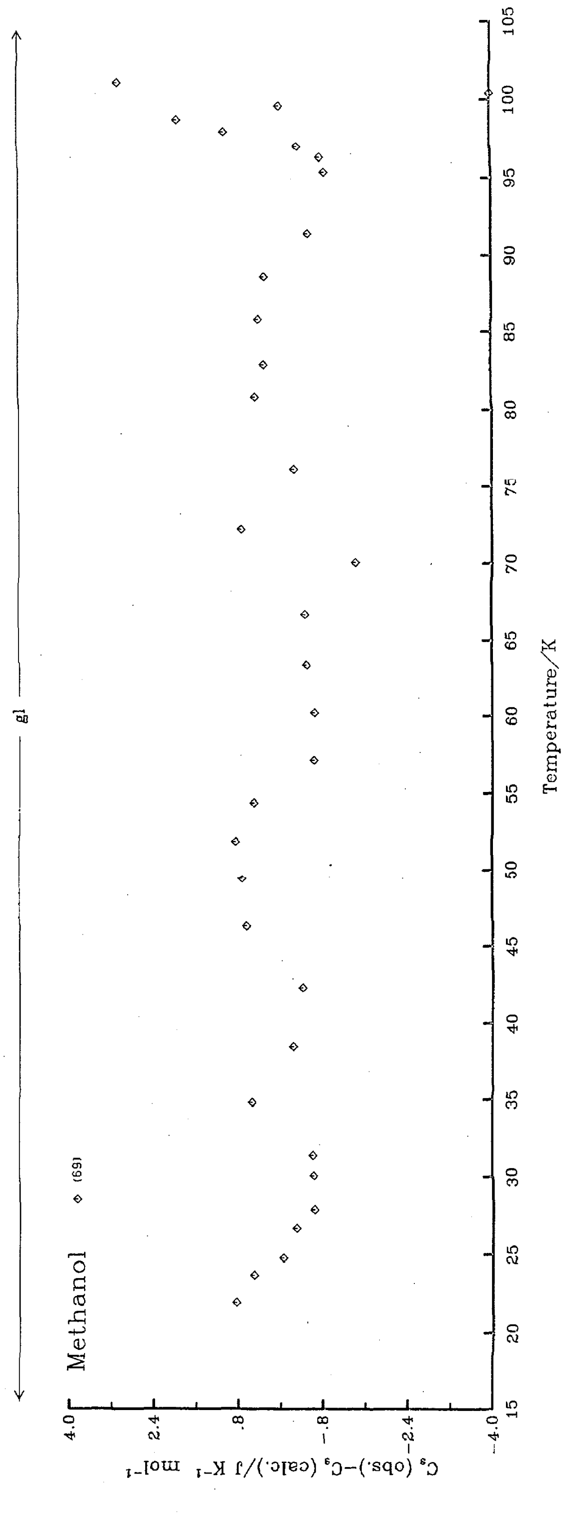

FIG. 7. Deviation plot for methanol, gl, 20–100 K.

3. Ethanol (Ethyl Alcohol)

In spite of the common industrial and laboratory uses of ethanol, the only detailed modern study of its thermodynamic properties below the melting point is that of Haida, Suga and Seki [67]. The existence of the glass form of ethanol has been known for many years [43, 45, 48, 122, 124, 127, 128] but Haida, Suga and Seki showed that its solid phase properties are more complicated than had been previously suspected. First they identified the solid phase transitions by the use of a DTA technique, and then they measured the heat capacities and transition enthalpies by the use of an adiabatic calorimeter.

Haida, Suga and Seki concluded that ethanol is monotropic, and that it also has at least three metastable phases. Figure 8 is a schematic Gibbs energy plot which shows the relationships among these phases. Haida, Suga and Seki [67] refer to the stable crystal by c,I and to the metastable crystal by c,II. It shows two kinds of glass – a glassy liquid formed by undercooling the liquid and a glassy crystal formed by cooling the metastable crystal.

The sequence of phase transitions observed on cooling ethanol below its equilibrium triple point and on subsequent heating are strongly dependent on sequence of steps and on the rates of cooling and heating. Very rapid cooling of the liquid to below 90 K produces the glassy liquid. On raising the temperature, a typical glass transition occurs at around 95 K. On further heating, the undercooled liquid changes partly or completely to the metastable crystal, which melts at 127.5 K. This melting is accompanied by some conversion to the stable crystal. Further heating completes the conversion to the stable crystal. It melts at 159.00 K. Slow cooling of the liquid will regenerate the stable crystal. An intermediate rate of cooling will produce the metastable crystal or a mixture of stable and metastable crystals. Further cooling of the metastable crystal produces the glassy crystal, whose glass transition temperature is 97 K. Haida, Suga and Seki feel that the glass phase studied by earlier workers was actually the glassy crystal.

Thermodynamic properties of crystalline and liquid ethanol have been reported by Rabinovich and Nikolaev [129] and Nikolaev, Rabinovich and Lebedev [66]. Their main objective was to determine the effects of deuterium substitution on the thermodynamic properties of organic compounds.

The liquid phase properties up to 390 K in table 16 are based primarily on the data of Haida, Suga, and Seki [67] and Fiock, Ginnings and Holton [111]. The procedure for incorporating the data of Fiock, Ginnings and Holton into the calculations is the same as that used for methanol and has been described in section 2.

In 1867 Hirn [130] investigated some properties of ethanol and several other organic liquids at temperatures above the normal boiling points. His principal objective was to measure the liquid volumes as functions of temperature. He also measured the specific heats by comparing the rate of cooling of a sample of liquid with the rate of cooling of a sample of water under similar conditions. The conditions used correspond to the measurement of the heat capacity at a constant pressure of 1490 kPa. Later Sutherland [131] recalculated the specific heats from his raw data by a method which corrected for some systematic side effects in the experimental procedure. The values calculated by Sutherland run from about 2.3 J K^{-1} mol^{-1} lower than the values calculated from the selected parameters at 353 K to about 8 J K^{-1} mol^{-1} higher at 393 K. The conversion of these values from 1490 kPa to the saturated vapor pressure has only a minor effect compared to these differences.

Storvick and Smith [132] measured the enthalpy of liquid and vapor ethanol under saturated conditions from 278 to 470 °F (409–516 K) and under superheated conditons from 250 to 500 °F (394–533 K). Their values for the enthalpy of the saturated liquid were fit to polynomials in temperature for two regions by a least squares calculation. The result, when converted to joules per mole with temperature in kelvins, is

$$H_T(\mathrm{l}) - H_{298.15}(\mathrm{l}) = 81788. - 500.31T + 0.91883T^2 - 2.2103 \times 10^{-4}T^3\ \mathrm{J\ mol^{-1}} \quad \text{for } T = 410 \text{ to } 500\ \mathrm{K}$$

$$H_T(\mathrm{l}) - H_{298.15}(\mathrm{l}) = -346148148. + 2060436.1T - 4088.067T^2 + 2.703845T^3\ \mathrm{J\ mol^{-1}} \quad \text{for } T = 500 \text{ to } 516\ \mathrm{K}\ .$$

The data in table 16 from 410 to 510 K were calculated from the equations above, the tabulated value of $H_{298.15}—H_0$, the density values of Ramsay and Young [133], and the vapor pressure values of Ambrose and Townsend [134] and Young [135]. The results are considerably less accurate that those at lower temperatures and no attempt was made to force continuity between 380 and 410 K. The value of C_p calculated by Sutherland at 413 K is 190. J K^{-1} mol^{-1} which is appreciably higher than the values in Table 16 at similar temperatures. Table 17 lists property values for the metastable crystal and glassy crystal derived from the measurements of Haida, Suga and Seki, while table 18 gives data for the glassy liquid and liquid states. The reference state for enthalpy and entropy in both these tables is the stable crystal at 0 K.

Green [136] reviewed the thermodynamic properties of the condensed and ideal gas phases of ethanol in 1961. He included a table of the thermodynamic properties of the crystal and liquid by graphically smoothing the data of Kelley [45] and Fiock, Ginnings and Holtan [111]. He also gave equations for the heat capacity of the liquid. He obtained an entropy of 161.2 J K^{-1} mol^{-1} for the liquid at 298.15 K. NBS Technical Note 270-3 [327] gives 160.7 J K^{-1} mol^{-1} and 111.46 J K^{-1} mol^{-1} as the entropy and heat capacity of the liquid at 298.15 K.

TABLE 13. Sources of Heat Capacity Data for Ethanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Favre & Silbermann	1847	l(293–351)	drop	H	not stated			[211]
Andrews	1848	l(298)	mixing	H	distilled over CaO,treated with charcoal			[104]
Hirn	1867	l(333–423)	cooling rate	C	not stated			[130]
von Reis	1881	l(289–347)	drop	H	not stated			[105]
Blumcke	1885	l(273–371)	drop (ice)	H	not stated			[137]
Sutherland	1888	l(333–423)	‡	C				[131]
Louguinine	1898	l(293–350)	drop	H	not stated			[138]
Bose & Mueller	1907	l(279–314)	drop	C	not stated			[106]
Walden	1907	l(289–293)	mixture	C	not stated			[107]
Batelli	1908	l(182–245)	isoperibol	C	95% ethanol, dried over CaO and Na, then distilled			[139]
Doroshevskii & Rakovskii	1908	l(294–372)	drop	H				[140]
Gibson, Parks & Latimer	1920	c(88–141),l(196–271) c,m*(86–96)	adiabatic	C	commercial sample est. 99.6 wt% pure, redistilled over Na			[43]
Williams & Daniels	1924	l(301–330)	adiabatic	C	99% pure sample, dried over Na, fract. distilled			[17]
Parks	1925	c(87–140),l(160–298) c,m*(87–110)	isoperibol	C	absolute ethanol, dist. over CaO and Ca, then fract. distilled			[48]
Kelley	1929	c(19–133),l(164–294) c,m*(18–108)	isoperibol	C	commercial sample, dried over CaO for one week, distilled, dried over CaO for 5 days, fract. distilled, 99.6%			[45]
Mitsukuri & Hara	1929	l(184–269)	isoperibol	C	not stated			[61]
Fiock, Ginnings & Holton	1931	l(313–383)	isoperibol	C	commercial sample, distilled over CaO, extractive dist. with benzene de–gas by refluxing & evacuation, final water content 0.047 wt%	8	corr	[111]
Blacet, Leighton & Bartlett	1931	l(303–343)	adiabatic	C	dried over CaO for 30 days, then distilled			[141]
Ernst, Watkins & Ruwe	1936	l(298)	Dewar flask	C	dried over Na, NaOH & Na, then distilled			[142]
Bykov	1939	l(298)						[143]
Cox & Smith	1959	l(286–303)	isoperibol	C	not stated			[144]
Storvick & Smith	1960	l(410–516)	flow	H	not stated	10	no	[132]
Swietoslawski & Zielenkiewicz	1960	l(294–339)	drop	H	not stated			[114]
Rabinovich & Nikolaev	1962	l(288–328)	adiabatic	C	carefully purified and dried	8	no	[129]
Hwa & Ziegler	1966	l(181–305)	adiabatic	C	commercial sample, purified 99.95^c mol%			[145]
Nikolaev, Rabinovich & Lebedev	1967	c(80–150),l(160–250) c,m(100–110)	adiabatic	C	carefully purified and dried			[66]
Fortier, Benson & Picker	1976	l(298)	flow	C	commercial sample			[146]
Haida, Suga & Seki	1977	c(14–155),l(159–301) c,m(14–108), gl(14–90)	adiabatic	C	sample from Tokyo Kagaku Seki Co. Ltd., then dried with molecular sieve, fract. distilled 99.86 mol%	233	I–68	[67]
Brown & Ziegler	1979	l(159–306)	adiabatic	C	commercial sample, dried, and distilled, 99.94 mol%	34	I–68	[147]

* Called a "glass" by the original authors but identified as a "glassy–crystal" by Haida, Suga and Seki [67].

‡ recalculation of data reported by Hirn [130].

TABLE 14. Reported Phase Transition Data for Ethanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Timmermans	1911	c⇌l	159.0	mp			[148]
Gibson, Parks & Latimer	1920	c⇌l	156.2	tp	4628.	c	[43]
Parks	1925	c⇌l	158.7	tp	4966.	c	[48]
		glass	97.	hc			
Mitsukuri	1926	c⇌l	157.93	mp	2720.	t	[59]
Kelley	1929	c⇌l	158.5	tp	5025.	c	[44]
		glass	96.	hc			
Bridgeman	1941	c⇌l	155.7*	mp			[149]
Sapgir	1929	c⇌l	159.1	mp			[150]
Dreisbach & Martin	1949	c⇌l	158.72	mp			[151]
Sackmann & Sauerwald	1950	c⇌l	159.0	mp			[152]
Corcoran, Kruse & Skolnik	1953	c⇌l	159.2	mp			[153]
Faucher & Koleske	1966	glass	100.	ml			[122]
Hwa & Ziegler	1966	c⇌l	159.015	tp			[145]
Carpenter, Davies & Matheson	1967	glass	96.	dt			[127]
		glass	80.8	vs			
Nikolaev, Rabinovich & Lebedev	1967	c⇌l	158.8	tp	4644.	c	[66]
Lesikar	1975	glass	97.2	dt			[123]
Lesikar	1975	glass	98.6	dt			[124]
Haida, Suga & Seki	1977	c⇌l	159.00	tp	4931.	c	[67]
		c,m⇌l	127.5	tp	659.	c	
		glass	97.	hc			
Brown & Ziegler	1979	c⇌l	159.00	tp			[147]
SELECTED VALUES		c⇌l	159.00±0.05		4931.±7		
		c,m⇌l	127.5±0.5		659.±15		

* Melting point reported at pressures 0 to 3400 MPa.

TABLE 15. Parameters for Heat Capacity of Ethanol

Phase	c	c	c	c	c	l	l
Data Points							
Number	3	17	24	20	64(8)	94	16
Temp./K	13.8 - 16.8	18.1 - 48.3	50.8 - 109.0	116.6 - 151.7	13.8 - 151.7	151.8 - 298.3	301.0 - 383.2
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 17.0	17.0 - 50.0	50.0 - 110.0	110.0 - 159.0	0 - 159.0	150.0 - 300.0	300.0 - 390.0
a_i		-7.63	-10.06	-8.12		88.45	166.49
b_i x 10		6.430	10.559	11.659		0.4709	-7.7781
c_i x 10^3		6.868	-6.728	-9.2085		-0.8260	2.0720
d_i x 10^5	116.4	-10.74	1.881	3.0817		0.31388	-0.02462
e_i x 10^7	-115.0						
Deviations							
Average, d	0.021	-0.016	0.004	0.004	0.000	-0.004	0.025
R.M.S., $r(\sigma)$	0.226	0.054	0.067	0.134	0.109(0.117)	0.090	0.192
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.20	0.3	0.5	0.6		0.3	0.5
$\delta(H-H_0)$	0.9	10.	32.	43.		61.	76.
$\delta(S)$	0.14	0.4	0.5	0.6		0.6	0.6
$\delta(G-H_0)/T$	0.08	0.15	0.19	0.20		0.20	0.20

Phase	gl & l	l	c,m	c,m	c,m	c,m	c,m
Data Points							
Number	118(8)	16	4	15	23	5	47(8)
Temp./K	96.4 - 383.2	301.0 - 383.2	13.9 - 17.8	19.5 - 50.5	53.2 - 87.0	89.1 - 96.5	13.9 - 96.5
Parameters for	C_s	C_p	C_s	C_s	C_s	C_s	C_s
Temp./K	96.455 390.0	300.0 - 390.0	0 - 19.0	19.0 - 52.0	52.0 - 89.0	89.0 - 96.59	0 - 96.59
a_i		148.45		-7.21	-42.2	-67914.6	
b_i x 10		-5.9300		7.536	27.80	22584.41	
c_i x 10^3		1.4421		3.535	-35.578	-25018.58	
d_i x 10^5		0.04682	235.9	-6.81	18.348	9239.89	
e_i x 10^7			-634.6				
Deviations							
Average, d	0.000	0.025	0.038	-0.021	-0.008	0.075	0.000
R.M.S., $r(\sigma)$	0.116(0.120)	0.192	0.067	0.096	0.117	0.65	0.163(0.176)
Estimated Uncertainty in Tabulated Values							
$\delta(C)$		0.5	0.2	0.3	0.4	1.5	
$\delta(H-H_0)$			1.2	10.	18.	21.	
$\delta(S)$			0.15	0.3	0.4	0.4	
$\delta(G-H_0)/T$			0.09	0.14	0.15	0.15	

Phase	c,m	gl	gl	gl	gl	gl	gl
Data Points							
Number	11(3)	4	28	17	3	52(8)	8
Temp./K	96.6 - 107.9	13.7 - 17.3	18.4 - 67.0	69.1 - 90.0	92.5 - 96.4	13.7 - 96.4	96.4 - 150
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	96.59 - 107.0	0 - 18.0	18.0 - 68.0	68.0 - 90.0	90.0 - 96.455	0 - 96.455	96.455 - 150.0
a_i	-115.11		-8.26	12.99	-167064.4		-21.85
b_i x 10	37.757		8.798	6.167	55122.3		27.864
c_i x 10^3	-18.256		-1.458	-7.506	-60607.3		-22.643
d_i x 10^5		230.0	-1.806	6.021	22213.2		5.952
e_i x 10^7		-611.3					
Deviations							
Average, d	0.000	0.084	-0.038	0.155	0.45	0.000	0.052
R.M.S., $r(\sigma)$	0.092(0.109)	0.205	0.134	0.213	1.56	0.205(0.022)	0.221
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.5	0.3	0.4	0.5	2.0		0.5
$\delta(H-H_0)$	22.	1.6	20.	23.	26.		27.
$\delta(S)$	0.4	0.22	0.6	0.6	0.6		0.6
$\delta(G-H_0)/T$	0.15	0.14	0.27	0.27	0.27	0.27	

TABLE 16. Thermodynamic Functions of Ethanol

C_2H_6O $M = 46.069$

T/K	$(G\text{-}H_0)/T$	$(H\text{-}H_0)/T$	$H\text{-}H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}		J K^{-1} mol^{-1}	
			Crystal			
0	0.000	0.00	0.0	0.00	0.00	0.00
10	-0.091	0.27	2.7	0.36	1.05	1.05
15	-0.298	0.87	13.0	1.16	3.35	3.35
20	-0.68	1.94	38.8	2.63	7.12	7.12
25	-1.27	3.37	84.3	4.64	11.06	11.06
30	-2.02	4.98	149.3	7.00	14.94	14.94
35	-2.91	6.67	233.5	9.59	18.68	18.68
40	-3.92	8.40	335.8	12.31	22.21	22.21
50	-6.16	11.79	589.4	17.95	28.26	28.26
60	-8.59	14.95	897.1	23.54	33.14	33.14
70	-11.12	17.86	1249.9	28.97	37.34	37.34
80	-13.68	20.52	1642.0	34.20	40.98	40.98
90	-16.24	22.98	2068.1	39.22	44.19	44.19
100	-18.78	25.25	2524.6	44.03	47.06	47.06
110	-21.29	27.35	3008.6	48.64	49.72	49.72
120	-23.75	29.33	3519.2	53.08	52.44	52.44
130	-26.17	31.22	4058.6	57.39	55.53	55.53
140	-28.56	33.08	4631.6	61.64	59.2	59.2
150	-30.90	34.96	5244.7	65.87	63.6	63.6
159.0	-32.99	36.72	5837.7	69.70	68.3	68.3
			Liquid			
159.0	-33.00	67.72	10768.	100.72	87.70	87.70
160	-33.43	67.85	10856.	101.27	87.70	87.70
170	-37.57	69.02	11734.	106.60	88.00	88.00
180	-41.55	70.09	12616.	111.64	88.47	88.47
190	-45.37	71.07	13504.	116.44	89.11	89.11
200	-49.04	72.00	14399.	121.03	89.94	89.94
210	-52.57	72.87	15303.	125.44	90.98	90.98
220	-55.98	73.72	16219.	129.7	92.25	92.25
230	-59.28	74.56	17149.	133.8	93.78	93.78
240	-62.47	75.40	18096.	137.9	95.56	95.56
250	-65.56	76.25	19062.	141.8	97.64	97.64
260	-68.57	77.11	20050.	145.7	100.02	100.02
270	-71.50	78.01	21063.	149.5	102.73	102.73
280	-74.35	78.95	22105.	153.3	105.78	105.78
290	-77.14	79.93	23180.	157.1	109.19	109.19
298.15	-79.36	80.77	24082.	160.1	112.25	112.25
300	-79.86	80.97	24291.	160.8	112.98	112.98
310	-82.54	82.07	25441.	164.6	117.16	117.16
320	-85.16	83.23	26635.	168.4	121.7	121.7
330	-87.74	84.47	27876.	172.2	126.6	126.6
340	-90.28	85.79	29168.	176.1	131.9	131.9
350	-92.79	87.19	30515.	180.0	137.5	137.6
360	-95.27	88.67	31920.	183.9	143.5	143.7
370	-97.72	90.23	33387.	188.0	149.9	150.2
380.	-100.14	91.89	34919.	192.0	156.6	157.0
390	-102.55	93.64	36270.	196.4	163.7	164.3
410		97.5	$400\underline{00}.$		$14\underline{0}.$	$14\underline{0}.$
420		98.7	$415\underline{00}.$		$15\underline{0}.$	$15\underline{0}.$
430		100.1	$431\underline{00}.$		$16\underline{0}.$	$17\underline{0}.$
440		101.8	$448\underline{00}.$		$18\underline{0}.$	$18\underline{0}.$
450		104.	$467\underline{00}.$		$19\underline{0}.$	$19\underline{0}.$
460		106.	$486\underline{00}.$		$20\underline{0}.$	$21\underline{0}.$
470		108.	$508\underline{00}.$		$21\underline{0}.$	$22\underline{0}.$
480		$11\underline{0}.$	$530\underline{00}.$		$22\underline{0}.$	$24\underline{0}.$
490		113.	$553\underline{00}.$		$23\underline{0}.$	$26\underline{0}.$
500		116.	$578\underline{00}.$		$24\underline{0}.$	$28\underline{0}.$
510		117.	$598\underline{00}.$		$41\underline{0}.$	$52\underline{0}.$

*Underlined digits are beyond the level of experimental significance.

TABLE 17. Thermodynamic Functions of Ethanol
C_2H_6O $M = 46.069$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	$J\ K^{-1}\ mol^{-1}$		$J\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$	
			Metastable Crystal		
0			2150.0	5.10	0.00
10	209.74	215.46	2154.6	5.73	1.72
15	137.73	144.68	2170.2	6.95	4.75
20	101.34	110.19	2203.8	8.85	8.73
25	79.07	90.30	2257.5	11.24	12.78
30	63.79	77.71	2331.4	13.92	16.74
40	43.64	63.4	2536.8	19.8	24.23
50	30.35	56.3	2812.9	25.9	30.79
60	20.46	52.5	3148.5	32.0	36.15
70	12.54	50.5	3534.2	37.9	41.00
80	5.86	49.6	3970.5	43.8	46.45
90	0.02	49.7	4469.	49.6	53.4
95	−2.67	50.0	4752.	52.7	65.1
100	−5.27	51.4	5137.	56.6	79.9
105	−7.81	52.7	5538	60.5	80.1

TABLE 18. Thermodynamic Functions of Ethanol
C_2H_6O $M = 46.069$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	$J\ K^{-1}\ mol^{-1}$		$J\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$	
			Glass and Liquid		
0			2577.0	8.80	0.00
10	248.74	258.15	2581.5	9.41	1.69
15	162.51	173.12	2596.8	10.61	4.67
20	119.01	131.49	2629.9	12.5	8.61
25	92.48	107.31	2682.8	14.8	12.54
30	74.38	91.84	2755.1	17.5	16.33
40	50.72	73.9	2954.5	23.1	23.44
50	35.35	64.4	3221.5	29.1	29.83
60	24.1	59.1	3548.3	35.0	35.38
70	15.3	56.1	3926.0	40.8	40.03
80	7.9	54.4	4350.7	46.5	45.12
90	1.5	53.7	4833.	52.2	51.6
95	−1.4	53.6	5089.	55.0	67.2
100	−4.18	55.38	5538.	59.56	89.88
105	−6.92	57.03	5988.	63.95	89.98
110	−9.61	58.52	6437.	68.13	89.89
120	−14.82	61.11	7334.	75.93	89.31
130	−19.79	63.25	8223.	83.05	88.48
140	−24.55	65.03	9104.	89.58	87.77
150	−29.09	66.53	9980.	95.62	87.52
160	−33.43	67.85	10856.	101.27	87.70
170	−37.57	69.02	11734.	106.60	88.00

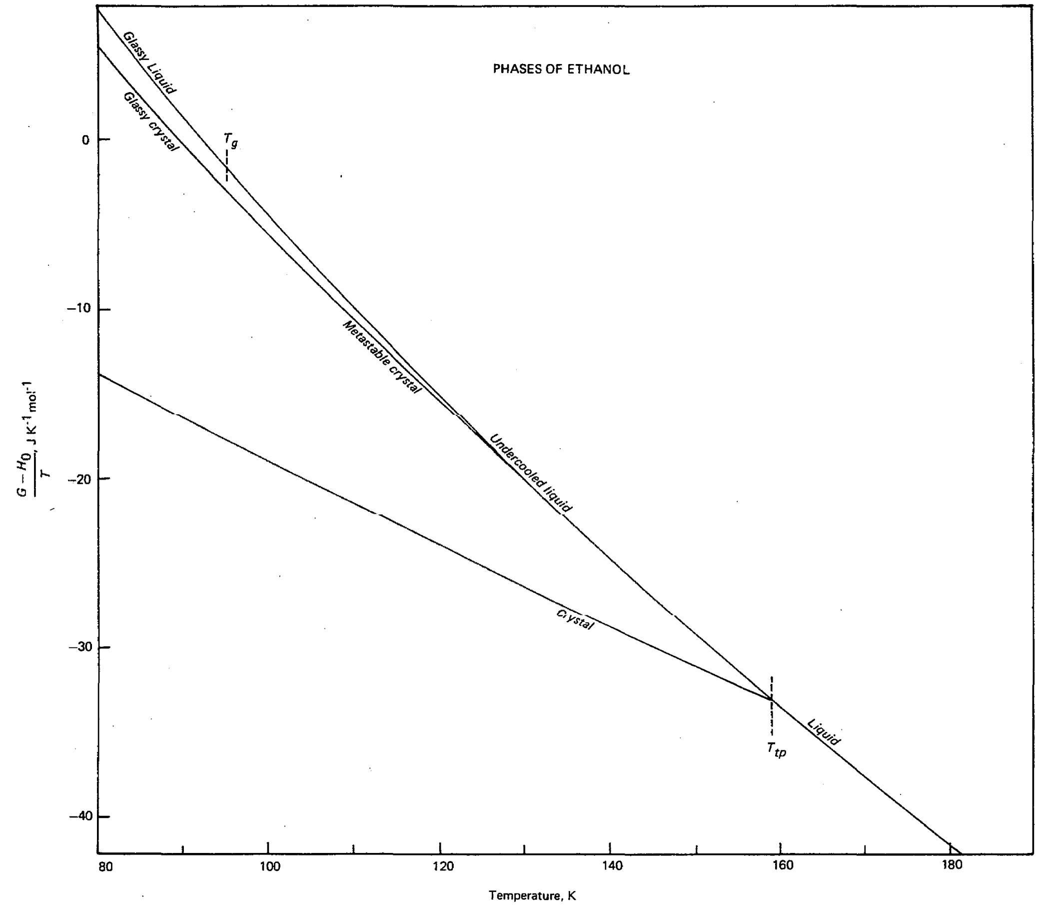

FIG. 8. Diagram of Gibbs energy of ethanol phases.

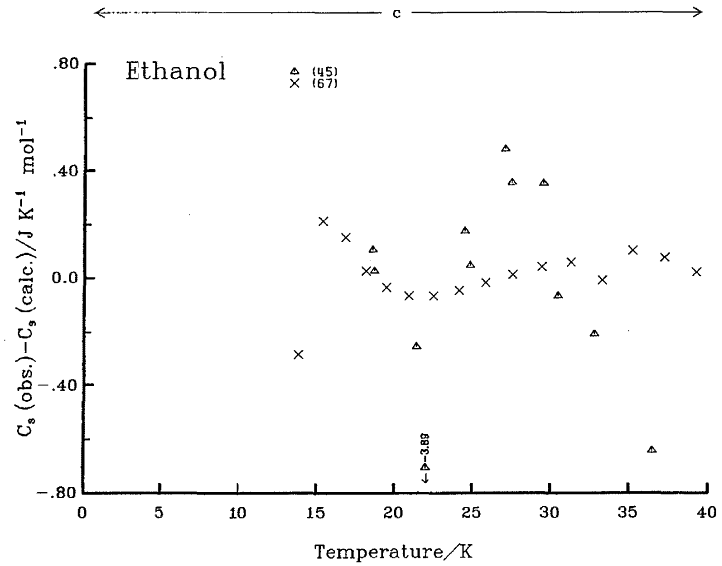

FIG. 9. Deviation plot for ethanol, c, 0–40 K.

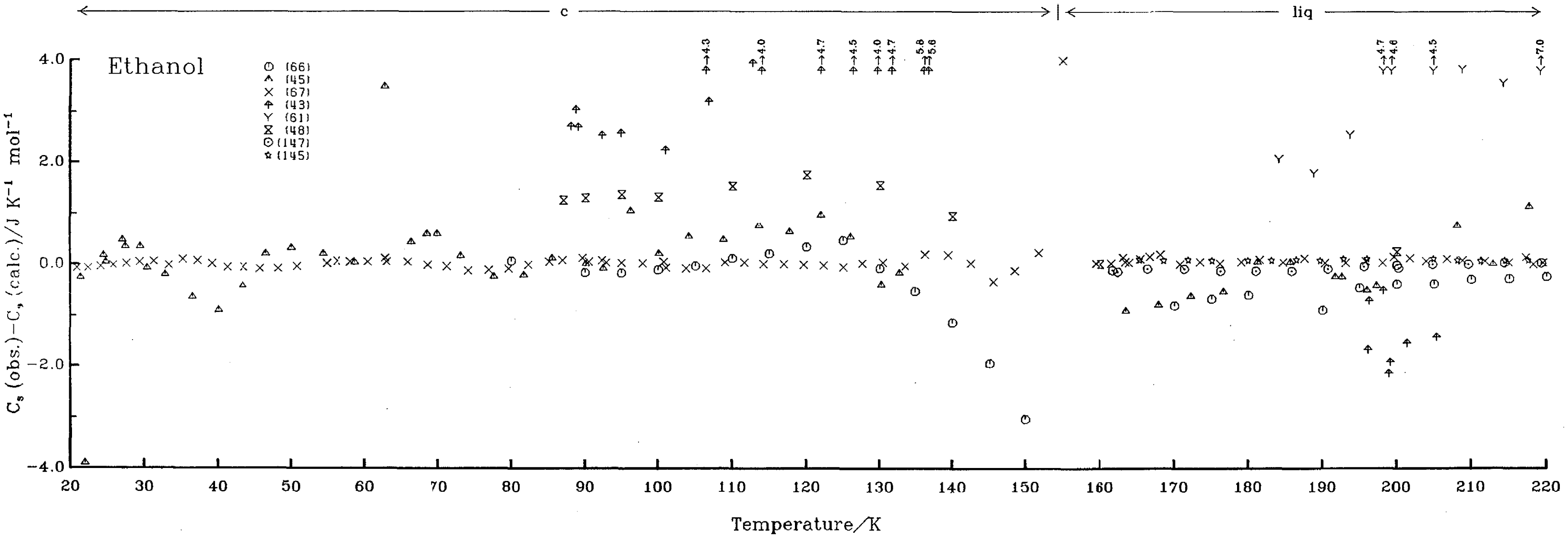

FIG. 10. Deviation plot for ethanol, c, l, 20–220 K.

FIG. 10. Deviation plot for ethanol, c,1, 20–220 K.

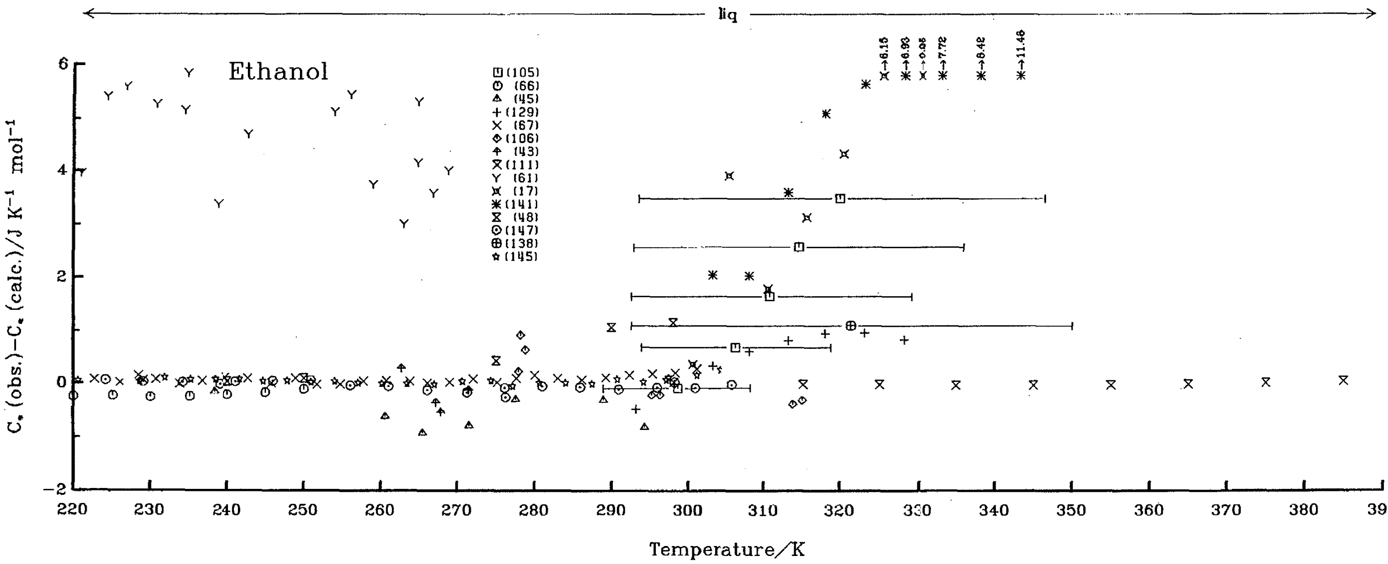

FIG. 11. Deviation plot for ethanol, 1, 220–420 K.

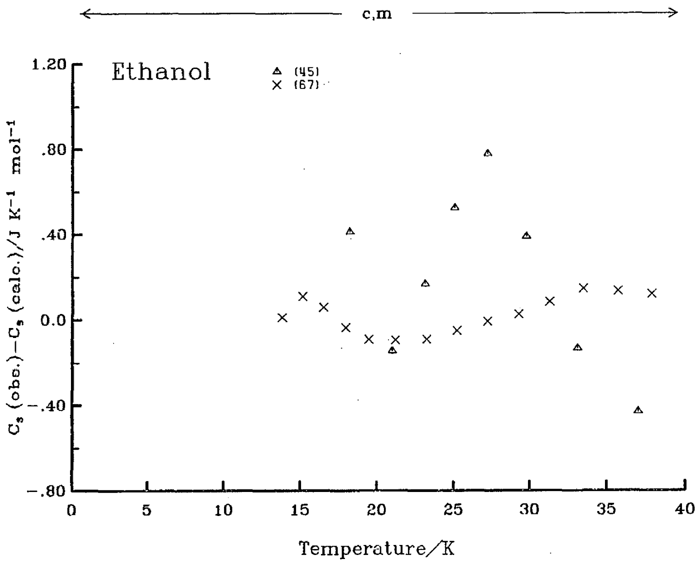

FIG. 12. Deviation plot for ethanol, c,m 0–40 K.

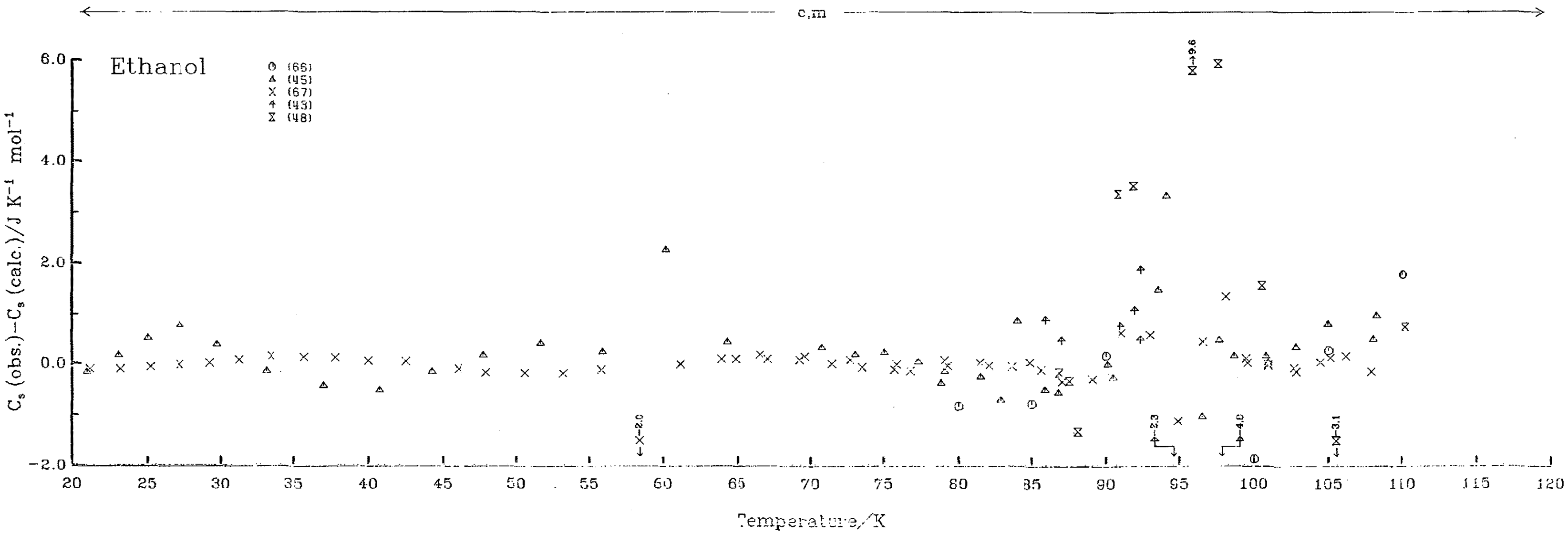

FIG. 13. Deviation plot for ethanol, c,m, 20–110 K.

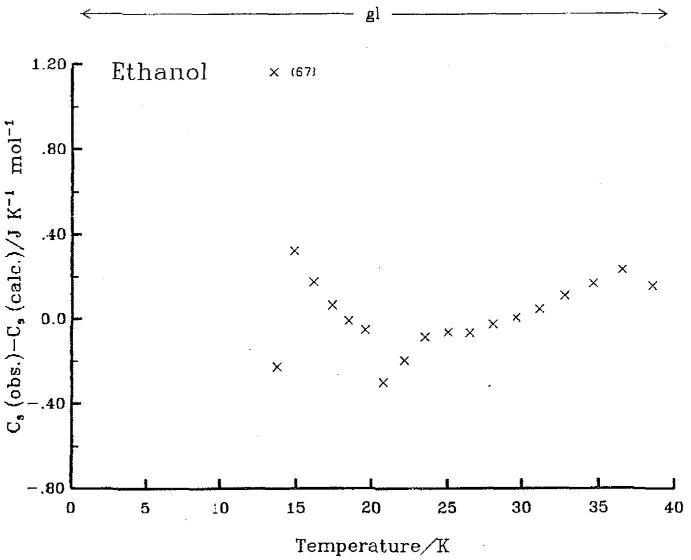

FIG. 14. Deviation plot for ethanol, gl, 0–40 K.

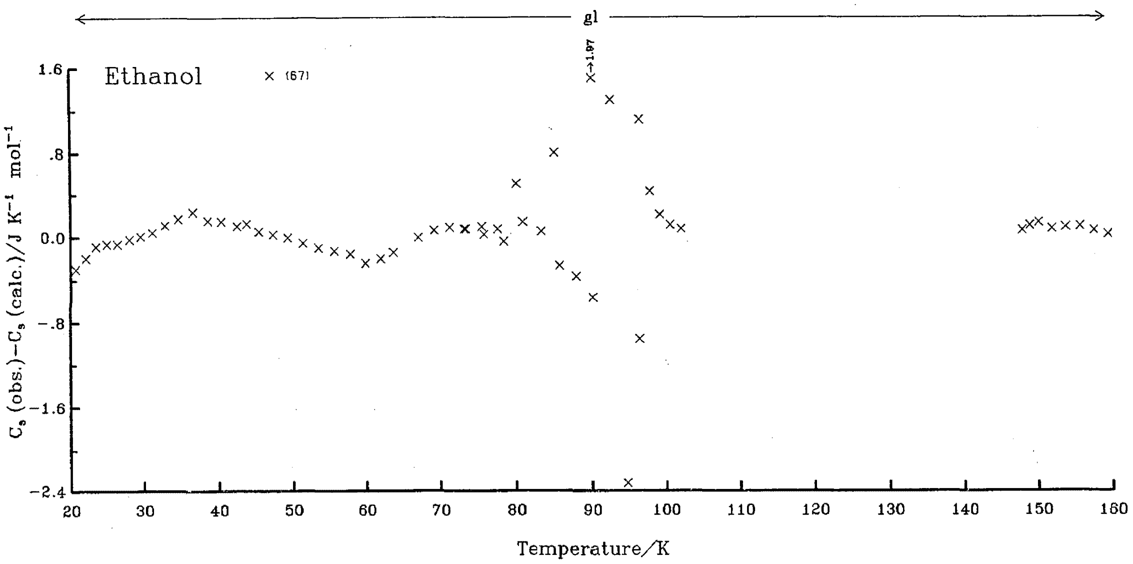

FIG. 15. Deviation plot for ethanol, gl, 20–160 K.

4. 1-Propanol (Propyl Alcohol)

The smoothed values of the thermodynamic properties of 1-propanol in the crystal, liquid, and glass states from 0 to 370 K were based on the measurements of Counsell, Lees, and Martin [12]. The values from 370 to 400 K were based on the measurements of Eucken and Eigen [154].

Eubank and Smith [155] measured enthalpy differences in the liquid phase from 300 to 506.7 °F (422–536 K) and in the gas from 300 to 540 °F (422–555 K) in a flow calorimeter. Graphical extrapolations gave values of enthalpy for the saturated liquid. The numerical values were not reported in the published article but are available from ADI at the Library of Congress. These were fit to a polynomial in temperature by the least squares technique. The result is,

$$H_T - H_{298.15} = -467631 + 3645.25T - 9.31405T^2 + 8.1438 \times 10^{-3}T^3 \text{ J mol}^{-1}$$

for T = 435 to 520 K

$$H_T - H_{298.15} = -889081060 + 5076528T - 966.153T^2 + 6.12922T^3 \text{ J mol}^{-1}$$

for T = 520 to 535 K

The values in table 22 from 430 to 530 were calculated from above equations and the vapor pressure and liquid densities of Martin, Campbell, and Seidell [156]. The uncertainties in these enthalpies are in the range of 100–200 J mol^{-1} and the uncertainties in heat capacities are in the range of 10–20 J K^{-1} mol^{-1}. No attempt was made to force continuity of these values with those at lower temperatures.

The glass phase of 1-propanol is readily formed by rapid cooling of the liquid. Values of the glass transition temperature measured by various techniques and summarized in table 19 ranges from 98 to 109 K.

TABLE 19. Sources of Heat Capacity Data for 1-Propanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
von Reis	1881	l(290–364)	drop	H	not stated			[105]
Schiff	1886	l(289–355)	drop	H	not stated			[16]
Louguinine	1898	l(295–363)	drop	H	not stated			[138]
Bose & Muller	1907	l(277–317)		C	not stated			[106]
Doroshevskii	1909	l(289–373)	drop	H				[108]
Dewar	1913	c(20–80)	drop	H	not stated			[157]
Gibson, Parks & Latimer	1920	l(166–275), gl(77–124)	adiabatic	C	commercial sample, fract. distilled over anhyd. K_2CO_3			[43]
Parks & Huffman	1926	c(88–128),l(152–275) gl(86–113)	isoperibol	C	refined sample from Eastman Kodak, distilled over CaO			[49]
Mitsukuri & Hara	1929	l(163–334)	isoperibol	C	not stated			[61]
Trew & Watkins	1933	l(298)	mixture	H				[158]
Philip	1939	l(301)	not stated	C	commercial source, distilled			[112]
Zhdanov	1941	l(278–319)						[159]
Eucken & Eigen	1951	l(303–393)	adiabatic	C	commercial grade sample, distilled under vac. several times, water content $< 0.1\%$	8	no	[154]
Swietoslawski & Zielenkiewicz	1960	l(294–347)	drop	H	not stated			[114]
Recko	1968	l(297–313)	adibatic	C	not stated			[161]
Eubank & Smith	1962	l(422–536)	flow	H	$>99\%$	8	no	[155]
Counsell, Lees & Martin	1968	c(11–143),l(154–361) gl(11–148)	adiabatic	C	commercial sample, fract. distilled twice, 99.75^c mol%	153	corr	[12]
Paz Andrade, Paz Fernandez & Recacho	1970	l(313)	Calvet	C	not stated			[116]
Fortier, Benson & Picker	1976	l(298)	flow	C	commercial sample, purified by gas chromatography			[146]

TABLE 20. Reported Phase Transition Data for 1-Propanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Gibson, Parks & Latimer	1920	glass	100.	hc			[43]
Parks & Huffman	1926	$c \rightleftharpoons l$	147.0	tp	5196.	c	[49]
Parks & Huffman	1927	glass	100.	hc			[50]
		glass	107.	sp			
Cady & Jones	1933	$c \rightleftharpoons l$	146.1	mp			[162]
Tschamler, Richter & Wettig	1949	$c \rightleftharpoons l$	146.7	mp			[163]
Sackmann & Sauerwald	1950	$c \rightleftharpoons l$	145.6	mp			[152]
Faucher & Koleske	1966	glass	109.	dt			[122]
Carpenter, Davies & Matheson	1967	glass	98.	dt			[127]
		glass	105.8	vs			
		glass	105.8	vs			
Counsell, Lees & Martin	1968	$c \rightleftharpoons l$	148.75	tp	5372.	c	[12]
		glass	100.	hc			
Lesikar	1975	glass	100.0	dt			[123]
Lesikar	1975	glass	102.4	dt			[124]
SELECTED VALUES		$c \rightleftharpoons l$	148.75 ± 0.02		$5372. \pm 20$		

TABLE 21. Parameters for Heat Capacity of 1-Propanol

Phase	c	c	c	c	c	l	l
Data Points							
Number	8	11	24	12	55(11)	21	18
Temp./K	11.3 - 22.3	24.7 - 59.9	62.1 - 117.4	120.4 - 142.7	11.3 - 142.7	153.9 - 245.1	250.4 - 318.4
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 24.0	24.0 - 60.0	60.0 - 120.0	120.0 -148.75	0 - 148.75	148.75 - 250.0	250.0 - 320.0
a_i		-11.844	1.21	28134.55		102.95	107.91
b_i x 10		10.975	5.3494	-8889.4197		0.8415	0.9802
c_i x 10^3		-7.234	3.8155	10541.9503		-1.0079	-1.3570
d_i x 10^5	177.1	8.414	-5.7065	-5550.8417		0.39433	0.48003
e_i x 10^7	-398.1	-6.790	2.0260	1095.5199			
Deviations							
Average, d	0.005	-0.115	-0.013	-0.027	-0.035	0.004	-0.006
R.M.S., $r(\sigma)$	0.106	0.193	0.206	0.197	0.185(0.197)	0.067	0.138
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.10	0.20	0.25	0.3		0.3	0.4
$\delta(H-H_0)$	1.3	7.3	17.	19.		41.	50.
$\delta(S)$	0.10	0.21	0.3	0.3		0.3	0.4
$\delta(G-H_0)/T$	0.05	0.08	0.09	0.09		0.10	0.10

Phase	l	l	l	l	l	l	gl
Data Points							
Number	14	53(8)	21	18	14	53(8)	10
Temp./K	322.0- 393.2	153.9 - 393.2	153.9 - 245.1	250.4- 318.4	322.0- 393.2	153.9 - 393.2	11.3- 27.4
Parameters for	C_s	C_s	C_p	C_p	C_p	C_p	C_s
Temp./K	320.0- 400.0	148.75- 400.0	148.75- 250.0	250.0- 320.0	320.0- 400.0	148.75- 400.0	0- 30.0
a_i	3.63		102.73	102.43	-27.85		
b_i x 10	2.3648		0.8762	1.5857	5.2320		
c_i x 10^3	0.8326		-1.0259	-1.5788	-0.0412		
d_i x 10^5	-0.02123		0.39739	0.50700	0.06795		215.9
e_i x 10^7							-479.1
Deviations							
Average, d	-0.003	0.000	0.004	-0.006	-0.003	0.000	0.343
R.M.S., $r(\sigma)$	0.45	0.197(0.21)3	0.067	0.138	0.45	0.197(0.213)	0.69
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.8		0.3	0.4	0.8		0.6
$\delta(H-H_0)$	81.						11.
$\delta(S)$	0.4						0.6
$\delta(G-H_0)/T$	0.10						0.24

Phase	gl	gl	gl	gl
Data Points				
Number	14	4	9	37(11)
Temp./K	30.3 - 88.6	93.7 -107.5	112.9 -148.3	11.3 -148.3
Parameters for	C_s	C_s	C_s	C_s
Temp./K	3 0.0 - 90.0	90.0 -110.0	110.0 -148.3	0 -148.3
a_i	-3.96	256533.1	-8651.01	
b_i x 10	10.657	-102732.81	2687.278	
c_i x 10^3	-16.038	153749.46	-3080.770	
d_i x 10^5	26.375	-101904.477	1563.996	
e_i x 10^7	-14.757	25245.02	-296.696	
Deviations				
Average, d	0.100	-1.03	0.004	0.109
R.M.S., $r(\sigma)$	0.71	3.29	0.310	1.12(1.33)
Estimated Uncertainty in Tabulated Values				
$\delta(C)$	0.8	3.0	0.4	
$\delta(H-H_0)$	49.	78.	79.	
$\delta(S)$	1.1	1.2	1.2	
$\delta(G-H_0)/T$	0.4	0.4	0.4	

TABLE 22. Thermodynamic Functions of 1-Propanol

C_3H_8O $M = 60.096$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}	C_p J K^{-1} mol^{-1}
			Crystal			
0	0.000	0.00	0.0	0.00	0.00	0.00
10	−0.128	0.36	3.6	0.49	1.37	1.37
15	−0.397	1.09	*16.4*	*1.49*	*3.96*	3.96
20	−0.862	2.27	45.4	3.13	7.80	7.80
25	−1.528	3.81	95.2	5.34	12.12	12.12
30	−2.37	5.54	166.3	7.92	16.29	16.29
35	−3.36	7.37	257.8	10.73	20.30	20.30
40	−4.47	9.22	369.0	13.69	24.13	24.13
50	−6.93	12.93	646.4	19.86	31.22	31.22
60	−9.60	16.50	990.1	26.11	37.34	37.34
70	−12.40	19.86	1390.4	32.27	42.64	42.64
80	−15.26	23.02	1841.5	38.28	47.51	47.51
90	−18.15	25.99	2339.1	44.14	51.95	51.95
100	−21.03	28.79	2879.4	49.83	56.05	56.05
110	−23.90	31.45	3459.5	55.35	59.93	59.93
120	−26.75	33.98	4077.8	60.73	63.75	63.75
130	−29.57	36.44	4737.6	66.01	68.21	68.21
140	−32.36	38.91	5447.8	71.27	75.30	75.30
148.75	−34.79	41.63	6193.0	76.42	100.23	100.23
			Liquid			
148.75	−34.79	77.75	11565.0	112.54	106.14	106.14
150	−35.44	77.99	11697.8	113.43	106.20	106.20
160	−40.53	79.77	12762.5	120.30	106.76	106.76
170	−45.42	81.37	13834.	126.79	107.50	107.50
180	*−50.11*	*82.85*	*14913.*	*132.96*	*108.44*	*108.44*
190	−54.63	84.23	16003.	138.85	109.60	109.60
200	−58.98	85.53	17106.	144.51	111.01	111.01
210	−63.19	86.78	18224.	149.97	112.69	112.69
220	−67.25	88.00	19361.	155.25	114.67	114.67
230	−71.19	89.2	20519.	160.40	116.96	116.96
240	−75.01	90.4	21701.	165.43	119.60	119.60
250	−78.73	91.6	22912.	170.38	122.61	122.61
260	−82.35	92.9	24155.	175.25	126.03	126.04
270	−85.88	94.2	25434.	180.08	129.93	129.94
280	−89.33	95.6	26755.	184.88	134.34	134.35
290	−92.70	97.0	28123.	189.68	139.29	139.29
298.15	−95.41	98.2	29276.	193.60	143.73	143.74
300	−96.02	98.5	29543.	194.49	144.79	144.80
310	−99.27	100.1	31021.	199.34	150.89	150.90
320	−102.47	101.8	32564.	204.23	157.62	157.64
330	−105.63	103.6	34176.	209.19	164.71	164.74
340	−108.75	105.5	35860.	214.22	171.94	171.98
350	−111.83	107.5	37617.	219.31	179.29	179.36
360	−114.88	*109.6*	*39449.*	*224.5*	*186.8*	*186.9*
370	−117.91	111.8	41357.	229.7	194.4	194.5
380	−120.91	114.1	43343.	235.0	202.1	202.3
390	−123.89	116.4	45408.	240.3	209.9	210.2
400	−126.85	118.9	47554.	245.7	217.9	218.3
430			$5442\underline{0}.$			
440			$5608\underline{0}.$			
450			$5802\underline{0}.$		$21\underline{0}.$	$21\underline{0}.$
460			$6029\underline{0}.$		$24\underline{0}.$	$24\underline{0}.$
470			$6295\underline{0}.$		$28\underline{0}.$	$28\underline{0}.$
480			$6605\underline{0}.$		$33\underline{0}.$	$33\underline{0}.$
490			$696\underline{00}.$		$38\underline{0}.$	$39\underline{0}.$
500			$737\underline{00}.$		$43\underline{0}.$	$44\underline{0}.$
510			$784\underline{00}.$		$49\underline{0}.$	$51\underline{0}.$
520			$837\underline{00}.$		$56\underline{0}.$	$58\underline{0}.$
530			$855\underline{00}.$			

*Underlined figures are beyond experimental significance.

TABLE 23. Thermodynamic Functions of 1-Propanol
C_3H_8O $M = 60.096$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
			Glass		
0			2992.8	12.51	0.00
10	286.6	299.7	2997.2	13.11	1.68
15	186.5	200.9	3012.8	14.33	4.86
20	136.07	152.42	3048.5	16.35	9.61
25	105.33	124.40	3110.1	19.08	15.02
30	84.33	106.57	3197.	22.2	19.5
35	68.88	94.37	3303.	25.5	22.8
40	56.88	85.63	3425.	28.8	26.1
50	39.10	74.40	3720.	35.3	33.0
60	26.14	68.09	4085.	41.9	40.1
70	15.94	64.60	4522.	48.7	47.1
80	7.44	62.81	5024.	55.4	53.2
90	0.10	62.0	5580.	61.9	57.5
95	-3.25	62.2	5909.	65.5	79.1
100	-6.5	63.8	6376.	70.2	105.
105	-9.6	65.9	6922.	75.6	110.
110	-12.8	67.8	7454.	80.5	104.
120	-18.8	71.0	8518.	89.8	106.8
130	-24.6	73.7	9580.	98.3	105.6
140	-30.13	75.97	10636.	106.10	105.97
148	-34.40	77.61	11486.	112.00	105.98

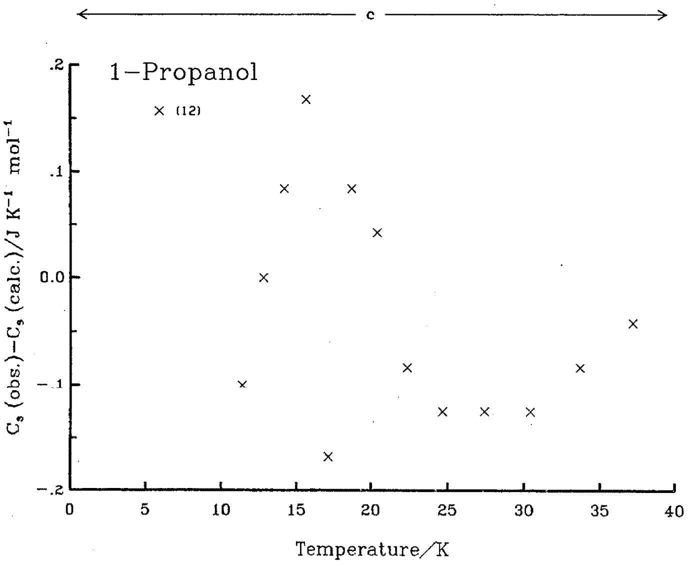

FIG. 16. Deviation plot for 1-propanol, c, 0–40 K.

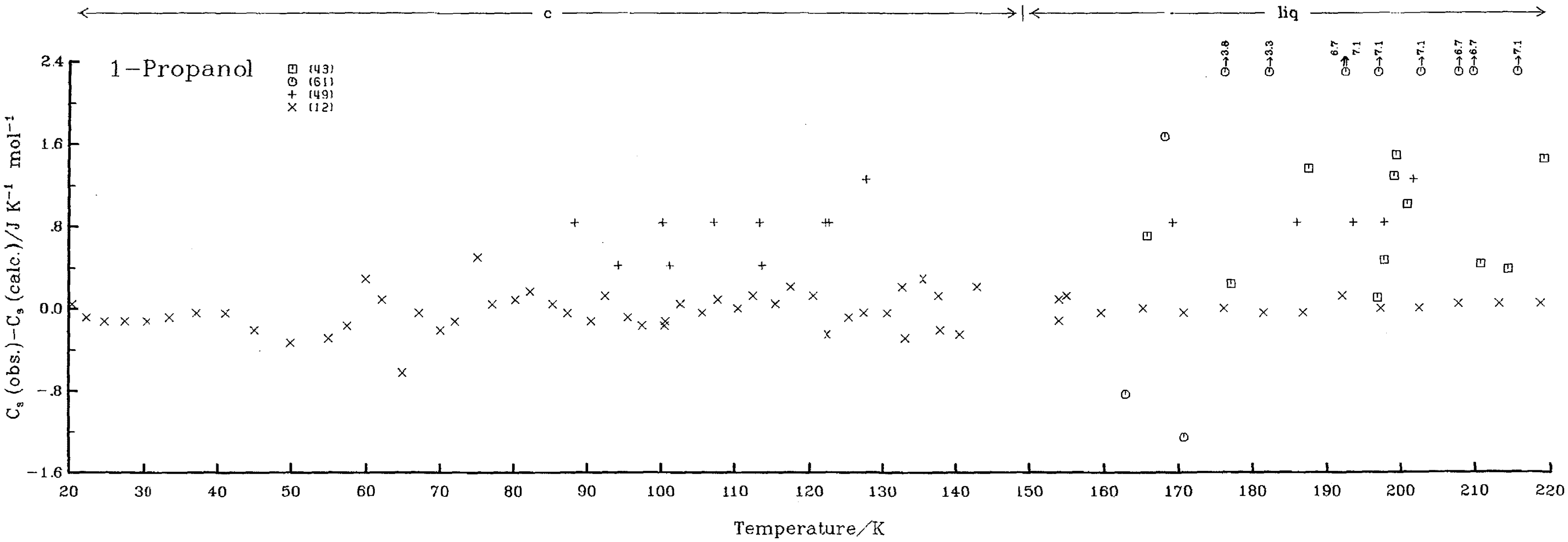

FIG. 17. Deviation plot for 1-propanol, c, 1, 20–220 K.

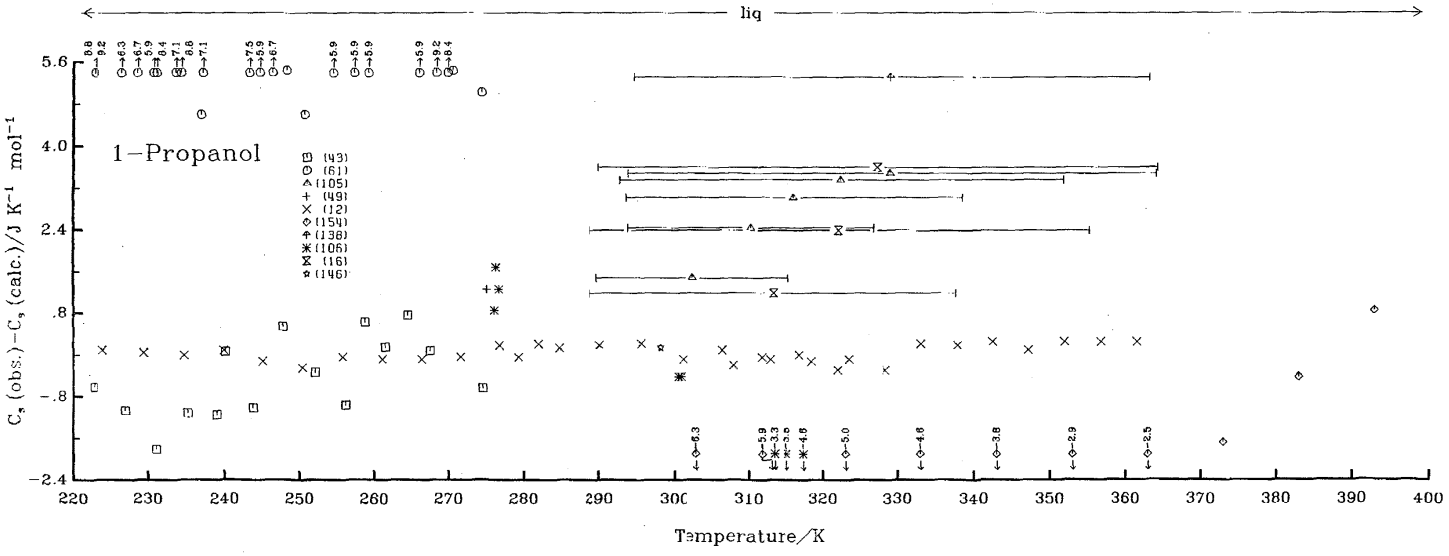

FIG. 18. Deviation plot for 1-propanol, 1, 220–400 K.

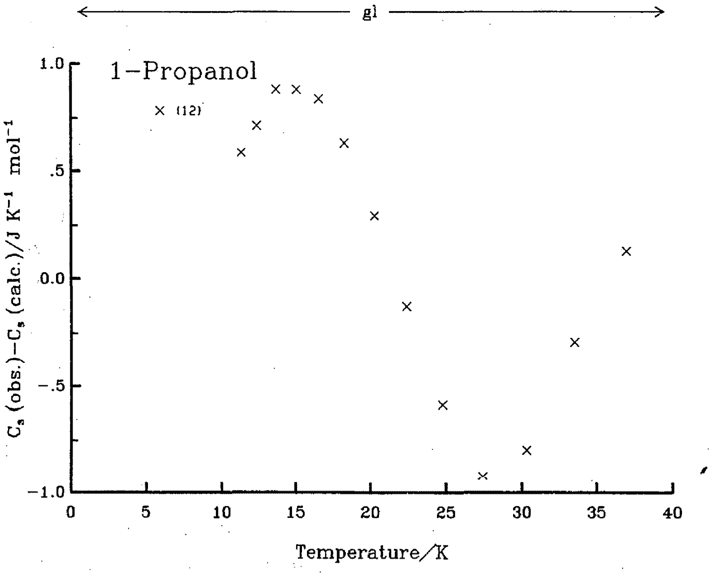

FIG. 19. Deviation plot for 1-propanol, gl, 0–40 K.

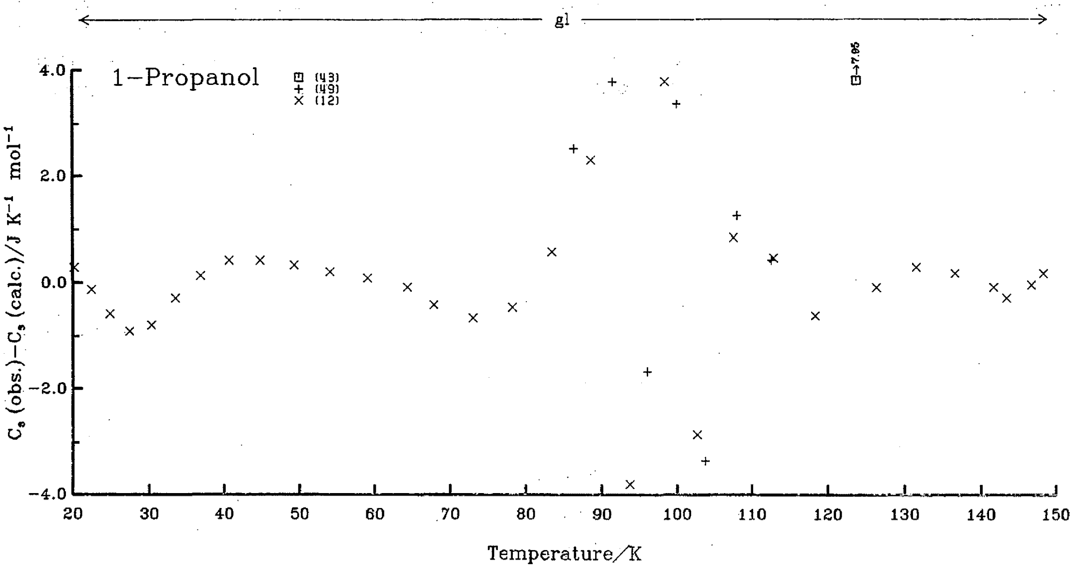

FIG. 20. Deviation plot for 1-propanol, gl, 20–150 K.

5. 2-Propanol (Isopropyl Alcohol)

Although several studies of low temperature thermodynamic properties of 2-propanol were made in earlier years [46, 53, 54] the more recent work of Andon, Counsell, and Martin [73] is clearly superior. The reported sample purities are similar for these studies, but the value obtained by Andon, Counsell, and Martin is more firmly established by the analysis of the melting curve as well as by gas chromatography. They did notice a rapid increase in heat capacity a few degrees below the melting point which was too large to be ascribed to impurities only. However, the point at 179.96 K was not included in our least squares fit. No reports of glass formation have been made for 2-propanol.

Ginnings and Corruccini [164] studied the thermal properties of saturated liquid 2-propanol by means of an ice calorimeter. They measured the heat evolved on cooling several samples from temperatures in the range of 55 to 200 °C down to 0 °C. Corrections for decomposition of the samples were applied to the higher temperature data. The heat transferred from the sample to the ice in the calorimeter is equivalent to $\int C_s \, dT$ taken from the initial to the final sample temperature. They calculated $H - H_{273.15}$ for the saturated liquid by use of the integrated form of equation (18). They estimated the liquid volume and dP/dT at higher temperatures by extrapolating the available lower temperature data. However, these values of V and dP/dT cancel out in their calculation of C_s. Therefore, their procedure is equivalent to a graphical differentiation of the observed heat evolved from the liquid samples.

The smoothed values of the thermodynamic properties in table 27 were obtained from the least squares fit of the data from references [73] and [164]. C_p was calculated from C_s by means of equation (13) with the vapor pressure data of Ambrose and Townsend [134] and the liquid volume selected by [126] and reported in reference [165].

Hoffman, San Jose and Reid [166] measured C_p directly for the liquid alcohol at temperatures from 80 to 180 °C and pressures from the equilibrium vapor pressure to 35 bars. Their values range from about 1.5 to 2.8 J K^{-1} mol^{-1} higher than those calculated from the parameters in table 26. The same relationship holds between the selected C_s and the C_s calculated from their measured C_p. These comparisons are included in Figure 24.

The smoothed values of C_s show an incipient inflection in the range of 300 to 370 K. It was also noticed by Ginnings and Corruccini. A similar trend can be seen in the C_p data also, but it is partially masked by the rapid increase in dC_p/dT at the upper end of this range.

TABLE 24. Sources of Heat Data Capacity for 2-Propanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Louguinine	1898	l(294–353)	drop	H	not stated			[138]
Doroshevskii	1909	l(289–373)	drop	H				[108]
Williams & Daniels	1924	l(304–327)	adiabatic	C	dried with CaO, distilled dried with BaO, then fract. distilled			[17]
Parks & Kelley	1925	c(71–153),l(195–293)	isoperibol	C	distilled twice over CaO 99.99^d wt%			[53]
Parks & Kelley	1928	c(71–153),l(195–293)	isoperibol	C	distilled twice over CaO 99.96^d wt%			[54]
Kelley	1929	c(19–170),l(188–293)	isoperibol	C	best grade, refluxed over CaO for 3 h., fract. distilled 3 times, 99.95%			[46]
Trew & Watkins	1933	l(298)	mixture	C	not stated			[158]
Philip	1939	l(303)	not stated	C	commercial sample, distilled			[112]
Zhdanov	1945	l(280–355)	drop	H				[167]
Ginnings & Corruccini	1948	l(273–473)	drop (ice)	H	refluxed over CaO, distilled	12	corr	[164]
Swietoslawski & Zielenkiewicz	1958	l(295–354)	drop	H	not stated			[160]
Katayama	1962							[115]
Andon, Counsell & Martin	1963	c(12–180),l(188–327)	adiabatic	C	purified & dried over CaH_2 99.96^c mol%	123	corr	[73]
Hoffman, San Jose & Reid	1977	l(383–463)	flow	C	not stated			[166]
Brown & Ziegler	1979	l(185–304)	adiabatic	C	dried over CaH_2, 99.84 mol%	26	I–68	[147]

TABLE 25. Reported Phase Transition Data for 2-Propanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Parks & Kelley	1925	$c \rightleftharpoons l$	184.6	tp	5301.	c	[53]
Parks & Kelley	1928	$c \rightleftharpoons l$	184.6	tp	5301.	c	[54]
Kelley	1929	$c \rightleftharpoons l$	184.70	tp	5372.	c	[47]
Cady & Jones	1933	$c \rightleftharpoons l$	186.6	mp			[162]
Ross, Dixon, Frolen & Termini	1963	$c \rightleftharpoons l$	185.30	tp			[168]
Andon, Counsell & Martin	1963	$c \rightleftharpoons l$	185.23	tp	5410.	c	[73]
Brown & Ziegler	1979	$c \rightleftharpoons l$	185.25	tp			[147]
SELECTED VALUES		$c \rightleftharpoons l$	185.26±0.05		5410.±15		

TABLE 26. Parameters for Heat Capacity of 2-Propanol

Phase	c	c	c	c	c	l	l
Data Points							
Number	4	25	14	20	63(11)	48	42
Temp./K	12.0 - 14.3	15.5 - 78.7	81.2 -127.3	130.6 -176.7	12.0 -176.7	188.3 -267.2	270.8 -353.2
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 15.0	15.0 - 80.0	80.0 -130.0	130.0 -185.26	0 -185.26	185.26-270.0	270.0 -360.0
a_i		-9.883	-71.985	1269.849		118.138	1452.168
b_i x 10		9.0301	34.7045	-361.2604		-0.7626	-137.8064
c_i x 10^3		2.5133	-40.7998	398.2850		-0.66886	45.94674
d_i x 10^5	53.81	-12.3976	24.0537	-192.86817		0.44125	-4.80248
e_i x 10^7	401.3	7.563	-5.3083	34.98965			
Deviations							
Average, d	0.100	-0.004	0.000	-0.004	0.000	-0.020	0.034
R.M.S., $r(\sigma)$	0.193	0.113	0.113	0.105	0.113(0.126)	0.120	0.402
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.04	0.10	0.12	0.12		0.2	0.3
$\delta(H-H_0)$	0.1	6.5	8.8	11.		28.	39.
$\delta(S)$	0.014	0.17	0.18	0.18		0.22	0.23
$\delta(G-H_0)/T$	0.005	0.09	0.09	0.09		0.09	0.09

Phase	l	l	l	l	l
Data Points					
Number	6	96(8)	42	6	96(8)
Temp./K	373.2 -473.2	188.3 -473.2	270.8 -353.2	373.2 -473.2	188.3 -473.2
Parameters for	C_s	C_s	C_p	C_p	C_p
Temp./K	360.0 -480.0	185.26-480.0	270.0 -360.0	360.0 -480.0	185.26-480.0
a_i	-252.35		1424.783	-746.05	
b_i x 10	22.0280		-134.9754	61.3915	
c_i x 10^3	-3.39361		44.97307	-13.86879	
d_i x 10^5	0.22365		-4.69105	1.15501	
Deviations					
Average, d	-0.088	0.000	0.034	-0.088	0.000
R.M.S.,$(r\sigma)$	0.233	0.283(0.296)	0.402	0.233	0.283(0.296)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.3		0.3	0.3	
$\delta(H-H_0)$	53.				
$\delta(S)$	0.25				
$\delta(G-H_0)/T$	0.09				

TABLE 27. Thermodynamic Functions of 2-Propanol

C_3H_8O $M = 60.096$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}		
			Crystal			
0	0.000	0.000	0.00	0.000	0.000	0.000
10	-0.065	0.215	2.15	0.280	0.939	0.939
15	-0.253	0.860	12.91	1.113	3.848	3.848
20	-0.667	2.168	43.36	2.835	8.312	8.312
25	-1.325	3.831	95.76	5.156	12.621	12.621
30	-2.182	5.641	169.24	7.824	16.73	16.73
35	-3.191	7.507	262.7	10.698	20.62	20.62
40	-4.316	9.376	375.0	13.692	24.26	24.26
50	-6.803	13.02	651.1	19.825	30.78	30.78
60	-9.485	16.46	987.5	25.94	36.37	36.37
70	-12.265	19.66	1376.2	31.92	41.28	41.28
80	-15.09	22.65	1812.3	37.74	45.95	45.95
90	-17.92	25.49	2294.4	43.41	50.40	50.40
100	-20.75	28.19	2819.1	48.94	54.52	54.52
110	-23.56	30.77	3384.4	54.32	58.52	58.52
120	-26.34	33.25	3989.6	59.59	62.53	62.53
130	-29.10	35.65	4634.8	64.75	66.51	66.51
140	-31.83	38.00	5319.6	69.82	70.45	70.45
150	-34.53	40.29	6043.8	74.82	74.41	74.41
160	-37.20	42.56	6809.7	79.76	78.98	78.98
170	-39.85	44.88	7630.2	84.73	85.62	85.62
180	-42.48	47.42	8536.4	89.91	96.60	96.60
185.26	-43.87	48.94	9066.0	92.81	105.14	105.14
			Liquid			
185.26	-43.87	78.14	14476.0	122.01	109.11	109.11
190	-45.86	78.92	14995.	124.77	109.77	109.77
200	-49.94	80.50	16100.	130.45	111.43	111.43
210	-53.91	82.02	17225.	135.93	113.49	113.49
220	-57.76	83.51	18372.	141.27	115.97	115.97
230	-61.50	84.98	19546.	146.48	118.90	118.90
240	-65.15	86.46	20751.	151.61	122.31	122.31
250	-68.71	87.97	21993.	156.68	126.21	126.21
260	-72.19	89.53	23277.	161.72	130.65	130.65
270	-75.60	91.14	24608.	166.74	135.64	135.64
280	-78.95	92.83	25993.	171.78	141.57	141.57
290	-82.23	94.63	27443.	176.87	148.63	148.63
298.15	-84.88	96.19	28680.	181.07	155.00	155.00
300	-85.47	96.56	28969.	182.04	156.51	156.51
310	-88.67	98.63	30576.	187.30	164.94	164.94
320	-91.84	100.94	32268.	192.68	173.63	173.65
330	-94.98	103.18	34048.	198.15	182.29	182.34
340	-98.09	105.63	35913.	203.72	190.63	190.74
350	-101.19	108.17	37859.	209.36	198.36	198.56
360	-104.28	110.77	39877.	215.05	205.19	205.52
370	-107.35	113.41	41960.	220.75	211.39	211.85
380	-110.41	116.06	44104.	226.47	217.40	217.95
390	113.46	118.74	46308.	232.19	223.24	223.92
400	-116.50	121.42	48569.	237.92	228.93	229.81
410	-119.53	124.11	50886.	243.64	234.47	235.70
420	-122.55	126.80	53258.	249.35	239.89	241.66
430	-125.57	129.50	55683.	255.06	245.2	247.8
440	-128.57	132.2	58161.	260.76	250.5	254.1
450	-131.57	134.9	60691.	266.44	255.5	260.6
460	-134.57	137.5	63271.	272.1	260.5	267.6
470	-137.55	140.2	65901.	277.8	265.5	274.9
480	-140.53	142.9	68581.	283.4	270.4	282.7

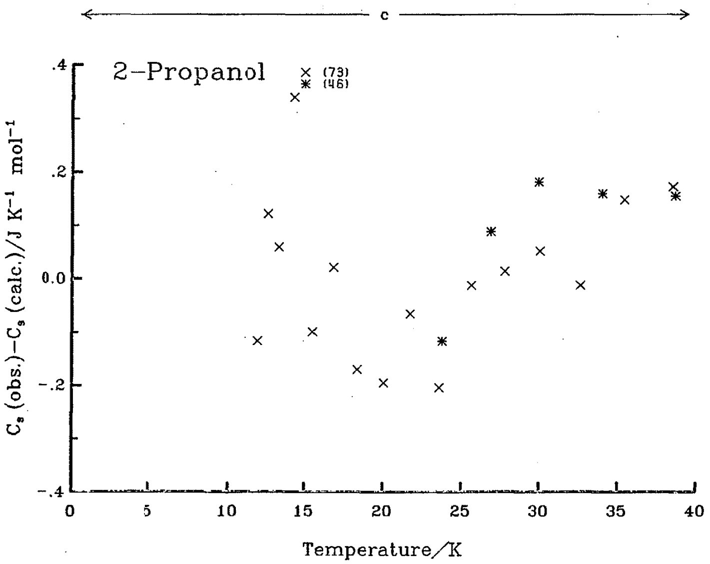

FIG. 21. Deviation plot for 2-propanol, c, 0–40 K.

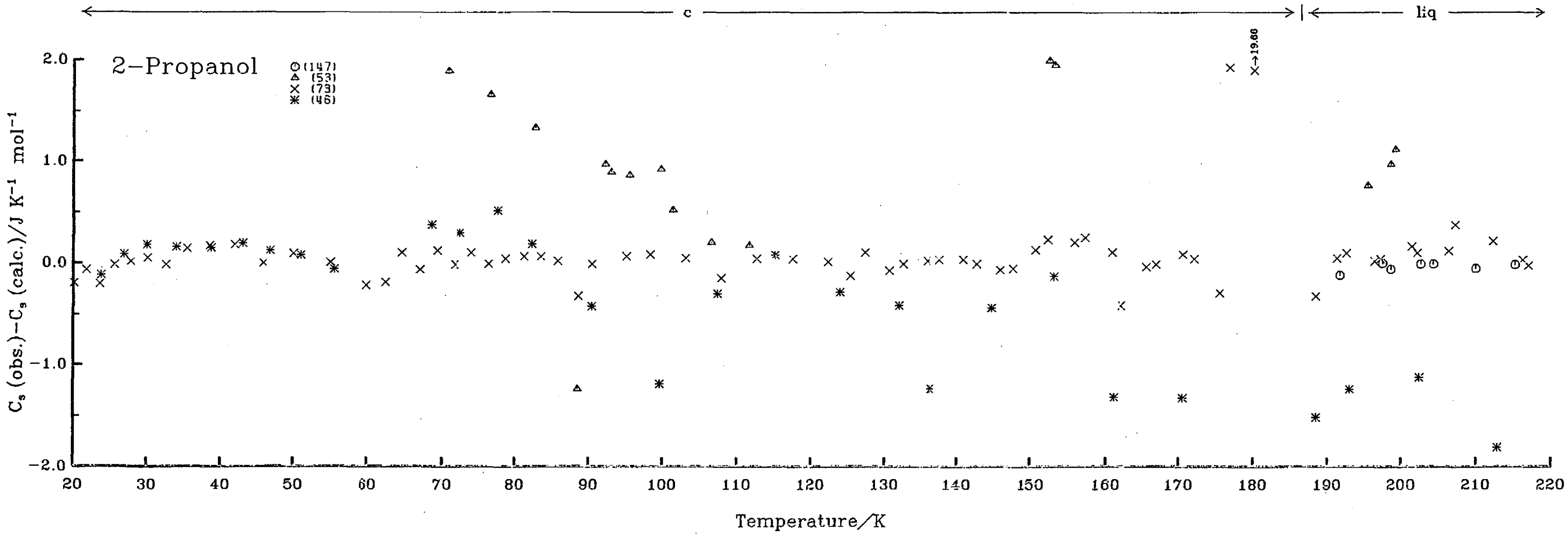

FIG. 22. Deviation plot for 2-propanol, c, l, 20–220 K.

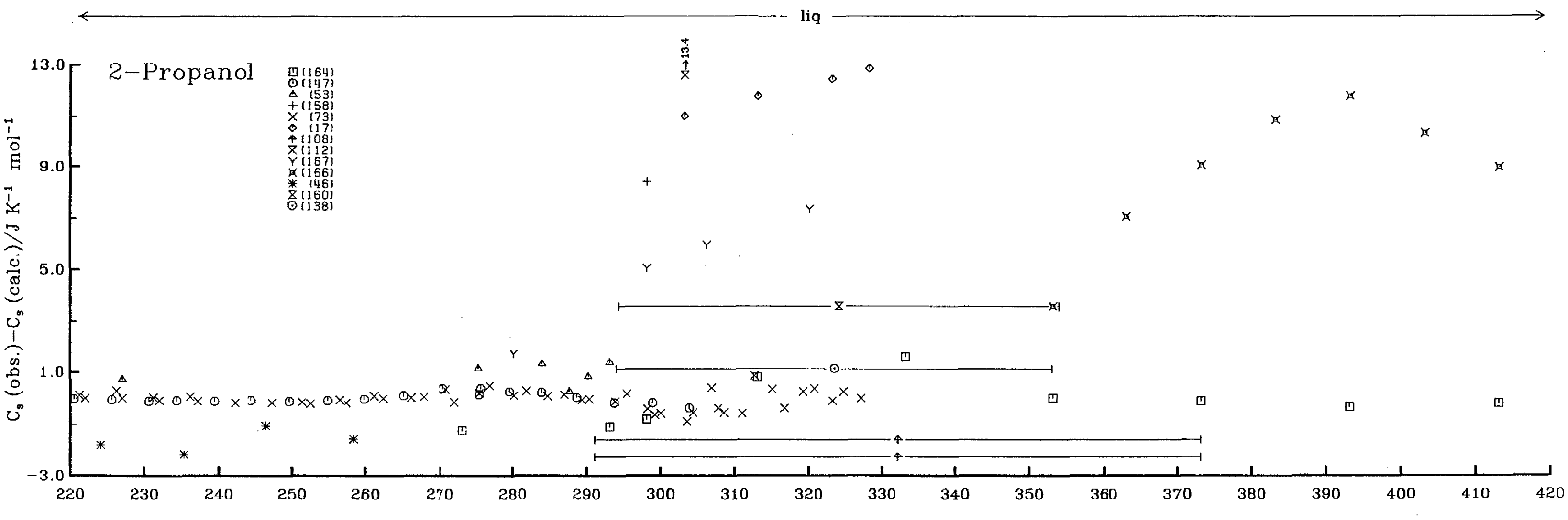

FIG. 23. Deviation plot for 2-propanol, l, 220–420 K.

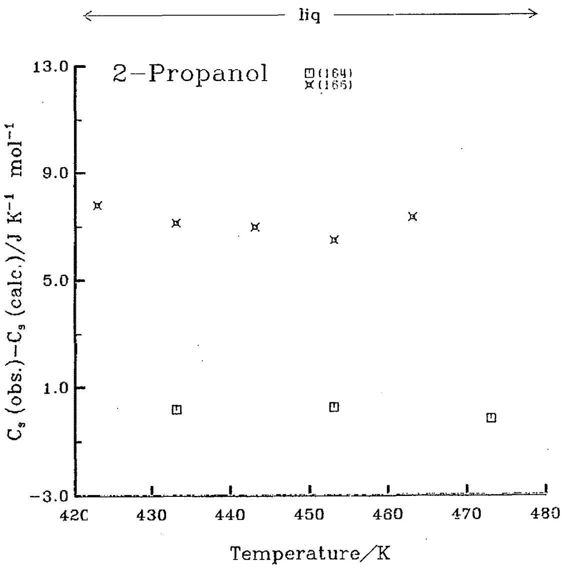

FIG. 24. Deviation plot for 2-propanol, l, 420–480 K.

6. 1-Butanol (Butyl Alcohol)

The only low temperature data are from Parks [48] and Counsell, Hales, and Martin [75]. The smoothed values in table 31 up to 320 K were obtained from a least squares fit to the latter set only. Parameters for the heat capacity equation at higher temperatures were obtained by a least squares fit to the $\bar{C}_s$ data for von Reis [105] and to C_s values calculated from the equation of Williams and Daniels [17]. In the second least squares calculation, the value of C_s and its temperature derivative were constrained to be continuous at 320 K with those calculated from the lower temperature region. Therefore the high temperature data did not affect the fit of the data of Counsell, Hales, and Martin in this procedure.

San Jose, Mellinger, and Reid [169] measured C_p at a fixed pressure of 15 bars from 293 to 465 K. A plot of their values, along with others at lower temperatures showed an inflection point at around 360 K so that the C_p curve becomes concave to the temperature axis at higher temperatures. They remarked that this behaviour was quite different than that observed for several hydrocarbons under similar conditions. Their data for 1-butanol appeared only in graphical form.

TABLE 28. Sources of Heat Capacity Data for 1-Butanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
von Reis	1881	l(290–352)	drop	H	not stated	6	no	[105]
Louguinine	1898	l(294–387)	drop	H	not stated			[138]
Williams & Daniels	1924	l(307–347)	adiabatic	C	Kahlbaum sample, dried over, CaO,distilled, dried over BaO, treated with Na,fract.dist.	4	no	[17]
Parks	1925	c(91–151),l(195–294)	isoperibol	C	commercial sample,dist. over Ca,fract.dist. twice			[48]
Trew & Watkins	1933	l(298)	mixture	C	not stated			[158]
Philip	1939	l(303)	not stated	C	commercial sample, distilled			[112]
Swietoslawski & Zielenkiewcz	1960	l(294–350)	drop	H	not stated			[114]
Counsell, Hales & Martin	1965	c(11–179),l(188–322)	adiabatic	C	99.94^g mol%, 99.92^c mol%	70	corr	[75]
Paz Andrade, Paz Fernandez & Recacho	1970	l(301–313)	Calvet	C				[116]

TABLE 29. Reported Phase Transition Data for 1-Butanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Timmermans	1921	$c \rightleftharpoons l$	183.4	mp			[170]
Parks	1925	$c \rightleftharpoons l$	183.9	tp	9282.	c	[48]
Timmermans & Martin	1928	$c \rightleftharpoons l$	183.0	mp			[171]
Cady & Jones	1933	$c \rightleftharpoons l$	182.8	mp			[162]
Bridgman	1941	$c \rightleftharpoons l$	183.4*	mp			[149]
Dreisbach & Martin	1949	$c \rightleftharpoons l$	183.83	mp			[151]
Tschamler, Richter & Wettig	1949	$c \rightleftharpoons l$	192.6	mp			[163]
Sackmann & Sauerwald	1950	$c \rightleftharpoons l$	189.	mp			[152]
Counsell, Hales & Martin	1965	$c \rightleftharpoons l$	184.54	tp	9372.	c	[75]
Faucher & Koleske	1966	glass	118.	ml			[122]
Lesikar	1975	glass	111.6	dt			[123]
Lesikar	1975	glass	112.8	dt			[124]
SELECTED VALUES		$c \rightleftharpoons l$	184.54±0.02		9372.±8		

*Melting point reported at pressures 0 to 3400 MPa.

TABLE 30. Parameters for Heat Capacity of 1-Butanol

Phase	c	c	c	c	c	l	l
Data Points							
Number	4	15	18	17	45(11)	11	14
Temp./K	11.2 - 14.3	15.5 - 62.0	66.9 -118.5	123.3 -177.7	11.2 -177.7	188.2 -246.0	251.6 -317.3
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 15.0	15.0 - 65.0	65.0 -120.0	120.0 -184.54	0 -184.54	184.54-250.0	250.0 -320.0
a_i		-2.83	3.27	-88.07		63.05	10.86
b_i x 10		1.086	3.203	32.852		9.829	14.982
c_i x 10^3		29.499	11.222	-27.0003		-5.1721	-6.7889
d_i x 10^5	158.6	-44.429	-12.1021	10.9759		1.0624	1.2187
e_i x 10^7	-257.1	21.390	3.7924	-1.6491			
Deviations							
Average, d	0.011	-0.015	-0.007	0.003	0.000	-0.008	-0.005
R.M.S.,r(σ)	0.060	0.139	0.120	0.067	0.096(0.113)	0.182	0.241
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.08	0.15	0.2	0.25		0.3	0.35
$\delta(H-H_0)$	0.3	7.5	13.	21.		30.	39.
$\delta(S)$	0.034	0.22	0.25	0.3		0.3	0.3
$\delta(G-H_0)/T$	0.015	0.11	0.11	0.11		0.11	0.11

Phase	l	l
Data Points		
Number	10	35(8)
Temp./K	322.3 -389.0	188.2 -246.0
Parameters for	C_s	C_s
Temp./K	320.0 -390.0	184.54-390.0
a_i	-172.38	
b_i x 10	12.742	
c_i x 10^3	-0.021	
d_i x 10^5	-0.1182	
Deviations		
Average, d	0.22	0.025
R.M.S., $r(\sigma)$	1.05	0.44(0.50)
$\delta(C)$	2.0	
$\delta(H-H_0)$	145.	
$\delta(S)$	0.5	
$\delta(G-H_0)/T$	0.12	

TABLE 31. Thermodynamic Functions of 1-Butanol
$C_4H_{10}O$ $M = 74.122$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.000	0.000
10	-0.119	0.345	3.45	0.464	1.329
15	-0.381	1.078	16.17	1.459	4.051
20	-0.85	2.29	45.89	3.14	7.93
25	-1.52	3.85	96.13	5.37	12.22
30	-2.38	5.61	168.40	7.99	16.71
35	-3.38	7.52	263.36	10.91	21.27
40	-4.52	9.52	381.0	14.04	25.75
50	-7.08	13.63	681.4	20.71	34.18
60	-9.93	17.69	1061.3	27.62	41.64
70	-12.95	21.59	1511.3	34.54	48.26
80	-16.08	25.31	2024.5	41.38	54.27
90	-19.26	28.83	2594.6	48.09	59.64
100	-22.48	32.15	3215.3	54.63	64.40
110	-25.69	35.28	3881.1	60.97	68.71
120	-28.89	38.24	4588.7	67.13	72.79
130	-32.06	41.05	5336.7	73.11	76.74
140	-35.20	43.74	6122.9	78.94	80.48
150	-38.31	46.31	6946.1	84.61	84.15
160	-41.37	48.79	7806.1	90.16	87.85
170	-44.40	51.20	8703.4	95.60	91.62
180	-47.40	53.55	9638.7	100.95	95.45
184.54	-48.74	54.60	10076.0	103.35	97.21
		Liquid			
184.54	-48.74	105.39	19448.0	154.13	135.07
190	-51.83	106.25	20187.9	158.08	135.96
200	-57.32	107.78	21556.	165.10	137.74
210	-62.61	109.25	22943.	171.87	139.76
220	-67.73	110.7	24352.	178.42	142.08
230	-72.68	112.1	25786.	184.80	144.78
240	-77.48	113.5	27249.	191.02	147.90
250	-82.15	115.0	28746.	197.13	151.52
260	-86.69	116.5	30281.	203.15	155.66
270	-91.11	118.0	31861.	209.11	160.34
280	-95.43	119.6	33490.	215.04	165.64
290	-99.66	121.3	35176.	220.95	171.62
298.15	-103.04	122.7	36597.	225.78	177.06
300	-103.80	123.1	36925.	226.88	178.37
310	-107.86	125.0	38746.	232.85	185.95
320	-111.86	127.0	40647.	238.89	194.44
330	-115.81	129.2	42637.	245.01	203.34
340	-119.70	131.5	44713.	251.21	212.0
350	-123.54	133.9	46875.	257.47	220.3
360	-127.35	136.4	49119.	263.8	228.5
370	-131.13	139.0	51443.	270.2	236.3
380	-134.9	141.7	53845.	276.6	243.9
390	-138.6	144.4	56321.	283.0	251.

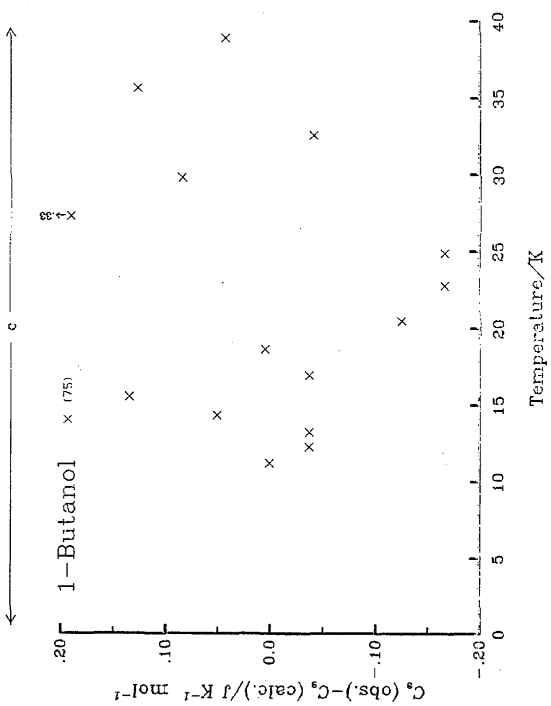

FIG. 25. Deviation plot for 1-butanol, c, 0–40 K.

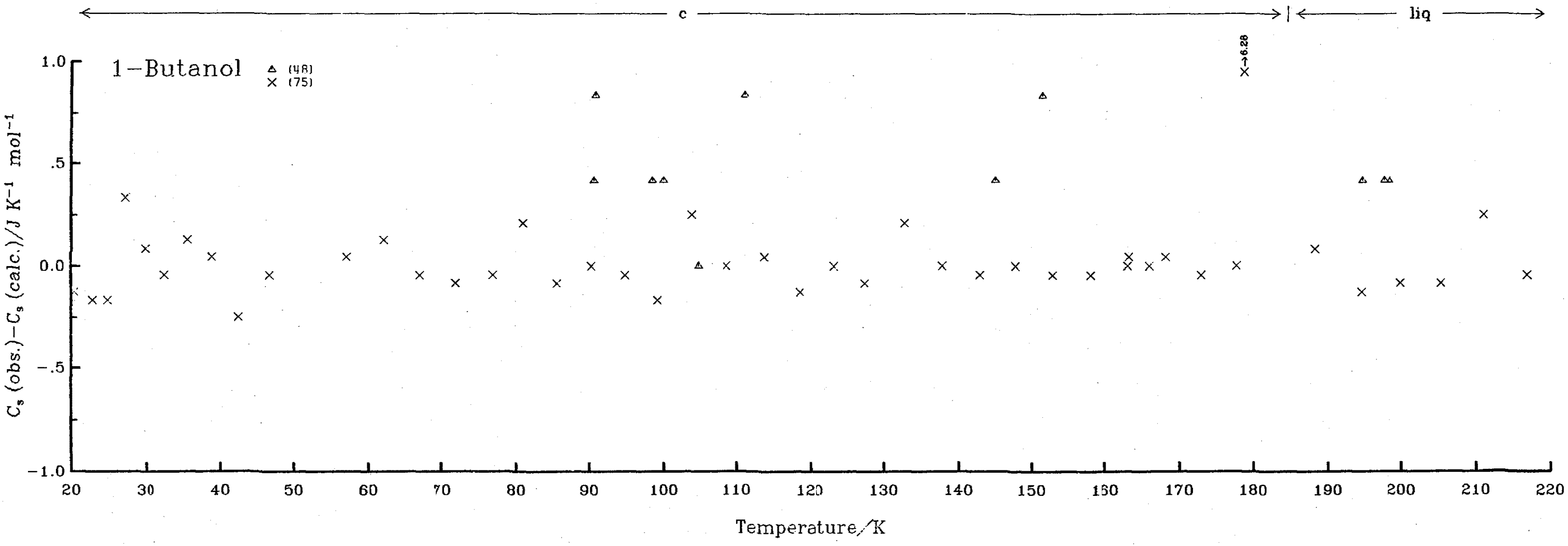

FIG. 26. Deviation plot for 1-butanol, c, l, 20–220 K.

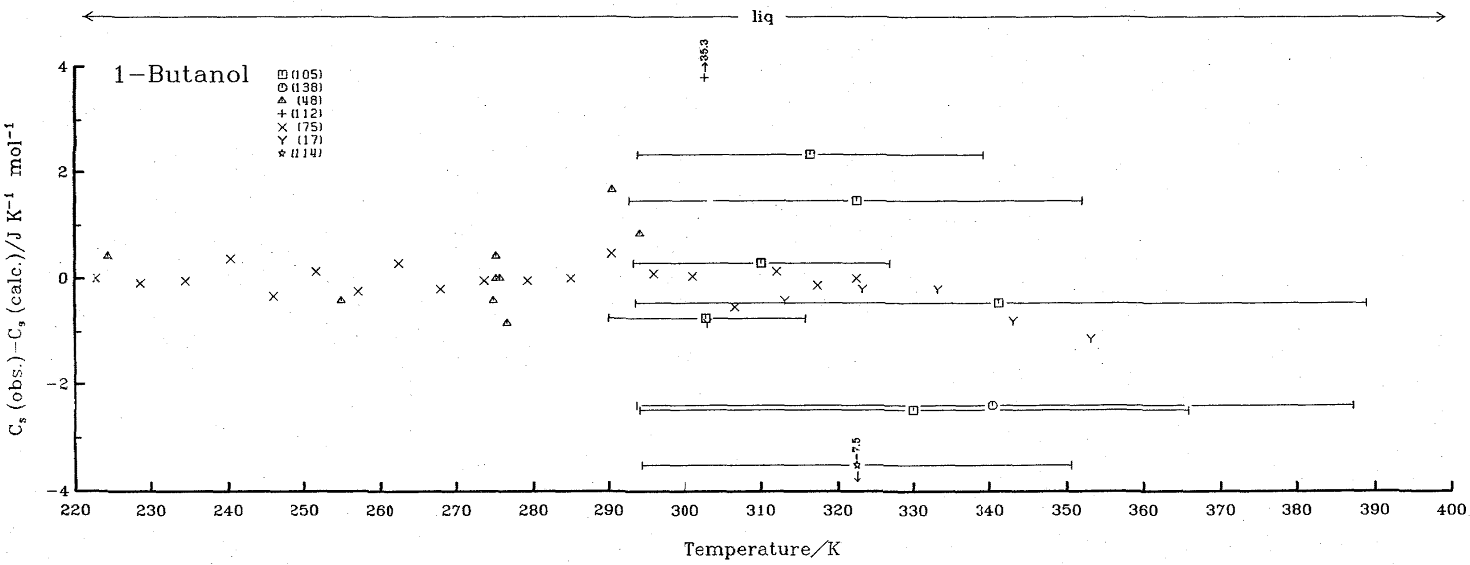

FIG 27. Deviation plot for 1-butanol, l, 220–400 K.

7. 2-Butanol (sec-Butyl Alcohol)

The 2-butanol molecule contains an asymmetrically substituted carbon atom, and therefore the compound exists as two optical isomers. Andon, Connett, Counsell, Lees, and Martin [72] measured the heat capacity, triple point and enthalpy of fusion of d-2-butanol in an adiabatic calorimeter. The specific rotation of their sample was $[\alpha]_D^{22.5} = 13.64°$. Sample purity was established both by gas chromatography and analysis of the melting curve. See Table 32. The heat capacity of the crystal showed a large pre-melting effect, which can be seen in Fig. 29, and therefore measured values above 150.46 K were not used in the least squares calculation of the parameters.

Parks, Thomas, and Light [56] measured the heat capacity of the liquid and glass forms of racemic 2-butanol down to 103 K using a Nernst type calorimeter. They could not prepare the crystals. The smoothed values of properties for the crystal, liquid and glass phases in tables 37 and 38 were derived from the measurements of Andon, Connett, Counsell, Lees and Martin [72]. The reference states for entropy, enthalpy, and Gibbs energy in these tables is the racemic crystal at 0 K. Crystallization of the racemic form was initiated by repeated thermal cycling for several days, and complete crystallization required fifteen days.

If we assume that the two enantiomers of 2-butanol form an ideal liquid solution, then the enthalpy of the liquid racemic mixture is the same as that of either pure enantiomer, and the entropy is greater by the amount $R \ln 2 = 5.76$ J K^{-1} mol^{-1}. With this assumption the comparison of Table 36 with 37 shows that the enthalpy of the racemic crystal at 0 K is 9.9 J mol^{-1} larger than the pure enantiomer at this temperature, and the entropy is 4.06 J K^{-1} mol^{-1} larger. This implies that the racemic crystal is a solid solution of D– and L– forms, but not a completely random one. The fact that the racemic crystal melts at a higher temperature than the pure enantiomers means that either the racemic crystal is a compound of the D– and L– forms or that it is a non-ideal solution of them. This latter conclusion is the simplest interpretation of the thermodynamic data.

TABLE 32. Sources of Heat Capacity Data for 2-Butanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
			dl–form					
Parks, Thomas & Light	1936	l(275–282) gl(103–182)	adiabatic	C	pure sample from H.E.Buc, Standard Oil Development Co.			[56]
Andon, Connett, Counsell,Lees & Martin	1971	c(12–179),l(188–345) gl(11–181)	adiabatic	C	analytical reag., fract. distilled 3 times, 99.95^g mol %	183	corr*	[72]
			d–form					
Andon, Connett, Counsell,Lees & Martin	1971	c(12–165),l(180–310)	adiabatic	C	prepared by Pickard & Kenyon's method, 99.85^g mol%	88	corr*	[72]
Conti, Gianni, Mateoli & Mengheri	1976	l(298)	Calvet	C	not stated			[172]

*Original scale was IPTS-48, Martin [173].

TABLE 33. Reported Phase Transition Data for 2-Butanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
		DL–2-Butanol					
Cady & Jones	1933	$c \rightleftharpoons l$	158.4	mp			[162]
Parks, Thomas & Light	1936	glass	115.	hc			[56]
Faucher & Koleske	1966	glass	127.	ml			[122]
Andon, Connett, Counsell, Lees & Martin	1971	$c \rightleftharpoons l$	184.70	tp	5971.	c	[72]
		glass	114.	hc			
Lesikar	1975	glass	122.0	dt			[124]
SELECTED VALUES		$c \rightleftharpoons l$	184.73±0.10		5971.±20		
		D–2–Butanol					
Andon, Connett, Counsell	1971	$c \rightleftharpoons l$	177.38	tp	6000.	c	[72]
SELECTED VALUES		$c \rightleftharpoons l$	177.38±0.10		6000.±25		

TABLE 34. Parameters for Heat Capacity of D-2-Butanol

Phase	c	c	c	c	c	c	l	l	c
Data Points									
Number	6	7	22	10	9*	54*(14)	24	11	35(8)
Temp./K	12.0 - 16.9	18.3 - 28.6	30.9 - 99.4	102.6 -132.1	138.9 -150.5	12.0 -150.5	180.1 -260.0	264.1 -309.7	180.1 -309.7
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 17.0	17.0 - 30.0	30.0 -100.0	100.0 -135.0	135.0 -177.38	0 -177.38		260.0 -310.0	177.38-310.0
a_i		15.258	-20.683	784.32	2212.32		72.89	-6116.29	
b_i x 10		-30.672	18.198	-255.044	-585.9952		6.9089	921.1594	
c_i x 10^3		244.087	-21.572	325.774	595.1279		-2.7628	-510.1399	
d_i x 10^5	272.5	-657.18	17.300	-179.6689	-266.0965		-0.0042	125.4087	
e_i x 10^7	-782.4	657.22	-5.614	36.7499	44.4965		0.21267	-11.44050	
Deviations									
Average, d	0.000	0.017	-0.004	-0.008	0.000	0.000	-0.004	0.008	0.000
R.M.S., $r(\sigma)$	0.075	0.046	0.075	0.155	0.105	0.092(0.105)	0.039	0.121	0.071(0.080)
Estimated Uncertainty in Tabulated Values									
$\delta(C)$	0.10	0.10	0.12	0.15	0.2		0.25	0.25	
$\delta(H\text{-}H_0)$	0.5	1.4	8.5	10.	13.		47.	49.	
$\delta(S)$	0.041	0.07	0.16	0.17	0.18		0.25	0.3	
$\delta(G\text{-}H_0)/T$	0.015	0.020	0.06	0.06	0.06		0.07	0.07	

*Includes one point extrapolated to the triple point

TABLE 35. Parameters for Heat Capacity of DL-2-Butanol

Phase	c	c	c	c	c	c	l
Data Points							
Number	4	6	17	25	19	71(14)	30
Temp./K	11.5 – 15.3	16.8 – 27.6	30.4 –100.6	105.3 –150.0	151.9 –171.4	11.5 –171.4	188.4 –258.7
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 16.0	16.0 30.0	30.0 105.0	105.0 –150.0	150.0 –184.73	0 –184.73	
a_i		–15.268	–14.798	266.91	–3046.77		–130.86
b_i x 10		22.055	15.536	–75.040	788.6677		42.5432
c_i x 10^3		–83.07	–14.642	94.4117	–750.2786		–26.1619
d_i x 10^5	310.4	255.25	9.401	–49.1948	318.1813		6.84184
e_i x 10^7	–832.0	–297.30	–2.4626	9.4947	–50.4627		–0.54093
Deviations							
Average, d	0.000	–0.008	0.000	0.000	0.004	0.000	0.002
R.M.S., $r(\sigma)$	0.100	0.033	0.088	0.063	0.142	0.092(0.105)	0.099
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.10	0.12	0.15	0.2	0.3		0.25
$\delta(H-H_0)$	0.5	1.7	11.	14.	18.		48.
$\delta(S)$	0.04	0.09	0.21	0.22	0.23		0.3
$\delta(G-H_0)/T$	0.015	0.024	0.08	0.09	0.09		0.09

Phase	l	l	gl	gl	gl	gl	gl
Data Points							
Number	30	60(8)	6	23	6	4	13
Temp./K	261.5 –345.4	188.4 –345.4	11.2 – 16.9	18.6 – 93.6	97.6 –116.0	119.1 –128.8	132.3 –180.6
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	260.0 –350.0	184.73–350.0	0 – 18.0	18.0 – 95.0	95.0 –117.0	117.0 –130.0	130.0 –185.0
a_i	–592.05			–10.41	106062.82	–1286035.3	1345.48
b_i x 10	136.3741			13.395	–41720.87	409421.53	–312.0688
c_i x 10^3	–92.7490			–11.510	61469.38	–488553.84	297.4959
d_i x 10^5	26.91763		407.3	8.708	–40183.33	259004.428	–125.6532
e_i x 10^7	–2.74159		–1267.2	–2.843	9835.47	–51471.847	19.9178
Deviations							
Average, d	0.004	0.003	0.084	0.000	–0.29	0.26	–0.008
R.M.S.,$(r\sigma)$	0.107	0.102(0.109)	0.155	0.268	1.11	1.14	0.084
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.3		0.15	0.25	2.0	2.0	0.3
$\delta(H-H_0)$	55.		1.0	19.	48.	55.	57.
$\delta(S)$	0.3		0.09	0.4	0.6	0.6	0.6
$\delta(G-H_0)/T$	0.09		0.033	0.21	0.22	0.22	0.22

Phase	gl
Data Points	
Number	52(14)
Temp./K	11.2 –180.6
Parameters for	C_s
Temp./K	0 –185.0
Deviations	
Average, d	0.008
R.M.S., $r(\sigma)$	0.460(0.540)

TABLE 36. Thermodynamic Functions of D-2-Butanol
$C_4H_{10}O$ $M = 74.122$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.00	0.000
10	-0.188	0.525	5.25	0.71	1.943
15	-0.568	1.507	22.61	2.08	5.236
20	-1.191	2.96	59.14	4.15	9.49
25	-2.037	4.73	118.15	6.76	14.12
30	-3.07	6.67	200.2	9.74	18.72
35	-4.25	8.72	305.1	12.97	23.16
40	-5.55	10.78	431.2	16.33	27.23
50	-8.39	14.81	740.6	23.20	34.49
60	-11.43	18.64	1118.3	30.07	40.94
70	-14.58	22.25	1557.7	36.83	46.86
80	-17.78	25.68	2054.4	43.46	52.42
90	-20.99	28.94	2605.0	49.94	57.65
100	-24.20	32.06	3205.9	56.26	62.44
110	-27.40	35.04	3854.4	62.44	67.36
120	-30.57	37.94	4553.1	68.52	72.30
130	-33.72	40.76	5298.3	74.48	76.62
140	-36.84	43.46	6084.1	80.30	80.58
150	-39.93	46.07	6910.4	86.00	84.65
160	-42.98	48.60	7776.2	91.59	88.48
170	-46.01	51.07	8681.1	97.07	92.67
177.38	-48.21	52.88	9379.7	101.09	96.92
		Liquid			
177.38	-48.21	86.71	15379.7	134.92	129.33
180	-49.49	87.33	15719.2	136.82	129.82
190	-54.27	89.62	17027.3	143.89	131.85
200	-58.93	91.79	18357.	150.71	134.25
210	-63.45	93.88	19714.	157.33	137.11
220	-67.87	95.92	21101.	163.78	140.54
230	-72.18	97.9	22527.	170.12	144.65
240	-76.39	100.0	23997.	176.38	149.54
250	-80.51	102.1	25521.	182.60	155.36
260	-84.56	104.3	27108.	188.82	162.20
270	-88.54	106.5	28768.	195.08	170.06
280	-92.45	109.0	30512.	201.43	178.95
290	-96.32	111.6	32350.	207.88	188.85
298.15	-99.44	113.8	33924.	213.23	197.45
300	-100.15	114.3	34292.	214.46	199.44
310	-103.95	117.2	36340.	221.17	210.17

TABLE 37. Thermodynamic Functions of DL-2-Butanol
$C_4H_{10}O$ $M = 74.122$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.00	0.000
10	-0.217	0.610	6.10	0.83	2.272
15	-0.662	1.777	26.65	2.44	6.264
20	-1.403	3.53	70.52	4.93	11.28
25	-2.406	5.57	139.29	7.98	16.22
30	-3.61	7.75	232.4	11.36	20.97
35	-4.97	9.95	348.3	14.92	25.30
40	-6.44	12.12	484.9	18.57	29.31
50	-9.60	16.29	814.7	25.90	36.49
60	-12.92	20.20	1211.9	33.12	42.82
70	-16.31	23.84	1669.1	40.16	48.54
80	-19.72	27.27	2181.2	46.99	53.83
90	-23.12	30.50	2744.6	53.62	58.80
100	-26.49	33.56	3356.4	60.06	63.53
110	-29.83	36.49	4014.4	66.33	68.08
120	-33.13	39.32	4718.6	72.45	72.75
130	-36.39	42.07	5469.1	78.46	77.32
140	-39.60	44.74	6264.2	84.35	81.66
150	-42.78	47.35	7102.0	90.12	85.92
160	-45.91	49.89	7983.2	95.81	90.36
170	-49.02	52.41	8910.4	101.43	95.08
180	-52.08	54.91	9882.9	106.99	99.18
184.73	-53.52	56.06	10355.1	109.58	100.35
		Liquid			
184.73	-53.52	88.38	16326.1	141.90	130.57
190	-56.02	89.57	17017.4	145.59	131.80
200	-60.67	91.7	18348.	152.41	134.33
210	-65.20	93.8	19705.	159.03	137.23
220	-69.61	95.9	21094.	165.50	140.66
230	-73.92	97.9	22521.	171.84	144.74
240	-78.13	100.0	23992.	178.10	149.60
250	-82.25	102.1	25515.	184.32	155.34
260	-86.30	104.2	27102.	190.54	162.05
270	-90.27	106.5	28760.	196.79	169.85
280	-94.19	108.9	30502.	203.13	178.73
290	-98.06	111.5	32338.	209.57	188.47
298.15	-101.18	113.7	33908.	214.91	196.89
300	-101.88	114.2	34274.	216.13	198.84
310	-105.68	117.1	36315.	222.82	209.48
320	-109.44	120.2	38463.	229.64	220.03
330	-113.19	123.4	40714.	236.57	230.01
340	-116.92	126.6	43060.	243.57	238.90
350	-120.64	130.0	45486.	250.60	246.13

TABLE 38. Thermodynamic Functions of DL-2-Butanol
$C_4H_{10}O$ M = 74.122

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
			Glass		
0			2995.9	9.72	0.00
10	289.59	300.35	3003.5	10.76	2.81
15	189.18	201.88	3028.2	12.70	7.33
20	138.37	153.89	3077.8	15.52	12.43
25	107.27	126.07	3151.8	18.80	17.13
30	85.97	108.29	3248.6	22.32	21.54
35	70.24	96.19	3366.8	25.95	25.68
40	57.99	87.63	3505.0	29.64	29.60
50	39.72	76.76	3838.1	37.04	36.90
60	26.32	70.69	4241.2	44.37	43.65
70	15.70	67.28	4709.7	51.58	50.00
80	6.85	65.50	5240.1	58.65	56.03
90	-0.82	64.77	5829.2	65.59	61.7
95	-4.32	64.68	6144.8	69.00	64.5
100	-7.64	64.78	6478.	72.42	69.3
105	-10.80	65.08	6834.	75.88	72.1
110	-13.84	65.4	7196.	79.3	73.7
115	-16.76	66.0	7595.	82.8	90.1
117.5	-18.19	66.8	7846.	85.0	112.1
120	-19.60	67.9	8144.	87.5	124.1
130	-25.2	72.2	9386.	97.4	124.55
140	30.7	75.9	10631.	106.6	124.67
150	-36.1	79.2	11882.0	115.27	125.65
160	-41.3	82.2	13144.4	123.41	126.85
170	-46.3	84.8	14419.3	131.14	128.15
180	-51.2	87.3	15709.0	138.51	129.91
185	-53.6	88.4	16361.5	142.09	131.19
190	-56.02	89.57	17017.4	145.59	131.80

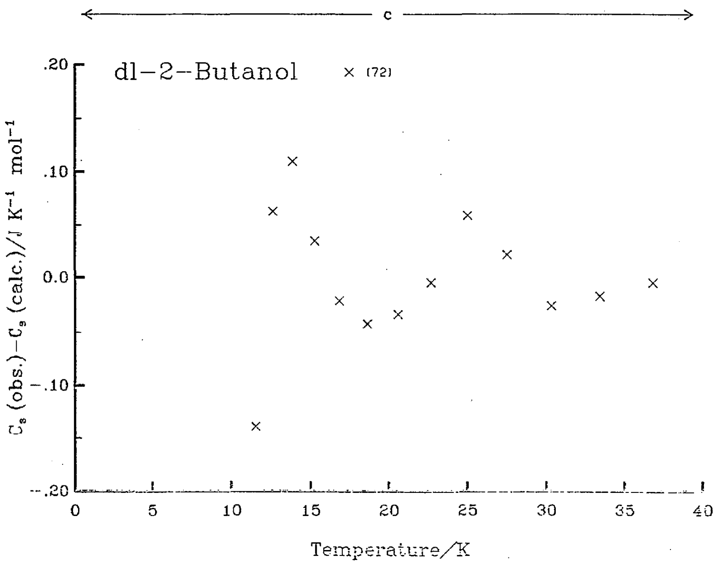

FIG. 28. Deviation plot for DL-2-butanol, c, 0–40 K.

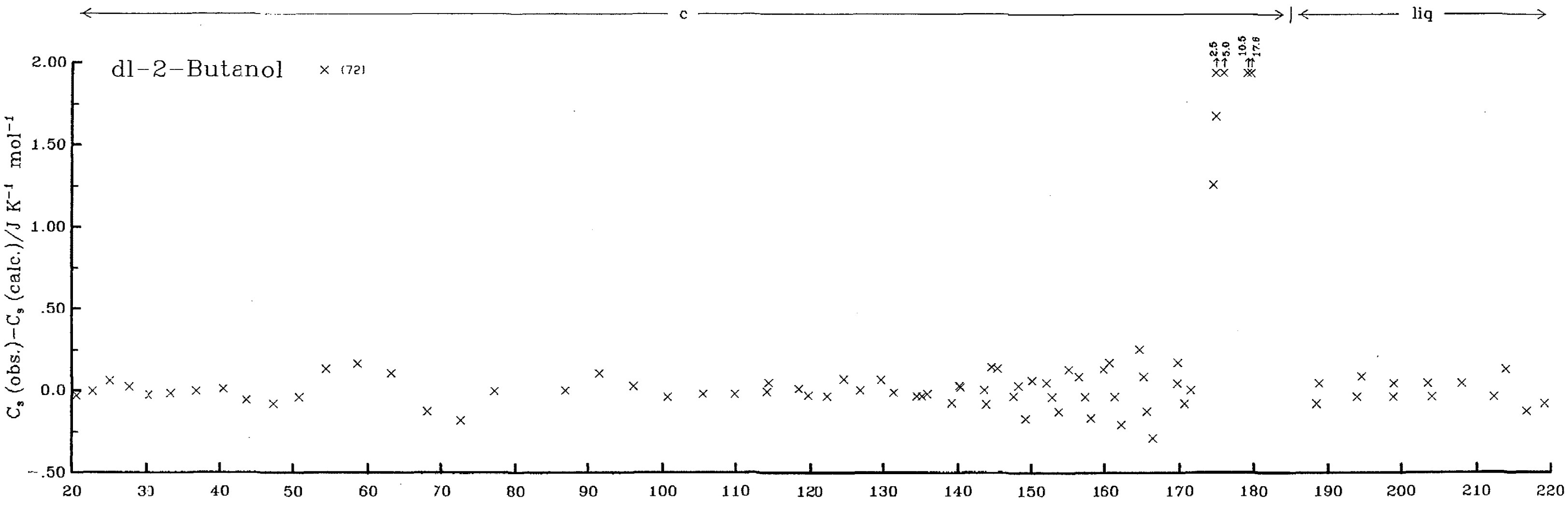

FIG. 29. Deviation plot for DL-2-butanol, 20–220 K.

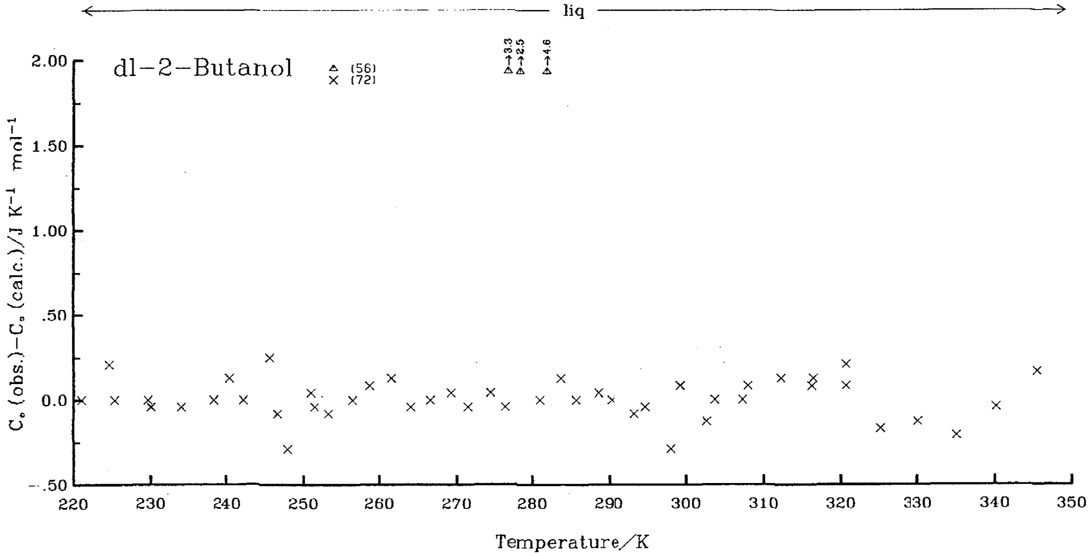

FIG. 30. Deviation plot for DL-2-butanol,220–350 K.

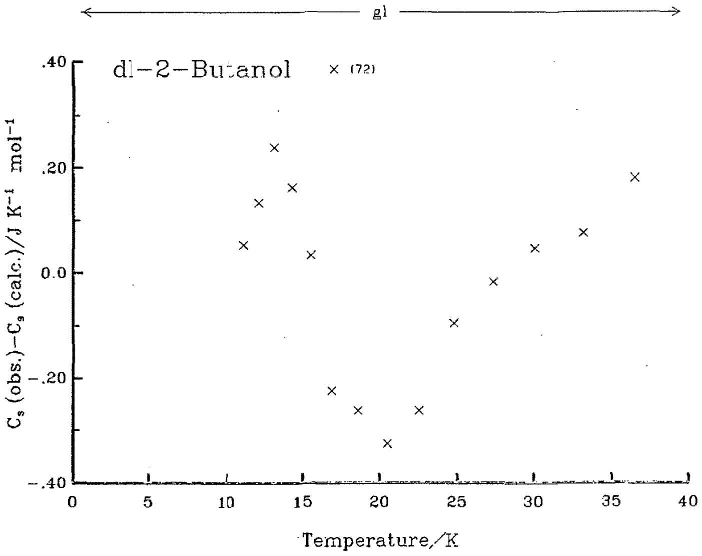

FIG. 31. Deviation plot for DL-2-butanol, gl, 0–40 K.

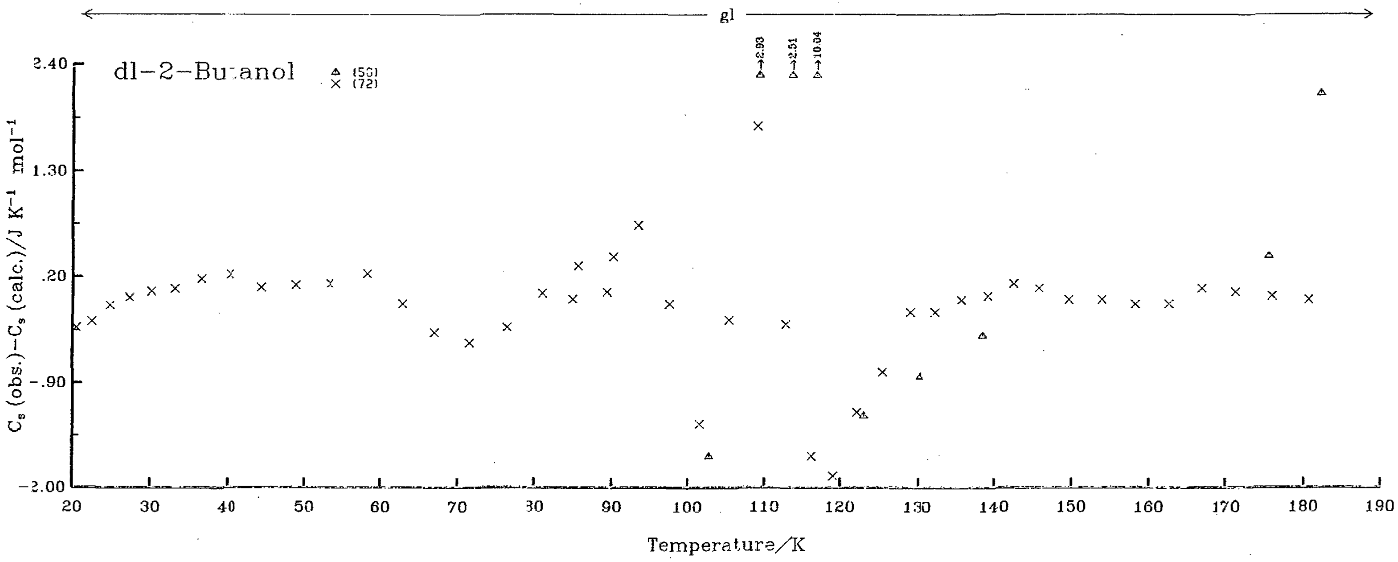

FIG. 32. Deviation plot for DL-2-butanol, gl, 20–180 K.

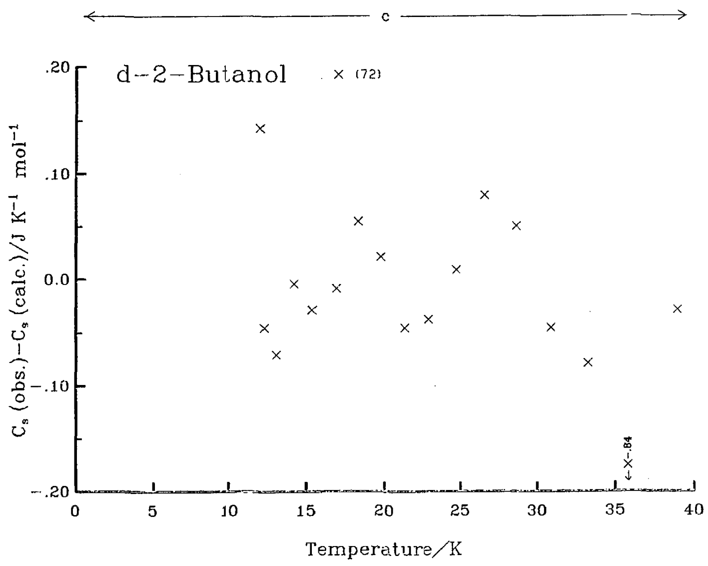

FIG. 33. Deviation plot for D-2-butanol, c, 0–40 K.

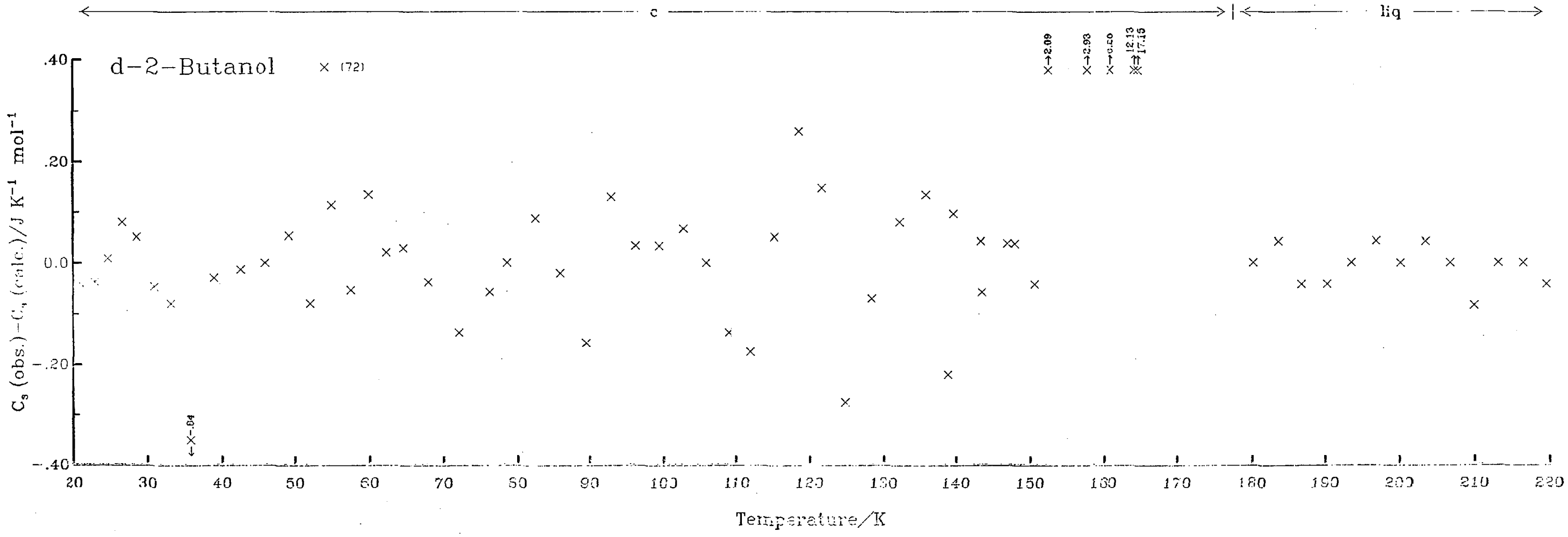

FIG. 34. Deviation plot for D-2-butanol, 20–220 K.

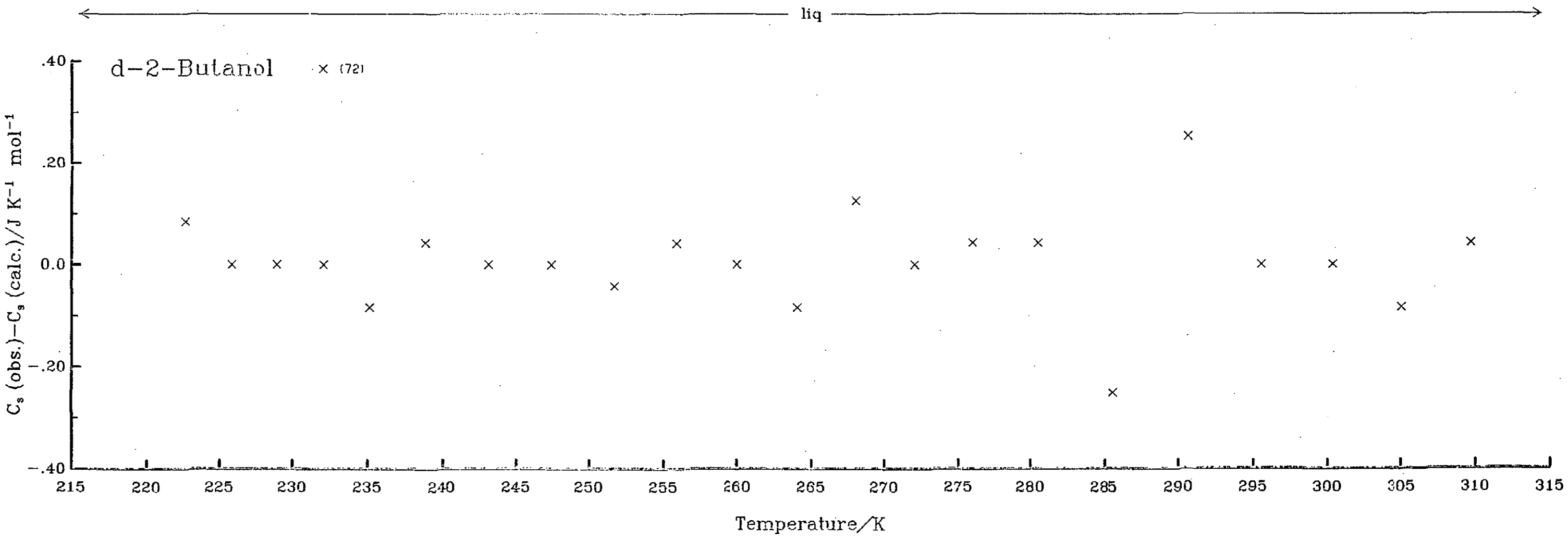

FIG. 35. Deviation plot for D-2-butanol, l, 220–310 K.

8. 2-Methyl-1-propanol (Isobutyl Alcohol)

The smoothed data for the crystal, glass, and liquid forms up to 355 K are based on the measurements of Counsell,Lees, and Martin [12], which were made along with those of propanol. The glass form resulted from the rapid cooling of the liquid. The sample then slowly crystallized on standing a few degrees above the glass transition temperature.

Table 39 lists several sets of measurements on liquid 2-methyl-1-propanol. The data of Williams and Daniels [17] overlap those of Counsell, Lees, and Martin [12], and lie from 0.3 J K^{-1} mol^{-1} higher at the low end to 1.7 J K^{-1} mol^{-1} higher at the upper end of the range. The measurements of Hoffman, San Jose and Reid [166] carry the available data up to 490 K. They measured C_p directly for the saturated liquid as well as for the liquid at pressures up to 40 bars. These data are converted to C_s by the use of the vapor pressure data of Ambrose and Townsend [134] and the liquid density from [126] up to 390 K. The coefficient of expansion of 2 methyl 1 propanol is assumed to be the same as that for 2-methyl-2-propanol at the same reduced temperature for the calculations at higher temperatures.

TABLE 39. Sources of Heat Capacity Data for 2-Methyl-1-propanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Schiff	1886	l(281-365)	drop	H	not stated			[16]
Louguinine	1898	l(294-382)	drop	H	not stated			[138]
Doroshevskii	1909	l(291-373)	drop	H				[108]
Williams & Daniels	1924	l(311-353)	adiabatic	C	U.S. Industrial Chemical Co. sample, dried over BaO			[17]
Zhdanov	1941	l(278-319)	drop	H				[159]
Kanda,Otsubo & Haseda	1950	c(103-170), l(175-230)	isoperibol	C				[58]
Otsubo, Haseda & Kanda	1955	gl,l(100-120)	adiabatic	C	not stated			[29]
Swietoslawski & Zielenkiewicz	1958	l(295-379)	drop	H	not stated			[160]
Swietoslawski & Zielenkiewcz	1960	l(294-351)	drop	H	not stated			[114]
Counsell, Lees & Martin	1968	c(11-163),l(175-355) gl(11-168)	adiabatic	C	fract. distilled 99.3^8 mol%	152	corr	[12]
Hoffman, San Jose & Reid	1977	l(383-493)	flow	C	not stated	12	no	[166]

TABLE 40. Reported Phase Transition Data for 2-Methyl-1-propanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Kanda, Otsubo & Haseda	1950	$c \rightleftharpoons l$	169.	tp	6070.	c	[58]
Otsubo, Haseda & Kanda	1955	glass	115.	hc			[29]
Faucher & Koleske	1966	glass	127.	ml			[122]
Counsell, Lees & Martin	1968	$c \rightleftharpoons l$	171.20	tp	6322.	c	[12]
		glass	120.	hc			
Lesikar	1975	glass	117.4	dt			[124]
SELECTED VALUES		$c \rightleftharpoons l$	171.20±0.01		6322.±10		

TABLE 41. Parameters for Heat Capacity of 2–Methyl–1–propanol

Phase	c	c	c	c	c	c	l
Data Points							
Number	4	14	6	13	10	47(14)	18
Temp./K	10.9 – 14.8	16.1 – 62.7	67.9 – 92.2	97.0 –138.4	143.6 –163.4	10.9 –163.4	175.3 –244.1
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 – 15.0	15.0 – 65.0	65.0 – 94.0	94.0 –140.0	140.0 –171.2	0 –171.2	171.2 –245.0
a_i		–8.992	–116.23	–34.63	6993.30		131.05
$b_i \times 10$		8.604	69.578	20.353	–1910.951		–1.0442
$c_i \times 10^3$		9.126	–123.893	–18.1697	1971.9620		0.0138
$d_i \times 10^5$	177.0	–26.096	106.434	9.3263	–902.1223		0.2789
$e_i \times 10^7$	–159.	16.700	–34.307	–1.8365	154.7099		
Deviations							
Average, d	0.034	–0.008	–0.013	–0.004	0.000	0.000	–0.023
R.M.S., $r(\sigma)$	0.067	0.100	0.084	0.034	0.088	0.080(0.096)	0.092
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.10	0.12	0.2	0.2	0.25		0.3
$\delta(H-H_0)$	0.4	6.0	8.4	12.	15.		28.
$\delta(S)$	0.039	0.18	0.19	0.21	0.22		0.24
$\delta(G-H_0)/T$	0.014	0.08	0.09	0.09	0.09		0.09

Phase	l	l	l	l	l	l	l
Data Points							
Number	44	16	78(8)	18	44	16	78(8)
Temp./K	248.6 –337.8	341.4 –493.2	175.3 –493.2	175.3 –244.1	248.6 –337.8	341.4 –493.2	175.3 –493.2
Parameters for	C_s	C_s	C_s	C_p	C_p	C_p	C_p
Temp./K	245.0 –340.0	340.0 –500.0	171.2 –500.0	171.2 –245.0	245.0 –340.0	340.0 –500.0	171.2 –500.0
a_i	536.98	–1243.49		124.19	517.05	–1463.47	
$b_i \times 10$	–43.4535	89.9145		–0.4656	–41.2886	107.9282	
$c_i \times 10^3$	14.3456	–17.9001		–0.4656	13.5657	–22.8111	
$d_i \times 10^5$	–1.2658	1.21123		0.3552	–1.1726	1.65740	
Deviations							
Average, d	0.029	–0.155	–0.004	–0.21	0.035	–0.160	0.000
R.M.S., $r(\sigma)$	0.296	0.79	0.333(0.348)	0.090	0.295	0.87	0.348(0.368)
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.4	0.6		0.3	0.4	0.6	
$\delta(H-H_0)$	47.	107.					
$\delta(S)$	0.3	0.4					
$\delta(G-H_0)/T$	0.09	0.10					

Phase	gl	gl	gl	gl	gl	gl
Data Points						
Number	6	16	3	3	11	39(14)
Temp./K	11.4 – 18.7	20.9 – 81.4	86.8 – 97.2	102.5 –112.5	117.2 –167.6	11.4 –167.6
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 – 20.0	20.0 – 85.0	85.0 –102.0	102.0 –115.0	115.0 –170.0	0 –170.0
a_i		–9.30	–3145.66	–828622.77	–2602.60	
$b_i \times 10$		12.354	1279.671	310235.082	769.750	
$c_i \times 10^3$		–6.373	–1910.302	–435049.628	–811.743	
$d_i \times 10^5$	395.7	–1.904	1258.532	270822.645	378.4079	
$e_i \times 10^7$	–1180.4	4.370	–306.084	–63138.889	–65.7054	
Deviations						
Average, d	0.084	–0.004	–0.038	–0.138	0.046	0.000
R.M.S., $r(\sigma)$	0.218	0.209	0.105	0.330	0.297	0.234(0.293)
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.2	0.2	0.25	0.5	0.35	
$\delta(H-H_0)$	1.7	13.	14.	15.	24.	
$\delta(S)$	0.13	0.3	0.32	0.33	0.35	
$\delta(G-H_0)/T$	0.05	0.14	0.14	0.14	0.15	

TABLE 42. Thermodynamic Functions of 2-Methyl-1-propanol
$C_4H_{10}O$ $M = 74.122$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}		
			Crystal			
0	0.000	0.000	0.00	0.00	0.000	0.000
10	-0.140	0.411	4.11	0.55	1.611	1.611
15	-0.458	1.332	19.99	1.79	5.169	5.169
20	-1.044	2.903	58.06	3.95	10.046	10.046
25	-1.893	4.810	120.2	6.70	14.80	14.80
30	-2.949	6.86	205.7	9.81	19.34	19.34
35	-4.163	8.95	313.2	13.11	23.62	23.62
40	-5.49	11.03	441.4	16.53	27.60	27.60
50	-8.39	15.07	753.6	23.47	34.66	34.66
60	-11.48	18.86	1131.3	30.34	40.76	40.76
70	-14.66	22.39	1567.6	37.05	46.44	46.44
80	-17.87	25.74	2059.3	43.61	51.90	51.90
90	-21.09	28.95	2605.3	50.03	57.25	57.25
100	-24.30	32.03	3202.5	56.32	62.10	62.10
110	-27.49	34.97	3846.4	62.45	66.64	66.64
120	-30.65	37.79	4534.9	68.44	71.04	71.04
130	-33.78	40.51	5266.9	74.30	75.34	75.34
140	-36.88	43.15	6041.4	80.04	79.55	79.55
150	-39.95	45.72	6857.8	85.67	83.74	83.74
160	-42.98	48.23	7717.5	91.21	88.45	88.45
170	-45.98	50.82	8639.5	96.80	97.09	97.09
171.20	-46.34	51.15	8757.0	97.49	98.69	98.69
			Liquid			
171.20	-46.34	88.08	15079.0	134.42	127.57	127.55
180	-50.80	90.04	16208.	140.85	128.97	128.96
190	-55.73	92.14	17506.	147.87	130.84	130.84
200	-60.51	94.13	18825.	154.63	133.03	133.03
210	-65.14	96.04	20168.	161.18	135.56	135.55
220	-69.66	97.9	21538.	167.55	138.44	138.43
230	-74.05	99.7	22938.	173.78	141.70	141.68
240	-78.33	101.6	24373.	179.88	145.34	145.33
250	-82.51	103.4	25846.	185.90	149.46	149.47
260	-86.60	105.3	27365.	191.86	154.47	154.49
270	-90.61	107.2	28939.	197.79	160.38	160.39
280	-94.55	109.2	30576.	203.75	167.11	167.11
290	-98.42	111.3	32284.	209.74	174.58	174.57
298.15	-101.53	113.1	33733.	214.67	181.16	181.15
300	-102.23	113.6	34070.	215.79	182.71	182.70
310	-105.99	115.9	35940.	221.92	191.44	191.44
320	-109.71	118.4	37901.	228.15	200.68	200.70
330	-113.39	121.1	39956.	234.47	210.36	210.43
340	-117.04	123.9	42110.	240.90	220.40	220.55
350	-120.68	126.8	44363.	247.43	230.07	230.27
360	-124.28	129.7	46709.	254.03	238.69	238.90
370	-127.88	132.8	49137.	260.68	246.35	246.56
380	-131.45	135.9	51637.	267.34	253.11	253.33
390	-135.01	139.0	54202.	273.99	259.06	259.31
400	-138.56	142.1	56824.	280.62	264.26	264.62
410	-142.09	145.1	59497.	287.20	268.79	269.34
420	-145.60	148.1	62214.	293.73	272.72	273.57
430	-149.09	151.1	64971.	300.18	276.12	277.42
440	-152.56	154.0	67764.	306.57	279.1	281.0
450	-156.00	156.9	70588.	312.87	281.6	284.4
460	-159.42	159.7	73443.	319.08	283.9	287.6
470	-162.81	162.4	76326.	325.21	285.9	290.9
480	-166.17	165.1	79238.	331.2	287.7	294.4
490	-169.49	167.7	82177.	337.2	289.5	298.0
500	-172.77	170.3	85146.	343.1	291.2	301.9

TABLE 43. Thermodynamic Functions of 2-Methyl-1-propanol
$C_4H_{10}O$ $M = 74.122$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
			Glass		
0			3223.5	2.34	0.00
10	319.7	323.10	3231.0	3.36	2.78
15	211.7	217.04	3255.7	5.30	7.38
20	157.1	165.31	3306.2	8.17	12.77
25	123.75	135.28	3382.0	11.53	17.48
30	100.90	116.02	3480.5	15.11	21.87
35	84.07	102.86	3600.2	18.79	25.97
40	70.98	93.49	3739.8	22.52	29.82
50	51.54	81.48	4073.9	29.94	36.89
60	37.35	74.60	4475.8	37.25	43.43
70	26.17	70.60	4942.3	44.43	49.91
80	16.90	68.45	5475.7	51.54	56.90
90	8.90	67.59	6083.0	58.69	64.41
100	1.79	67.65	6764.6	65.86	72.51
110	−4.70	68.72	7560.	73.42	95.6
120	−10.84	72.63	8715.	83.46	121.72
130	−16.80	76.45	9939.	93.25	122.70
140	−22.59	79.77	11167.	102.36	123.11
150	−28.20	82.69	12404.	110.89	124.36
160	−33.62	85.36	13657.	118.98	126.30
170	−38.87	87.80	14926.	126.67	127.18

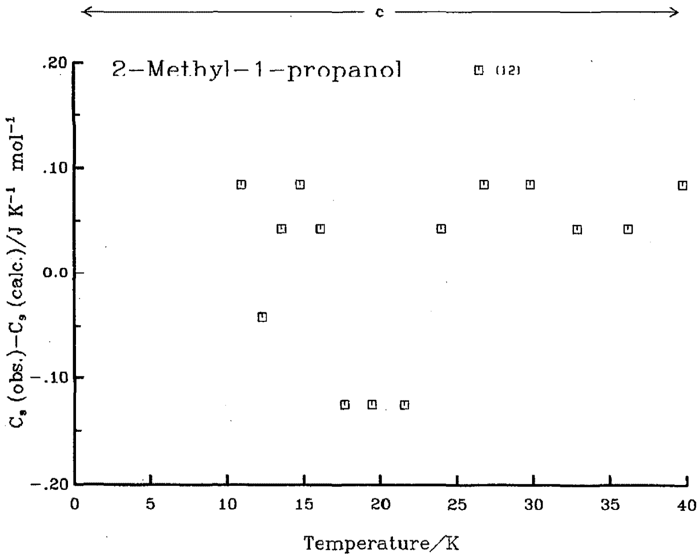

FIG. 36. Deviation plot for 2-methyl-1-propanol, c, 0–40 K.

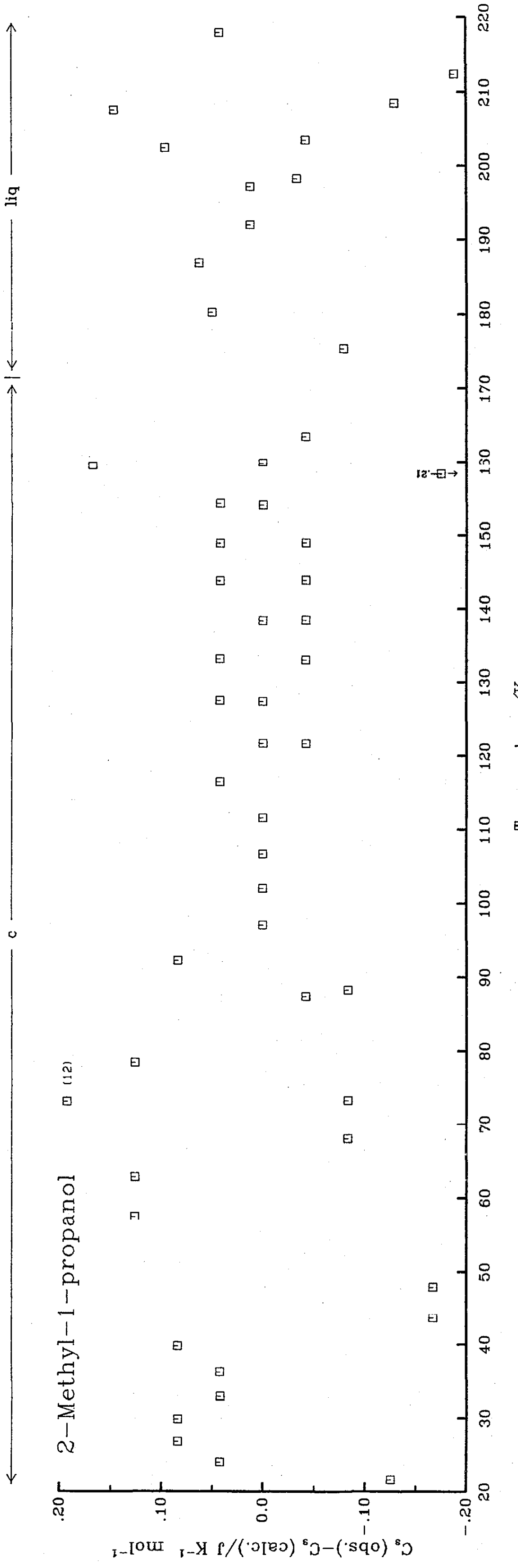

FIG. 37. Deviation plot for 2-methyl-1-propanol, c,l, 20–220 K.

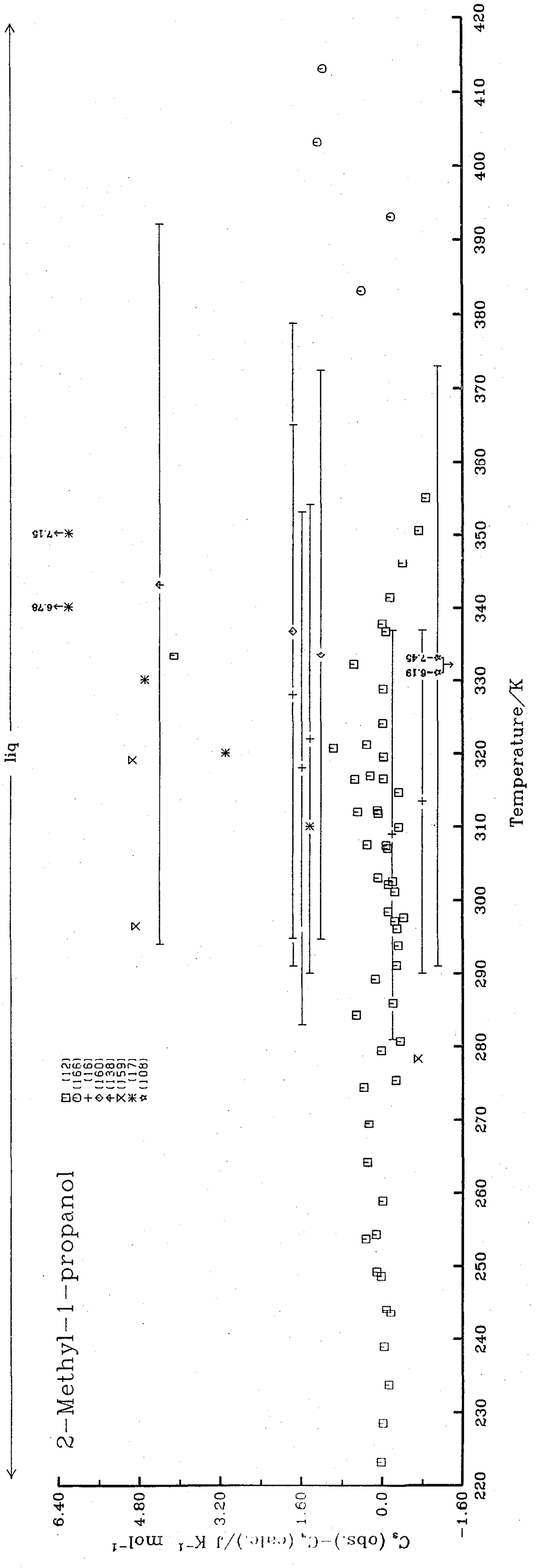

FIG. 38. Deviation plot for 2-methyl-1-propanol, l, 220–420 K.

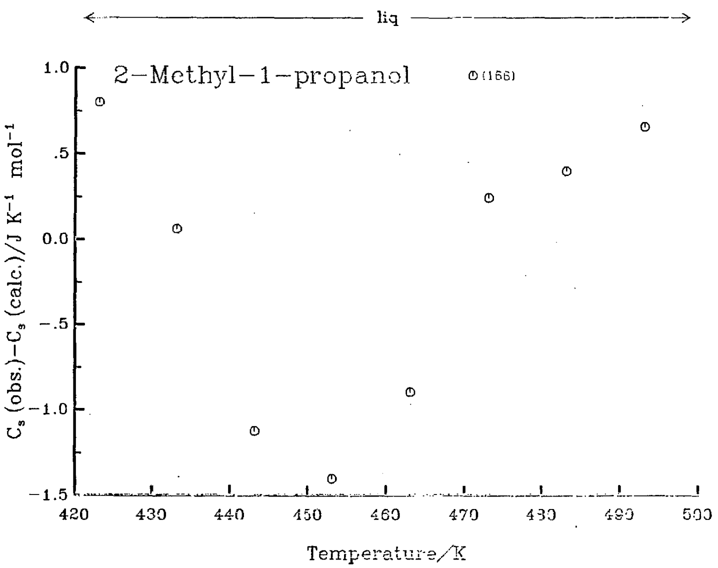

FIG. 39. Deviation plot for 2-methyl-1-propanol, l, 240–490 K.

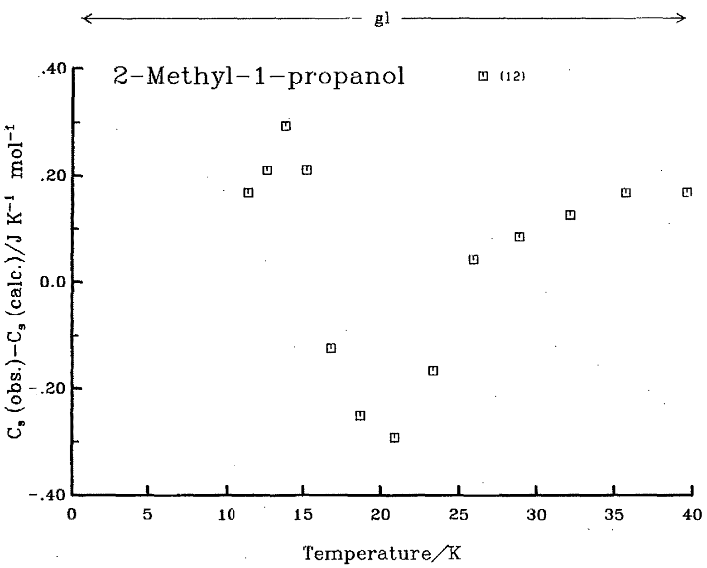

FIG. 40. Deviation plot for 2-methyl-1-propanol, gl, 0–40 K.

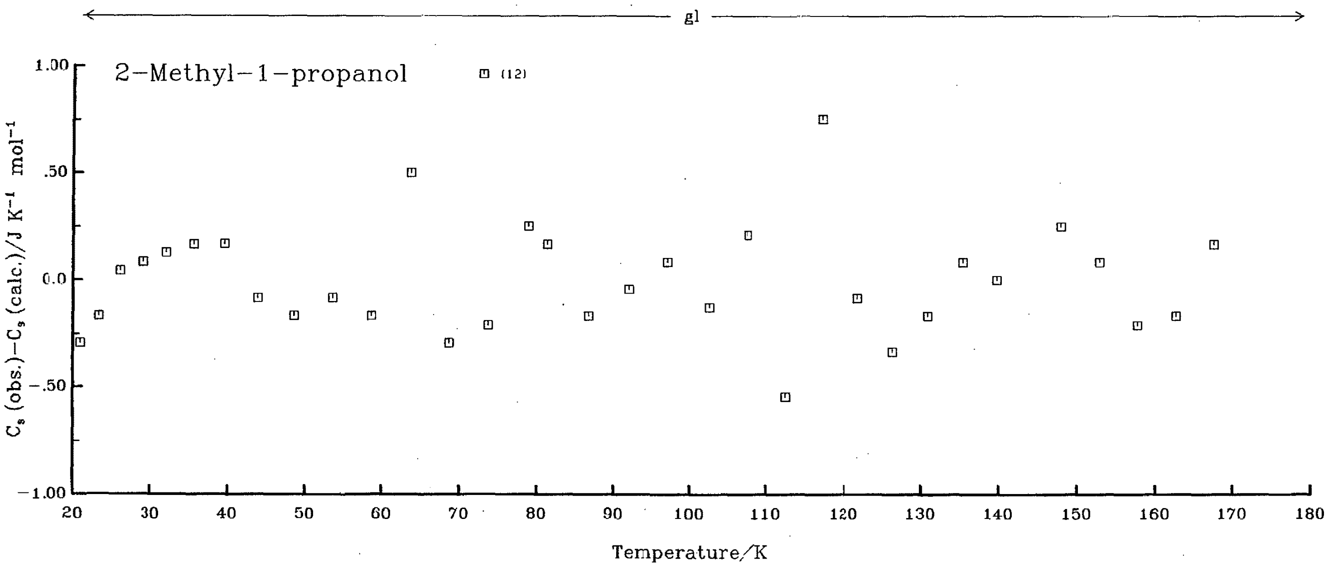

FIG. 41. Deviation plot for 2-methyl-1-propanol, gl, 20–170 K.

9. 2-Methyl-2-Propanol(tert-Butyl Alcohol)

Because of its convenient melting point and suitability as a solvent, 2-methyl-2-propanol has often been recommended as a solvent for the cryoscopic determination of molecular weights [174], [175], [176], [177]. Atkins [174] had difficulty in obtaining a reproducible melting point. He attributed this difficulty to the existence of two crystalline phases. Parks, Warren, and Greene [177] found some disadvantages in using 2-methyl-2-propanol as a solvent because of its hygroscopicity, its tendency to undercool, and the formation of mixed crystals with secondary and tertiary alcohols. These problems could be partially alleviated by using carefully purified alcohol. Getman [175] found that a reproducible melting point could be achieved by storing the alcohol at a temperature below its melting point between measurements. In their study of the 2-methyl-2-propanol-benzene-water system, Simonsen and Washburn [178] also noted the existence of two crystalline forms of the alcohol which had different melting points.

Parks and Anderson [8] did not observe a second crystal phase during their heat capacity measurements. However, they did not make a close study in the vicinity of the melting point. Smyth and McNeight [101] did not find any evidence of a crystal phase transition in their measurement of dielectric constant as a function of temperature.

During the course of his heat capacity measurements Oetting [62] did observe a definite and reproducible transition from crystal II to crystal I at 286.14 K. He obtained 297.97 K as the c–l–g triple point of crystal I. The rapid increase in heat capacity associated with the pre-melting phenomenon began about 10 degrees below the triple point. He also obtained some evidence for the existence of a third form which he called crystal III. Because of the uncertainty of the nature of this form, we designate it by c,x here. In one series of measurements starting with c,II, he observed a transition at 281.54 K and measured the enthalpy change associated with it. In another series, starting with a sample obtained by slow cooling of c,I, he observed an absorption of heat just below the triple point which appeared to indicate a phase change. After that, the sample appeared to consist of c,I. He also obtained some measurements of heat capacity of c,x which were close to, but measurably different from, c,I. These can be represented as a linear function of temperature, within the experimental uncertainty, using the parameters listed for c,x in table 46. However, since these measurements could not be reproduced at will, Oetting did not feel that the existence of the third crystalline form was unequivocally established.

Figure 42 is a graph of the Gibbs energy of various forms of 2-methyl-2-propanol relative to that for c,II at the same temperature. Lines marked c,I, c,III (a), and liq are calculated from Oetting's measurements of triple point temperatures, enthalpies of transition and heat capacity (through use of the parameters in table 46). The vertical lines show the extent of experimental measurements, so that some extrapolation has been used in Figure 42. The curve for c,III (a) was drawn on the assumption that it is in equilibrium with c,II at 281.54 K. From this interpretation we must conclude that 2-methyl-2-propanol is monotropic, with c,II stable up to 281.54 K, c,III (a) the stable form from 281.54 to around 294.47 K, and c,I stable from there to the observed triple point of 298.97 K. The transition from c,II to c,I observed by Oetting occurs in the metastable region for these two forms. The melting point of 298.2 K observed by some other investigators probably refers to c,II.

Recently Jannelli, Lopez, and Azzi [176] described a thermal analysis study of 2-methyl-2-propanol and several systems containing small amounts of solutes in 2-methyl-2-propanol. They observed changes in the slopes of time-temperature plots obtained by cooling initially liquid samples. By this means they identified three melting points, 298.88, 298.15 and 294.81 K, for the pure alcohol. Allowing for the effect of dissolved air, the highest one corresponds closely to the triple point of c,I reported by Oetting and others. The next lower one corresponds to the expected metastable melting point of c,II. The transition of c,I to c,II at 287.25 K can also be seen in their cooling curves. The authors assumed that the crystals which formed from the liquid at 294.81 K were the same as those designated as c,III by Oetting. They also observed the formation of c,I and c,II from solutions of carbon tetrachloride, n-heptane, and sulfalone in 2-methyl-2-propanol. The formation of the third crystal was seen only in solutions of sulfalone, however. They calculated the cryoscopic constants from their measurements, and then calculated the enthalpies of fusion of the three crystalline forms of 2-methyl-2-propanol.

The curve labeled c,III (b) in Figure 42 is based on the assumption that the crystal is in equilibrium with the liquid at 294.81 K and that the heat capacity of the crystal corresponds to that measured for c,III (a) (his c,III) by Oetting. The enthalpy of fusion obtained by Jannelli, Lopez and Azzi is also used. It appears that, even allowing for the effect of errors in measurements and of the assumptions and extrapolations made in Figure 42, the melting point of 294.81 K assigned to the third crystalline form by Jannelli, Lopez, and Azzi is not compatible with the observations of Oetting. The simplest reconciliation of the data now available is the assumption that Jannelli, Lopez, and Azzi observed the formation of a fourth metastable crystalline form at 294.81 K.

Because of these uncertainties, smoothed values of thermodynamic properties are given for only the c,II, c,I, and liquid phases in table 47.

The selected properties for 2-methyl-2-propanol in the liquid phase are derived from Oetting's data from the triple point to 331 K, and from the data of Hoffman, San Jose, and Reid [166] from 353 to 453 K. The measured values of C_p for the saturated liquid are converted to C_s by use of the vapor pressure data of Ambrose and Townsend [134] and the densities from references [126] and [165].

TABLE 44. Sources of Heat Capacity Data for 2-Methyl-2-propanol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
de Forcrand	1903	c(251–287), l(299–318)	drop	H	commercial sample, recryst. several times, dist. over Na			[179]
Parks & Anderson	1926	c(87–275),l(300)	isoperibol	C	distilled over CaO, 8 fract. crystalizations			[8]
Oetting	1963	c(16–297),l(304–331)	adiabatic	C	Eastman Kodak sample, fract. dist., then fract. cryst. 99.91^c mol%	138	corr	[62]
Hoffman, San Jose & Reid	1977	l(353–453)	flow	C	not stated	11	no	[166]
de Visser, Perron & Desnoyers	1977			C	commercial sample, no further purification			[180]

TABLE 45. Reported Phase Transition Data for 2-Methyl-2-propanol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
de Forcrand	1903	c,I⇌l	298.7	mp	6485.	c	[179]
Atkins	1911	c,I⇌l	298.7	mp	5816.	t	[174]
		c,II⇌l	298.15	mp	5816.	t	
Parks & Anderson	1926	c,I⇌l	298.5	tp	6954.	c	[8]
Cady & Jones	1933	c,I⇌l	298.85	mp			[162]
Timmermans & Delcourt	1934	c,I⇌l	298.70	mp			[181]
Parks, Waren & Greene	1935	c,I⇌l	298.6	mp	6620.	t	[177]
Smyth & McNeight	1936	c,I⇌l	297.9	mp			[101]
Getman	1940	c,I⇌l	298.3	mp	6611.	t	[175]
Simonsen & Washburn	1946	c,I⇌l	298.81	mp			[178]
		c,II⇌l	298.2	mp	5816.	t	
Dreisbach & Martin	1949	c,I⇌l	298.48	mp			[151]
De Vries & Soffer	1951	c,I⇌l	298.81	mp			[182]
Barnard	1959	c,I⇌l	298.65	mp			[183]
Oetting	1963	c,x⇌c,II	281.54	tp	649.	c	[62]
		c,II⇌c,I	286.13	tp	828.	c	
		c,x⇌c,I	294.46	tp	490.	c	
		c,I⇌l	298.96	tp	6703.	c	
Faucher & Koleske	1966	glass	180.*	ml			[122]
Jannelli, Lopez & Azzi	1979	c,II⇌c,I	287.25	mp			[176]
		c,II⇌c,y	282.	mp			
		c,y⇌l	294.81	mp	6180.	t	
		c,II⇌l	298.15	mp	4606.	t	
		c,I⇌l	298.77	mp	6640.	t	
SELECTED VALUES		c,x⇌c,II	281.54±0.2		649.±20		
		c,II⇌c,I	286.13±0.1		828.±10		
		c,I⇌l	298.96±0.06		6703.±10		

*Extrapolated from measurements on solutions.

TABLE 46. Parameters for Heat Capacity of 2-Methyl-2-propanol

Phase	c,II	c,II	c,II	c,II	c,II	c,II	c,I
Data Points							
Number	5	17	35	21	42	122(14)	6(2)
Temp./K	15.5 - 22.9	25.1 - 95.9	101.1 -199.7	202.7 -253.0	256.5 -291.0	15.5 -291.0	283.1 -290.8
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 24.0	24.0 -100.0	100.0 -200.0	200.0 -255.0	255.0 -286.13	0 -286.13	286.13-298.96
a_i		-14.88	-19.51	214.69	426274.88		-26.4
b_i x 10		14.793	11.972	-39.267	-63885.578		5.778
c_i x 10^3		-13.663	-5.4203	36.2899	35896.567		
d_i x 10^5	233.6	7.693	1.5220	-13.4687	-8961.0197		
e_i x 10^7	-558.5	-1.308	-0.09598	1.9130	838.7442		
Deviations							
Average, d	0.021	0.008	-0.008	-0.004	0.167*	0.004*	0.000
R.M.S., $r(\sigma)$	0.180	0.163	0.197	0.255	0.80*	0.431(0.460)*	0.68(0.96)
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.12	0.4	0.5	0.6	1.0		2.0
$\delta(H-H_0)$	1.0	30.	59.	67.	74.		88.
$\delta(S)$	0.06	0.6	0.7	0.7	0.7		0.7
$\delta(G-H_0)/T$	0.026	0.27	0.3	0.3	0.3		0.3

*For data up to 285.3 K only.

Phase	l	l	l	l	l	l	l
Data Points							
Number	12	4	8	23(8)	11	4	8
Temp./K	303.6 -326.0	331.3 -373.2	373.2 -453.2	303.6 -453.2	303.6 -326.0	331.3 -373.2	373.2 -453.2
Parameters for	C_s	C_s	C_s	C_s	C_p	C_p	C_p
Temp./K	298.96-330.0	330.0 -380.0	380.0 -460.0	298.96-460.0	298.96-330.0	330.0 -380.0	380.0 -460.0
a_i	-9118.36	-2292.88	1925.62		-8595.65	-2060.58	1281.91
b_i x 10	856.4127	189.6792	-129.694		806.5898	171.0201	-78.873
c_i x 10^3	-263.4313	-47.3800	33.0694		-247.6079	-42.4438	19.6369
d_i x 10^5	27.24348	4.00491	-2.73660		25.56905	3.57598	-1.54682
Deviations							
Average, d	0.013	-0.040	-0.021	0.000	0.010	-0.026	-0.028
R.M.S., $r(\sigma)$	0.234	0.266	0.273	0.246(0.301)	0.232	0.228	0.295
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.4	0.5	0.6		0.4	0.5	0.6
$\delta(H-H_0)$	97.	101.	111.				
$\delta(S)$	0.7	0.7	0.7				
$\delta(G-H_0)/T$	0.3	0.3	0.3				

Phase	l	c,x
Data Points		
Number	23(8)	8(2)
Temp./K	303.6 -453.2	282.6 -290.2
Parameters for	C_p	C_s
Temp./K	298.96-460.0	281.5 -294.5
a_i		-119.71
b_i x 10		8.9615
Deviations		
Average, d	0.000	0.00
R.M.S., $r(\sigma)$	0.244(0.302)	1.01(1.16)
Estimated Uncertainty in Tabulated Values		
$\delta(C)$		3.

TABLE 47. Thermodynamic Functions of 2-Methyl-2-propanol

$C_4H_{10}O$ $M = 74.122$

T/K	$(G\text{-}H_0)/T$	$(H\text{-}H_0)/T$	$H\text{-}H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}		J K^{-1} mol^{-1}	
			Crystal II			
0	0.00	0.00	0.0	0.00	0.00	0.00
10	-0.17	0.47	4.7	0.64	1.78	1.78
15	-0.52	1.41	21.1	1.92	5.06	5.06
20	-1.11	2.88	57.7	4.00	9.75	9.75
25	-1.95	4.76	119.1	6.71	14.71	14.71
30	-3.00	6.80	203.9	9.80	19.17	19.17
35	-4.20	8.86	310.2	13.06	23.26	23.26
40	-5.52	10.90	436.0	16.42	27.02	27.02
50	-8.37	14.81	740.5	23.19	33.73	33.73
60	-11.40	18.46	1107.8	29.87	39.61	39.61
70	-14.51	21.87	1531.0	36.38	44.97	44.97
80	-17.64	25.08	2006.3	42.72	50.05	50.05
90	-20.77	28.13	2531.9	48.90	55.09	55.09
100	-23.89	31.08	3108.5	54.97	60.27	60.27
110	-26.99	33.98	3737.3	60.96	65.45	65.45
120	-30.06	36.81	4416.7	66.87	70.41	70.41
130	-33.12	39.58	5145.0	72.70	75.22	75.22
140	-36.15	42.29	5920.8	78.44	79.94	79.94
150	-39.16	44.96	6743.6	84.12	84.62	84.62
160	-42.15	47.58	7613.4	89.73	89.33	89.33
170	-45.11	50.18	8530.6	95.29	94.13	94.13
180	-48.05	52.76	9496.	100.81	99.06	99.06
190	-50.97	55.33	10512.	106.30	104.17	104.17
200	-53.88	57.90	11581.	111.78	109.52	109.52
210	-56.76	60.49	12704.	117.26	115.17	115.17
220	-59.64	63.12	13885.	122.75	121.23	121.23
230	-62.50	65.78	15130.	128.29	127.88	127.88
240	-65.36	68.52	16446.	133.88	135.35	135.35
250	-68.21	71.36	17841.	139.58	143.91	143.91
260	-71.07	74.35	19331.	145.42	154.9	154.9
270	-73.94	77.6	20953.	151.5	169.6	169.6
280	-76.82	81.2	22725.	158.0	185.7	185.7
286.13	-78.61	83.6	23909.	162.2	202.3	202.3
			Crystal I			
286.13	-78.61	86.5	24737.	165.1	138.9	138.9
290	-79.77	87.2	25279.	166.9	141.2	141.2
295	-81.27	88.1	25992.	169.4	144.1	144.1
298.15	-82.21	88.7	26448.	170.9	145.9	145.9
298.96	-82.45	88.9	26567.	171.3	146.3	146.3
			Liquid			
298.96	-82.45	111.3	33270.	193.7	219.7	219.8
300	-82.84	111.7	33499.	194.50	220.94	220.98
310	-86.55	115.4	35761.	201.91	230.79	230.79
320	-90.27	119.1	38110.	209.37	238.62	238.64
330	-93.99	122.8	40534.	216.82	246.08	246.06
340	-97.71	126.6	43034.	224.28	253.17	253.10
350	-101.42	130.3	45599.	231.70	258.95	258.96
360	-105.13	133.9	48217.	239.07	263.65	263.84
370	-108.83	137.5	50879.	246.34	267.54	267.95
380	-112.53	141.0	53579.	253.52	270.8	271.5
390	-116.21	144.4	56314.	260.60	274.1	275.1
400	-119.87	147.7	59086.	267.6	277.5	278.9
410	-123.51	151.0	61897.	274.5	281.0	283.0
420	-127.13	154.2	64747.	281.3	284.4	287.2
430	-130.7	157.3	67635.	288.0	287.5	291.4
440	-134.3	160.4	70558.	294.7	290.2	295.6
450	-137.8	163.4	73512.	301.2	292.2	299.6
460	-141.4	166.3	76492.	307.6	293.5	303.3

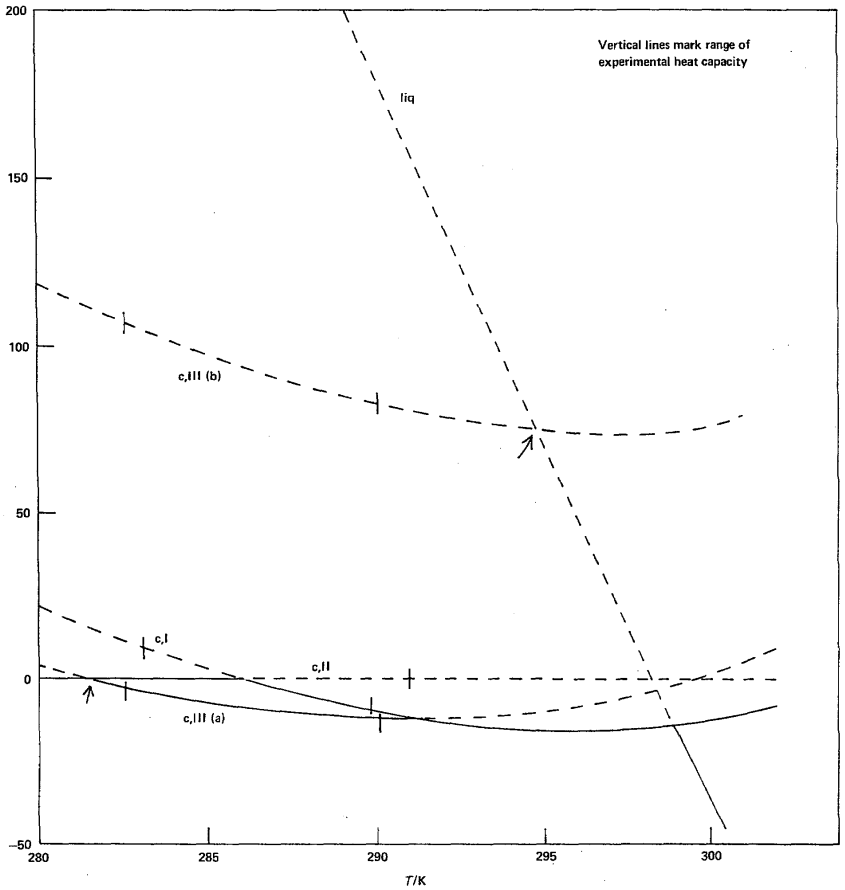

FIG. 42. Gibbs energy of various forms of 2-methyl-2-propanol relative to c,II.

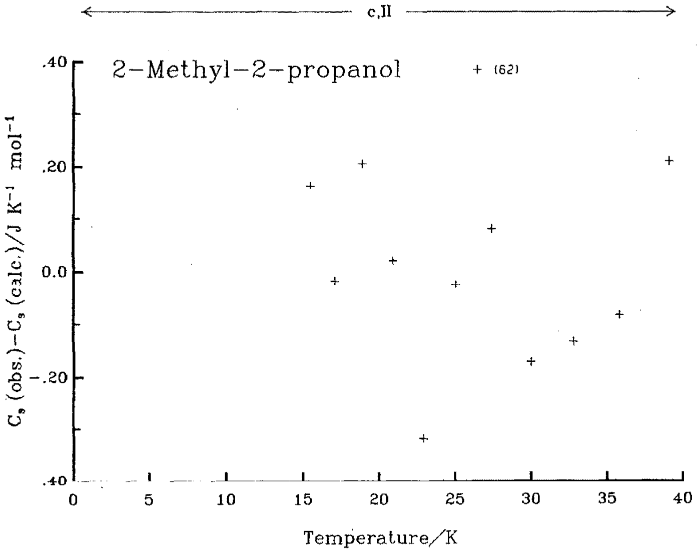

FIG. 43. Deviation plot for 2-methyl-2-propanol, c,II 0–40 K.

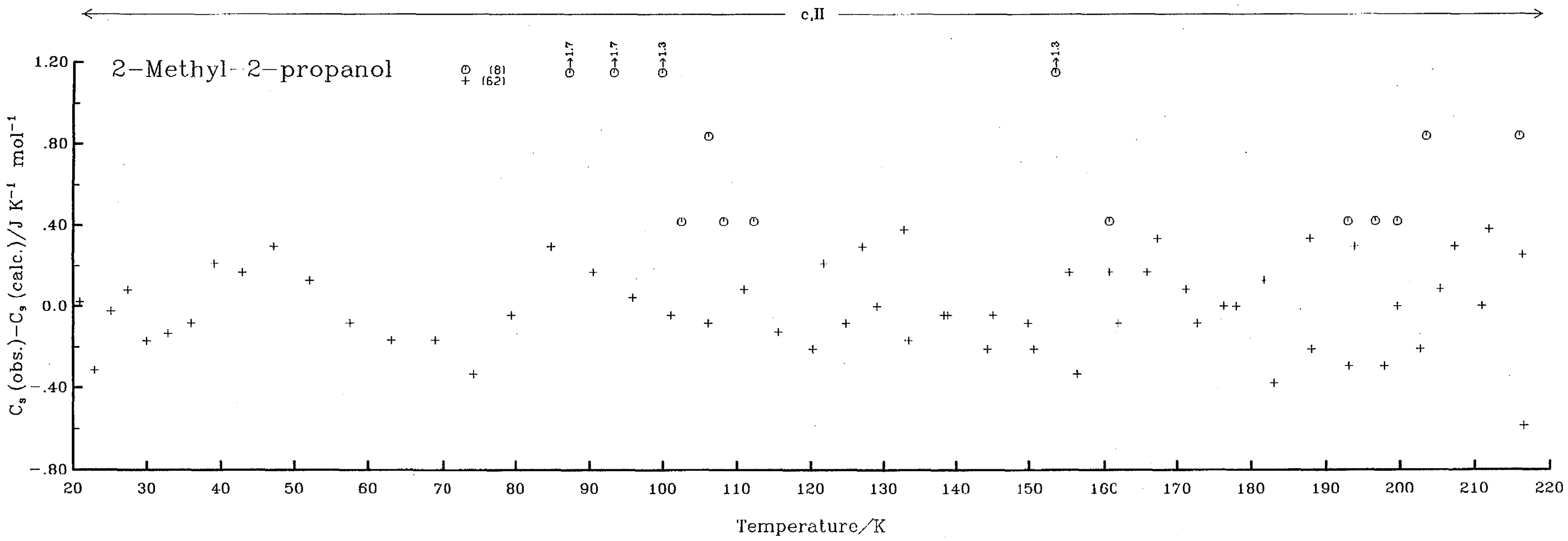

FIG. 44. Deviation plot for 2-methyl-2-propanol, c,II, 20–220 K.

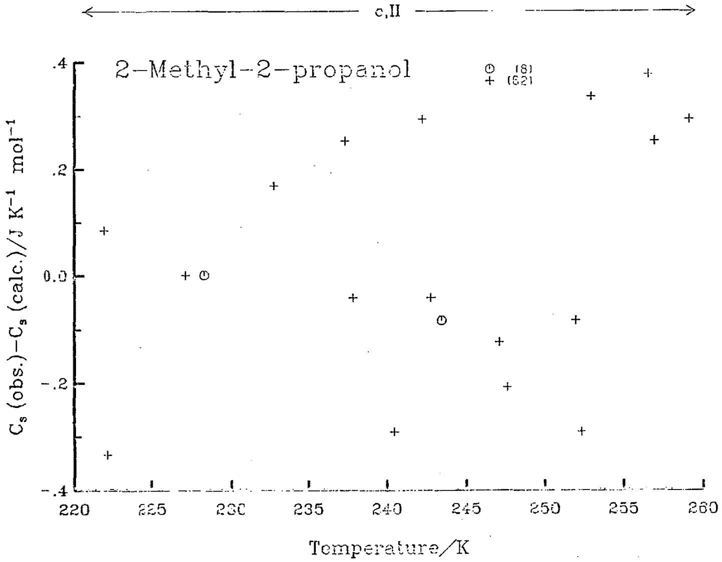

FIG. 45. Deviation plot for 2-methyl-2-propanol, c,II, 220–260 K.

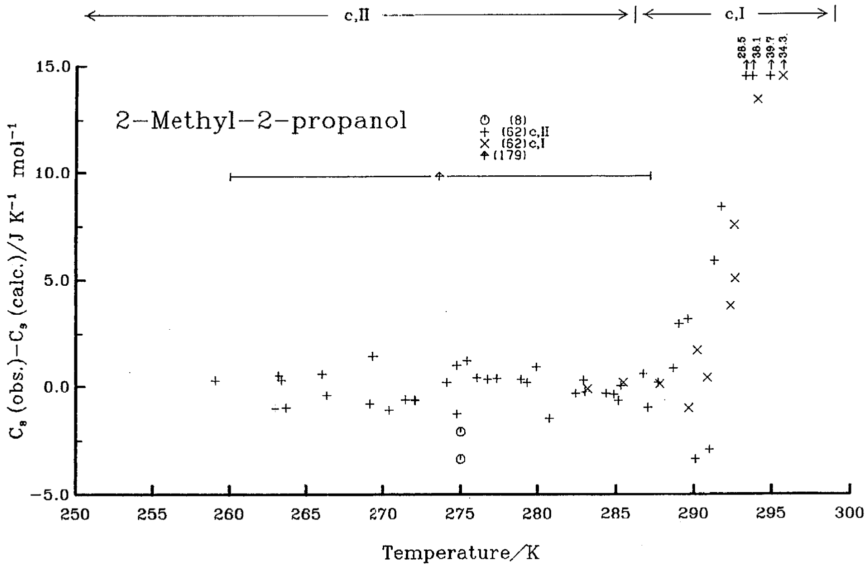

FIG. 46. Deviation plot for 2-methyl-2-propanol, c,II, c,I, 260–298 K.

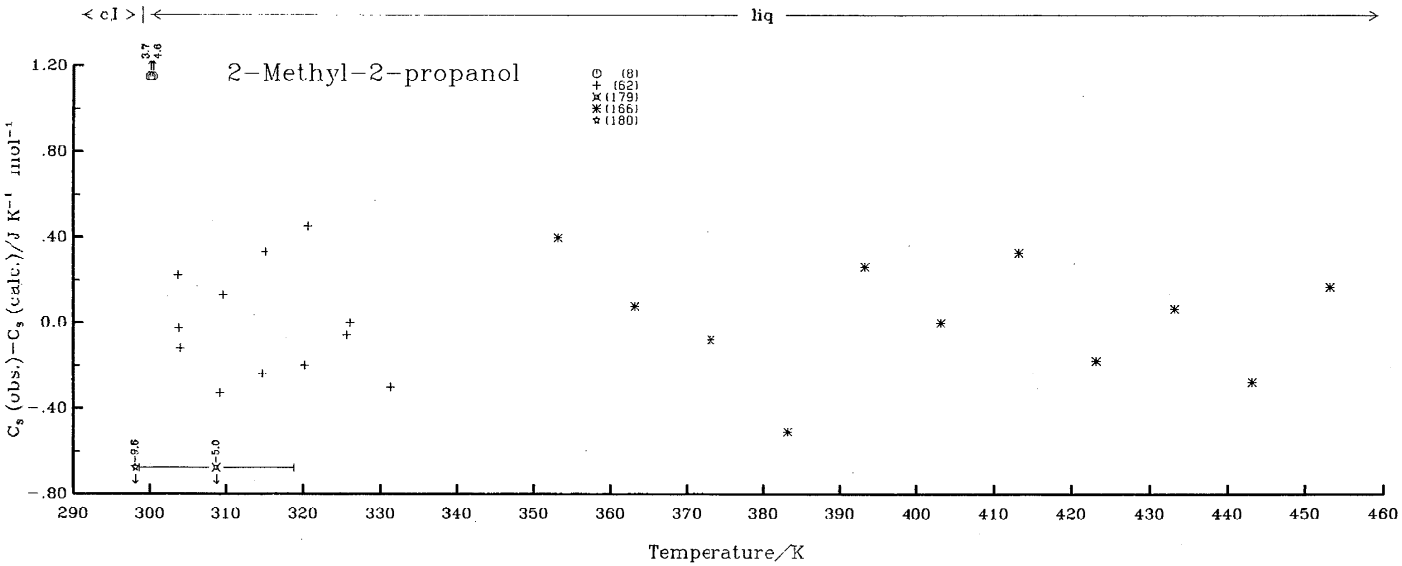

FIG. 47. Deviation plot for 2-methyl-2-propanol, l, 293–450 K.

10. 1,2-Ethanediol (Ethylene Glycol)

The only two sources of heat capacity data for 1,2-ethanediol in the crystalline phase are those of Parks and Kelley [53] and Nikolaev and Rabinovich [65]. Since the sample used by Parks and Kelley contained about 1.5% water the selected values of properties of the crystal in table 51 are based entirely on the data of Nikolaev and Rabinovich. They took special precautions to exclude water from their sample. They reported only the smoothed values of heat capacity at multiples of 5 K. These values are treated as observed data in the least squares calculations of the parameters. The conditions of measurement were not sufficiently well defined to justify a temperature scale correction. Nikolaev and Rabinovich also measured the heat capacity of deuterated 1,2-ethanediol, CH_2OD-CH_2OD.

Since the measurements extended only to 80 K, the values of entropy and enthalpy at 80 K are estimated by the group additivity method described in section 1.2.b. Parks, Kelley and Huffman [6] estimated the entropy at 90 K to be 35.6 J K^{-1} mol^{-1} in good agreement with the value in table 51.

Because of its tendency to undercool, the values of the melting point and triple point of 1,2-ethanediol have not been accurately determined. de Forcrand [184] measured the enthalpy of fusion by warming crystalline samples from 2 to 9 degrees below the melting point to about 20 degrees above in a drop calorimeter. The uncertainty in the melting point and in the heat capacity of the solid near the melting point gives rise to a large uncertainty in the reported enthalpies of fusion shown in table 49. The selected value is close to that reported by Nikolaev and Rabinovich, but increased in the direction of the earlier measurements.

Data from a number of sources, identified in table 48, are combined to establish the heat capacity and derived properties of the liquid. The heat capacity values of Parks and Kelley [53] were decreased by 1.5% in order to correct for the presence of water in the sample. The smoothed heat capacity values reported by Nikolaev and Rabinovich [66] and Rabinovich and Nikolaev [129] are included in the data set. The values of Nikolaev and Rabinovich at the high end of their temperature range are larger than other values. Above 300 K their values are given a reduced weight or omitted from the least squares calculation. Thus the selected values above 300 K are determined largely by the mean heat capacities of Todd [185], and de Forcrand [184] obtained from drop calorimeters and from the recent measurements of Stephens and Tamplin [193] obtained with a differential scanning calorimeter.

NBS Technical Note 270-3 [327] reports an entropy of 166.9 J K^{-1} mol^{-1} and a heat capacity of 149.8 J K^{-1} mol^{-1} at 298.15 K.

TABLE 48. Sources of Heat Capacity Data for 1,2-Ethanediol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
de Heen	1884	l(290–369)	drop	H	not stated			[187]
Louguinine	1898	l(295–469)	drop	H	not stated			[138]
de Forcrand	1901	l(250–412)	drop	H	not stated	3	no	[184]
Louguinine	1902	l(293–460)	drop	H	not stated	1	no	[186]
Schwers	1909	l(293–310)	drop	H	acetate ester saponified with methanol & HCl, purified by fract. dist. to const. b.p.			[188]
Parks & Kelley	1925	c(88–277),l(262–293)	isoperibol	C	chem. pure sample, fract. distilled, 99 mol% (impurity mainly water)	6	no	[53]
Todd	1929	l(300–448)	drop	H	fract. distilled	3	no	[185]
Neumann & Kurlyankin	1932	l(293–351)		C				[189]
Crutzen, Jost & Sieg	1957	l(293,338)	Dewar flask	C	commercial sample,fract. dist., dried with anhyd. Na_2SO_4, dist. at reduced press., dried with silical gel			[190]
Rabinovich & Nikolaev	1962	l(283–328)	adiabatic	C	carefully purified & dried	10	no	[129]
Tungusov & Mishchenko	1965	l(298)	Dewar flask	C	"pure" sample, dist. and fraction boiling over 0.2–0.3° taken			[191]
Nikolaev & Rabinovich	1967	c(80–245),l(265–310)	adiabatic	C	fract.distilled with water excluded	43	no	[65]
Paz Andrade, Paz Fernandez & Recacho	1970	l(301–313)	Calvet	C	not stated	2	no	[116]
Kawaizumi, Otake Nomura & Miyohara	1972							[192]
Stephens & Tamplin	1979	l(273–493)	DSC	C	Union Carbide, 99.9^8 %	15	no	[1]

TABLE 49. Reported Phase Transition Data for 1,2-Ethanediol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Ladenburg & Krugel	1899	c$\rightleftharpoons$l	255.8	mp			[194]
Ladenburg & Krugel	1900	c$\rightleftharpoons$l	257.6	mp			[195]
de Forcrand	1901	c$\rightleftharpoons$l	261.7	mp	11130.	c	[184]
Parks & Kelley	1925	c$\rightleftharpoons$l	260.8	tp	11630.	c	[53]
Timmermans & Hennaut-Roland	1935	c$\rightleftharpoons$l	260.6	mp			[196]
Gallaugher & Hilbert	1936	c$\rightleftharpoons$l	260.0	mp			[197]
Nikolaev, Rabinovich & Lebedev	1967	c$\rightleftharpoons$l	260.6	tp	9958.	c	[66]
Angell, Sare & Sare	1978	glass	185.	dt			[125]
SELECTED VALUES		c$\rightleftharpoons$l	260.6±0.2		10210.±400		

TABLE 50. Parameters for Heat Capacity of 1,2-Ethanediol

Phase	c	c	c	c	l
Data Points					
Number	11	20	3	34(11)	28(4)
Temp./K	80.0 –125.0	130.0 –225.0	230.0 –245.0	80.0 –245.0	262.0 –493.2
Parameters for	C_s	C_s	C_s	C_s	C_s
Temp./K	80.0 –130.0	130.0 –230.0	230.0 –260.6	80.0 –260.6	260.6 –490.0
a_i	–84.77	–75.07	–6867.61		63.03
b_i x 10	29.384	20.411	1007.096		2.3482
c_i x 10^3	–23.111	–11.0277	–483.8049		0.2912
d_i x 10^5	6.6764	2.2495	77.1132		–0.03635
Deviations					
Average, d	0.034	0.063	0.080	0.071	0.000
R.M.S., $r(\sigma)$	0.088	0.184	0.234	0.159(0.180)	0.154(0.160)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.25	0.3	0.4		0.8
$\delta(H\text{-}H_0)$	101.	105.	106.		220.
$\delta(S)$	1.5	1.5	1.5		2.2
$\delta(G\text{-}H_0)/T$	1.4	1.4	1.4		1.4

TABLE 51. Thermodynamic Functions of 1,2-Ethanediol
$C_2H_6O_2$ $M = 62.068$

T/K	(G-H_0)/T J K^{-1} mol^{-1}	(H-H_0)/T J K^{-1} mol^{-1}	H-H_0 J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
80	-11.3	19.9	1590.	31.2	36.57
90	-13.79	22.00	1980.0	35.78	41.16
100	-16.21	24.10	2409.8	40.31	44.72
110	-18.61	26.11	2872.1	44.72	47.67
120	-20.96	28.02	3362.5	48.98	50.41
130	-23.28	29.85	3880.9	53.13	53.33
140	-25.55	31.64	4429.2	57.19	56.27
150	-27.80	33.37	5005.2	61.16	58.89
160	-30.00	35.04	5606.4	65.04	61.34
170	-32.18	36.66	6231.7	68.83	63.73
180	-34.32	38.23	6881.4	72.55	66.22
190	-36.43	39.77	7556.9	76.20	68.93
200	-38.50	41.31	8261.2	79.81	72.00
210	-40.56	42.85	8998.6	83.41	75.57
220	-42.59	44.43	9774.6	87.02	79.76
230	-44.60	46.07	10596.3	90.67	84.71
240	-46.60	47.87	11488.0	94.46	95.66
250	-48.59	50.23	12557.1	98.82	120.92
260	-50.63	53.73	13969.5	104.36	165.09
260.6	-50.75	53.99	14069.6	104.74	168.44
		Liquid			
260.6	-50.75	93.17	24279.	143.92	137.57
270	-54.08	94.76	25586.	148.8	140.51
280	-57.56	96.45	27007.	154.0	143.63
290	-60.97	98.1	28459.	159.1	146.75
298.15	-63.71	99.5	29665.	163.2	149.29
300	-64.33	99.8	29942.	164.1	149.87
310	-67.63	101.5	31456.	169.1	153.0
320	-70.88	103.1	33002.	174.0	156.1
330	-74.07	104.8	34578.	178.9	159.2
340	-77.2	106.4	36185.	183.7	162.2
350	-80.3	108.1	37823.	188.4	165.3
360	-83.4	109.7	39491.	193.1	168.3
370	-86.4	111.3	41190.	197.8	171.4
380	-89.4	112.9	42918.	202.4	174.4
390	-92.4	114.6	44677.	206.9	177.3
400	-95.3	116.2	46465.	211.5	180.3
410	-98.2	117.8	48283.	215.9	183.2
420	-101.0	119.4	50129.	220.4	186.1
430	-103.9	120.9	52004.	224.8	189.
440	-106.7	122.5	53908.	229.2	192.
450	-109.4	124.1	55839.	234.	195.
460	-112.2	126.	57799.	238.	197.
470	-114.9	127.	59785.	242.	200.
480	-117.6	129.	61798.	246.	203.
490	-120.3	130.	63837.	251.	205.

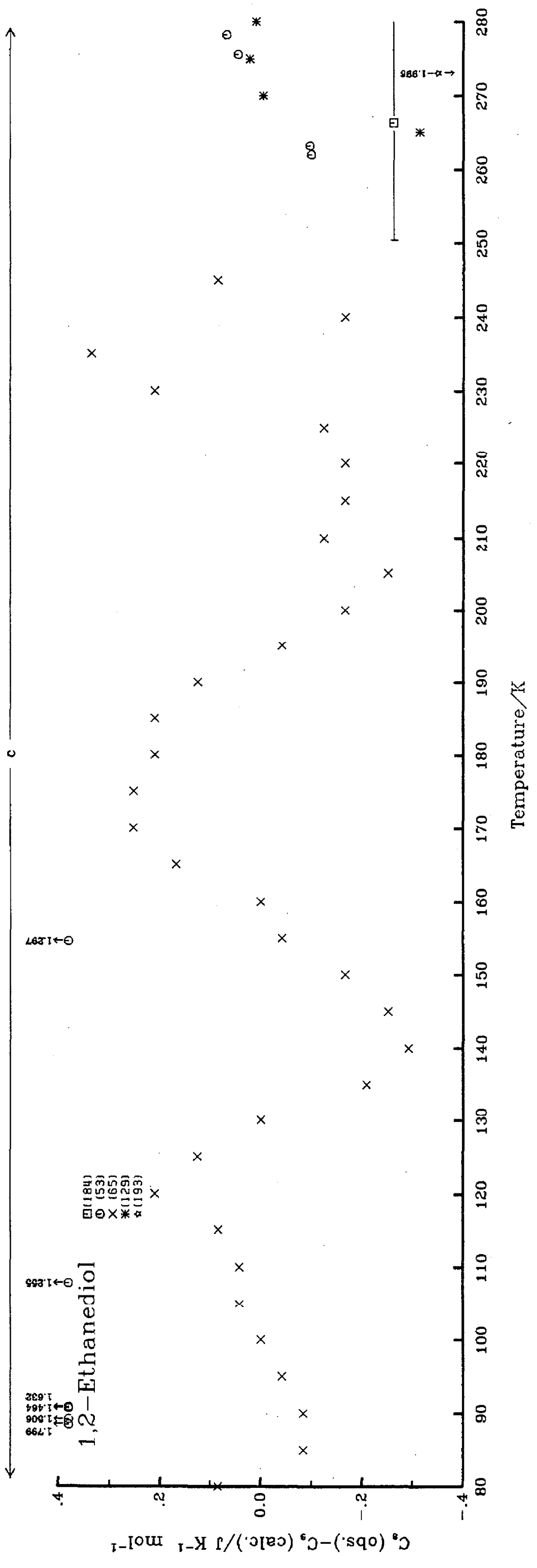

FIG. 48. Deviation plot for 1,2-ethanediol, c, 80–250 K.

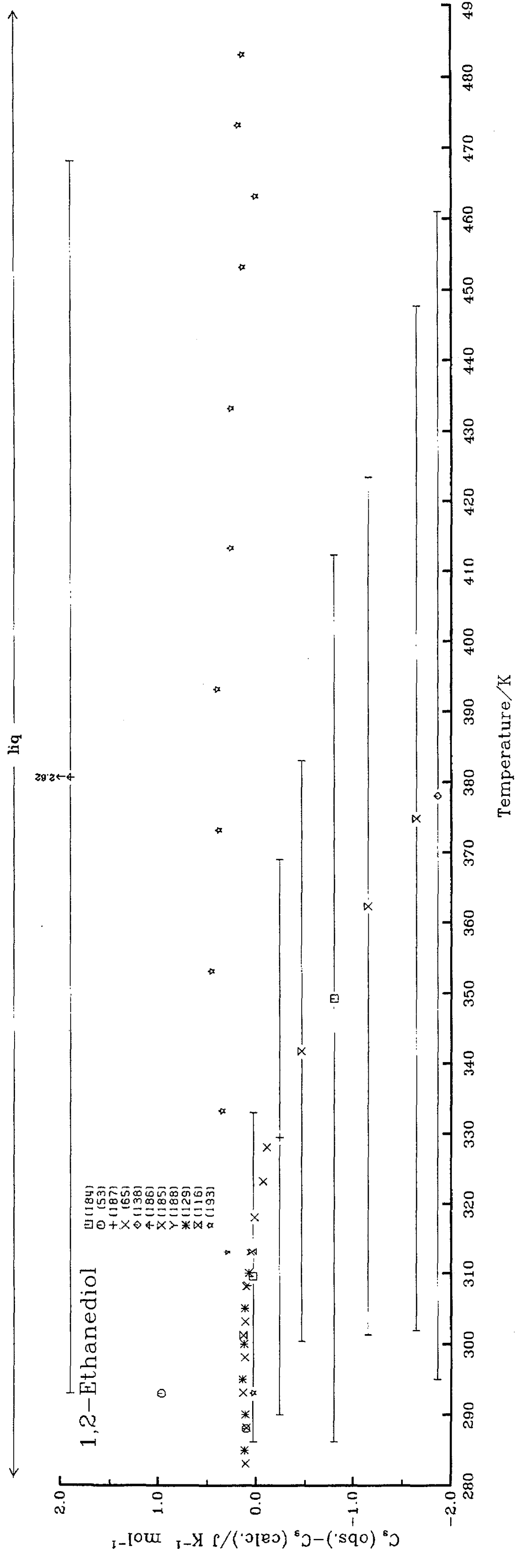

FIG. 49. Deviation plot for 1,2-ethanediol, 1, 260–380 K.

11. 1,2-Propanediol (Propylene Glycol)

1,2-Propanediol contains an asymmetric carbon atom, and therefore it exists in two optically active forms. On cooling, the racemic mixture does not crystallize but forms a glass. Howard [198] crystallized the pure d- and l-isomers by cooling the melts. By using seed crystals both the active forms and the racemic mixtures could then be crystallized neat or from solution in a variety of solvents.

The racemic mixture melts in the range 241.6 to 243.8 K. The d-isomer partially melts in the range 237.6 to 240 K, then solidifies, and melts completely between 241.7 and 243.5 K. This suggests that the d-isomer exists in two allotropic forms.

Parks and Huffman [50] investigated properties of several organic glasses and speculated on the reasons for their observations. These included the measurement of the heat capacity of racemic 1,2-propanediol in the glass and liquid forms using their Nernst type calorimeter. They estimated the calorimetric uncertainty in these measurements to be about 1% and the precision somewhat better, except in the region of the glass transition, from 145 to 165 K. Although they took care to obtain a pure sample, they had no quantitative measure of purity.

Parks and Huffman made three series of measurements on the same sample, going from low to high temperatures in each case. In one series, the glass was formed by cooling from 250 to 91 K in about one hour. Measurements were then made up to 277 K. In a second series, the sample was cooled to 133 K in about the same amount of time and measurements made to 164 K.

In a third series, the sample was first cooled slowly over a period of 50 hours to 136 K. Measurements were then made from 141 to 205 K. There seemed to be no systematic differences between the results of these three series of measurements above 165 K. At lower temperatures the heat capacity of the sample obtained by slow cooling was about 1% lower than the heat capacity of the the other two, and the increase in heat capacity in the transition region a little steeper.

On the basis of the calorimetric measurements, they found a glass transition temperature of 162 K. They also measured approximately the coefficient of expansion through this region and found a marked increase near 170 K. They noticed a "softening point" at 185 K. Finally, based on the time needed to attain thermal equilibrium in the calorimeter, they concluded that the thermal conductivity of the sample decreased markedly in the glass transition region, with a minimum at around 160 K.

Todd [185] reported values of the mean heat capacity of the liquid obtained in a drop calorimeter between 301 and 445 K. His estimated accuracy was 1% or better.

A satisfactory fit of the available data could not be obtained while maintaining the continuity constraints at the boundaries between regions. Therefore the heat capacity parameters were obtained from two independent calculations. For the region from 91.1 to 204.6 K the data reported by Parks and Huffman from the fast cooling experiments were combined with those from the slow cooling experiments above 165 K to form the data set. Data for the 194.3 to 445.5 K range consisted of those of Parks and Huffman from 194.3 to 276.6 K and the mean values of Todd. The overlap in these two calculations gave near continuity at 210 K. No data are available from 205 and 275 K so the data calculated for this region are more uncertain. The reference state for entropy and enthalpy in table 54 is the glass at 90 K. The data are insufficient for the calculation of the Gibbs energy.

TABLE 52. Sources of Heat Capacity Data for 1,2-Propanediol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Parks & Huffman	1927	gl &l(191–277)	isoperibol	C	high-grade sample fract. distilled at 4 torr	33	no	[50]
Todd	1929	l(300–445)	drop	H	fract. distilled	3	no	[185]
Kawaizumi, Otake, Nomura & Miyohara	1972							[192]

TABLE 53. Parameters for Heat Capacity of 1,2-Propanediol

Phase	gl	gl	l	gl & l	l
Data Points					
Number	15	4	10	29(11)	11(3)
Temp./K	91.1 -153.5	160.3 -164.1	167.1 -204.6	91.1 -204.6	194.3 -445.5*
Parameters for	C_s	C_s	C_s	C_s	C_s
Temp./K	90.0 -154.0	154.0 -166.0	166.0 -210.0	90.0 -210.0	210.0 -440.0
a_i	371.58	-1683911.8	37680.92		88.31
$b_i \times 10$	-124.891	443954.87	-7832.361		3.100
$c_i \times 10^3$	173.461	-437766.866	6118.504		0.0826
$d_i \times 10^5$	-102.8130	191368.399	-2120.987		
$e_i \times 10^7$	22.6399	-31293.754	275.3595		
Deviations					
Average, d	0.008	0.494	-0.138	0.000	0.067
R.M.S., $r(\sigma)$	0.218	1.72	1.13	0.75	0.326(0.385)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.25	2.0	1.0		0.5
$\delta(H-H_{90})$	16.	29.	53.		126.
$\delta(S-S_{90})$	0.13	0.20	0.3		0.48

*Upper temperature for an enthalpy measurement.

TABLE 54. Thermodynamic Functions of 1,2-Propanediol
$C_3H_8O_2$ $M = 76.095$

T/K	H-H_{90} J mol^{-1}	S-S_{90} J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
	Glass and Liquid		
90	0.0	0.00	51.63
100	535.4	5.64	55.55
110	1111.6	11.13	59.69
120	1728.2	16.49	63.58
130	2382.6	21.72	67.30
140	3075.8	26.86	71.49
150	3817.7	31.98	77.3
152	3973.8	33.01	78.8
154	4133.0	34.05	80.4
156	4298.0	35.11	86.
158	4482.	36.29	99.
160	4697.	37.64	116.
162	4948.	39.2	135.
164	5233.	40.9	149.
170	6145.	46.4	149.8
180	7627.	54.9	148.1
190	9121.	63.0	150.7
200	10638.	70.7	152.4
210	12171.	78.2	155.
220	13759.	85.6	161.
240	17039.	99.9	167.
260	20458.	113.5	174.
270	22221.	120.2	178.
280	24019.	126.7	181.6
290	25853.	133.2	185.2
298.15	27374.	138.3	188.1
300	27722.	139.5	188.7
310	29628.	145.8	192.3
320	31569.	151.9	196.0
330	33547.	158.0	199.6
340	35561.	164.0	203.3
360	39700.	175.8	210.6
380	43986.	187.4	218.
400	48422.	198.8	226.
420	53008.	210.	233.
440	57746.	221.	241.

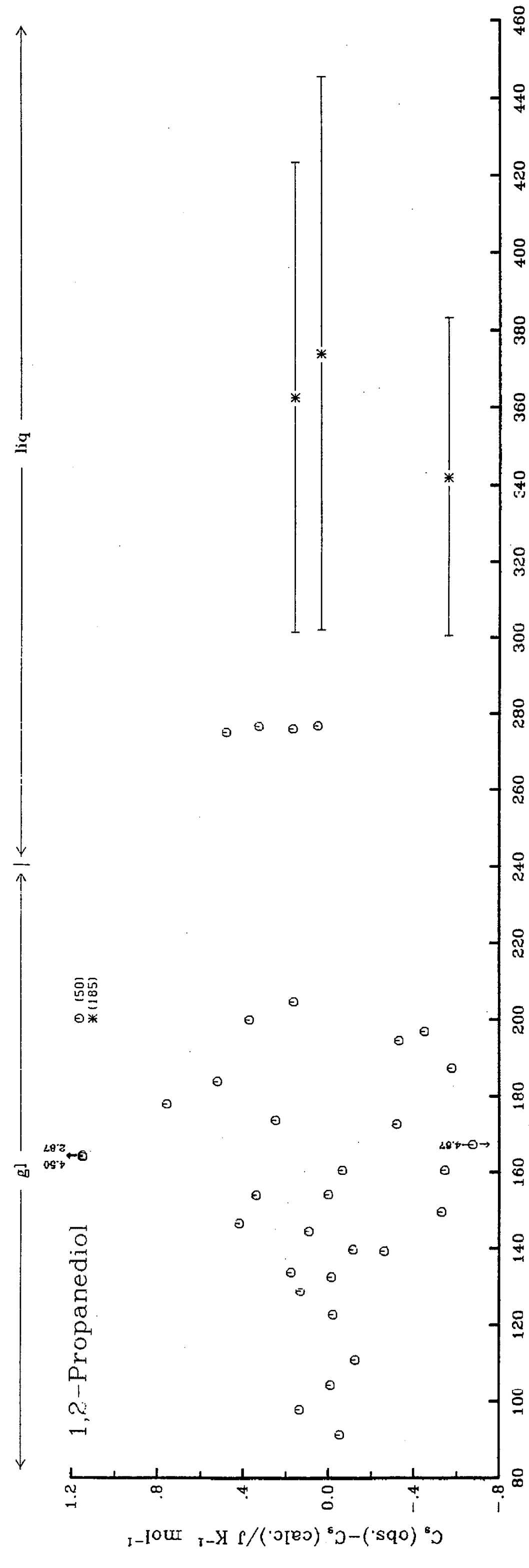

FIG. 50. Deviation plot for 1,2-propanediol, gl, l, 90–440 K.

12. 1,2,3-Propanetriol (Glycerol)

The thermodynamic properties of 1,2,3-propanetriol have been studied extensively. It occurs in the form of esters in most living organisms (Lawrie [199], Miner and Dalton [200], and Newman [201]) and is a major industrial chemical. Propanetriol readily forms a glass and has often been taken as a model for the study of organic glasses.

1,2,3-propanetriol is easily obtained in a pure state, except for the presence of water. Most of the water can be removed by heating the material to around 50 °C for a few days in a high vacuum. When 1,2,3-propanetriol is cooled from room temperature down to 180 K, it normally forms a glass. The glass transition temperature is 187 K. Various procedures have been used to prepare the crystalline form. Most investigators have found that when the glass is warmed slowly, crystallization starts somewhere between 190 and 291.8 K, the melting point. Otsubo, Haseda, and Kanda [29] stated that crystals do not form spontaneously unless the sample is first cooled to 180 K or below. In any case, crystallization occurs very slowly below 250 K. Once started, complete crystallization is generally achieved by storing the sample for several days at a few degrees below the melting point. Initiation of crystallization is helped by the addition of a seed crystal. Small amounts of water inhibit crystallization.

1,2,3-Propanetriol exists in only one crystalline form, and its heat capacity follows a smooth curve up to the triple point, in a manner typical of organic crystals. Table 55 identifies three sets of measurements of the heat capacity of crystalline 1,2,3-propanetriol. These are fairly old but do not appear to contain large errors.

Gibson and Giauque [41] encountered difficulty when crystallizing 1,2,3-propanetriol the first time, but after that found it much easier. They calibrated their thermometer against a copper–constantan thermocouple furnished by Eastman and Rodebush. Their temperature scale was defined at ten fixed points. These were the boiling points of nitrogen and oxygen at three pressures each, the sublimation temperature of carbon dioxide at two pressures, and the freezing points of mercury and water. Differences between their scale and the IPTS-68 were determined at these ten points, and the differences at intermediate temperatures were assumed to be linear functions of temperature between adjacent fixed points. The heat capacities reported by Gibson and Giauque were then converted to the IPTS-68 scale by the procedure of Douglas [32].

Simon and Lange [39] measured the heat capacity of crystalline 1,2,3-propanetriol in the narrow temperature range of 10.6 to 12.9 K. They did this to extend the data of Gibson and Giauque to lower temperatures and to compare the heat capacities of the crystalline and glass forms as close to 0 K as they could reach at that time.

Ahlberg, Blanchard, and Lundberg [84] closed the gap between the data of Simon and Lange and that of Gibson and Giauque and carried the measurements on down to 3 K. Their sample of 1,2,3-propanetriol was distilled under reduced pressure and its purity was confirmed by absence of pre-melting effects. They used a helium gas thermometer for temperature measurements up to 20 K and a copper–constantan thermocouple above 20 K. Their scale was fixed at the normal boiling point of hydrogen, taken to be 20.39 K, and the ice point at 273.17 K. Their heat capacity values were converted to the IPTS-68 basis by assuming a linear difference in temperature scales for intermediate temperatures.

At around 80 to 82 K the heat capacity values of Ahlberg, Blanchard, and Lundberg, are very close to those of Gibson and Giauque. However, they diverge increasingly at lower temperatures and differ by 1.6 $J K^{-1} mol^{-1}$ (4%) at 70 K. The data of Ahlberg, Blanchard, and Lundberg do not show any systematic deviations from those of Simon and Lange.

In spite of the large amount of data on 1,2,3-propanetriol, reliable heat capacity measurements much above the melting point are scarce. The highest temperature measurements were made by Berthelot [202] in 1879. He measured the heat removed from samples starting at temperatures in the range of 100 to 195 °C by dissolving them in water near room temperature. He derived the heat capacity from these measurements and expressed it by the function, $C_s = 200. + 0.59t$ $J K^{-1} mol^{-1}$ where t is temperature in degrees C. However, these values run 8 to 40 $J K^{-1} mol^{-1}$ higher than other values in this range and were not used in the final selection. Rabinovich and Nikolaev [129] measured the heat capacity of normal and deuterated 1,2,3-propanetriol using an isoperibol calorimeter similar to that of Skuratov. They did not give much information about the experimental procedure or sample purity. The selected values above 328 K are based largely on those of Omelchenko [203]. He did not measure them but compiled them from other sources, mostly Russian. The liquid phase data are combined with the glass phase data for the least squares calculation of the parameters so the calculated values are continuous above 190 K. The data are very uncertain above 330 K.

The melting point is difficult to determine accurately because of the slow approach to crystal–liquid equilibrium and the difficulty in removing all traces of water. Significant measurements are summarized in table 56. The value reported by Volmer and Marder [204] is selected because they carefully protected the dry sample from atmospheric moisture during the measurement, and, since their value is higher than the others, it is most likely correct. Berthelot [202] calculated the enthalpy of fusion from the difference between heats of solution of solid and liquid in water. de Forcrand reported a value but did not give any experimental details. Pushkin and Glagoleva [205] measured the cryoscopic constant for the depression of the freezing point caused by small amounts of water.

They obtained 3.1 K $\mathrm{mol^{-1}}$. The only direct measurements of enthalpy of fusion are those of Gibson and Giauque and of Volmer and Marder. An average of these two is selected.

Much research has been done on the properties of the glass form of 1,2,3-propanetriol. Specific questions which have been raised are: what is the residual entropy: what is the functional dependence of heat capacity on temperature near absolute zero, and what kinds of molecular phenomena give rise to the glass transition? 1,2,3-propanetriol glass has been recommended as a cryogenic heat transfer medium, and some recent studies at low temperatures have been made to obtain information for design purposes.

The early studies of Simon [38], Gibson and Giauque [41], Simon and Lange [39], and Ahlberg, Blanchard and Lundberg [84] were undertaken primarily to obtain the residual entropy of 1,2,3-propanetriol glass. They inspired many subsequent investigations on organic glasses in general. Kauzman [25] reviewed state of knowledge of organic glasses, including 1,2,3-propanetriol, in 1948. Samsoen [206], McMillan [207], and Carpenter, Davis and Matheson [127] have studied the kinetics of crystallization and certain other properties of 1,2,3-propanetriol. There have been several studies of 1,2,3-propanetriol - water mixtures. Yannas [208] and Bohon and Conway [209] are recent examples. Bohon and Conway reviewed earlier work, and their DTA measurements showed that the behavior of 1,2,3-propanetriol-water system in the liquid and glass phases is very complex. They found that the T_g for pure 1,2,3-propanetriol varies from 191–197 K to 195–204 K as the heating rate is changed from 5 to 60 K $\mathrm{min^{-1}}$. Other investigators have found similar time and rate dependent effects on the properties of 1,2,3-propanetriol glass. This contributes to the spread of T_g values listed in table 56.

Ahlberg, Blanchard, and Lundberg [84] measured the heat capacity of two samples of 1,2,3-propanetriol glass at low temperatures. One sample was cooled rapidly from the melt, and the other was prepared by melting the crystals and then cooling them slowly to 2.3 K. They found the small difference of 0.5 J $\mathrm{K^{-1}\,mol^{-1}}$ at 19 K, but no significiant difference below 14 K. The application of equation (12) to the selected properties previously reported are 23.4±0.5 J $\mathrm{K^{-1}\,mol^{-1}}$ by Gibson and Giauque [41], 19.2±1.2 J $\mathrm{K^{-1}\,mol^{-1}}$ by Simon and Lange [39], and 19.4 J $\mathrm{K^{-1}\,mol^{-1}}$ by Ahlberg, Blanchard, and Lundberg [84].

Oblad and Newton [210] measured the changes in enthalpy in liquid and glass 1,2,3-propanetriol between 292.6 K and temperatures in the range of 167 to 193 K in a drop calorimeter. They observed the effect of holding the sample for various lengths of time at the lower temperatures. The enthalpy changes were independent of these times (up to 24 hours) at temperatures down to 183 K. In this range the derived heat capacities agreed well with those of Gibson and Giauque. At lower temperatures, increasing equilibration times gave larger enthalpy changes and correspondingly larger heat capacities. At 177 K five days were required to reach equilibrium. They concluded that if equilibrium could be attained at temperatures down to absolute zero, the residual entropy would be much smaller than that calculated from observed heat capacities, and possibly zero. However, they did not report their data in a form suitable for quantitative comparison with the heat capacity calculated from the parameters in table 57.

Craig, Massena, and Mallya [211] evaluated 1,2,3-propanetriol glass for use as heat transfer medium in low temperature calorimetry and measured its heat capacity down to 1.5 K. They obtained the Debye characteristic temperature of 126 K. At very low temperatures, the acoustical contributions to the heat capacity of a solid should fit the equation $C_s/T^3 = a + bT^2$. A plot of C_s/T^3 versus T^2 for their data, however, shows a minimum at about 2 K. The increase in C_s/T^3 below 2 K must reflect other types of contributions. They discussed several possibilities. Leadbetter and Wycherley [212] measured the heat capacity of the glass from 1.88 to 25.1 K. They confirmed the minimum in C_s/T^3 at 2 K, and also verified earlier measurements in this region. They published their data only in graphical form. The numerical values which we include in our least squares fit were obtained directly from Prof. Leadbetter. They removed water and air from their sample and stored it over P_2O_5 but made no further attempt at purification. The germanium thermometer used in their measurements was calibrated on the IPTS-68 from 15 to 20 K and by comparison with a constant volume gas thermometer at lower temperatures.

The available heat capacity values for glycerol range from around 0.032 J $\mathrm{K^{-1}\,mol^{-1}}$ at 1.45 K to 215 J $\mathrm{K^{-1}\,mol^{-1}}$ at 282 K. *Because of the wide temperature* range and the complicated temperature dependence, fitting these data to polynomials in temperature was difficult. In order to accomplish it, the complete data set, ranging from 1.5 to 453 K, was separated into six regions. It was necessary to use terms containing powers of temperature from 2 to 6 for the lowest temperature region. The next region used powers of temperature from 0 to 5 and the remaining four from 0 to 4. The two lowest regions were fit separately but with constraints to force continuity at the boundary. The remaining four were combined together in a single calculation by the method described in section 1.5 of the Introduction. The deviations between observed and calculated heat capacities are largest in the glass transition region, but the experimental uncertainty is largest there also. Both the experimental and calculated heat capacity shows a slight maximum at 194 K.

TABLE 55. Sources of Heat Capacity Data for 1,2,3-Propanetriol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Berthelot	1879	l(393–468)	drop	H	not stated			[202]
Emo	1881	l(298)			not stated			[213]
Simon	1922	gl(19–294)	isoperibol	C	contains 1.3% water			[38]
Gibson & Giauque	1923	c(70–280),l(291–299) gl(70–282)	isoperibol	C	distilled under reduced pressure, 99.67^c mol%	73	corr	[41]
Simon & Lange	1926	c(11–13),gl(11–13)	isoperibol	C	dried in vacuum	10	no	[39]
Samsoen & Mondain-Monval	1926	gl(83–214)	drop	H	not stated			[214]
Ernst, Watkins & Ruwe	1936	l(298)	Dewar flask	C	distill under reduced press.			[142]
Ahlberg, Blanchard & Lundberg	1937	c(3–87),gl(2–95)	isoperibol	C	Baker Co. sample, c.p. grade distill under reduced press.	67	corr	[84]
Oblad & Newton	1937	gl(167–193)	drop	H	distill under reduced press. 0.2% water in some samples			[210]
Otsubo, Haseda & Kanda	1955	gl(160–200)	adiabatic	C	not stated			[29]
Omelchenko	1962	l(283–453)		C		7	no	[203]
Rabinovich & Nikolaev	1962	l(283–328)	isoperibol	C	carefully purified & dried	10	no	[129]
Craig, Massena & Mallya	1965	gl(1–4)	isoperibol	C	commercial c.p. sample	87	no	[211]
Paz Andrade, Paz Fernandez & Recacho	1970	l(301–313)	Calvet	C	not stated	1	no	[116]
Leadbetter & Wycherley	1970	gl(2–25)	isoperibol	C	98 %	52	I–68	[212]

TABLE 56. Reported Phase Transition Data for 1,2,3-Propanetriol

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Berthelot	1879	$c \rightleftharpoons l$	286.	mp	16360.	c	[202]
de Forcrand	1900	$c \rightleftharpoons l$			16320.	c	[215]
Simon	1922	glass	190.	hc			[38]
Pushin & Glagoleva	1922	$c \rightleftharpoons l$	291.2	mp	21000.	t	[205]
Gibson & Giauque	1923	$c \rightleftharpoons l$	291.00	tp	18301	c	[41]
		glass	190.	hc			
Parks & Huffman	1927	glass	221.	sp			[50]
Volmer & Marder	1931	$c \rightleftharpoons l$	291.8	mp	18477	c	[204]
Samsoen	1928	$c \rightleftharpoons l$	291.22	mp			[206]
Allbright	1937	$c \rightleftharpoons l$	291.33	mp			[216]
Otsubo, Haseda & Kanda	1955	glass	180.	hc			[29]
McMillan	1965	glass	187.	dt			[207]
Carpenter, Davies & Matheson	1967	glass	181.9	dt			[127]
SELECTED VALUES		$c \rightleftharpoons l$	291.8±0.2		18370.±180		

TABLE 57. Parameters for Heat Capacity of 1,2,3-Propanetriol

Phase	c	c	c	c	c	gl	gl
Data Points							
Number	14	28	11	10	63(11)	156(5)	40(2)
Temp./K	3.1 - 12.9	14.6 - 92.6	93.9 -193.7	204.1 - 280.0	3.1 -280.0	1.4 - 15.9	16.9 - 94.9
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 13.0	13.0 - 93.0	93.0 -200.0	200.0 291.8	0 291.8	0 16.0	16.0 100.
a_i		-1.96	-99.16	7468.90			-4.538
b_i x 10		0.864	37.205	-1329.606			4.6390
c_i x 10^3		18.981	-34.9194	892.8764		2.006	9.1002
d_i x 10^5	66.86	-22.247	15.9569	-265.1344		-95.40	-8.8543
e_i x 10^7	154.0	8.254	-2.6911	29.4565		5604.8	-3.388
f_i x 10^9						-44865.	4.680
g_i x 10^{11}						110782.	
Deviations							
Average, d	-0.005	0.004	-0.009	0.028	0.000	-0.000004	0.117
R.M.S., $r(\sigma)$	0.015	0.289	0.170	1.43	0.091	0.00295 (0.0030)	0.427(0.452)
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.02	0.3	0.35	1.0		0.015	0.4
$\delta(H-H_0)$	0.2	24.	44.	102.		0.2	34.
$\delta(S)$	0.029	0.6	0.6	0.8		0.037	0.7
$\delta(G-H_0)/T$	0.013	0.33	0.3	0.4		0.023	0.4

Phase	gl	gl	gl	gl & l	gl & l
Data Points					
Number	6	8	5	29	48(14)
Temp./K	102.0 -125.6	135.9 -173.5	179.8 -195.6	201.0 -453.2	102.0 -453.2
Parameters for	c_s	c_s	c_s	c_s	c_s
Temp./K	100.0 -130.0	130.0 -178.0	178.0 -200.0	200.0 -440.0	100.0 -440.0
a_i	2370.61	718.23	3152929.71	-182.20	
b_i x 10	808.944	-173.088	-664882.017	43.267	
c_i x 10^3	-1013.849	167.493	525131.020	-20.788	
d_i x 10^5	565.879	-70.694	-184108.535	4.9046	
e_i x 10^7	-118.189	11.301	24177.0482	-0.43126	
Deviations					
Average, d	-0.008	0.080	1.67	0.138	0.000
R.M.S., $r(\sigma)$	0.138	0.406	4.56	1.33	1.52(1.72)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.4	0.4	2.0	1.0	
$\delta(H-H_0)$	36.	46.	64.	283.*	
$\delta(S-S_0)$	0.7	0.8	0.8	1.0*	
$\delta(G-H_0)/T$	0.4	0.4	0.4	0.4*	

*Uncertainties relative to crystal at 0 K.

TABLE 58. Thermodynamic Functions of 1,2,3-Propanetriol
$C_3H_8O_3$ $M = 92.094$

T/K	$(G\text{-}H_0)/T$	$(H\text{-}H_0)/T$	$H\text{-}H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
		Crystal			
0	0.000	0.000	0.00	0.00	0.000
10	-0.063	0.198	1.98	0.26	0.823
15	-0.227	0.714	10.71	0.94	2.898
20	-0.547	1.60	32.05	2.15	5.713
25	-1.02	2.74	68.5	3.76	8.909
30	-1.64	4.05	121.6	5.69	12.377
35	-2.37	5.50	192.5	7.87	16.02
40	-3.20	7.05	281.9	10.25	19.74
50	-5.12	10.33	516.6	15.46	27.16
60	-7.31	13.73	823.8	21.04	34.20
70	-9.68	17.12	1198.4	26.80	40.61
80	-12.18	20.42	1633.7	32.60	46.33
90	-14.77	23.6	2123.3	38.36	51.54
100	-17.42	26.6	2663.3	44.05	56.35
110	-20.09	29.5	3248.3	49.62	60.56
120	-22.78	32.3	3873.	55.06	64.39
130	-25.47	34.9	4536.	60.36	68.08
140	-28.15	37.4	5235.	65.54	71.77
150	-30.81	39.8	5971.	70.62	75.54
160	-33.45	42.2	6746.	75.61	79.41
170	-36.08	44.5	7560.	80.55	83.35
180	-38.68	46.7	8413.	85.42	87.2
190	-41.27	49.0	9304.	90.24	90.9
200	-43.84	51.1	10230.	94.99	94.1
210	-46.39	53.3	11188.	99.66	97.7
220	-48.91	55.4	12184.	104.3	101.6
230	-51.42	57.5	13220.	108.9	105.4
240	-53.9	59.5	14291.	113.5	108.8
250	-56.4	61.6	15397.	118.0	112.7
260	-58.8	63.7	16551.	122.5	118.5
270	-61.3	65.9	17780.	127.1	128.2
280	-63.7	68.3	19138.	132.1	144.8
290	-66.2	71.4	20710.	137.6	171.6
291.80	-66.6	72.0	21024.	138.7	177.9
		Liquid			
291.80	-66.6	135.0	39394.	201.6	216.2
298.15	-69.5	136.8	40776.	206.3	219.0
300	-70.4	137.3	41182.	207.7	219.8
310	-74.9	140.0	43402.	214.9	224.2
320	-79.4	142.7	45666.	222.1	228.6
330	-83.9	145.4	47973.	229.2	232.9
340	-88.2	148.0	50324.	236.2	237.2
350	-92.6	150.6	52717.	243.2	241.3
360	-96.8	153.2	55149.	250.0	245.2
370	-101.1	155.7	57620.	256.8	248.9
380	-105.3	158.2	60126.	263.5	252.2
390	-109.4	160.7	62662.	270.1	255.
400	-113.5	163.1	65224.	276.6	257.
410	-117.6	165.4	67806.	282.9	259.
420	-121.6	167.6	70401.	289.	260.
430	-125.5	170.	72999.	295.	260.
440	-129.5	172.	75591.	301.	259.

TABLE 59. Thermodynamic Functions of 1,2,3-Propanetriol
$C_3H_8O_3$ $M = 92.094$

T/K	$(G\text{-}H_0)/T$	$(H\text{-}H_0)/T$	$H\text{-}H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
			Glass		
0			9535.	20.87	0.00000
1	9514.1297	9535.001	9535.001	20.87082	0.00157
1.5	6335.7961	6356.668	9535.002	20.87183	0.00380
2	4746.6289	4767.502	9535.005	20.87343	0.00799
3	3157.4605	3178.340	9535.021	20.87974	0.02760
4	2362.874	2383.767	9535.068	20.89313	0.0731
5	1886.118	1907.036	9535.180	20.91774	0.1583
6	1568.276	1589.234	9535.402	20.95786	0.2954
8	1170.952	1192.051	9536.410	21.09968	0.7559
10	932.519	953.860	9538.598	21.3408	1.4727
12	773.515	795.204	9542.446	21.6890	2.407
14	659.883	682.024	9548.341	22.1412	3.519
15	614.406	636.81	9552.17	22.4053	4.155
20	455.006	479.08	9581.57	24.073	7.633
25	358.986	385.15	9628.79	26.165	11.277
30	294.599	323.15	9694.5	28.551	15.018
35	248.251	279.40	9779.0	31.149	18.787
40	213.156	247.06	9882.3	33.902	22.52
45	185.546	222.31	10004.1	36.767	26.17
50	163.169	202.88	10143.8	39.708	29.68
60	128.857	174.56	10473.8	45.71	36.18
70	103.490	155.21	10864.7	51.72	41.89
80	83.716	141.37	11309.3	57.65	46.94
90	67.69	131.14	11802.8	63.46	51.78
100	54.28	123.47	12346.9	69.18	57.23
110	42.80	117.67	12943.6	74.87	61.65
120	32.76	113.14	13576.4	80.37	64.91
130	23.86	109.56	14242.9	85.70	68.38
140	15.84	106.75	14944.5	90.90	72.16
150	8.56	104.59	15688.4	96.03	76.7
155	5.14	103.73	16077.9	98.59	79.1
160	1.86	103.00	16479.7	101.14	81.6
165	-1.30	102.39	16894.	103.69	84.2
170	-4.35	101.90	17322.	106.2	87.0
175	-7.30	101.51	17764.	108.8	89.8
180	-10.15	101.25	18225.	111.4	98.5
182.5	-11.55	101.3	18493.	112.9	117.
185	-12.93	101.7	18814.	114.6	140.
187.5	-14.30	102.3	19189.	116.6	160.
190	-15.66	103.2	19607.	118.9	173.9
195	-18.37	105.2	20505.	123.5	180.6
200	-21.05	107.0	21391.	128.0	175.1
210	-26.35	110.3	23166.	136.7	180.0
220	-31.56	113.6	24990.	145.2	184.8
230	-36.68	116.8	26861.	153.5	189.3
240	-41.72	119.9	28776.	161.6	193.7
250	-46.67	122.9	30735.	169.6	198.1
260	-51.55	125.9	32738.	177.5	202.4
270	-56.36	128.8	34784.	185.2	206.7
280	-61.10	131.7	36873.	192.8	211.1
290	-65.77	134.5	39005.	200.3	215.4

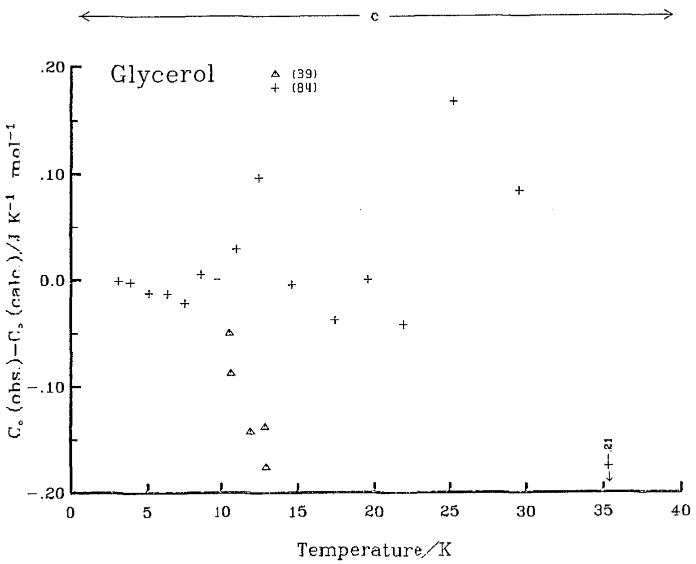

FIG. 51. Deviation plot for 1,2,3-propanetriol (glycerol), c, 0–35 K.

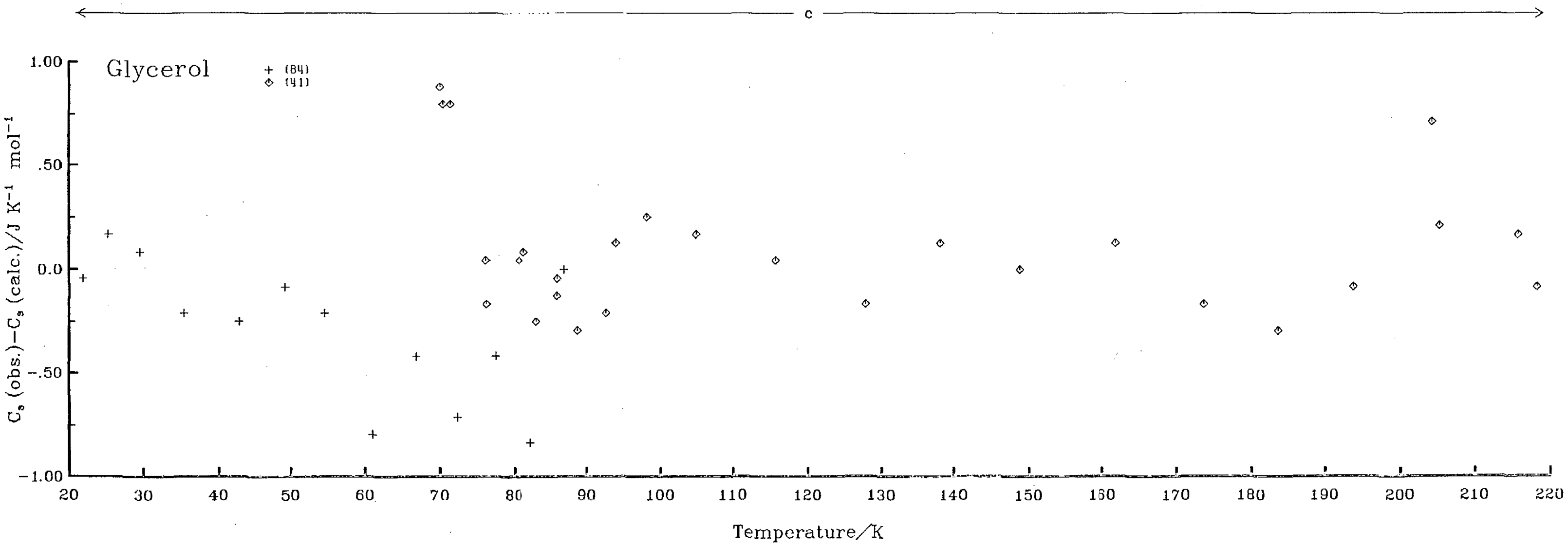

FIG. 52. Deviation plot for 1,2,3-propanetriol (glycerol), c, 20–220 K.

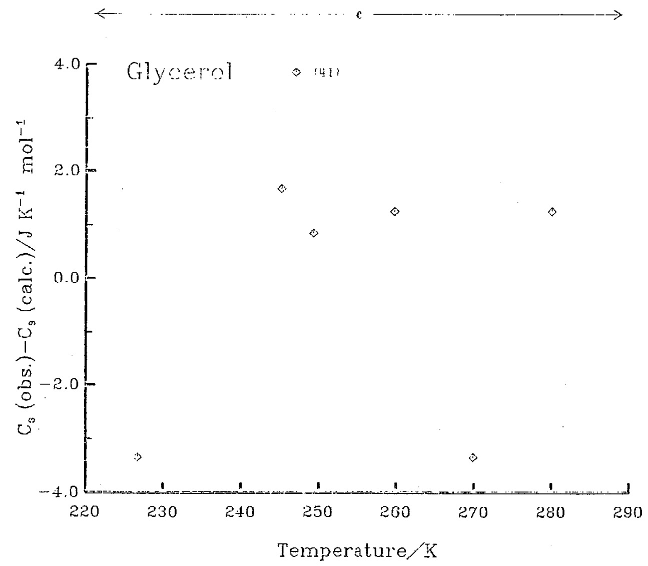

FIG. 53. Deviation plot for 1,2,3-propanetriol (glycerol), c, 330–380 K.

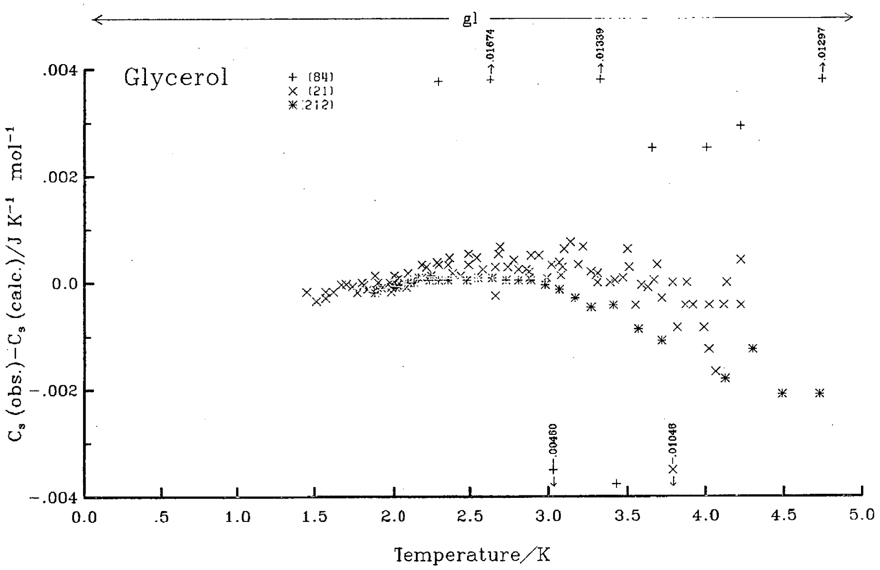

FIG. 54. Deviation plot for 1,2,3-propanetriol (glycerol), c, 0–10 K.

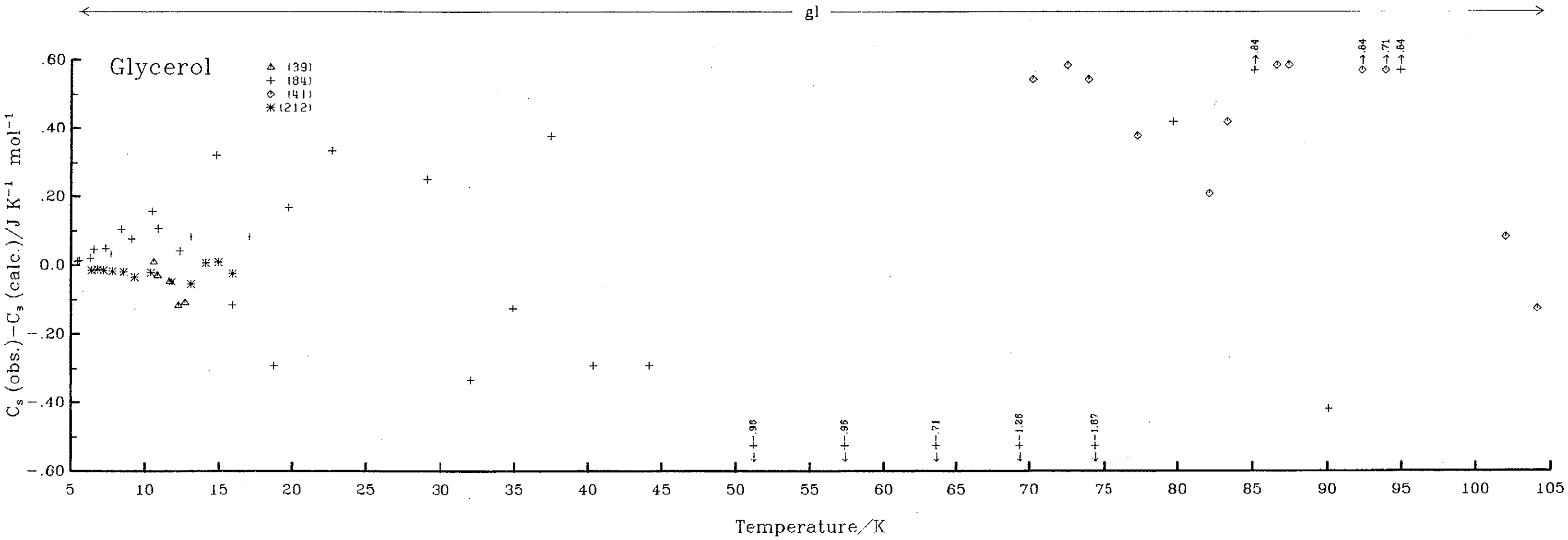

FIG. 55. Deviation plot for 1,2,3-propanetriol (glycerol), c, 10–105 K.

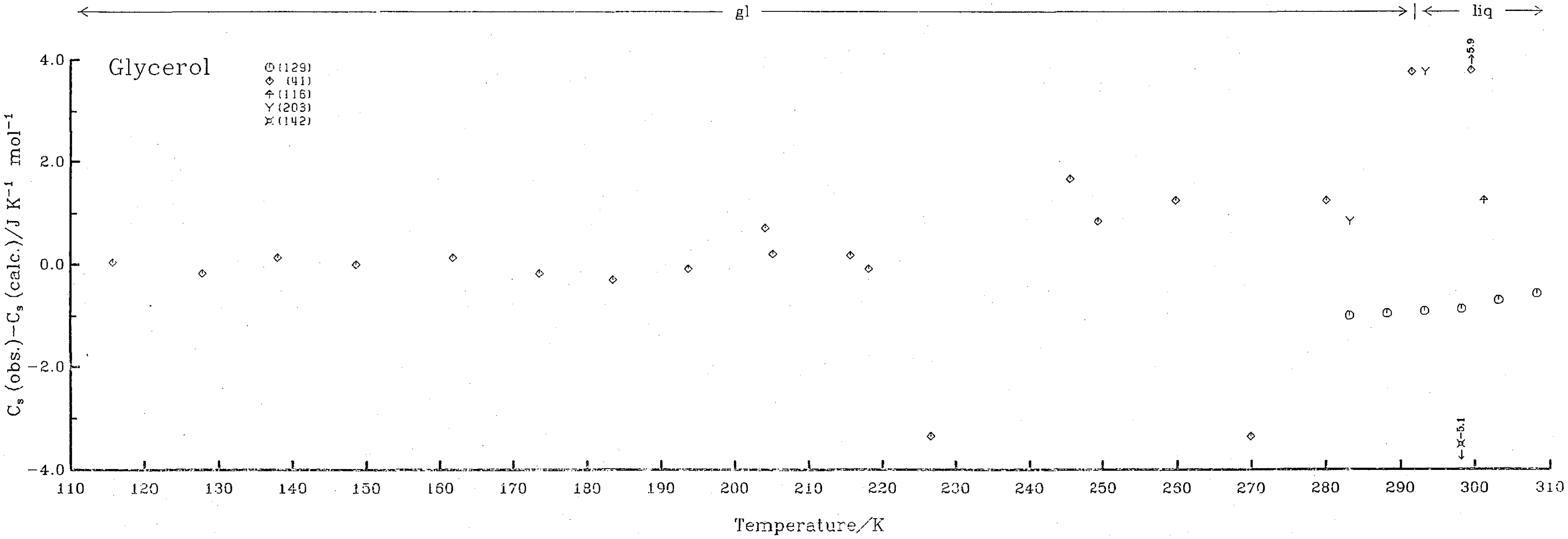

FIG. 56. Deviation plot for 1,2,3-propanetriol (glycerol), gl, l, 110–310 K.

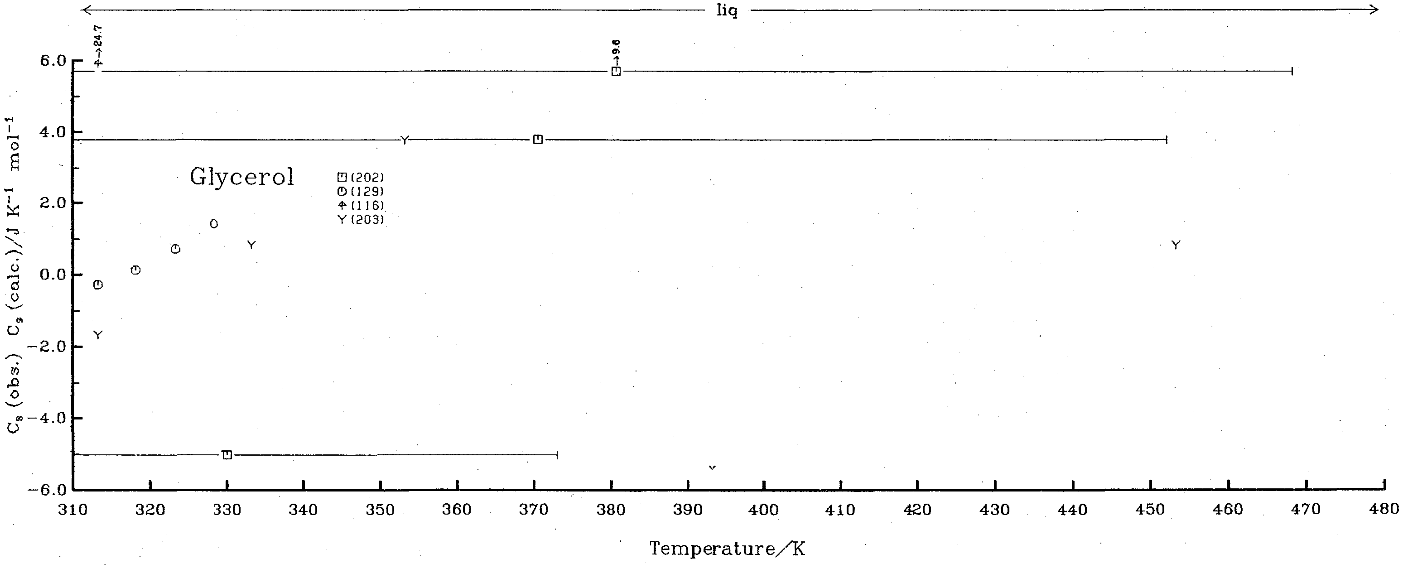

FIG. 57. Deviation plot for 1,2,3-propanetriol (glycerol), l, 310–450 K.

13. meso-1,2,3,4-Butanetetrol (Erythritol)

1,2,3,4-Butanetetrol contains two asymmetric carbon atoms and therefore exists as two diastereoisomers. The meso isomer melts in the range of 119 to 121 °C and is commonly called erythritol. The optically active isomers melt at about 88 to 89 °C and are commonly called d- and l-threitol.

Parks and Anderson [8] measured the heat capacity of solid erythritol from 87 to 292 K in a Nernst type calorimeter. They used an Eastman sample without further treatment. It melted at 118.9 °C. They estimated the uncertainty of less than 1% in their measurements. Spaght, Thomas, and Parks [217] measured the heat capacities and enthalpies of fusion of ten organic compounds, including solid and liquid erythritol, in the range of 30 to 200 °C by the use of a copper–jacketed conduction calorimeter. A commercial (Pfanstiehl) sample of erythritol was used, without further purification, in these measurements. The authors did not report the directly measured values but instead gave a table of smoothed values of heat capacity read from a graph of the observed data. They estimated an accuracy of better than 3% for the tabulated values. They also obtained a melting point of 118.4 °C and an enthalpy of fusion of 42.3 kJ mol^{-1}.

The foregoing two sets of data are combined for the least squares calculation of the parameters in table 61. Louguinine [218] measured the mean heat capacity of erythritol betweeen 20.5 and 100.0 °C in a drop calorimeter. Pushin and Glagoleva [205] determined the phase diagram for the water–erythritol system. They obtained a melting point of 116.6 ° for their sample of erythritol, but it probably contained some water.

The entropy and enthalpy at 80 K in table 62 were estimated by the group additivity procedure.

TABLE 60. Sources of Heat Capacity Data for meso–1,2,3,4–Butanetetrol

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Louguinine	1892	c(294–273)	drop	H	not stated			[218]
Parks & Anderson	1926	c(87–292)	isoperibol	C	Eastman Kodak sample, no further treatment	16	no	[8]
Spaght, Thomas & Parks	1932	c(303–393), l(403–423)	conduction	C	commercial sample, no further treatment	11	no	[217]

TABLE 61. Parameters for Heat Capacity of 1,2,3,4–Butanetetrol

Phase	c	c	c	l
Data Points				
Number	15	9	24(6)	3(2)
Temp./K	87.0 –289.0	291.7 –373.2	87.0 –373.2	403.2 –423.2
Parameters for	C_s	C_s	C_s	C_s
Temp./K	80.0 –290.0	290.0 –391.6	80.0 –391.6	391.6 –430.0
a_i	–3.92	765.7		247.7
b_i x 10	8.134	–65.65		2.51
c_i x 10^3	–1.643	21.788		
d_i x 10^5	0.2776	–2.1846		
Deviations				
Average, d	–0.004	0.025	0.000	0.000
R.M.S., $r(\sigma)$	0.218	9.557	0.272(0.305)	0.000
Estimated Uncertainty in Tabulated Values				
$\delta(C)$	1.0	5.0		10.
$\delta(H–H_0)$	290.	580.		1500.
$\delta(S)$	3.3	3.6		4.8
$\delta(G–H_0)/T$	4.0	4.0		4.0

TABLE 62. Thermodynamic Functions of meso-1,2,3,4-Butanetetrol
$C_4H_{10}O_4$ $M = 122.121$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
			Crystal		
80	-13.78	21.2	1700.	35.02	52.06
90	-16.50	25.0	2250.	41.50	58.00
100	-19.32	28.6	2859.	47.91	63.77
110	-22.21	32.0	3525.	54.25	69.37
120	-25.14	35.4	4246.	60.52	74.83
130	-28.10	38.6	5021.	66.72	80.2
140	-31.08	41.8	5849.	72.85	85.4
150	-34.1	44.9	6728.	78.9	90.5
160	-37.1	47.9	7658.	84.9	95.5
170	-40.0	50.8	8638.	90.9	100.5
180	-43.0	53.7	9668.	96.7	105.4
190	-46.0	56.6	10747.	102.6	110.4
200	-49.0	59.4	11875.	108.4	115.2
210	-52.0	62.2	13052.	114.1	120.1
220	-54.9	64.9	14278.	119.8	125.1
230	-57.9	67.6	15554.	125.5	130.0
240	-60.8	70.3	16879.	131.1	135.0
250	-63.7	73.0	18255.	136.7	140.1
260	-66.6	75.7	19682.	142.3	145.3
270	-69.5	78.4	21161.	147.9	150.6
280	-72.4	81.0	22693.	153.5	156.0
290	-75.3	83.7	24280.	159.0	161.5
298.15	-77.7	85.9	25615.	163.6	166.2
300	-78.2	86.4	25924.	164.6	167.3
310	-81.1	89.1	27627.	170.2	173.6
320	-84.0	91.9	29396.	175.8	180.1
330	-86.8	94.6	31231.	181.5	186.9
340	-89.7	97.5	33134.	187.1	193.7
350	-92.6	100.3	35104.	192.9	200.3
360	-95.4	103.	37139.	198.6	206.8
370	-98.3	106.	39238.	204.3	212.9
380	-101.2	109.	41395.	210.1	218.
390	-104.0	112.	43605.	215.8	223.
391.6	-104.5	112.	43963.	216.7	224.
			Liquid		
391.6	-104.5	220.	86303.	324.9	346.
400	-109.2	223.	89218.	332.	348.
410	-114.7	226.	92712.	341.	351.
420	-120.2	229.	96230.	349.	353.
430	-125.6	232.	99774.	358.	356.

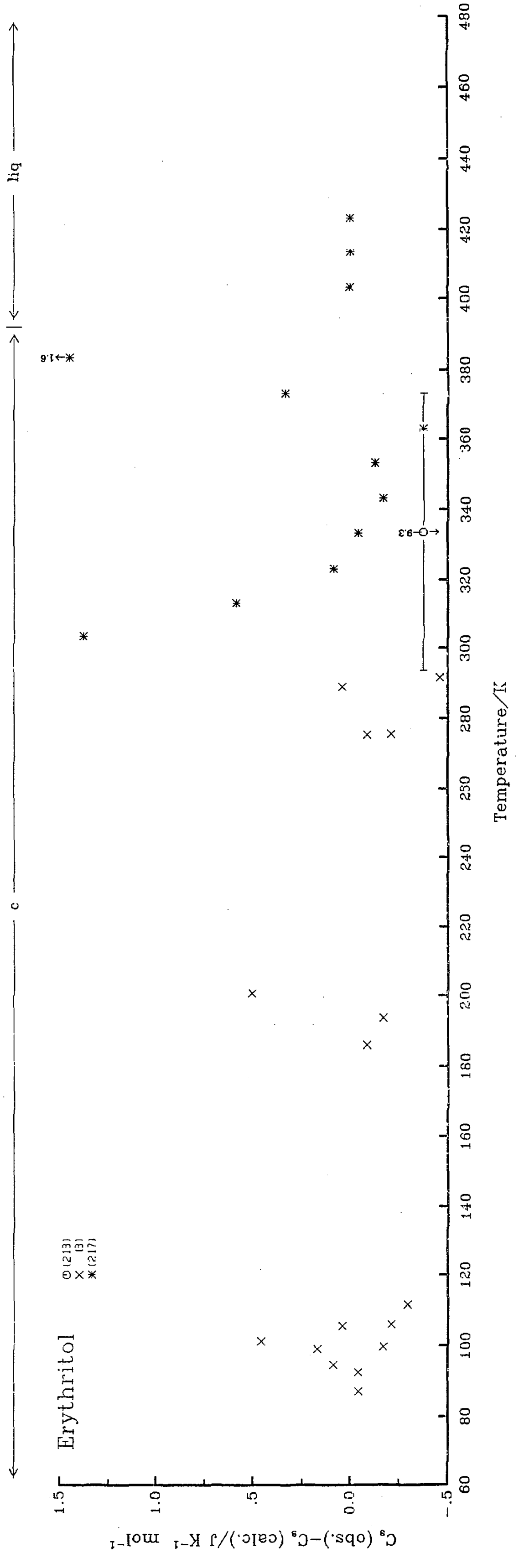

FIG. 58. Deviation plot for 1,2,3,4-butanetetrol (erythritol), c, 80–440 K.

14. Dimethyl Ether (Methoxymethane)

All of the heat capacity and phase transition values were taken from Kennedy, Sagenkahn and Aston [79]. They measured temperatures with a helium gas thermometer described by Aston, Willihnganz and Messerly [78]. It was calibrated at three fixed points: the boiling point of H_2 (20.35 K), the boiling point of O_2 (90.221 K) and the freezing point of water (273.16 K). Their data were converted to IPTS-68 on the assumption that the difference between their scale and IPTS-68 was a linear function of temperature between the fixed points. The vapor pressure values used to convert C_s to C_p were calculated from the equation given by Kennedy, Sagenkahn, and Aston. The liquid volumes were taken from Maas and Boomer [219]. Maas and Boomer also reported a melting point of 135.2 K.

TABLE 63. Sources of Heat Capacity Data for Dimethyl Ether

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Kennedy, Sagenkahn & Aston	1941	c(14–128),l(137–245)	isoperibol	C	sample dried by passing gas over Al_2O_3 two times, then distill, 99.59 %	58	corr	[79]

TABLE 64. Parameters for Heat Capacity of Dimethyl Ether

Phase	c	c	c	c	c	l	l
Data Points							
Number	5	11	5	5	26(8)	32(4)	32(4)
Temp./K	13.7 – 24.3	28.2 – 68.3	74.1 – 96.9	102.7 –127.8	13.7 –127.8	137.2 –245.5	137.2 –245.5
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_p
Temp./K	0 – 25.0	25.0 – 70.0	70.0 –100.0	100.0 –131.64	0 –131.64	131.64–250.0	131.64–250.0
a_i		–13.96	–37.49	–56.54		73.56	72.32
b_i x 10		12.783	21.255	22.298		4.473	4.700
c_i x 10^3		–8.898	–18.698	–15.065		–2.7429	–2.8789
d_i x 10^5	188.42	3.276	6.845	4.0762		0.5739	0.6009
e_i x 10^7	–422.1						
Deviations							
Average, d	0.013	–0.021	0.004	0.004	0.000	0.000	0.000
R.M.S., $r(\sigma)$	0.071	0.142	0.042	0.029	0.096(0.117)	0.239(0.255)	0.239(0.255)
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.08	0.15	0.2	0.25		0.4	0.4
$\delta(H-H_0)$	0.9	6.8	9.	12.		63.	
$\delta(S)$	0.053	0.16	0.18	0.19		0.4	
$\delta(G-H_0)/T$	0.018	0.06	0.06	0.06		0.09	

TABLE 65. Thermodynamic Functions of Dimethyl Ether

C_2H_6O $M = 46.069$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}	C_p J K^{-1} mol^{-1}
			Crystal			
0	0.000	0.000	0.00	0.00	0.00	0.00
10	-0.136	0.387	3.87	0.52	1.46	1.46
15	-0.423	1.162	17.44	1.59	4.22	4.22
20	-0.918	2.418	48.4	3.34	8.32	8.32
25	-1.629	4.06	101.6	5.69	12.95	12.95
30	-2.531	5.91	177.2	8.44	17.27	17.27
35	-3.585	7.82	273.7	11.41	21.29	21.29
40	-4.75	9.74	389.6	14.50	25.03	25.03
45	-6.01	11.64	523.6	17.65	28.53	28.53
50	-7.33	13.49	674.6	20.83	31.81	31.81
60	-10.11	17.05	1023.1	27.16	37.78	37.78
70	-12.99	20.40	1428.2	33.40	43.16	43.16
80	-15.93	23.55	1884.1	39.48	47.93	47.93
90	-18.87	26.50	2385.2	45.38	52.25	52.25
100	-21.81	29.29	2929.0	51.10	56.53	56.53
110	-24.73	31.96	3515.7	56.69	60.71	60.71
120	-27.62	34.52	4142.1	62.14	64.54	64.54
130	-30.48	36.97	4806.2	67.45	68.29	68.29
131.64	-30.95	37.37	4918.7	68.31	68.91	68.91
			Liquid			
131.64	-30.95	74.86	9854.7	105.81	98.00	98.01
140	-35.60	76.25	10675.	111.85	98.17	98.18
150	-40.91	77.71	11657.	118.62	98.31	98.33
160	-45.97	79.0	12641.	124.97	98.42	98.43
170	-50.79	80.1	13625.	130.94	98.53	98.54
180	-55.40	81.2	14612.	136.58	98.67	98.69
190	-59.82	82.1	15599.	141.92	98.89	98.91
200	-64.05	83.0	16590.	147.00	99.22	99.24
210	-68.11	83.7	17585.	151.85	99.7	99.7
220	-72.02	84.5	18585.	156.50	100.3	100.4
230	-75.79	85.2	19594.	160.98	101.2	101.2
240	-79.42	85.9	20612.	165.31	102.3	102.4
250	-82.93	86.6	21644.	169.51	103.6	103.8

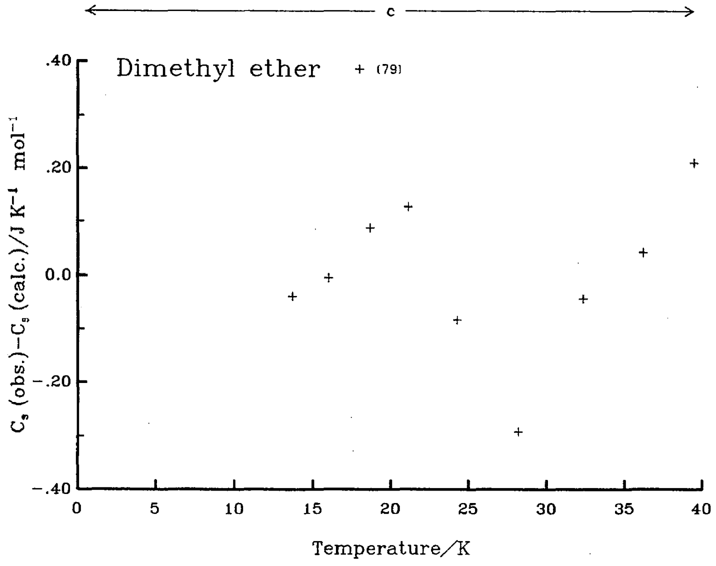

FIG. 59. Deviation plot for dimethyl ether, c, 0–40 K.

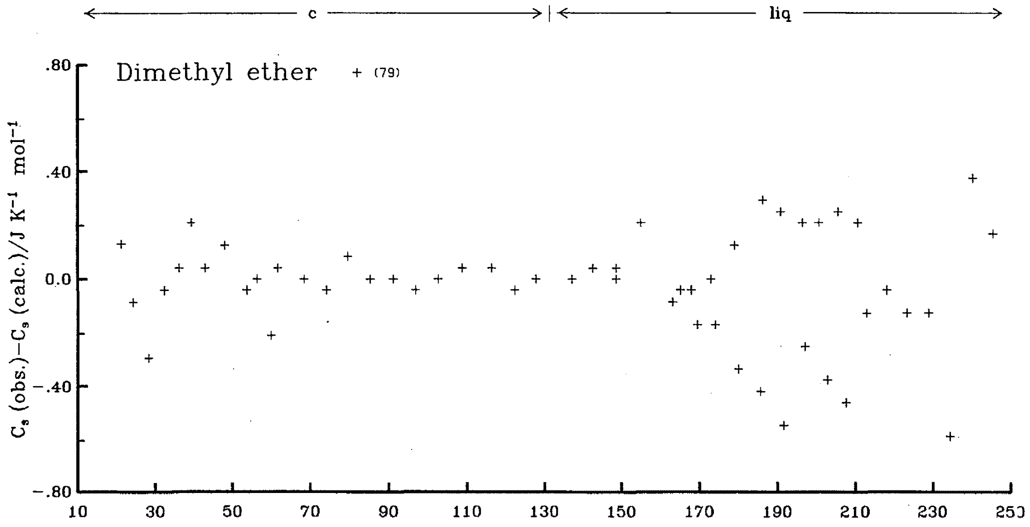

FIG. 60. Deviation plot for dimethyl ether, c,l, 20–250 K.

15. Diethyl Ether (Ethoxyethane)

References to several sources of heat capacity and transition data are collected in tables 66 and 67. However, the parameters in table 68 and the calculated thermodynamic properties in table 36 up to 300 K are all based on the data of Counsell, Lee, and Martin [76].

On crystallization, diethyl ether first forms a metastable crystal, which changes to the stable crystal on further cooling. Temperatures were measured with a platinum resistance thermometer, which, according to Counsell [220] was calibrated on the IPTS-48 above 90 K. Their reported heat capacity values above 90 K were converted to IPTS-68.

The only significant thermal measurements above 300 K are those of Hirn [130], Regnault [221], and Eubank and Smith [155]. The measurements of Hirn, and the subsequent calculations of Sutherland [131] were described briefly in section 3. Eubank and Smith measured the enthalpy of the liquid and gas at equilibrium from 348 K to the critical temperature, and also the enthalpy of the single phases up to pressures of 6200 kPa. The parameters for the enthalpy of liquid diethyl ether at saturation, relative to 300 K, were obtained by a least squares fit of dH/dT calculated from the heat capacity of Regnault at 303 and 308 K and from the heat capacity of Hirn (recalculated by Sutherland) and from the enthalpy (converted to $H_T - H_{348}$) of Eubank and Smith. Heat capacities were converted to dH/dT through the use of equations (16), (18), and (21). An equation similar to (34) was used for the enthalpy data. This procedure gives, for the temperature range of 300 to 466 K,

$$H_T\,(\mathrm{l})-H_{300}(\mathrm{l}) = 87069-1330.8T+6.164T^2-0.011553T^3 + 8.5645 \times 10^{-6}T^4 \quad \mathrm{J\,K^{-1}\,mol^{-1}}.$$

The calculation was constrained to reproduce the value of dH/dT at 300 K calculated from the parameters for the low temperature region. The properties of diethyl ether from 300 to 460 K in table 68 were calculated from this enthalpy equation. The heat capacity at equilibrium vapor pressure, C_s, was calculated using equation (20) and the entropy was calculated from equation (24). Values of the vapor pressure and liquid volume required for these calculations were taken from Schnaible and Smith [222].

TABLE 66. Sources of Heat Capacity Data for Diethyl Ether

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Favre & Silbermann	1846	l(290–305)	drop	H	not stated			[223]
Andrews	1848	l(298)	mixing	H	not stated			[104]
Regnault	1862	l(273–308)	drop	H		2	no	[221]
Hirn	1867	l(353–393)	cooling rate	C	not stated			[130]
de Heen	1888	l(453–458)	cooling rate	C	not stated			[224]
Sutherland	1888	l(353–393)	*	C	not stated	3	no	[131]
Battelli	1908	l(182–271)	Dewar flask	C	distilled over $CaCl_2$			[139]
Keyes & Beattie	1924	l(274–287)	isoperibol	C	treated with H_2SO_4, dried with $CaCl_2$, distilled over Na			
Parks & Huffman	1926	c(76–135),l(164–290)	isoperibol	C	Eastman Kodak sample,treated with Na twice, fract. distilled			[49]
Bennewitz & Wendroth	1927	l(303–488)	isoperibol	C	not stated			[226]
Aoyama & Kanda	1935	c(80–137),l(159–253)	adiabatic	C	commercial sample			[57]
Kurnakov & Voskresenskaya	1936							[227]
Mazur	1938	l(160–295)	isoperibol	C	not stated			[228]
Eubank & Smith	1962	l(339–467)	flow	H	>99.9%			[155]
Counsell, Lee & Martin	1971	c(16–151),l(160–300) c,m(140–145)	adiabatic	C	commercial sample, 99.92^c mol% 99.10^g wt%	121	corr	[76]

* Recalculation of data reported by Hirn [130].

TABLE 67. Reported Phase Transition Data for Diethyl Ether

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Beckmann & Waentig	1910	c$\rightleftharpoons$l	156.	mp	8490.	t	[229]
Mitsukuri & Hara	1926	c$\rightleftharpoons$l	150.61	mp	5860.	t	[59]
Parks & Huffman	1926	c$\rightleftharpoons$l	156.8	tp	7320.	c	[49]
		c,m$\rightleftharpoons$l	149.7	tp			
Sapgir	1929	c$\rightleftharpoons$l	156.8		7110.	t	[150]
		c,m$\rightleftharpoons$l	149.8				
Timmermans	1934	c$\rightleftharpoons$l	157.0	mp	7538.	t	[230]
McNeight & Smyth	1936	c$\rightleftharpoons$l	156.8	mp			[231]
		c,m$\rightleftharpoons$l	149.8	mp			
Brooks & Pilcher	1959	c$\rightleftharpoons$l	157.2	mp	6904.	c	[232]
Counsell, Lee & Martin	1971	c$\rightleftharpoons$l	156.92	tp	7190.	c	[76]
		c,m$\rightleftharpoons$l	149.86	tp	6820.	c	
Lesikar	1975	glass	93.4	dt			[124]
Lesikar	1976	glass	92.6	dt			[219]
Angell, Sare & Sare	1978	glass	87.	dt			[125]
SELECTED VALUES		c$\rightleftharpoons$l	156.92±0.05		7190.±20		

TABLE 68. Parameters for Heat Capacity of Diethyl Ether

Phase	c	c	c	c	c
Data Points					
Number	5	18	32	8	63(8)
Temp./K	15.8 - 20.7	22.5 - 61.1	62.8 -155.1	119.1 -148.3	15.8 -148.3
Parameters for	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 21.0	21.0 - 62.0	62.0 -116.0	116.0 -156.92	0 -156.92
a_i		-10.955	3.065	68.815	
b_i x 10		10.9659	8.3250	-0.2937	
c_i x 10^3		2.1706	-0.2522	-0.0511	
d_i x 10^5	287.63	-5.876	-0.9804	1.0391	
e_i x 10^7	-727.6				
Deviations					
Average, *d*	0.013	0.000	0.000	-0.018	0.000
R.M.S., $r(\sigma)$	0.054	0.073	0.134	0.63	0.100(0.106)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.04	0.10	0.15	0.20	
$\delta(H-H_0)$	0.2	4.1	9.	12.	
$\delta(S)$	0.018	0.11	0.14	0.16	
$\delta(G-H_0)/T$	0.009	0.043	0.05	0.05	

Phase	l	l	c,m
Data Points			
Number	58(4)	58(4)	6(3)
Temp./K	151.1 -294.4	151.1 -294.4	139.8 -145.0
Parameters for	C_s	C_p	C_s
Temp./K	156.92-300.0	156.92-300.0	140.0 -149.86
a_i	73.76	70.42	4098.4
b_i x 10	8.1622	8.6594	579.24
c_i x 10^3	-2.8924	-3.1345	209.59
d_i x 10^5	0.42417	0.46274	
Deviations			
Average, *d*	0.000	0.000	0.000
R.M.S., $r(\sigma)$	0.059(0.063)	0.063(0.067)	0.427(0.602)
Estimated Uncertainty in Tabulated Values			
$\delta(C)$	0.20	0.20	0.6
$\delta(H-H_0)$	40.		
$\delta(S)$	0.22		
$\delta(G-H_0)/T$	0.06		

TABLE 69. Thermodynamic Functions of Diethyl Ether

$C_4H_{10}O$ $M = 74.122$

T/K	$(G\text{-}H_0)/T$	$(H\text{-}H_0)/T$	$H\text{-}H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}		J K^{-1} mol^{-1}	
			Crystal			
0	0.000	0.000	0.00	0.00	0.000	0.000
10	-0.203	0.574	5.74	0.78	2.149	2.149
15	-0.625	1.690	25.35	2.31	6.024	6.024
20	-1.335	3.424	68.49	4.76	11.369	11.369
25	-2.325	5.568	139.2	7.89	16.898	16.898
30	-3.545	7.909	237.3	11.45	22.31	22.31
35	-4.946	10.344	362.0	15.29	27.57	27.57
40	-6.489	12.81	512.6	19.30	32.62	32.62
45	-8.141	15.29	687.8	23.43	37.43	37.43
50	-9.878	17.73	886.4	27.61	41.96	41.96
60	-13.532	22.45	1347.3	35.99	49.96	49.96
70	-17.330	26.88	1881.3	44.21	56.74	56.74
80	-21.191	31.01	2480.6	52.20	63.03	63.03
90	-25.070	34.89	3140.2	59.96	68.80	68.80
100	-28.937	38.55	3854.6	67.48	73.99	73.99
110	-32.773	41.98	4617.8	74.75	78.54	78.54
120	-36.566	45.19	5423.2	81.76	82.51	82.51
130	-40.304	48.23	6270.0	88.53	86.96	86.96
140	-43.986	51.18	7165.2	95.17	92.21	92.21
150	-47.617	54.11	8117.1	101.73	98.33	98.33
156.92	-50.104	56.17	8813.8	106.27	103.10	103.10
			Liquid			
156.92	-50.104	101.97	16001.8	152.08	147.01	147.00
160	-52.094	102.85	16456.	154.94	147.68	147.68
170	-58.411	105.55	17943.	163.96	149.77	149.78
180	-64.516	108.06	19450.	172.57	151.70	151.72
190	-70.42	110.40	20977.	180.83	153.52	153.53
200	-76.14	112.6	22521.	188.74	155.24	155.25
210	-81.69	114.7	24081.	196.36	156.89	156.89
220	-87.07	116.6	25658.	203.70	158.50	158.49
230	-92.29	118.5	27251.	210.78	160.09	160.07
240	-97.37	120.3	28860.	217.62	161.69	161.67
250	-102.31	121.9	30486.	224.26	163.32	163.30
260	-107.13	123.6	32128.	230.69	165.00	165.00
270	-111.82	125.1	33787.	236.95	166.77	166.80
280	-116.39	126.7	35465.	243.05	168.7	168.7
290	-120.86	128.1	37162.	249.01	170.7	170.8
298.15	-124.44	129.3	38563.	253.76	172.4	172.6
300	-125.22	129.6	38882.	254.83	172.8	173.0
310	-129.5	131.1	40651.	260.6	180.0	180.4
320	-133.6	132.8	42493.	266.4	186.7	187.3
330	-137.8	134.5	44401.	272.3	193.1	193.8
340	-141.7	136.4	46374.	278.1	199.	200.
350	-145.7	138.3	$4841\underline{0}.$	284.0	205.	207.
360	-149.6	140.3	$5052\underline{0}.$	289.9	212.	214.
380	-157.1	144.6	$5494\underline{0}.$	302.	226.	229.
400	-164.5	149.	$5969\underline{0}.$	314.	244.	248.
420	-171.8	154.	$6486\underline{0}.$	326.	267.	274.
440	-178.	160.	$7058\underline{0}.$	338.	297.	311.
460	-182.	167.	$7699\underline{0}.$	350.	334.	414.

*Underlined figures are beyond experimental significance.

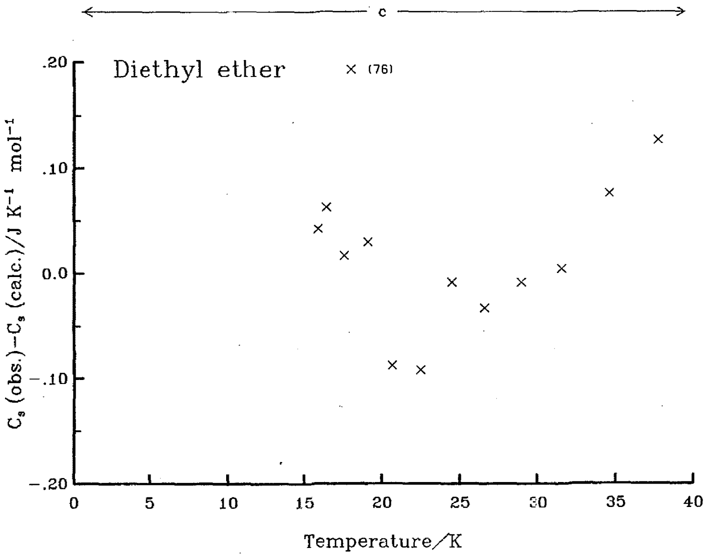

FIG. 61. Deviation plot for diethyl ether, c, 0–40 K.

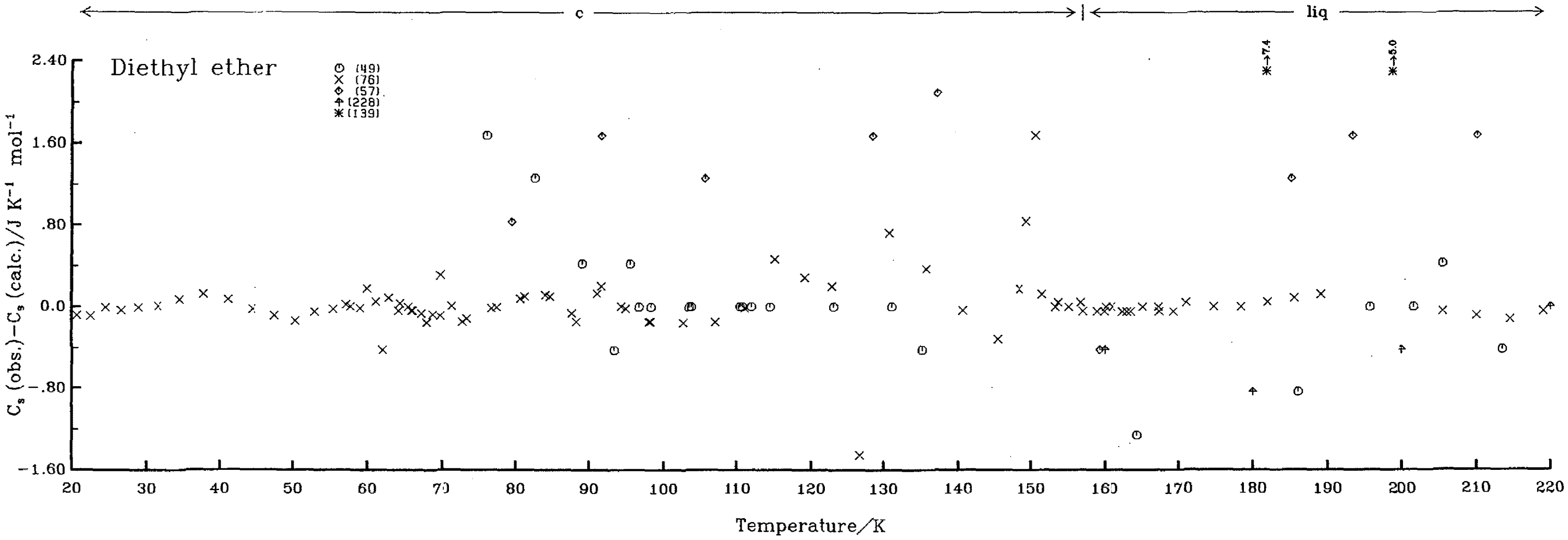

FIG. 62. Deviation plot for diethyl ether, c, l, 20–220 K.

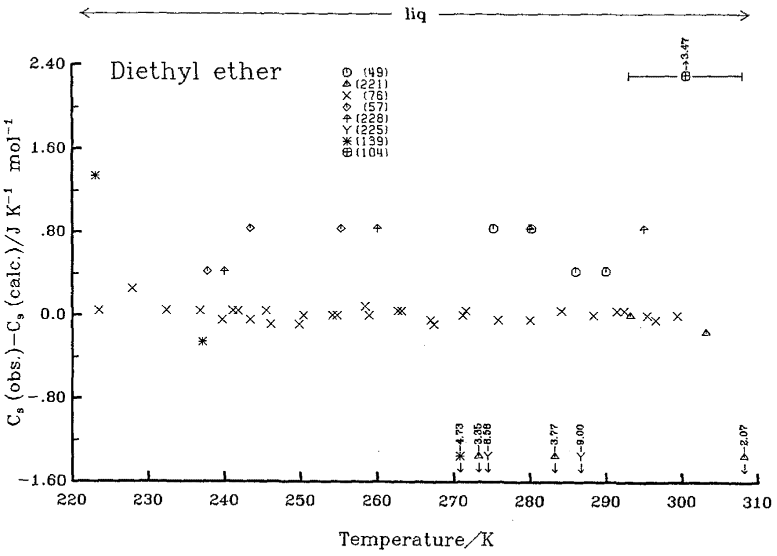

FIG. 63. Deviation plot for diethyl ether, l, 220–310 K.

16. Methyl Propyl Ether(1-Methoxypropane)

Andon and Martin [74] published low temperature heat capacity values for six alkyl ethers, including methyl propyl ether. All values reported in tables 71 and 72 are based on their measurements.

TABLE 70. Sources of Heat Capacity Data for Methyl Propyl Ether

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Andon & Martin	1975	c(16–127),l(138–309)	adiabatic	C	purified by distillation 99.9^c mol %	154	I-68	[74]

TABLE 71. Parameters for Heat Capacity of Methyl Propyl Ether

Phase	c	c	c	c	c
Data Points					
Number	3	13	13	7	36(8)
Temp./K	16.0 - 18.5	20.1 - 59.1	62.9 -113.8	118.3 -127.3	16.0 -127.3
Parameters for	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 20.0	20.0 - 60.0	60.0 -114.0	114.0 -133.97	0 -133.97
a_i		-6.896	-5.423	-688.582	
b_i x 10		7.9039	10.0537	184.8283	
c_i x 10^3		6.022	-2.3704	-151.2922	
d_i x 10^5	300.93	-7.302	0.0330	42.2939	
e_i x 10^7	-833.6				
Deviations					
Average, d	0.018	-0.009	0.004	-0.007	0.000
R.M.S., $r(\sigma)$	0.040	0.048	0.056	0.128	0.058(0.067)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.06	0.10	0.12	0.15	
$\delta(H-H_0)$	0.3	4.0	7.6	8.	
$\delta(S)$	0.026	0.11	0.14	0.14	
$\delta(G-H_0)/T$	0.015	0.05	0.05	0.05	

Phase	1	1	1	1
Data Points				
Number	17	82	18	117(8)
Temp./K	137.7 -154.6	157.8 -249.0	253.2 -308.2	137.7 -308.2
Parameters for	C_s	C_s	C_s	C_s
Temp./K	133.97-155.0	155.0 -250.0	250.0 -320.0	133.97-320.0
a_i	156.07	126.87	20.28	
b_i x 10	-2.5898	1.5910	12.6940	
c_i x 10^3	1.0397	-0.7092	-4.4752	
d_i x 10^5	0.0362	0.2084	0.62047	
Deviations				
Average, d	0.006	-0.012	0.000	0.000
R.M.S., $r(\sigma)$	0.043	0.052	0.050	0.050(0.051)
Estimated Uncertainty in Tabulated Values				
$\delta(C)$	0.2	0.2	0.25	
$\delta(H-H_0)$	22.	32.	37.	
$\delta(S)$	0.19	0.23	0.23	
$\delta(G-H_0)/T$	0.015	0.06	0.06	

TABLE 72. Thermodynamic Functions of Methyl Propyl Ether
$C_4H_{10}O$ $M = 74.122$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.00	0.00
10	-0.209	0.586	5.86	0.79	2.18
15	-0.635	1.695	25.43	2.33	5.94
20	-1.339	3.351	67.02	4.69	10.74
25	-2.293	5.302	132.6	7.60	15.49
30	-3.443	7.40	221.9	10.84	20.26
35	-4.747	9.58	335.2	14.32	25.01
40	-6.170	11.80	471.9	17.97	29.68
45	-7.69	14.04	631.7	21.73	34.21
50	-9.28	16.27	813.7	25.56	38.55
60	-12.64	20.66	1239.7	33.30	46.43
70	-16.14	24.85	1739.5	40.99	53.45
80	-19.72	28.84	2307.2	48.56	60.00
90	-23.34	32.65	2938.1	55.99	66.10
100	-26.97	36.28	3627.6	63.25	71.74
110	-30.59	39.74	4371.4	70.33	76.93
120	-34.19	43.02	5162.8	77.22	81.32
130	-37.76	46.15	5999.6	83.91	86.27
133.97	-39.17	47.38	6347.0	86.54	88.86
		Liquid			
133.97	-39.17	104.63	14017.0	143.80	140.91
140	-43.81	106.20	14867.5	150.00	141.18
150	-51.22	108.55	16282.4	159.77	141.84
160	-58.29	110.66	17705.0	168.95	142.71
170	-65.06	112.57	19136.8	177.63	143.66
180	-71.54	114.32	20578.4	185.87	144.68
190	-77.77	115.95	22030.7	193.72	145.79
200	-83.75	117.47	23495.	201.23	146.99
210	-89.52	118.91	24971.	208.43	148.31
220	-95.08	120.28	26461.	215.36	149.74
230	-100.46	121.59	27966.	222.05	151.30
240	-105.66	122.87	29488.	228.53	153.01
250	-110.70	124.11	31027.	234.81	154.9
260	-115.59	125.3	32586.	240.92	156.9
270	-120.35	126.5	34164.	246.88	158.9
280	-124.97	127.7	35764.	252.70	161.1
290	-129.47	128.9	37386.	258.4	163.4
298.15	-133.06	129.9	38726.	262.9	165.4
300	-133.86	130.1	39032.	264.0	165.9
310	-138.15	131.3	40704.	269.5	168.6
320	-142.34	132.5	42404.	274.9	171.5

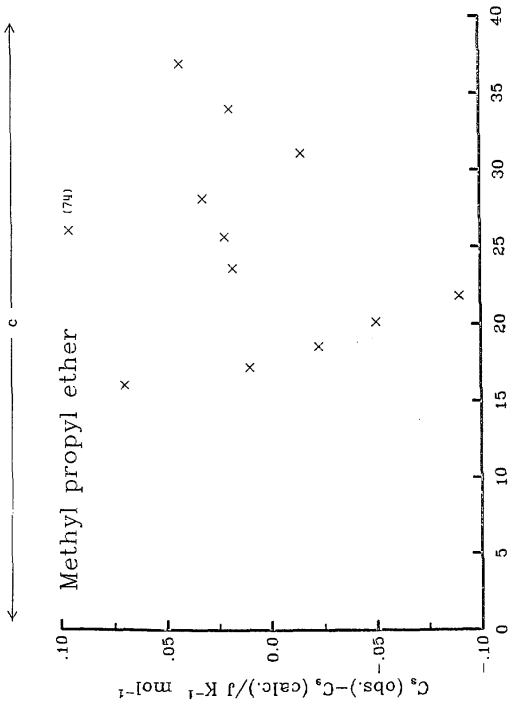

FIG. 64. Deviation plot for methyl propyl ether, c, 0–40 K.

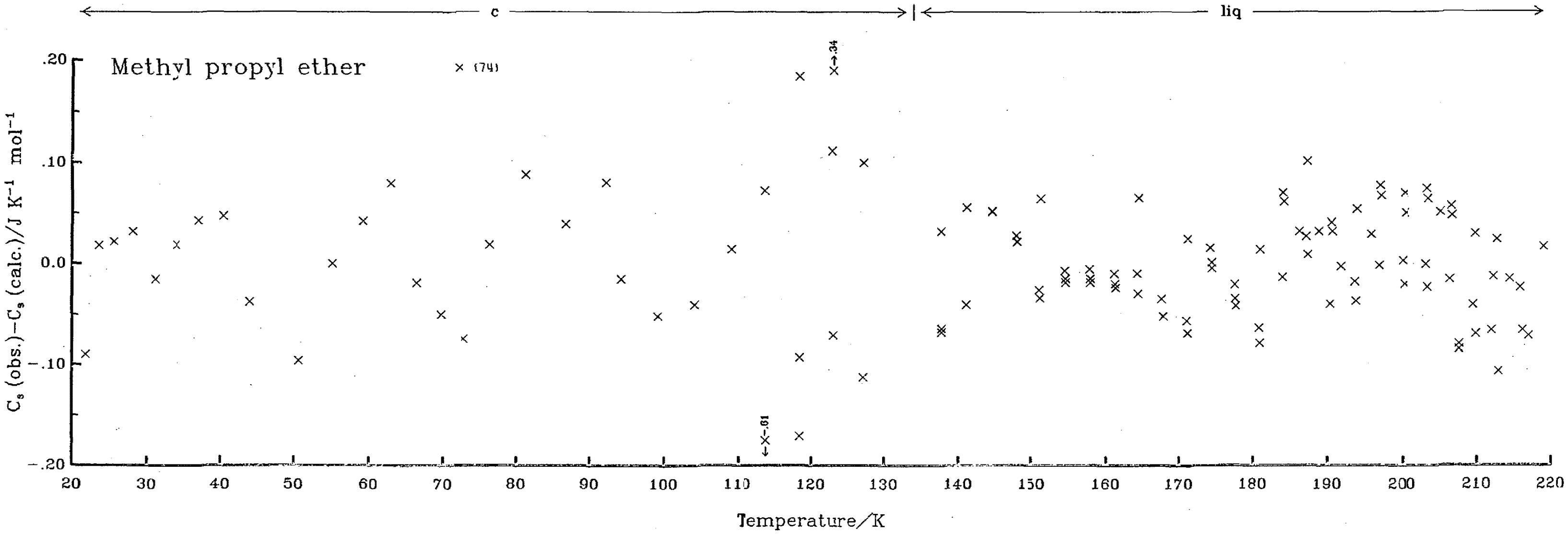

Fig. 65. Deviation plot for methyl propyl ether c, l, 20–220 K.

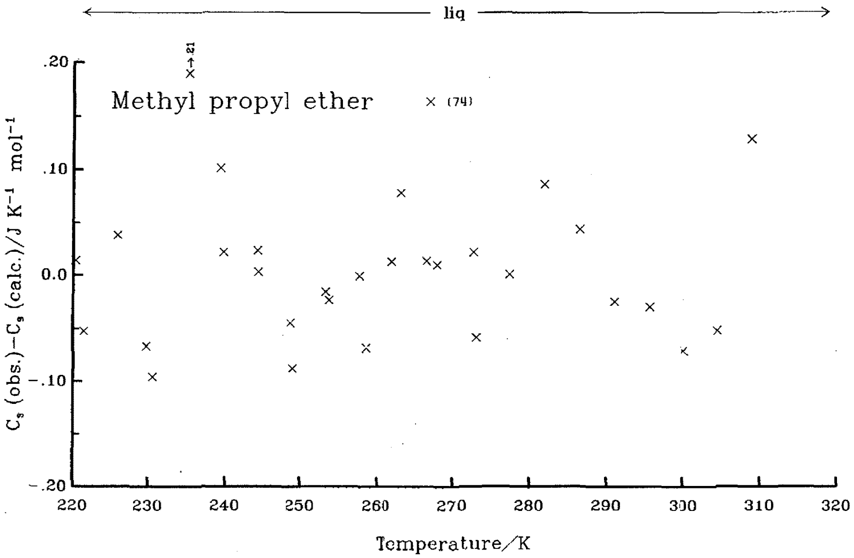

Fig. 66. Deviation plot for methyl propyl ether, l, 220–310 K.

17. Isopropyl Methyl Ether (2-Methoxypropane)

All data for this compound were from Andon and Martin [74]. Initially methyl isopropyl ether crystallized in a metastable form, which changed to the stable crystal on further cooling. Andon and Martin report a triple point of 123.06 K for the metastable crystal, and an enthalpy of fusion of 5100 J mol^{-1}.

TABLE 73. Sources of Heat Capacity Data for Isopropyl Methyl Ether

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Andon & Martin	1975	c(13–121),l(130–311)	adiabatic	C	purified by distillation 99.90^{c} mol %	110	I–68	[74]

TABLE 74. Parameters for Heat Capacity of Isopropyl Methyl Ether

Phase	c	c	c	c	c
Data Points					
Number	5	14	20	9	48(8)
Temp./K	12.7 – 18.3	21.1 – 49.4	52.3 –104.9	108.9 –121.4	12.7 –121.4
Parameters for	C_s	C_s	C_s	C_s	C_s
Temp./K	0 – 19.0	19.0 – 50.0	50.0 –105.0	105.0 –127.93	0 –127.93
a_i		–8.593	–4.972	–591.741	
b_i x 10		9.3061	11.7142	174.4368	
c_i x 10^3		8.0309	–5.9471	–156.2299	
d_i x 10^5	343.25	–13.4996	1.9270	48.1467	
e_i x 10^7	–957.8				
Deviations					
Average, d	0.035	–0.016	0.026	–0.011	0.007
R.M.S., $r(\sigma)$	0.172	0.114	0.130	0.209	0.143(0.155)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.10	0.12	0.2	0.3	
$\delta(H-H_0)$	0.6	3.8	12.	14.	
$\delta(S)$	0.05	0.12	0.19	0.20	
$\delta(G-H_0)/T$	0.015	0.04	0.06	0.06	

Phase	l	l	l	l
Data Points				
Number	16	24	22	62(8)
Temp./K	130.2 –159.2	162.2 –229.9	233.3 –311.4	130.2 –311.4
Parameters for	C_s	C_s	C_s	C_s
Temp./K	127.93–160.0	160.0 –230.0	230.0 –320.0	127.93–320.0
a_i	276.76	163.37	109.32	
b_i x 10	–27.6261	4.6059	2.2221	
c_i x 10^3	17.7306	2.2429	–0.6289	
d_i x 10^5	–3.6986	–0.2428	0.15933	
Deviations				
Average, d	–0.010	0.025	–0.019	0.000
R.M.S., $r(\sigma)$	0.114	0.133	0.156	0.135(0.147)
Estimated Uncertainty in Tabulated Values				
$\delta(C)$	0.25	0.3	0.4	
$\delta(H-H_0)$	34.	40.	51.	
$\delta(S)$	0.28	0.3	0.3	
$\delta(G-H_0)/T$	0.06	0.07	0.07	

TABLE 75. Thermodynamic Functions of Isopropyl Methyl Ether
$C_4H_{10}O$ M = 74.122

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.00	0.00
10	-0.238	0.667	6.67	0.90	2.47
15	-0.723	1.926	28.90	2.65	6.74
20	-1.522	3.800	76.01	5.32	12.15
25	-2.604	6.015	150.4	8.62	17.58
30	-3.909	8.39	251.7	12.30	22.91
35	-5.385	10.83	379.1	16.22	28.03
40	-6.991	13.29	531.4	20.28	32.84
45	-8.70	15.71	706.8	24.40	37.25
50	-10.47	18.06	903.0	28.53	41.14
60	-14.16	22.49	1349.5	36.66	48.07
70	-17.94	26.61	1862.7	44.55	54.50
80	-21.75	30.48	2438.2	52.23	60.55
90	-25.56	34.14	3072.7	59.70	66.33
100	-29.33	37.64	3764.3	66.98	71.97
110	-33.08	41.02	4511.9	74.10	77.51
120	-36.79	44.31	5316.6	81.10	83.77
127.93	-39.71	46.96	6007.7	86.67	91.01
		Liquid			
127.93	-39.71	92.69	11857.7	132.40	136.08
130	-41.20	93.38	12139.3	134.58	136.01
140	-48.24	96.42	13499.1	144.66	136.02
150	-54.98	99.08	14861.3	154.06	136.48
160	-61.45	101.43	16229.4	162.89	137.15
170	-67.67	103.56	17604.7	171.23	137.96
180	-73.64	105.50	18989.	179.14	138.97
190	-79.40	107.29	20385.	186.68	140.17
200	-84.94	108.97	21793.	193.91	141.54
210	-90.30	110.55	23216.	200.85	143.07
220	-95.47	112.07	24655.	207.54	144.7
230	-100.49	113.53	26112.	214.02	146.5
240	-105.35	114.94	27586.	220.29	148.5
250	-110.07	116.3	29081.	226.39	150.5
260	-114.66	117.7	30596.	232.34	152.6
270	-119.13	119.0	32133.	238.1	154.8
280	-123.48	120.3	33693.	243.8	157.2
290	-127.72	121.6	35278.	249.4	159.7
298.15	-131.11	122.7	36588.	253.8	161.9
300	-131.87	123.0	36888.	254.8	162.4
310	-135.92	124.3	38526.	260.2	165.2
320	-139.89	125.6	40193.	265.5	168.2

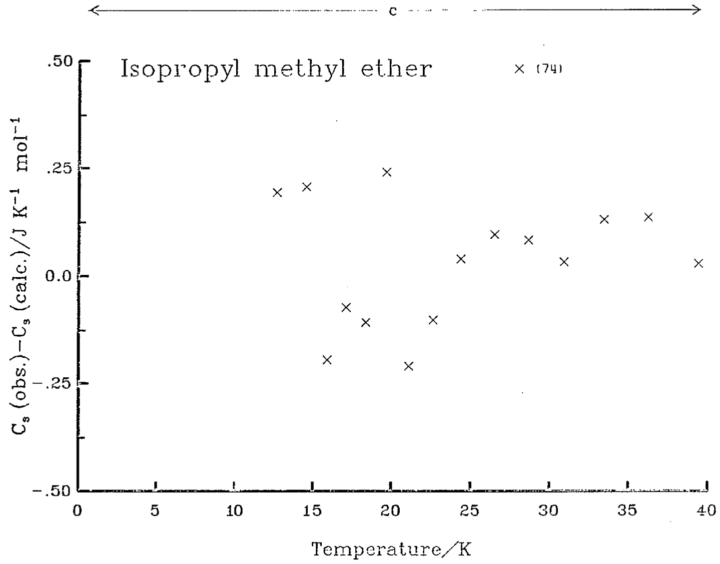

FIG. 67. Deviation plot for isopropyl methyl ether, c, 0–40 K.

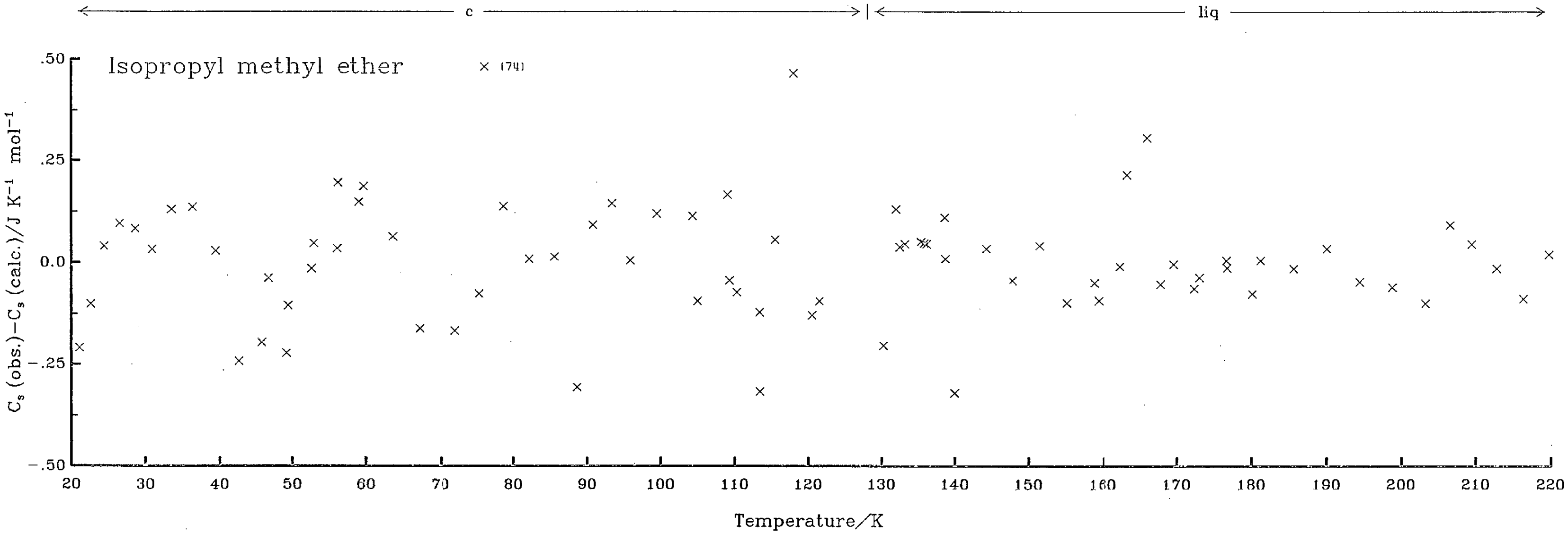

FIG. 68. Deviation plot for isopropyl methyl ether, c,l, 20–220 K.

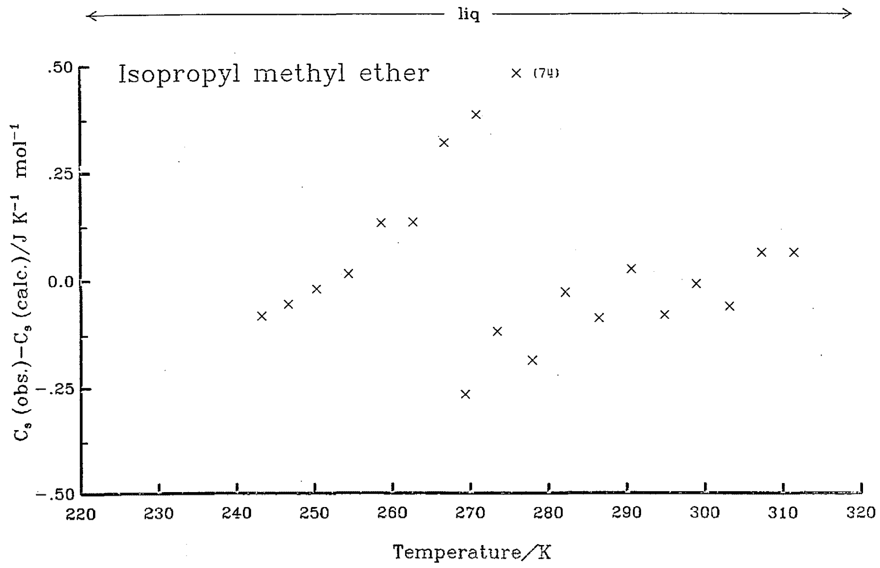

FIG. 69. Deviation plot for isopropyl methyl ether, l, 220–320 K.

18. Dimethoxymethane

McEachern and Kilpatrick [83] are the only source of data for this compound. They carried out a careful analysis of the melting curve and calculated the amount of impurity in their sample from this analysis, as well as from gas chromatography and the heat capacity in the pre-melting region. They concluded that the sample contained both solid insoluble and solid soluble impurities.

TABLE 76. Sources of Heat Capacity Data for Dimethoxymethane

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
McEachern & Kilpatrick	1964	c(16–166),l(171–308)	isoperibol	C	commercial sample, fract. dist. dried over Na, >99.9^g %, 99.94^c mol %, 99.91 mol %(from C_s)	100	corr	[83]

TABLE 77. Parameters for Heat Capacity of Dimethoxymethane

Phase	c	c	c	c	c	l
Data Points						
Number	3	6	23	37	69(8)	31(4)
Temp./K	16.1 - 20.4	23.1 - 41.7	46.0 -123.6	130.3 -166.6	16.1 -166.6	171.1 -307.8
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 23.0	23.0 - 45.0	45.0 -125.0	125.0 -168.03	0 -168.03	168.03-310.0
a_i		-3.119	-23.59	135.74		166.60
b_i x 10		1.8151	16.9208	-20.1222		-3.3310
c_i x 10^3		27.585	-9.2276	19.4502		1.3526
d_i x 10^5	212.65	-27.613	2.0580	-5.3343		-0.09892
e_i x 10^7	-485.4					
Deviations						
Average, d	0.025	-0.009	0.002	-0.002	0.000	0.000
R.M.S., $r(\sigma)$	0.093	0.074	0.096	0.347	0.205(0.218)	0.165(0.177)
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.1	0.12	0.15	0.25		0.3
$\delta(H-H_0)$	0.7	2.7	12.	16.		46.
$\delta(S)$	0.05	0.09	0.18	0.19		0.27
$\delta(G-H_0)/T$	0.019	0.029	0.06	0.06		0.08

TABLE 78. Thermodynamic Functions of Dimethoxymethane $C_3H_8O_2$ $M = 76.095$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.00	0.00
10	-0.153	0.435	4.35	0.59	1.64
15	-0.475	1.303	19.54	1.78	4.72
20	-1.029	2.700	53.99	3.73	9.25
25	-1.821	4.516	112.9	6.34	14.34
30	-2.825	6.60	197.9	9.42	19.70
35	-4.010	8.86	310.1	12.87	25.19
40	-5.35	11.24	449.7	16.59	30.61
45	-6.81	13.68	615.7	20.49	35.75
50	-8.38	16.13	806.5	24.51	40.52
60	-11.75	20.93	1255.8	32.68	49.16
70	-15.32	25.51	1786.0	40.84	56.70
80	-19.01	29.83	2386.6	48.85	63.26
90	-22.76	33.87	3048.3	56.63	68.96
100	-26.53	37.63	3763.2	64.16	73.92
110	-30.28	41.13	4524.7	71.42	78.28
120	-34.00	44.39	5327.2	78.40	82.14
130	-37.68	47.43	6166.4	85.11	85.67
140	-41.30	50.28	7039.5	91.58	88.88
150	-44.86	52.95	7942.0	97.81	91.50
160	-48.36	55.42	8866.5	103.77	93.22
168.03	-51.11	57.24	9617.7	108.35	93.72
		Liquid			
168.03	-51.11	106.82	17949.7	157.94	144.13
170	-52.36	107.26	18233.7	159.62	144.20
180	-58.55	109.32	19678.	167.87	144.70
190	-64.51	111.20	21128.	175.72	145.35
200	-70.26	112.93	22586.	183.19	146.17
210	-75.81	114.53	24052.	190.35	147.14
220	-81.18	116.04	25529.	197.22	148.25
230	-86.37	117.47	27018.	203.83	149.50
240	-91.39	118.83	28519.	210.22	150.9
250	-96.27	120.14	30036.	216.41	152.4
260	-101.01	121.4	31568.	222.42	154.0
270	-105.61	122.7	33117.	228.27	155.8
280	-110.10	123.9	34684.	234.0	157.7
290	-114.46	125.1	36271.	239.5	159.6
298.15	-117.94	126.0	37578.	244.0	161.3
300	-118.72	126.3	37877.	245.0	161.7
310	-122.88	127.4	39505.	250.3	163.9

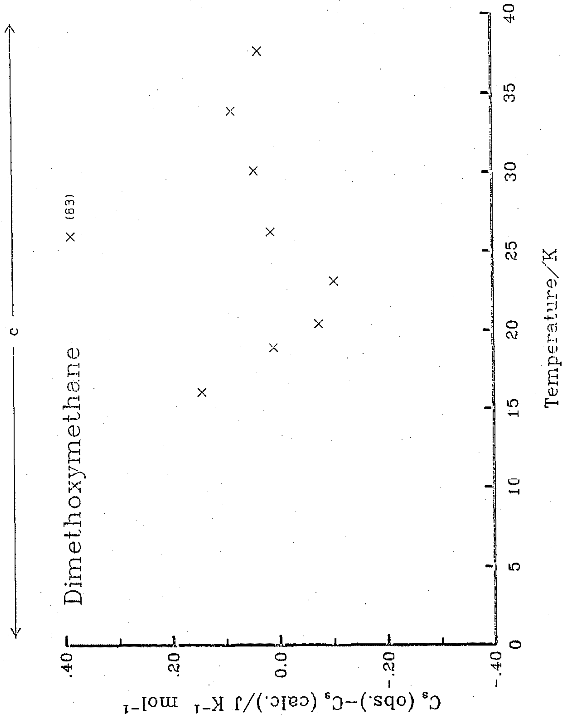

FIG. 70. Deviation plot for dimethoxymethane, c, 0–40 K.

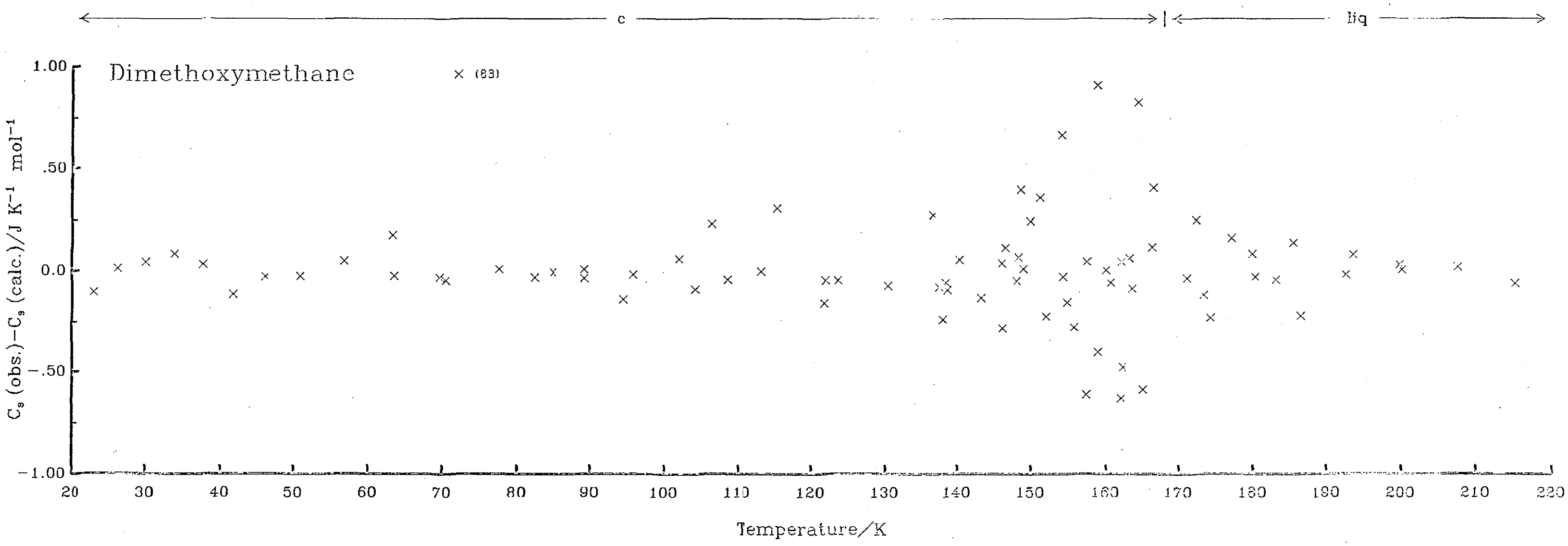

FIG. 71. Deviation plot for dimethoxymethane, c,l, 20–220 K.

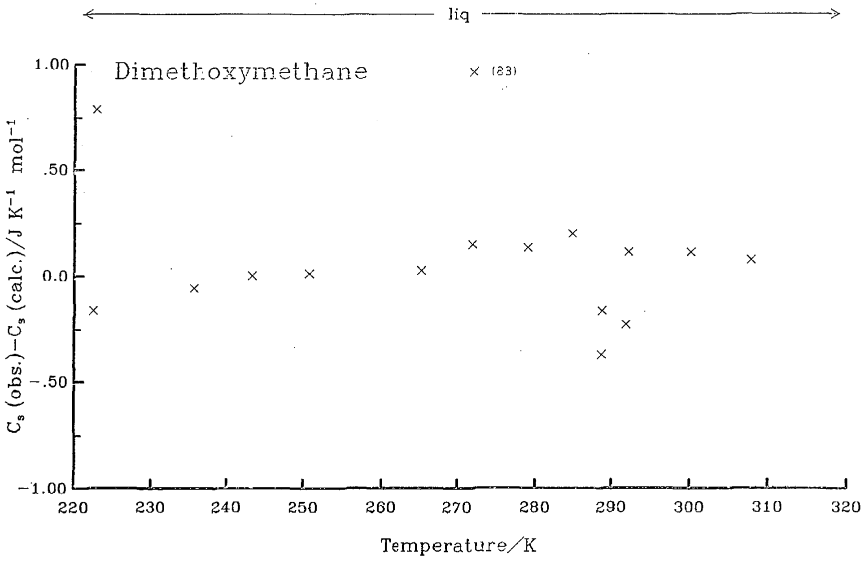

FIG. 72. Deviation plot for dimethoxymethane, l, 220–310 K.

19. Propanone (Acetone)

The heat capacity of propanone has been reported by a large number of investigators, who are listed in table 79. None of these have used modern calorimetric techniques of high accuracy. Figures 73 through 75 therefore show quite a large scatter among different investigators, as well as among data from the same investigator in many cases.

The selected values for the crystals, in table 82, are based primarily on the data of Kelley [46]. He measured the heat capacity down to 17.8 K using liquid hydrogen as the refrigerant in the same apparatus used for methanol, ethanol and 2-propanol. He noticed a small "hump" in the heat capacity curve around 126 K and attributed this to a solid phase transition. When the high temperature form was cooled through this temperature the conversion to the low temperature form was quite slow. The enthalpy of transition was very small. No subsequent observations of this transition have been reported in the literature.

Mueller and Kearns [236] pointed out that it is difficult to remove all traces of water from propanone. This may account, in part, for the poor agreement among melting points listed in table 80. Witschonke [235] obtained a melting point of 178.13 K for acetone of 99.0% purity by extrapolation of the melting curve. He then calculated the value of 178.6 K for the hypothetical pure material. The selected enthalpy of fusion was obtained by correcting the value of Kelley [46] to 178.5 K.

The heat capacity values selected for the liquid are based primarily on those of Kelley [46], Staveley, Tupman and Hart [238] and Low and Moelwyn-Hughes [239]. These data extend only up to 320 K.

Eubank and Smith [155] measured the enthalpy of liquid and gas from 394 to 533 K and at pressures up to 62 bars. The values of enthalpy listed for the saturated liquid from 380 to 500 K in table 82 were derived from their data. However, values of the liquid volume in this range needed to convert enthalpy to heat capacity are not available.

TABLE 79. Sources of Heat Capacity Data for Propanone

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
von Reis	1881	l(290–353)	drop	H	not stated			[105]
Walden	1907	l(290–293)	mixture	C	not stated			[107]
Bramley	1916	l(273–293)	drop	H	not stated			[238]
Trehin	1921	l(297–319)	Dewar flask	C	bisulfite derivative prepared and decomposed,distilled over $CaCl_2$	7	no	[239]
Maass & Waldbauer	1925	c(93–173)	drop	H	Kahlbaum sample, purified with $NaHSO_3$			[109]
Parks & Kelley	1925	c(70–153),l(193–289)	isoperibol	C	National Aniline & Chemical Co. sample, reagent grade	10	no	[53]
Williams & Daniels	1925	l(293–313)	adiabatic	C	Eastman Kodak sample, dried, fract. distilled	2	no	[89]
Parks & Kelley	1928	c(70–153),l(193–289)	isoperibol	C	National Aniline & Chemical Co. sample			[54]
Kelley	1929	c(18–163),l(180–297)	isoperibol	C	Eastman Kodak sample,dried over $CaCl_2$ for 7 days, fract. distilled 3 times	43	no	[46]
Mitsukuri & Hara	1929	l(205–256)	isoperibol	C	not stated			[61]
Trew	1932	l(298)	drop	H	fract. distilled to constant b.p.	1	no	[240]
Trew & Watkins	1933	l(298)	drop	H	not stated	1	no	[158]
Philip	1939	l(303)	not stated	C	commercial sample, distilled	1	no	[112]
Staveley, Tupman & Hart	1955	l(288–324)	adiabatic	C	commercial sample,treated 3–4 days with $KMnO_4$, distilled over K_2CO_3, fract. distilled	10	no	[236]
Low&Moelwyn-Hughes	1962	l(253–308)	adiabatic	C	commercial sample, treated 3–4 days with $KMnO_4$, distilled over K_2CO_3, fract. distilled	7	no	[237]
Eubank & Smith	1962	l(394–509)	flow	H	99.5%			[155]
Deshpande & Bhatgadde	1971	l(295–315)	adiabatic	C	distilled			[117]
Saluja, Peacock & Fuchs	1979	l(298)	Dewar flask	C	commercial sample, 99–99.8%[c]			[241]

TABLE 80. Reported Phase Transition Data for Propanone

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Maass and Waldbauer	1925	c,I$\rightleftharpoons$l	178.55	tp	4761.	c	[109]
Parks & Kelley	1925	c,I$\rightleftharpoons$l	177.6	tp	5690.	c	[53]
Mitsukuri & Hara	1926	c,I$\rightleftharpoons$l	179.37	mp	5440.	t	[59]
Mitsukuri & Aoki	1926	c,I$\rightleftharpoons$l	179.42	mp		t	[60]
Timmermans	1928	c,I$\rightleftharpoons$l	178.35	mp			[242]
Parks & Kelley	1928	c,I$\rightleftharpoons$l	177.6	tp	5690.	c	[54]
Kelley	1929	c,II$\rightleftharpoons$c,I	126.	tp	42.	c	[46]
		c,I$\rightleftharpoons$l	176.65	tp	5715.	c	
Sapgir	1929	c,I$\rightleftharpoons$l	178.35	mp			[150]
McNeight & Smyth	1936	c,I$\rightleftharpoons$l	178.2	mp			[231]
Dreisbach & Martin	1949	c,I$\rightleftharpoons$l	177.96	mp			[151]
Witschonke	1954	c,I$\rightleftharpoons$l	178.6	mp			[235]
Mueller & Kearns	1958	c,I$\rightleftharpoons$l	178.28	mp	5669.	t	[234]
Lesikar	1976	glass	100.	dt			[233]
Angell, Sarc & Sarc	1978	glass	93.	dt			[125]
SELECTED VALUES		c,II$\rightleftharpoons$c,I	126.0±2		42.±10		
		c,I$\rightleftharpoons$l	178.5±0.3		5774.-120		

TABLE 81. Parameters for Heat Capacity of Propanone

Phase	c,II	c,II	c,II	c,II	c,II
Data Points					
Number	4	10	5	3	22(8)
Temp./K	17.8 - 27.0	30.7 - 74.3	78.4 -100.7	107.7 -119.1	17.8 -119.1
Parameters for	c_S	c_S	c_S	c_S	c_S
Temp./K	0 - 30.0	30.0 - 75.0	75.0 -105.0	105.0 -126.0	0 -126.0
a_i		-6.08	-29.61	274.4	
b_i x 10		8.348	21.892	-64.883	
c_i x 10^3		3.57	-20.001	62.548	
d_i x 10^5	206.7	-5.28	7.641	-18.536	
e_i x 10^7	-432.8				
Deviations					
Average, d	0.163	-0.042	0.046	0.013	0.050
R.M.S., $r(\sigma)$	0.54	0.318	0.121	0.021	0.381(0.48)
Estimated Uncertainty in Tabulated Values					
$\delta(C)$	0.6	0.6	0.8	0.8	
$\delta(H-H_0)$	7.4	28.	37.	41.	
$\delta(S)$	0.4	0.7	0.7	0.7	
$\delta(G-H_0)/T$	0.17	0.25	0.3	0.3	

Phase	c,I	l	l	l
Data Points				
Number	5(3)	15	38	53(6)
Temp./K	126.6 -163.3	180.3 -242.8	253.2 -319.5	180.3 -319.5
Parameters for	C_s	C_s	C_s	C_s
Temp./K	126.0 -178.5	178.5 -250.0	250.0 -320.0	178.5 -320.0
a_i	44.5	235.1	242.9	
b_i x 10	3.848	-15.650	-12.278	
c_i x 10^3	-0.871	6.694	3.624	
d_i x 10^5		-0.912	-0.2732	
Deviations				
Average, d	0.000	-0.024	0.033	0.000
R.M.S., $r(\sigma)$	0.013(0.17)	0.495	1.09	0.93(0.98)
Estimated Uncertainty in Tabulated Values				
$\delta(C)$	1.0	1.2	1.5	
$\delta(H-H_0)$	69.	170.	200.	
$\delta(S)$	0.8	1.1	1.1	
$\delta(G-H_0)/T$	0.26	0.3	0.3	

TABLE 82. Thermodynamic Functions of Propanone

C_3H_6O $M = 58.080$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal II			
0	0.00	0.00	0.0	0.00	0.00
10	-0.15	0.43	4.3	0.58	1.63
15	-0.47	1.31	19.6	1.78	4.79
20	-1.03	2.75	55.0	3.78	9.61
25	-1.85	4.69	117.3	6.54	15.39
30	-2.90	6.94	208.2	9.84	20.75
35	-4.14	9.24	323.3	13.38	25.25
40	-5.52	11.51	460.5	17.04	29.64
45	-7.01	13.77	619.5	20.78	33.90
50	-8.57	15.99	799.3	24.56	37.98
60	-11.87	20.29	1217.3	32.16	45.46
70	-15.31	24.35	1704.4	39.66	51.74
80	-18.81	28.09	2247.2	46.90	56.64
90	-22.32	31.51	2836.1	53.83	61.11
100	-25.80	34.70	3469.9	60.50	65.7
110	-29.25	37.74	4152.	67.00	70.8
120	-32.67	40.73	4887.	73.39	76.2
126.0	-34.70	42.49	5353.	77.2	79.1
		Crystal I			
126.0	-34.70	42.82	5395.	77.5	79.2
130	-36.05	43.9	5713.	80.0	79.8
140	-39.41	46.6	6519.	86.0	81.3
150	-42.7	48.9	7339.	91.6	82.6
160	-45.9	51.1	8171.	97.0	83.8
170	-49.1	53.0	9013.	102.1	84.7
178.5	-51.7	54.5	9737.	106.3	85.4
		Liquid			
178.5	-51.7	86.9	15511.	138.6	117.2
180	-52.4	87.1	15686.	139.6	117.1
190	-57.2	88.7	16856.	145.9	116.8
200	-61.8	90.1	18024.	151.9	116.9
210	-66.2	91.4	19195.	157.6	117.2
220	-70.5	92.6	20369.	163.1	117.7
230	-74.6	93.7	21549.	168.3	118.3
240	-78.6	94.7	22735.	173.4	119.0
250	-82.5	95.7	23929.	178.2	119.7
260	-86.3	96.7	25131.	183.0	120.6
270	-90.0	97.6	26343.	187.5	121.8
280	-93.5	98.5	27568.	192.0	123.3
290	-97.0	99.3	28809.	196.3	125.0
298.15	-99.8	100.1	29834.	199.8	126.6
300	-100.4	100.2	30068.	200.6	127.0
310	-103.7	101.1	31349.	204.8	129.
320	-106.9	102.0	32652.	208.9	132.
380			38600.		
400			40300.		
420			42200.		
440			44300.		
460			47000.		
480			50400.		
500			54600.		

*Underlined figures are beyond experimental significance.

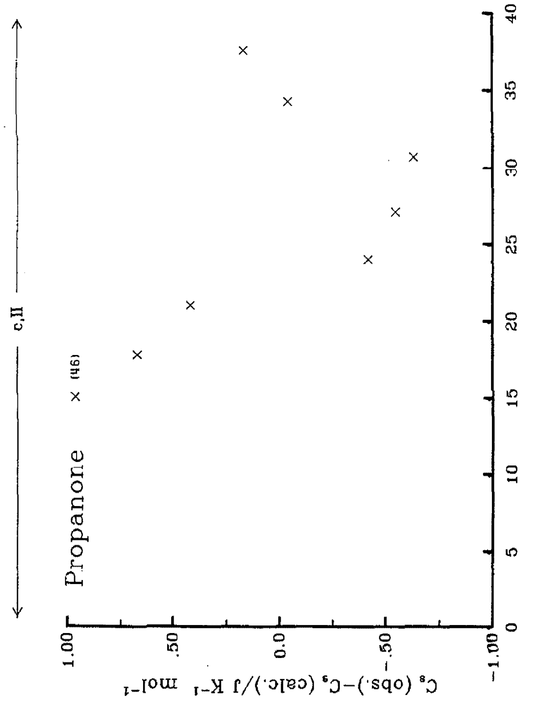

FIG. 73. Deviation plot for propanone, c,II, 0–40 K.

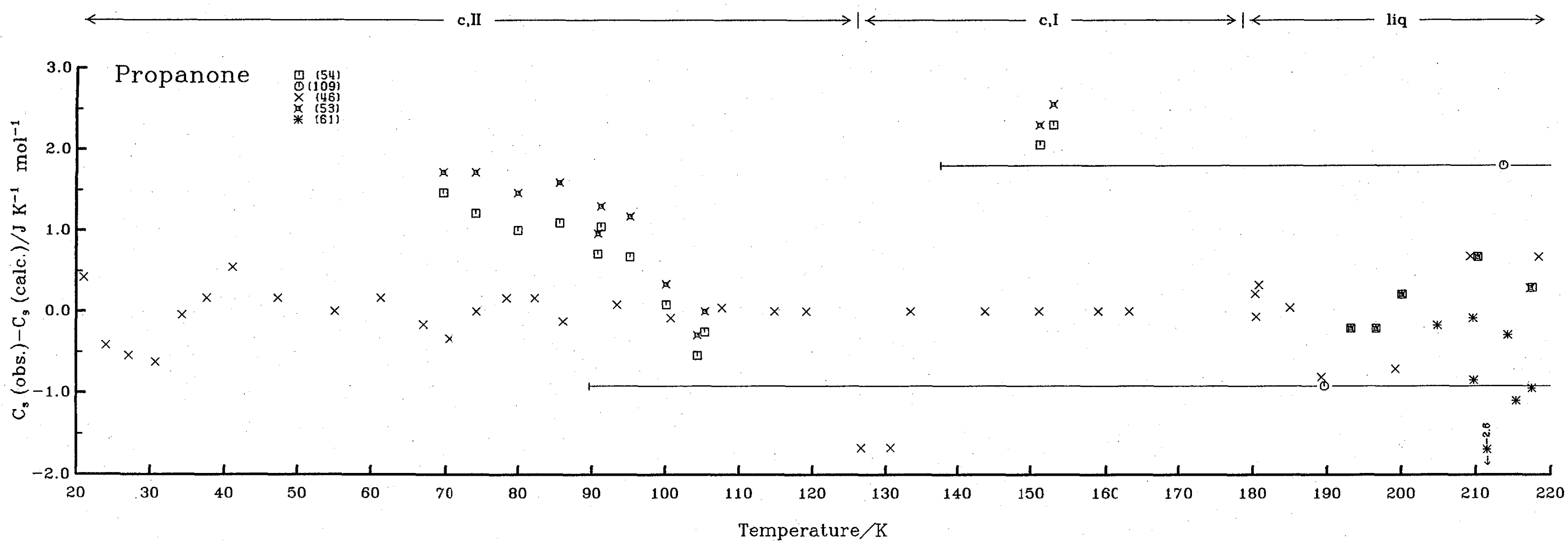

FIG. 74. Deviation plot for propanone, c,II, c,I, l, 20–220 K.

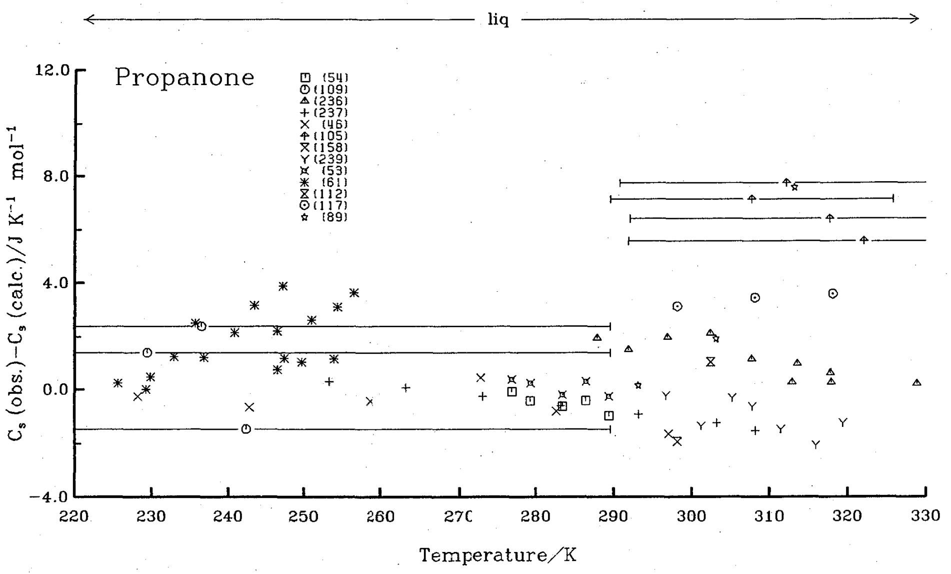

FIG. 75. Deviation plot for propanone, l, 220–230 K.

20. Butanone (Ethyl Methyl Ketone)

The thermodynamic properties up to 340 K in table 86 were derived from the heat capacity data of Sinke and Oetting [64] and Andon, Counsell, and Martin [13] and on the triple point and enthalpy of fusion obtained by Andon, Counsell, and Martin. On the average these two sets of data are in close agreement, although both scatter more in the liquid range than in the crystal. Parameters in equation (32) were calculated for C_p, which were calculated from C_s through the use of auxiliary data from Felsing, Shofner, and Garlock [243] and the TRC tables [244]. The difference between C_p and C_s were mostly within the experimental uncertainties.

Eubank and Smith [155] measured the enthalpy of the liquid and gas phases in the range of 422 to 561 K and up to a pressure of 62 bars. The enthalpy values at 400 K and above in table 86 were calculated from these data. Values for the liquid volumes needed to convert enthalpy to heat capacity values are not available in this range.

TABLE 83. Sources of Heat Capacity Data for Butanone

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Louguinine	1898	l(293–351)	drop	H	not stated			[138]
Kolosovskii & Udovenko	1934	l(297)	differential	C	not stated			[245]
Parks, Kennedy, Gates, Mosley, Moore & Renquist	1956	c(80–170),l(190–300)	isoperibol	C	sample from Shell Development Co., 99.7^c mol%			[55]
Eubank & Smith	1962	l(422–535)	flow	H	Eastman Kodak product			[155]
Sinke & Oetting	1964	c(13–185),l(192–338)	adiabatic	C	commercial sample,dried with $CaSO_4$, distilled, 99.78 mol%	118	corr	[64]
Andon, Counsell & Martin	1968	c(11–180),l(191–320)	adiabatic	C	fract. distilled, dried over	72	corr	[13]
Grollier & Benson	1975	l(298)	flow	C	Fisher Scientific Co. sample reagent grade,purified chromatographically, $>99.9^g$ mol%			[246]
Roux, Perron & Desnoyers	1978	l(277–313)	flow	C	commercial sample, A.C.S.grade $>99.8\%^c$			[247]

TABLE 84. Reported Phase Transition Data for Butanone

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Dreisbach & Martin	1949	$c\rightleftharpoons l$	186.05	mp			[151]
Randall & McKenna	1951	$c\rightleftharpoons l$	186.82	mp			[248]
Parks, Kennedy, Gates, Mosley,Moore & Renquist	1956	$c\rightleftharpoons l$	186.13	tp	8485.	c	[55]
Sinke & Oetting	1964	$c\rightleftharpoons l$	186.51	tp	8439.	c	[64]
Collerson,Counsell,Handley Martin & Sprake	1965	$c\rightleftharpoons l$	186.49	mp			[249]
Andon, Counsell & Martin	1968	$c\rightleftharpoons l$	186.505	tp	8385.	c	[13]
Lesikar	1976	glass	111.4	dt			[233]
SELECTED VALUES		$c\rightleftharpoons l$	186.505 ± 0.01		$8385.\pm10$		

TABLE 85. Parameters for Heat Capacity of Butanone

Phase	c	c	c	c	c	*l*	*l*
Data Points							
Number	15	27	46	7	95(8)	43	52
Temp./K	11.1 – 23.3	25.2 – 79.0	84.2 –159.2	164.3–180.4	11.1 –180.4	190.8 –259.9	265.0 –338.4
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 – 25.0	25.0 – 80.0	80.0 –160.0	160.0–186.505	0 –186.505	186.505–260.0	260.0 –340.0
a_i		–21.38	–5.93	–2291.59		72.44	175.75
b_i x 10		19.951	12.870	430.894		9.8839	–3.3089
c_i x 10^3		–17.386	–6.9224	–261.6021		–4.4105	1.1527
d_i x 10^5	278.1	6.763	1.7319	53.4182		0.6980	–0.07797
e_i x 10^7	–633.8						
Deviations							
Average, *d*	–0.059	–0.038	0.008	0.017	–0.025	–0.013	0.008
R.M.S., $r(\sigma)$	0.293	0.251	0.100	0.172	0.222(0.230)	0.222	0.213
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.2	0.2	0.2	0.25		0.3	0.4
$\delta(H–H_0)$	2.8	11.	20.	21.		34.	47.
$\delta(S)$	0.17	0.29	0.32	0.32		0.34	0.36
$\delta(G–H_0)/T$	0.06	0.11	0.12	0.12		0.12	0.12

Phase	1	1	1	1
Data Points				
Number	95(6)	43	52	95(6)
Temp./K	190.8 –338.4	190.8 –259.9	265.0 –338.4	190.8 –338.4
Parameters for	C_s	C_p	C_p	C_p
Temp./K	186.505–340.0	186.505–260.0	260.0 –340.0	186.505–340.0
a_i		73.27	177.45	
b_i x 10		9.7701	–3.4566	
c_i x 10^3		–4.3591	1.1918	
d_i x 10^5		0.6903	–0.08084	
Deviations				
Average, *d*	0.000	–0.013	0.008	0.000
R.M.S., $r(\sigma)$	0.218(0.222)	0.222	0.209	0.213(0.222)
Estimated Uncertainty in Tabulated Values				
$\delta(C)$		0.3	0.4	

TABLE 86. Thermodynamic Functions of Butanone

C_4H_8O $M = 72.107$

T/K	$(G\text{-}H_0)/T$	$(H\text{-}H_0)/T$	$H\text{-}H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}		J K^{-1} mol^{-1}	
0	0.000	0.000	0.0	0.00	0.00	0.00
10	-0.200	0.568	5.7	0.77	2.15	2.15
15	-0.622	1.705	25.6	2.33	6.18	6.18
20	-1.347	3.53	70.7	4.88	12.11	12.11
25	-2.383	5.91	147.8	8.29	18.70	18.70
30	-3.692	8.55	256.4	12.24	24.65	24.65
35	-5.212	11.24	393.4	16.45	30.05	30.05
40	-6.89	13.90	556.0	20.79	34.93	34.93
45	-8.67	16.49	741.9	25.16	39.36	39.36
50	-10.54	18.98	948.9	29.52	43.36	43.36
60	-14.42	23.64	1418.5	38.06	50.34	50.34
70	-18.39	27.89	1952.3	46.28	56.28	56.28
80	-22.37	31.78	2542.0	54.15	61.58	61.58
90	-26.32	35.36	3182.7	61.69	66.45	66.45
100	-30.22	38.70	3869.6	68.92	70.86	70.86
110	-34.06	41.81	4598.8	75.87	74.93	74.93
120	-37.82	44.73	5367.4	82.55	78.75	78.75
130	-41.51	47.49	6173.5	89.00	82.44	82.44
140	-45.13	50.12	7016.1	95.24	86.09	86.09
150	-48.67	52.64	7895.6	101.31	89.82	89.82
160	-52.15	55.08	8813.1	107.23	93.72	93.72
170	-55.56	57.47	9769.8	113.03	97.74	97.74
180	-58.91	59.86	10775.1	118.77	103.94	103.94
186.505	-61.07	61.51	11471.7	122.57	110.66	110.66
			Liquid			
186.505	-61.07	106.47	19856.7	167.53	148.65	148.64
190	-63.05	107.25	20376.6	170.30	148.89	148.89
200	-68.60	109.34	21868.8	177.95	149.54	149.53
210	-73.99	111.27	23367.2	185.26	150.14	150.13
220	-79.21	113.05	24872.	192.26	150.74	150.73
230	-84.27	114.71	26382.	198.97	151.38	151.37
240	-89.18	116.25	27900.	205.43	152.10	152.10
250	-93.96	117.70	29425.	211.66	152.94	152.94
260	-98.60	119.07	30959.	217.67	153.95	153.94
270	-103.12	120.39	32504.	223.50	155.09	155.09
280	-107.52	121.65	34061.	229.17	156.36	156.36
290	-111.81	122.87	35632.	234.68	157.72	157.72
298.15	-115.23	123.84	36922.	239.06	158.90	158.91
300	-115.99	124.06	37217.	240.05	159.17	159.19
310	-120.08	125.21	38816.	245.29	160.72	160.74
320	-124.07	126.4	40432.	250.42	162.35	162.39
330	-127.97	127.5	42065.	255.44	164.1	164.1
340	-131.79	128.6	43716.	260.37	165.9	165.9
400			$516\underline{00}.$			
420			$541\underline{00}.$			
440			$568\underline{00}.$			
460			$597\underline{00}.$			
480			$632\underline{00}.$			
500			$673\underline{00}.$			
520			$721\underline{00}.$			

*Underlined figures are beyond experimental significance.

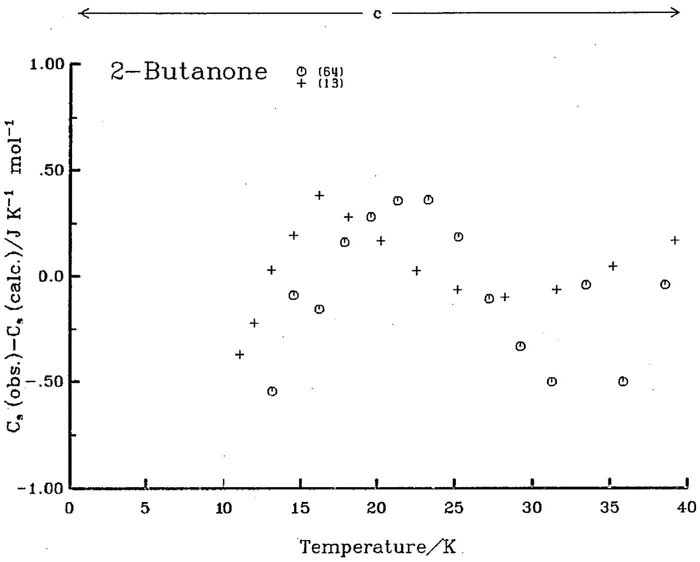

FIG. 76. Deviation plot for butanone, c, 0–40 K.

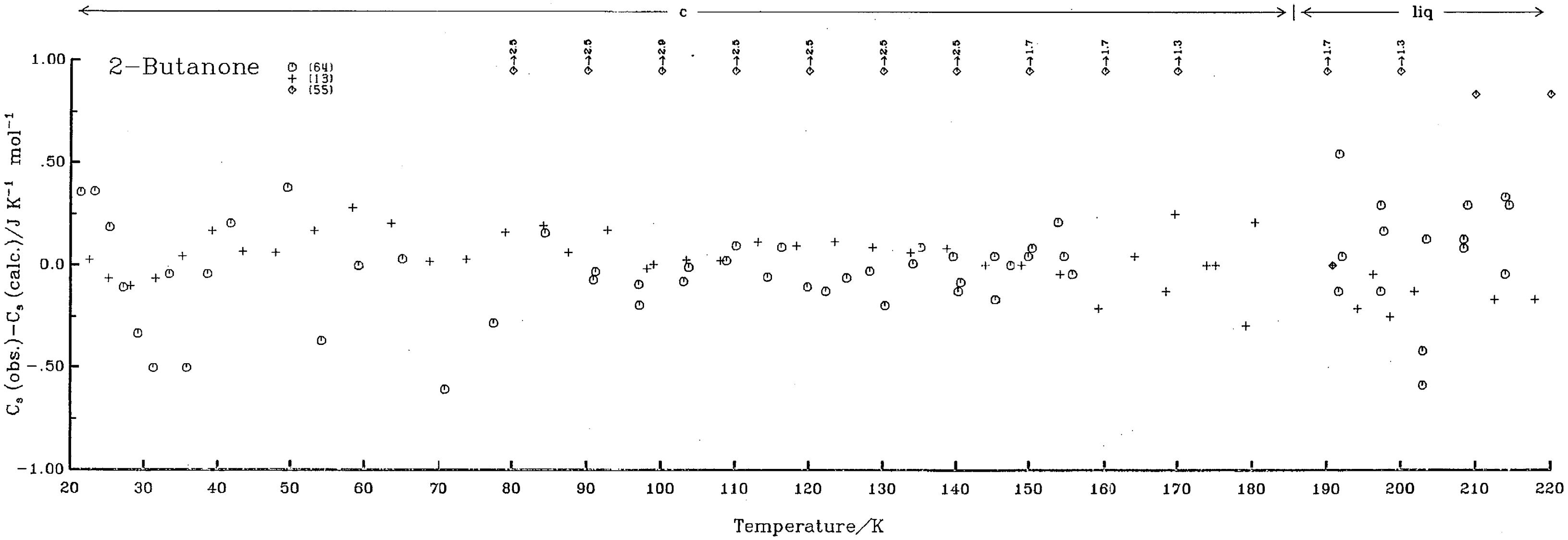

FIG. 77. Deviation plot for butanone, c,l, 20–220 K.

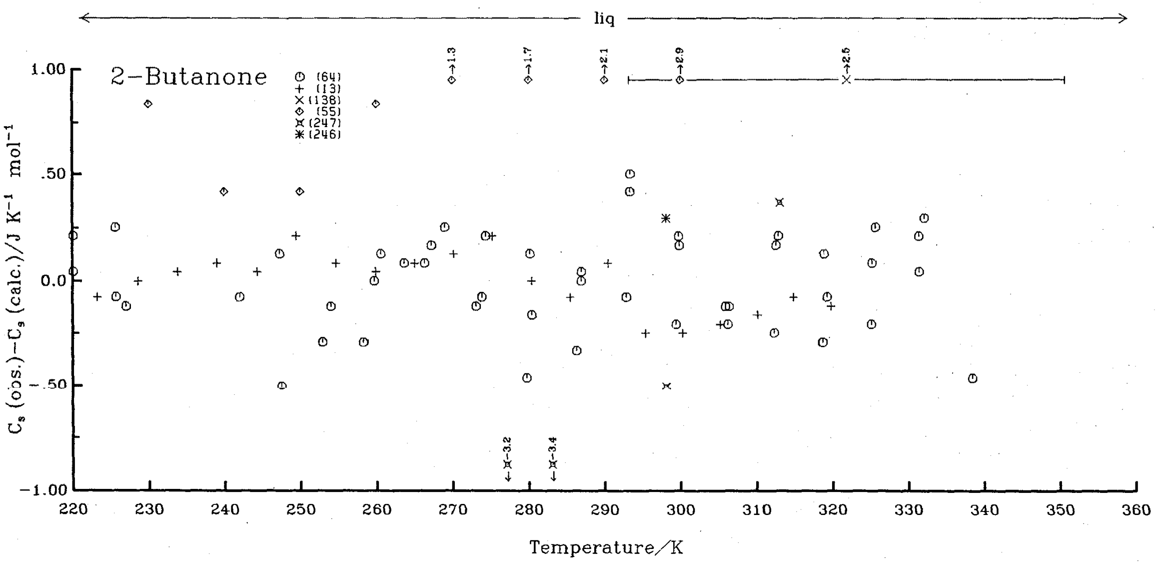

FIG. 78. Deviation plot for butanone, l, 220–340 K.

21. Butanal (Butyraldehyde)

All of the selected properties were taken from those reported by Parks, Kennedy, Gates, Mosley, Moore, and Renquist [55]. They also reported measurements for butanone and five other alcohols and aldehydes containing more than four carbon atoms per molecule. They gave only the graphically smoothed values of heat capacity at multiples of 10 K. These values were used for the least squares fit for butanal.

They obtained 176.2 K for the melting point of their sample, which corresponded to 176.8 K for a pure sample. Timmermans [250] reported 176.1 K. Parks et al. estimated the entropy at 90 K to be 43.93 J K^{-1} mol^{-1} by the method of Kelley, Parks, and Huffman [7]. This is quite close to the value in table 89, which was calculated by the procedure described in section 1.2.b.

The heat capacity values reported by Parks et al. for butanone were around 1.0 to 1.5 J K^{-1} mol^{-1} higher than the more accurate values of Sinke and Oetting [64] and Andon, Counsell, and Martin [13] (see Fig. 77 and 78). This observation, along with the low purity of the sample, gives an appreciable uncertainty to the heat capacity of butanal.

TABLE 87. Sources of Heat Capacity Data for Butanal

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Parks, Kennedy, Gates, Mosley, Moore & Renquist	1956	c(80–150),l(180–300)	isoperibol	C	Eastman Kodak sample, dried with CaCl$_2$, then distilled, 97.7^c mol %	29	no	[55]

TABLE 88. Parameters for Heat Capacity of Butanal

Phase	c	l	l	l
Data Points				
Number	8(2)	7	6	13(6)
Temp./K	80.0 -180.0	180.0 -245.0	250.0-300.0	180.0 -300.0
Parameters for	C_s	C_s	C_s	C_s
Temp./K	80.0 -176.8	176.8 -245.0	245.0-300.0	176.8 -300.0
a_i	17.19	246.02	2041.8	
$b_i \times 10$	4.913	-13.787	-208.660	
$c_i \times 10^3$		6.288	75.6165	
$d_i \times 10^5$		-0.9320	-8.9751	
Deviations				
Average, d	0.000	-0.021	0.025	0.000
R.M.S., $r(\sigma)$	0.121(0.140)	0.050	0.234	0.159(0.205)
Estimated Uncertainty in Tabulated Values				
$\delta(C)$	0.4	0.8	1.0	
$\delta(H-H_0)$	303.	317.	322.	
$\delta(S)$	2.0	2.1	2.1	
$\delta(G-H_0)/T$	0.5	0.5	0.5	

TABLE 89. Thermodynamic Functions of Butanal

C_4H_8O $M = 72.107$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
		Crystal			
80	-16.1	27.9	2234.	44.06	56.49
90	-19.6	31.4	2824.	51.00	61.41
100	-23.1	34.6	3462.	57.72	66.32
110	-26.5	37.7	4150.	64.27	71.23
120	-30.0	40.7	4887.	70.68	76.15
130	-33.3	43.6	5673.	76.97	81.06
140	-36.7	46.5	6508.	83.16	85.97
150	-40.0	49.3	7392.	89.26	90.88
160	-43.2	52.0	8326.	95.28	95.80
170	-46.5	54.8	9308.	101.23	100.71
176.8	-48.7	56.6	10004.	105.25	104.05
		Liquid			
176.8	-48.7	119.4	21108.	168.05	147.31
180	-50.8	119.9	21580.	170.7	147.23
190	-57.3	121.3	23051.	178.7	147.14
200	-63.6	122.6	24523.	186.2	147.24
210	-69.6	123.8	25997.	193.4	147.5
220	-75.4	124.9	27473.	200.3	147.8
230	-81.0	125.9	28953.	206.8	148.2
240	-86.3	126.8	30436.	213.2	148.5
250	-91.5	127.7	31923.	219.2	149.0
260	-96.6	128.5	33421.	225.1	150.9
270	-101.4	129.4	34943.	230.8	153.9
280	-106.1	130.4	36500.	236.5	157.4
290	-110.7	131.4	38092.	242.1	161.1
298.15	-114.4	132.2	39416.	246.6	163.7
300	-115.2	132.4	39719.	247.6	164.2

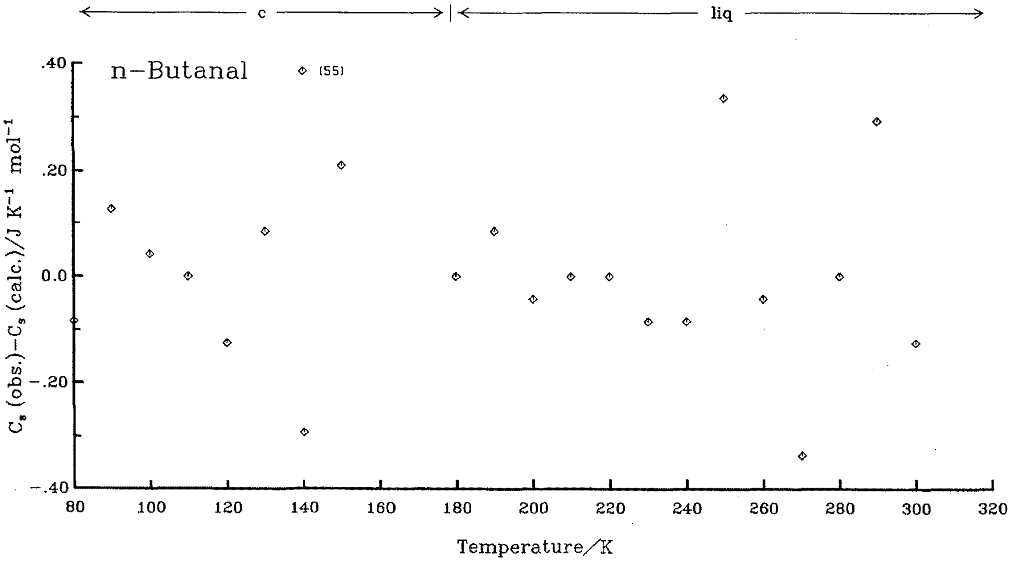

FIG. 79. Deviation plot for butanal, c, l, 80–300 K.

22. Methanoic Acid (Formic Acid)

Although several older sources of data are listed in table 90, the values of Stout and Fisher [80] were the basis of the selected values up through 300 K. They took considerable care in the purification and storage of their sample and used a high precision isoperibol type calorimeter based on the design of Giauque. They also applied a correction for the vaporization of liquid in the calorimeter.

The thermometer used by Stout and Fisher was calibrated in terms of a scale described by Kemp and Giauque [251]. Unfortunately there is no direct link from this scale to the IPTS-68. Therefore, the temperatures obtained by Stout and Fisher were simply multiplied by the ratio 273.15/273.10 to convert from the T_0 they used to 273.15 K.

Most of the points obtained by Gibson, Latimer, and Parks [42] were considerably higher than the ones selected here. Values above 300 K were based on the data of von Reis [105] and Schiff [16] using drop calorimeters. The uncertainties in these results are much greater than in those of Stout and Fisher, however.

Good agreement is seen among values of the triple points and melting points reported by several investigators. There is no systematic difference between the melting point and the triple point for methanoic acid.

It is easy to predict that methanoic acid molecules are extensively linked by hydrogen bonds in the crystal state. Pauling [252] thought it very probable that the molecules existed as hydrogen bonded dimers in the crystal, and because of the symmetry, that these would be randomly distributed between two orientations. If so then the crystal would have an entropy of $(1/2)R \ln 2 = 2.88$ J K^{-1} mol^{-1} at 0 K. For this reason, Stout and Fisher added this constant to the entropy calculated from observed heat capacities. However, Holtzberg, Post, and Fankuchen [253] found that methanoic acid existed as an infinite chain in the crystal. Therefore the $(1/2)R \ln 2$ term was not included in the entropy values in table 93.

NBS Technical Note 270-3 [327] reports an entropy of 128.95 J K^{-1} mol^{-1} and a heat capacity of 81.6 J K^{-1} mol^{-1} for the liquid at 298.15 K.

TABLE 90. Sources of Heat Capacity Data for Methanoic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Favre & Silbermann	1846	l(293–372)	drop	H	not stated			[223]
von Reis	1881	l(313–373)	drop	H	not stated	4	no	[105]
Schiff	1886	l(290–356)	drop	H	not stated	6	no	[16]
Luedeking	1886	l(289–323)	drop	H	Kahlbaum sample, distilled over $CaCl_2$, fract. distilled			[254]
Massol & Guillot	1895	c(268–278) l(276–353)	drop	H	not stated			[255]
Gibson, Latimer & Parks	1920	c(71–275),l(286–292)	isoperibol	C	comercial sample,distilled over B_2O_3 twice, recryst. in vacuo twice			[42]
Radulescu & Jula	1934	l(290)	Dewar flask	C	not stated			[256]
Stout & Fisher	1941	c(15–275),l(275–300)	isoperibol	C	sample prepared from NH_4CHO_2 distilled at low temp., dried with $CaSO_4$, 99.994^c mol%	53	no*	

* Corrected to $T_0 = 273.15$ K.

TABLE 91. Reported Phase Transition Data for Methanoic Acid

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Berthelot	1875	c⇌l	281.8	mp	10140.	c	[257]
Coolidge	1930	c⇌l	281.40	tp	12700.	c	[258]
Timmermans & Hennaut-Roland	1930	c⇌l	281.55	mp			[119]
Lange	1940	c⇌l	281.55	mp	12720.	t	[259]
Stout & Fisher	1941	c⇌l	281.45	tp	12682.	c	[80]
Dreisbach & Martin	1949	c⇌l	281.50	mp			[151]
Johnson & Cole	1951	c⇌l	281.55	mp			[260]
Kuznetsova & Bergman	1956	c⇌l	281.45	mp			[261]
Pinfold & Sebba	1956	c⇌l	281.45	mp			[262]
Lebedeva	1964	c⇌l	281.45	mp			[128]
SELECTED VALUES		c⇌l	281.45±0.1		12682.±40		

TABLE 92. Parameters for Heat Capacity of Methanoic Acid

Phase	c	c	c	c	c	l
Data Points						
Number	3	6	22	13	44(8)	19(3)
Temp./K	15.1 - 19.7	22.3 - 38.4	42.7 -177.8	185.0 -268.7	15.1 -268.7	275.3 -380.0
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 22.0	22.0 - 40.0	40.0 -180.0	180.0 -281.45	0 -281.45	281.45-385.0*
a_i		2.07	-8.85	33.18		70.37
b_i x 10		-3.445	6.8781	0.1471		1.206
c_i x 10^3		28.062	-3.0809	0.5065		-0.0767
d_i x 10^5	89.4	-29.83	0.5665	-0.06965		
e_i x 10^7	-197.5					
Deviations						
Average, d	-0.025	0.013	0.000	-0.008	0.000	0.000
R.M.S., $r(\sigma)$	0.054	0.067	0.054	0.084	0.067(0.071)	0.59(0.65)
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.12	0.15	0.15	0.2		1.2
$\delta(H-H_0)$	0.8	2.8	21.	29.		134.
$\delta(S)$	0.05	0.10	0.25	0.3		0.5
$\delta(G-H_0)/T$	0.019	0.03	0.11	0.11		0.13

*Upper temperature for enthalpy measurement.

TABLE 93. Thermodynamic Functions of Methanoic Acid
CH_2O_2 $M = 46.026$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.000	0.000
10	-0.065	0.184	1.84	0.249	0.697
15	-0.201	0.554	8.32	0.756	2.017
20	-0.438	1.156	23.12	1.594	3.99
25	-0.778	1.953	48.82	2.731	6.34
30	-1.216	2.897	86.92	4.113	8.94
35	-1.741	3.95	138.3	5.69	11.60
40	-2.341	5.07	202.6	7.41	14.10
45	-3.003	6.20	278.9	9.20	16.38
50	-3.714	7.32	366.2	11.04	18.55
60	-5.246	9.53	572.1	14.78	22.55
70	-6.876	11.66	815.9	18.53	26.14
80	-8.565	13.67	1093.7	22.24	29.36
90	-10.287	15.58	1401.9	25.86	32.23
100	-12.022	17.37	1737.2	29.39	34.79
110	-13.757	19.06	2096.7	32.82	37.07
120	-15.485	20.65	2477.8	36.13	39.11
130	-17.197	22.14	2878.2	39.34	40.94
140	-18.890	23.54	3296.1	42.43	42.60
150	-20.560	24.87	3729.8	45.43	44.12
160	-22.205	26.11	4178.2	48.32	45.53
170	-23.823	27.30	4640.2	51.12	46.87
180	-25.416	28.42	5115.	53.83	48.17
190	-26.981	29.49	5604.	56.47	49.48
200	-28.520	30.53	6105.	59.05	50.81
210	-30.034	31.52	6620.	61.56	52.16
220	-31.52	32.49	7148.	64.02	53.51
230	-32.99	33.44	7690.	66.42	54.88
240	-34.43	34.36	8246.	68.79	56.26
250	-35.85	35.26	8815.	71.11	57.63
260	-37.25	36.15	9399.	73.40	59.00
270	-38.63	37.02	9995.	75.65	60.37
280	-39.99	37.88	10606.	77.87	61.72
281.45	-40.19	38.00	10696.	78.19	61.91
		Liquid			
281.45	-40.19	83.70	23558.	123.89	98.24
290	-42.70	84.14	24400.	126.84	98.89
298.15	-45.04	84.55	25209.	129.59	99.51
300	-45.56	84.64	25393.	130.21	99.65
310	-48.35	85.14	26393.	133.49	100.39
320	-51.06	85.63	27401.	136.68	101.1
330	-53.70	86.11	28415.	139.81	101.8
340	-56.28	86.58	29437.	142.9	102.5
350	-58.79	87.0	30465.	145.8	103.2
360	-61.3	87.5	31501.	148.8	103.8
370	-63.7	88.0	32542.	151.6	104.5
380	-66.0	88.4	33590.	154.4	105.1

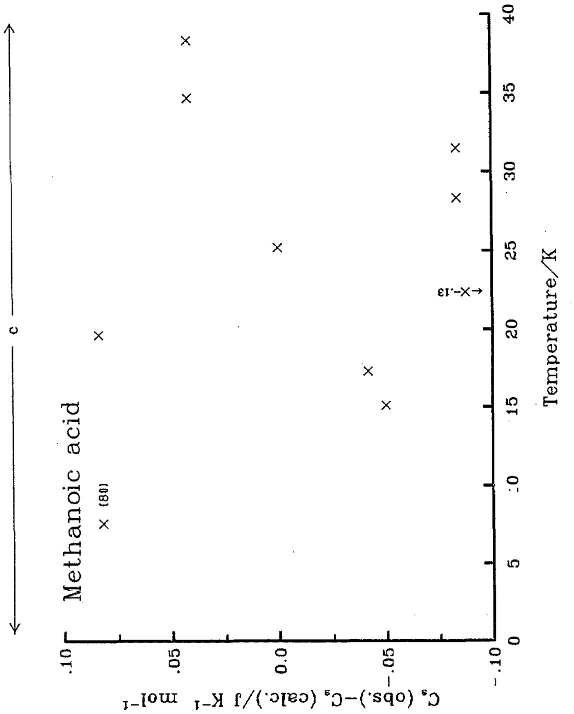

FIG. 80. Deviation plot for methanoic acid, c, 0–40 K.

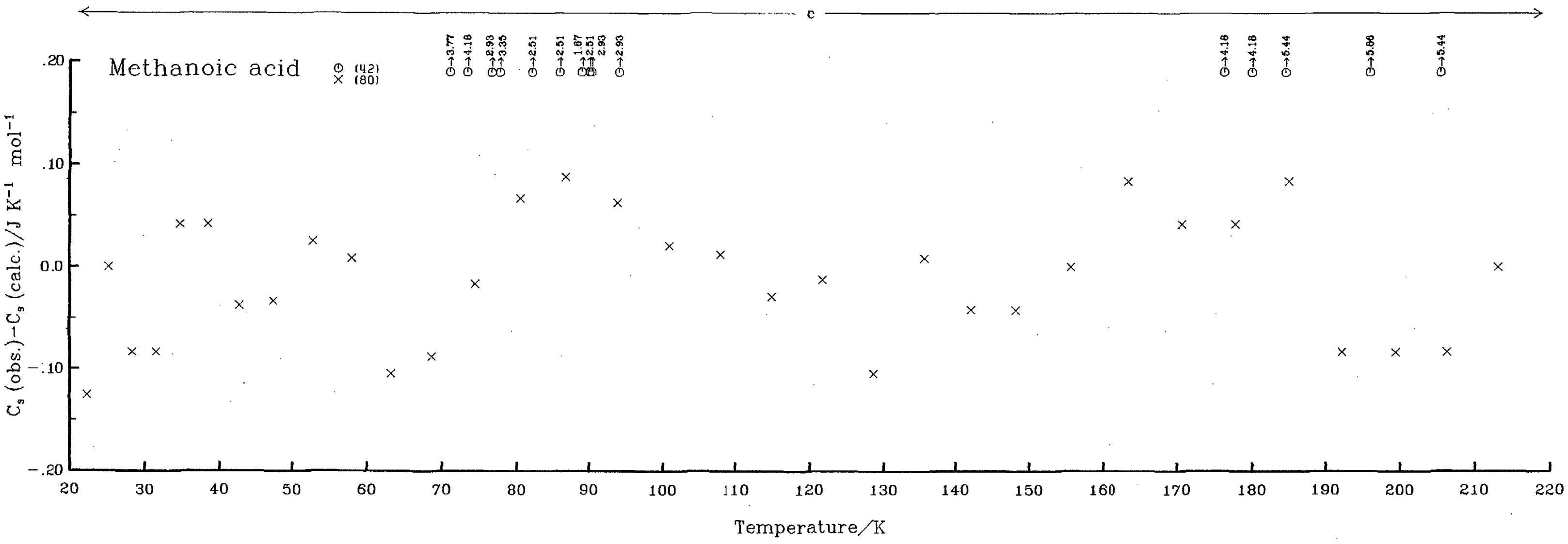

FIG. 81. Deviation plot for methanoic acid, c, 20–220 K.

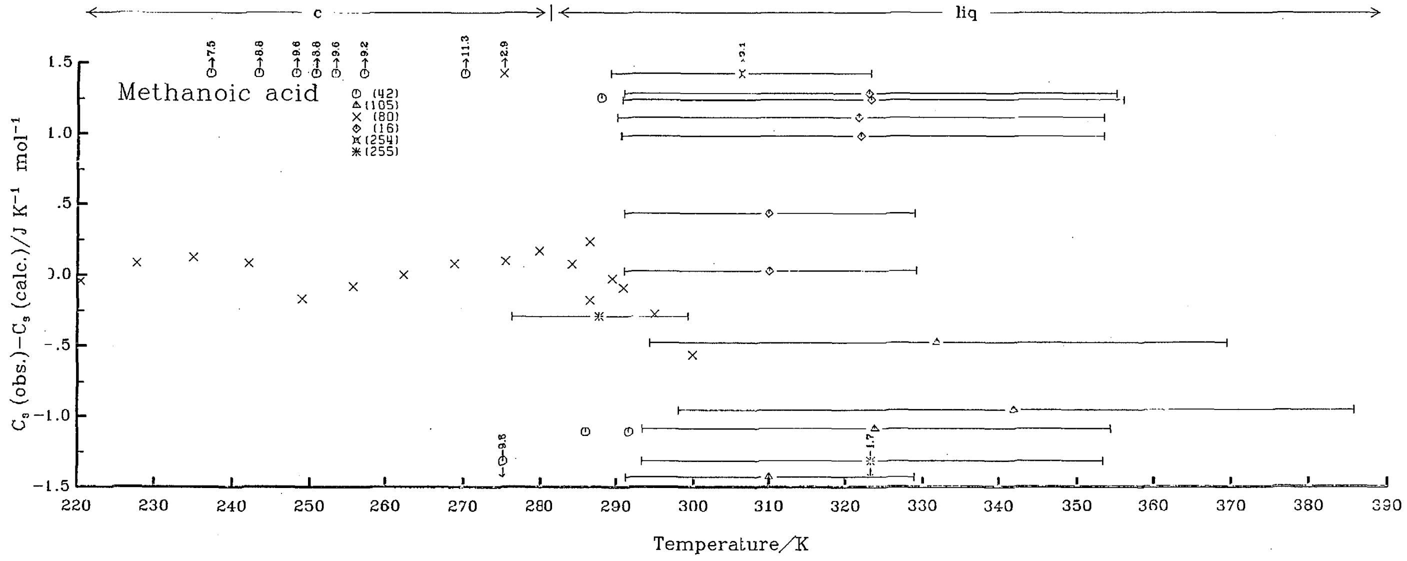

FIG. 82. Deviation plot for methanoic acid, c,l, 220–390 K.

23. Ethanoic Acid (Acetic Acid)

In spite of the widespread use of ethanoic acid for many purposes, no modern calorimetric studies have been made on its thermodynamic properties. This situation represents a major gap in the knowledge of thermodynamic properties of organic compounds. The data in table 97 are based on the specific heat and enthalpy of fusion measurements of Parks and Kelley [53] up to 295 K and on the drop calorimetric measurements of von Reis [105] and Schiff [16] at higher temperatures. Dewar [157] obtained 28.22 J K^{-1} mol^{-1} for $\bar{C}_s$ between 20.4 and 77.4 K from measurements in a drop calorimter using the vaporization of liquid hydrogen.

Careful drying is required to obtain a good melting point of ethanoic acid. A number of careful measurements have been made and reported. The entries in table 95 are a sample. Hess and Haber [263] have reviewed the melting point determinations prior to 1937. Only one measurement has been made at conditions corresponding to a g–l–c triple point, and it is only an approximate one.

Parks and Kelley [53] estimated the entropy at 90 K to be 76.8 J K^{-1} mol^{-1}. Later Parks, Kelley, and Huffman [6] calculated 42.7 J K^{-1} mol^{-1} by means of their empirical procedure. The value in table 97 using the group additivity method explained in section 1.2.b is 39.0 J K^{-1} mol^{-1}.

NBS Technical Note 270–3 [327] reports an entropy of 159.8 J K^{-1} mol^{-1} and a heat capacity of 124.3 J K^{-1} mol^{-1} at 298.15 K.

TABLE 94. Sources of Heat Capacity Data for Ethanoic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Favre & Silbermann	1846	l(290–390)	drop	H	not stated			[223]
Marignac	1876	l(293–323)	drop	H	not stated			[264]
Berthelot	1877	l(296–395)	drop	H	not stated			[265]
von Reis	1880	l(293–334)	drop	H	not stated			[266]
von Reis	1881	l(323–363)	drop	H	not stated	3	no	[105]
Schiff	1886	l(289–384)	drop	H	not stated	6	no	[16]
Luedeking	1886	l(293–323)	drop	H	Kahlbaum sample, distilled over $CaCl_2$, fract. distilled			[254]
Massol & Guillot	1895	c(277–281), l(285–294)	drop	H	not stated			[255]
de Forcrand	1903	c(251–285)	drop	H	not stated			[267]
Baud	1912	l(290)	drop	H	not stated			[268]
Dewar	1913	c(20–80)	drop	H	not stated			[157]
Parks & Kelley	1925	c(87–275),l(293–295)	isoperibol	C	fract. cryst. twice, 99.9mol%	17	no	[53]
Neumann	1932	l(297–353)		C				[269]
Radulescu & Jula	1934	l(289)	Dewar flask	C	not stated			[256]
Swietoslawski & Zielenkiewicz	1958	l(295–402)	drop	H	not stated			[160]

TABLE 95. Reported Phase Transition Data for Ethanoic Acid

Author	Year	Transition	*T*	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
de Forcrand	1903	$c \rightleftharpoons l$	289.77	mp	11000.	c	[267]
Meyer	1910	$c \rightleftharpoons l$	289.69	mp	11540.	c	[270]
Parks & Kelley	1925	$c \rightleftharpoons l$	289.80	tp	11730.	c	[53]
Timmermans & Hennaut-Roland	1930	$c \rightleftharpoons l$	289.70	mp			[119]
Kolthoff & Willman	1934	$c \rightleftharpoons l$	289.77	mp			[271]
Hess & Haber	1937	$c \rightleftharpoons l$	289.78	mp			[263]
Pool, Harwood & Ralston	1945	$c \rightleftharpoons l$	289.78	mp			[272]
Dreisbach & Martin	1949	$c \rightleftharpoons l$	289.80	mp			[151]
Gindin & Kazakova	1952	$c \rightleftharpoons l$	290.00	mp			[273]
Potter & Ritter	1954	$c \rightleftharpoons l$	289.69	mp			[274]
Usanovich, Bilyalov & Krasnomolova	1955	$c \rightleftharpoons l$	289.82	mp			[275]
Lebedeva	1964	$c \rightleftharpoons l$	289.75	mp			[128]
SELECTED VALUES		$c \rightleftharpoons l$	289.80±0.05		11730.±50		

TABLE 96. Parameters for Heat Capacity of Ethanoic Acid

Phase	c	l
Data Points		
Number	15(5)	11(4)
Temp./K	87.4 -274.7	292.6 -384.1*
Parameters for	C_s	C_s
Temp./K	85.0 -289.80	289.80-385.0
a_i	38.15	956.62
b_i x 10	-1.8664	-77.058
c_i x 10^3	5.6208	23.034
d_i x 10^5	-3.12207	-2.2000
e_i x 10^7	0.56891	
Deviations		
Average, d	0.000	0.000
R.M.S., $r(\sigma)$	0.372(0.441)	0.58(0.68)
Estimated Uncertainty in Tabulated Values		
$\delta(C)$	0.4	2.0
$\delta(H-H_0)$	130.	245.
$\delta(S)$	2.1	2.1
$\delta(G-H_0)/T$	0.9	0.9

*Upper temperature for enthalpy measurement.

TABLE 97. Thermodynamic Functions of Ethanoic Acid
$C_2H_4O_2$ M = 60.062

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
90	-15.0	24.0	2160.	39.0	47.85
100	-17.66	26.50	2650.1	44.16	50.16
110	-20.29	28.75	3163.0	49.05	52.41
120	-22.89	30.82	3697.9	53.70	54.54
130	-25.43	32.72	4253.4	58.15	56.54
140	-27.92	34.49	4828.	62.40	58.37
150	-30.35	36.1	5420.	66.49	60.05
160	-32.74	37.7	6029.	70.4	61.58
170	-35.06	39.1	6652.	74.2	62.99
180	-37.34	40.5	7288.	77.8	64.31
190	-39.56	41.8	7938.	81.3	65.60
200	-41.7	43.0	8600.	84.7	66.91
210	-43.9	44.2	9276.	88.0	68.34
220	-45.9	45.3	9968.	91.3	69.97
230	-48.0	46.4	10677.	94.4	71.91
240	-50.0	47.5	11407.	97.5	74.27
250	-51.9	48.7	12164.	100.6	77.2
260	-53.9	49.8	12954.	103.7	80.8
270	-55.8	51.1	13784.	106.8	85.3
280	-57.7	52.4	14664.	110.0	90.9
289.80	-59.5	53.8	15586.	113.3	97.5
		Liquid			
289.80	-59.5	94.3	27318.	153.8	122.5
290	-59.6	94.3	27342.	153.8	122.5
298.15	-62.2	95.1	28341.	157.2	123.6
300	-62.8	95.2	28574.	158.0	123.9
310	-65.9	96.2	29823.	162.1	126.0
320	-69.0	97.2	31096.	166.1	128.5
330	-72.0	98.2	32396.	170.1	131.5
340	-74.9	99.2	33726.	174.1	134.7
350	-77.8	100.3	35090.	178.1	138.
360	-80.7	101.4	36486.	182.0	141.
370	-83.4	102.5	37916.	185.9	144.
380	-86.2	103.6	39375.	189.8	147.

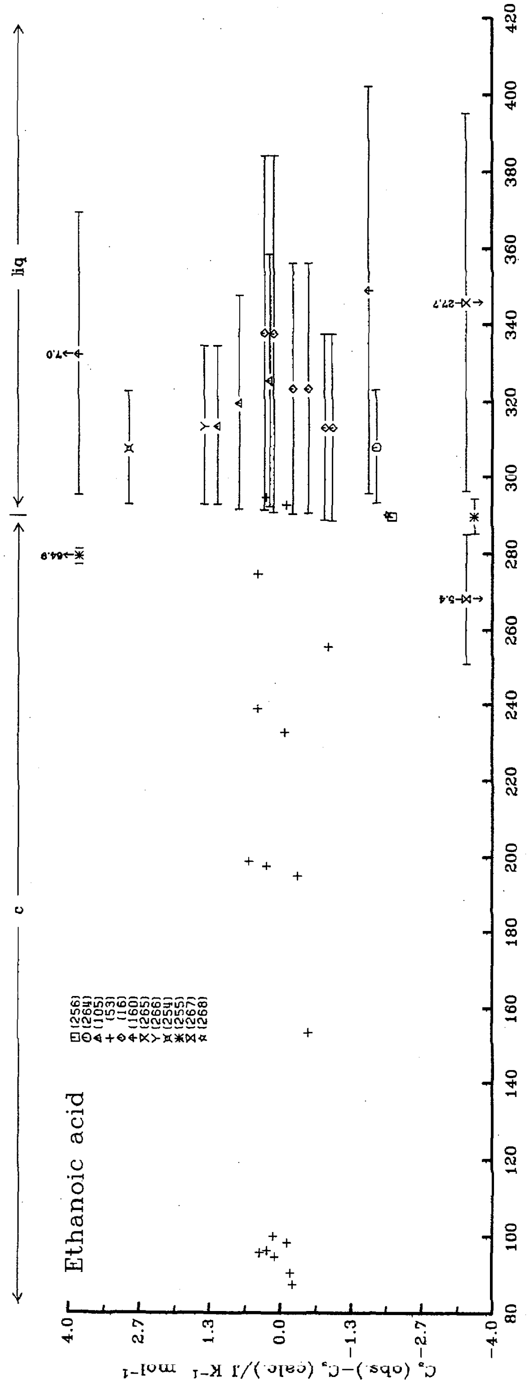

FIG. 83. Deviation plot for ethanoic acid c,l, 30–200 K.

24. Propanoic Acid (Propionic Acid)

Most of the usable heat capacity values were measured in drop calorimeters for the liquid phase. Only two have been published since 1902, and these were not of high accuracy. The values in table 101, based on these data, have a high uncertainty. The entropy and enthalpy values listed there are relative to the liquid at 290 K.

Massol and Faucon [276] reported a value of 226 $J\ K^{-1}\ mol^{-1}$ for $\bar{C}_s$ for the solid in the range of 227 to 253.4 K. This is much larger than would be predicted from the heat capacity of the liquid, or of the solid forms of ethanoic and butanoic acids. It is probable that some melting occurred during the measurement.

Melting points reported in the literature range from 250.2 to 252.9 K. Several of the more accurate ones are listed in table 99. The value of Dreisbach and Martin [151] appears best. Reported enthalpies of fusion show a wide discrepancy and all are much lower than ethanoic and butanoic acids. However, this may be qualitatively correct since some alternation of enthalpies of fusion between odd and even carbon number compounds is probable.

TABLE 98. Sources of Heat Capacity Data for Propanoic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Luedeking	1886	l(285–323)	drop	H	Kahlbaum sample, distilled over $CaCl_2$, fract. distilled			[254]
Schiff	1886	l(288–384)	drop	H	not stated	8	no	[16]
Guillot	1895	l(288–384)	drop	H	not stated	1	no	[277]
Louguinine	1902	l(294–409)	drop	H	prepared from ethyl propanoate	1	no	[278]
Massol & Faucon	1909	c(227–253)	drop	H	not stated			[276]
Radulescu & Jula	1934	l(289)	Dewar flask	C	not stated	1		[256]
Konicek & Wadso	1971	l(295–301)	drop	H	commercial sample, dried with molecular sieve, fract. dist. $>99.8\%^c$	1		[279]

TABLE 99. Reported Phase Transition Data for Propanoic Acid

Author	Year	Transition	*T*	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Massol & Faucon	1909	$c \rightleftharpoons l$	253.4	mp	7240* 5910‡	c c	[276]
Timmermans	1927	$c \rightleftharpoons l$	251.7	mp			[250]
Timmermans	1934	$c \rightleftharpoons l$	252.4	mp			[221]
Timmermans	1935	$c \rightleftharpoons l$			7530	t	[280]
Dreisbach & Martin	1949	$c \rightleftharpoons l$	252.49	mp			[151]
Timmermans	1952	$c \rightleftharpoons l$	252.5	mp			[281]
Gindin & Kazakova	1952	$c \rightleftharpoons l$	251.5	mp			[273]

* By direct calorimetry.

‡ By difference between heats of solution of crystal and liquid.

TABLE 100. Parameters for Heat Capacity of Propanoic Acid

Phase	1
Data Points	
Number	12(3)
Temp./K	288.0* - 409.0‡
Parameters for	C_s
Temp./K	290.0 - 400.0
a_i	569.2
$b_i \times 10$	-28.462
$c_i \times 10^3$	4.861
Deviations	
Average, d	0.000
R.M.S., $r(\sigma)$	1.91(1.65)
Estimated Uncertainty in Tabulated Values	
$\delta(C)$	2.0

*Lower temperature for enthalpy measurement.
‡Upper temperature for enthalpy measurement.

TABLE 101. Thermodynamic Functions of Propanoic Acid
$C_3H_6O_2$ M = 72.063

T/K	H-H_{290} J mol^{-1}	S-S_{290} J K^{-1} mol^{-1}	C_s
	Liquid		
290	0.	0.0	153.
298.15	1244.	4.2	152.7
300	1526.	5.2	152.8
320	4610.	15.1	156.2
340	7800.	24.8	163.5
360	11170.	34.4	175.
380	14810.	44.	190.
400	18780.	54.	208.

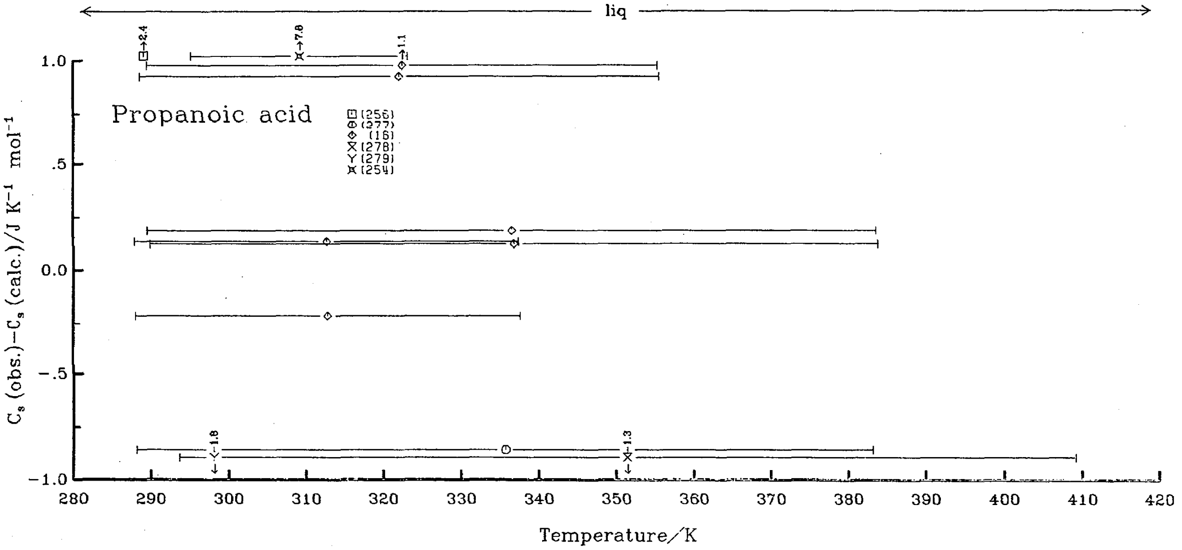

FIG. 84. Deviation plot for propanoic acid, 1, 290–410 K.

25. Butanoic Acid (Butyric Acid)

The thermodynamic properties of the crystal phase are calculated from the data of Parks and Anderson [8]. Their estimate of sample purity (see Table 102) was made by comparison of their observed melting point with a table of melting points of butanoic acid–water mixtures published by Faucon [282]. However, the melting point of pure butanoic acid used by Faucon to prepare the table is two degrees higher than the currently accepted value. If the only impurity in the sample used by Parks and Anderson was water its purity may have been greater than 99.1%.

Parks and Anderson found a maximum in the heat capacity near 221 K. However, they measured only two points for the solid at higher temperatures. The one at 226.2 K was 40 J K^{-1} mol^{-1} lower than the maximum. At the next point 231.5 K the heat capacity had started to increase again. The heat capacity between 231.5 and the melting point, 267.89 K, was calculated by a linear extrapolation of the two observed values. These values are, therefore, quite uncertain.

By a downward extrapolation of their heat capacity values Parks and Anderson calculated the entropy at 90 K to be 82.4 J K^{-1} mol^{-1}. Parks, Kelley, and Huffman [6] later revised this to 53.6 J K^{-1} mol^{-1}. The value in table 105, which was estimated by the group contribution method of section 1.2.b, is 49.8 J K^{-1} mol^{-1}.

The properties off the liquid phase were fit to the data of Parks and Anderson [8] in combination with some earlier data at higher temperatures measured with drop calorimeters. Table 103 summarizes several reported melting points. The value of Dreisbach and Martin was selected.

TABLE 102. Sources of Heat Capacity Data for Butanoic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Favre & Silbermann	1846	l(290–430)	drop	H	not stated			[223]
von Reis	1881	l(292–448)	drop	H	not stated			[105]
Schiff	1886	l(296–323)	drop	H	not stated	8	no	[16]
Luedeking	1886	l(289–411)	drop	H	Kahlbaum sample, distilled over $CaCl_2$, fract. distilled			[254]
Parks & Anderson	1926	c(89–232),l(275–291)	isoperibol	C	twelve successive fract. crystallizations, 99.1 %	23	no	[8]
Konicek & Wadso	1971	l(295–301)	drop	H	commercial sample, fract. dist. fract. cryst., dried with molecular sieve, dist. red. pressure, >99.8%^{c}			[281]

TABLE 103. Reported Phase Transition Data for Butanoic Acid

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Faucon	1910	$c \rightleftharpoons l$	270.03	mp			[282]
Parks & Anderson	1926	$c \rightleftharpoons l$	267.4	tp	11080.	c	[8]
Timmermans & Hennaut-Roland	1932	$c \rightleftharpoons l$	267.75	mp			[283]
Belcher	1938	$c \rightleftharpoons l$	267.78	mp			[284]
Dreisbach & Martin	1949	$c \rightleftharpoons l$	267.97	mp			[151]
Costello & Bowden	1958	$c \rightleftharpoons l$	267.8	mp			[285]
Lebedeva	1964	$c \rightleftharpoons l$	267.9	mp			[128]
Radwan & Hanna	1976	$c \rightleftharpoons l$	267.60	mp			[286]
SELECTED VALUES		$c \rightleftharpoons l$	267.97±0.05		11080.±50		

TABLE 104. Parameters for Heat Capacity of Butanoic Acid

Phase	c	c	c	c	c	l
Data Points						
Number	7	8	3	18(11)	1(1)	13(3)
Temp./K	89.2 -161.4	186.0 -215.9	221.0 -231.5	89.2 -231.5	231.5	274.8 -410.8*
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	90.0 -170.0	170.0 -220.0	220.0 -231.5		231.5 -267.89	267.89–410.0
a_i	-156.11	22439.08	-13643826.9		-13.2	210.3
b_i x 10	63.912	-4735.214	2331071.63		6.430	-5.793
c_i x 10^3	-72.276	3754.146	-1490578.05			1.5867
d_i x 10^5	38.2035	-1321.3116	422731.750			
e_i x 10^7	-7.3815	174.5950	-44857.2276			
Deviations						
Average, d	0.000	0.002	-0.017	0.000		0.000
R.M.S., $r(\sigma)$	0.071	0.226	0.025	0.151(0.230)		0.172(0.189)
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.25	0.6	1.2		2.0	1.5
$\delta(H-H_0)$	201.	203.	204.		216.	315.
$\delta(S)$	2.0	2.0	2.0		2.0	2.1
$\delta(G-H_0)$	0.8	0.8	0.8		0.8	0.8

*Upper temperature for enthalpy measurement.

TABLE 105. Thermodynamic Functions of Butanoic Acid
$C_4H_8O_2$ $M = 118.089$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
90	-19.6	30.2	2720.	49.8	63.74
100	-22.95	33.82	3381.6	56.77	68.47
110	-26.33	37.16	4088.1	63.50	72.80
120	-29.70	40.31	4837.7	70.02	77.15
130	-33.05	43.32	5632.1	76.37	81.79
140	-36.37	46.25	6474.7	82.61	86.78
150	-39.66	49.12	7368.7	88.78	92.04
160	-42.92	51.97	8315.	94.89	97.28
170	-46.15	54.8	9313.	100.93	102.05
180	-49.36	57.6	10361.	106.9	108.95
190	-52.55	60.5	11501.	113.1	119.3
200	-55.7	63.8	12751.	119.5	130.9
210	-58.9	67.3	14131.	126.2	146.2
215	-60.5	69.2	14888.	129.8	157.1
220	-62.2	71.4	15708.	133.6	171.7
222	-62.8	72.3	16054.	135.1	169.6
224	-63.5	73.1	16378.	136.6	152.6
226	-64.1	73.7	16663.	137.8	133.2
228	-64.8	74.2	16915.	139.0	120.7
230	-65.4	74.6	17155.	140.0	122.3
240	-68.6	77.2	18524.	145.8	141.
260	-75.0	82.6	21475.	157.6	154.
267.97	-77.5	84.8	22723.	162.3	159.
		Liquid			
267.97	-77.5	126.1	33802.	203.7	169.0
270	-78.5	126.5	34146.	205.0	169.6
280	-83.2	128.1	35856.	211.2	172.5
290	-87.7	129.6	37597.	217.3	175.7
298.15	-91.3	130.9	39041.	222.2	178.6
300	-92.1	131.2	39372.	223.3	179.3
310	-96.4	132.9	41184.	229.3	183.2
320	-100.7	134.5	43037.	235.2	187.4
330	-104.8	136.2	44933.	241.0	191.9
340	-108.9	137.9	46877.	246.8	196.8
350	-112.9	139.6	48870.	252.6	201.9
360	-116.9	141.4	50916.	258.3	207.
370	-120.8	143.3	53019.	264.1	213.
380	-124.6	145.2	55181.	269.9	219.
390	-128.4	147.2	57405.	275.6	226.
400	-132.2	149.2	59696.	281.4	232.
410	-135.9	151.4	62055.	287.3	240.

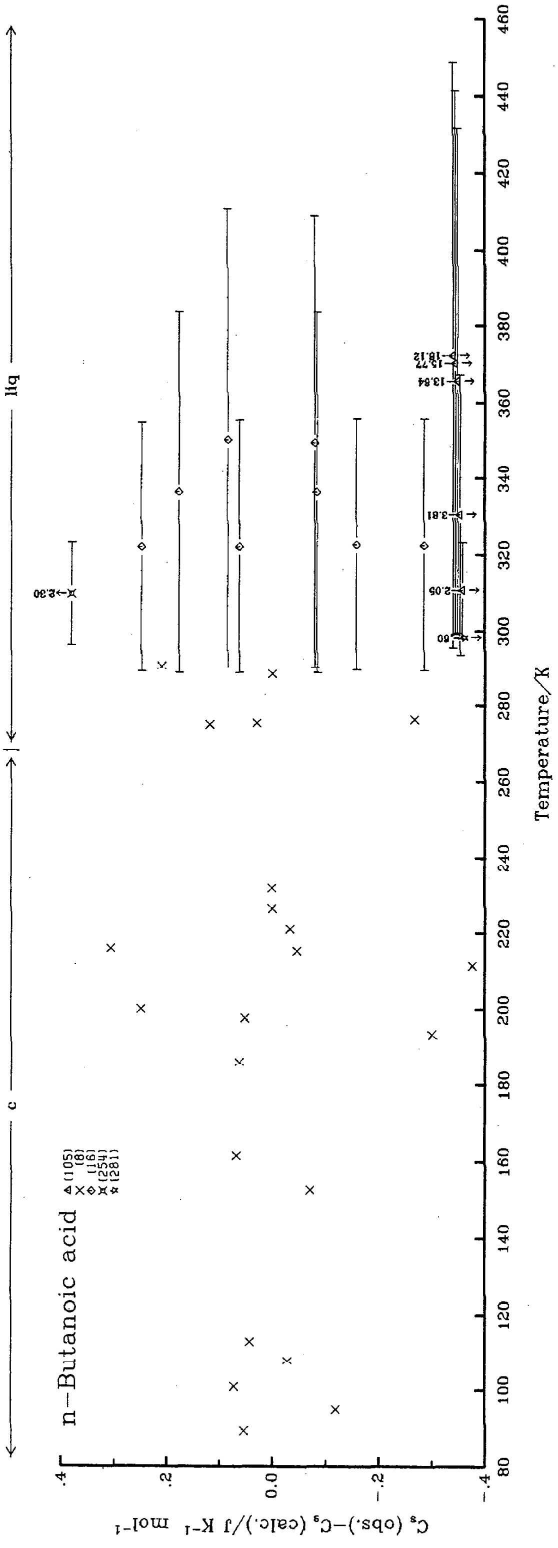

FIG. 85. Deviation plot for butanoic acid, c,l, 90–410 K.

26. Ethanedioic Acid (Oxalic Acid)

Ethanedioic acid can be crystallized in anhydrous and hydrated forms. On heating, the anhydrous form decomposes before it melts. A melting point of 373.7 - 374.2 K has been reported for the dihydrate [287]. A few scattered measurements of heat capacity have been given for both forms.

The only low temperature data are the mean heat capacity values obtained by Nernst, Koref, and Lindeman [37] in 1910 with a copper block drop calorimeter, and a few measurements made by Nernst [35], [36] at about this same time with an electrically heated isoperibol calorimeter. Hess [288] and Satoh and Sogabe [289] have also obtained some mean heat capacity values for the anhydrous acid between upper temperatures up to 313 K and the lower temperature of 273 K using ice calorimeters.

Bradley and Cotson [290] studied the vapor pressure of anhydrous and hydrated ethanedioic acid in the range of about 303 to 323 K. From these data they calculated the enthalpy of dehydration of one mole of the dihydrate to the anhydrous crystal and gaseous water to be 57.3 kJ mol^{-1}. They also found two crystalline forms of the anhydrous acid. Crystal II (their α-form) is orthorhombic and thermodynamically stable at room temperature. Crystal I (their β-form) is monoclinic and metastable at room temperature. Noyes and Webbe [292] and Granovskaya [292] measured the vapor pressure of the anhydrous acid.

Parks and Kelley [53] calculated the entropy of the anhydrous acid by extraolation of the data of Nernst and co-workers. This was later revised by Parks, Kelley, and Huffman to 120 J K^{-1} mol^{-1} at 298.2 K. The enthalpy and entropy of ethanedioic acid in table 108 at 90 K were calculated by equations (4) and (5). This value of S_{90}, in combination with the heat capacity parameters in table 107, give an entropy of 109.8 J K^{-1} mol^{-1} at 298.15 K. None of estimation procedures described here is suitable for the dihydrate.

Since most of the heat capacity values available for both forms are mean values covering large temperature ranges, and all of them are of doubtful accuracy, the values listed in tables 108 and 109 are uncertain. NBS Technical Note 270-3 [327] lists the heat capacity of crystalline oxalic acid as 91. J K^{-1} mol^{-1} at 298.15 K.

TABLE 106. Sources of Heat Capacity Data for Ethanedioic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
			Anhydrous					
Hess	1888	c(273–367)	drop(ice)	H	recrystallized from water, dried by heating to constant wt.			[288]
Nernst	1910	c(98–208)	isoperibol	C	not stated			[35]
Nernst, Koref & Lindemann	1910	c(84–320)	drop	H		3	no	[37]
Nernst	1911	c(84–202)	isoperibol	C	not stated	9	no	[36]
Satoh & Sogabe	1939	c(303–373)	drop(ice)	H	Kahlbaum sample, dried at 90 °C to constant wt.	1	no	[289]
David	1964	c(298–373)	DTA	C	not stated			[293]
			Dihydrate					
Nernst	1910	c(98–208)	isoperibol	C	not stated			[35]
Nernst, Koref & Lindemann	1910	c(83–320)	drop	H		3	no	[37]
Nernst	1911	c(84–198)	isoperibol	C	not stated	7	no	[36]

TABLE 107. Parameters for Heat Capacity of Ethanedioic Acid

	Anhydrous	Dihydrate
Phase	c	c
Data Points		
Number	13(4)	10(4)
Temp./K	84.2 -372.0*	84.2 -319.8*
Parameters for	C_s	C_s
Temp./K	80.0 -370.0	80.0 -320.0
a_i	21.85	20.46
b_i x 10	2.608	6.393
c_i x 10^3	-0.0704	-0.6442
d_i x 10^5	0.0508	0.1381
Deviations		
Average, d	0.000	0.000
R.M.S., $r(\sigma)$	1.12(1.29)	1.94(2.37)
Estimated Uncertainty in Tabulated Values		
$\delta(C)$	1.0	1.5
$\delta(H-H_0)$	420.	
$\delta(S)$	3.4	
$\delta(G-H_0)/T$	1.2	

*Upper temperature for enthalpy measurement.

TABLE 108. Thermodynamic Functions of Ethanedioic Acid, Anhydrous

$C_2H_2O_4$ $M = 90.035$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
			Crystal		
80	-13.6	20.8	1668.	34.5	38.2
90	-16.2	22.9	2060.	39.1	40.3
100	-18.7	24.7	2473.	43.4	42.3
120	-23.5	28.0	3361.	51.5	46.5
140	-28.1	31.0	4335.	59.0	50.8
160	-32.4	33.7	5395.	66.1	55.
170	-34.5	35.0	5958.	69.5	57
180	-36.5	36.4	6544.	72.9	60.
190	-38.5	37.7	7154.	76.2	62.
200	-40.5	38.9	7786.	79.4	64.
210	-42.4	40.2	8443.	82.6	67.
220	-44.3	41.5	9124.	85.8	69.
240	-48.0	44.0	10562.	92.0	74.
260	-51.6	46.6	12104.	98.2	80.
270	-53.4	47.8	12915.	101.3	83.
280	-55.2	49.1	13755.	104.3	85.
290	-56.9	50.4	14623.	107.4	88.
298.15	-58.3	51.5	15353.	109.8	91.
300	-58.7	51.7	15521.	110.4	91.
320	-62.1	54.4	17408.	116.	97.
340	-65.5	57.1	19422.	123.	104.
360	-68.8	59.9	21570.	129.	111.

TABLE 109. Thermodynamic Functions of Ethanedioic Acid, Dihydrate

$C_2H_2O_4 \cdot 2H_2O$ $M = 126.066$

T/K	$H-H_{90}$	$S-S_{90}$	C_s
	J mol^{-1}	J K^{-1} mol^{-1}	
	Crystal		
80	0.	0.0	68.2
90	710.	8.4	73.8
100	1476.	16.4	79.3
120	3172.	31.9	90.3
140	5086.	46.6	101.1
160	7217.	60.8	112.
170	8363.	67.7	117.
180	9563.	74.6	123.
190	10817.	81.4	128.
200	12126.	88.1	134.
210	13489.	94.7	139.
220	14908.	101.3	145.
240	17912.	114.4	156.
260	21145.	127.3	167.
270	22848.	133.8	173.
280	24611.	140.2	179.
290	26434.	146.6	185.
298.15	27965.	151.8	190.
300	28318.	153.	192.
320	32276.	166.	204.

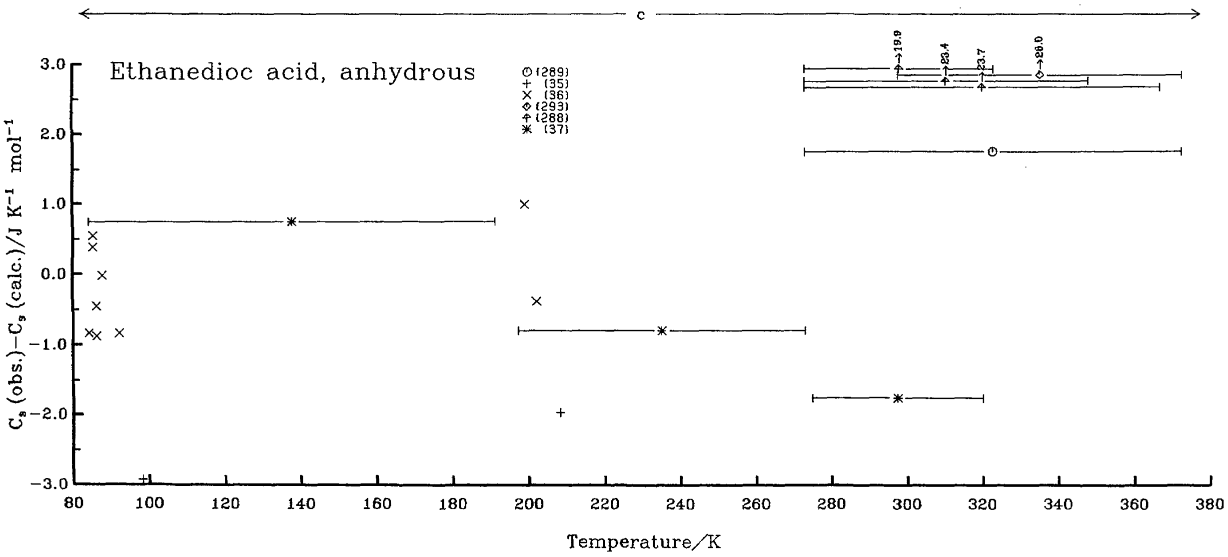

FIG. 86. Deviation plot for ethanedioic acid (oxalic acid), anhydrous, c, 80–380 K.

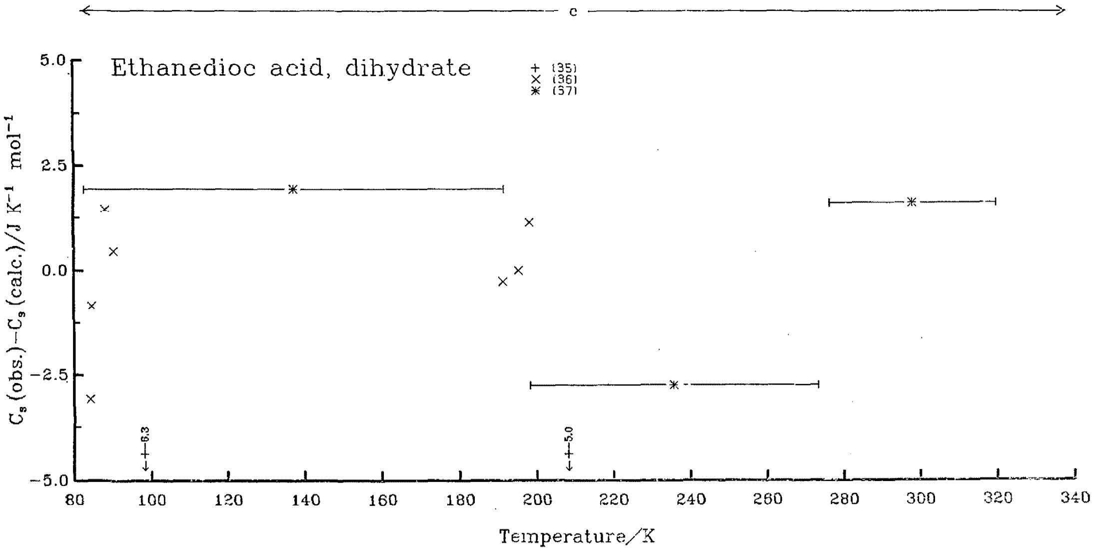

FIG. 87. Deviation plot for ethanedioic acid (oxalic acid), dihydrate, c, 80–320 K.

27. 1,4-Butanedioic Acid (Succinic Acid)

1,4-Butanedioic acid is enantiotropic. Crystal I (identified as the α-form in the prior literature) is triclinic [294] and crystal II (previously identified as the β-form) is monoclinic [295]. The transition temperature is 410 K [296]. Crystal I can be obtained at room temperature by rapid quenching from around 440 K. It then slowly reverts to crystal II during a period of several weeks. Removal of all water from 1,4-butanedioic acid requires special techniques [71]. Some decomposition or formation of the anhydride probably takes place on melting. These phenomena account for the variations reported in the melting point (see Table 111). The sample used by Wilhoit and Shiao [297] was carefully purified by a series of recrystallizations from several solvents followed by sublimation under high vacuum. Usol'tseva, Kobenina and Pobedinskaya [298] measured the enthalpy of fusion with a DTA type calorimeter. It included the effect of formation of some anhydride.

Two low temperature studies have been made on the heat capacity. The data in Table 113 up to 325 K are based entirely on the modern work of Vanderzee and Westrum [71]. The agreement with the values of Parks and Huffman [51] is within the expected uncertainty of the older measurements, except in the vicinity of 272 K. The "hump" observed by Parks and Huffman in this region was undoubtedly caused by the melting of ice present as an impurity in their sample.

The parameters for heat capacity above 325 K were obtained by a least squares fit to the mean heat capacity data identified in Table 110. The procedure used forced continuity with the low temperature data at 323 K. No distinction was made between crystals I and II in these calculations.

TABLE 110. Sources of Heat Capacity Data for 1,4-Butanedioic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Kopp	1865	c(292–324)	drop	H	not stated	1	no	[299]
de Heen	1883	c(323–423)	drop	H	not stated	2	no	[300]
Hess	1888	c(273–423)	drop	H	recrystallized from water dried by heating to constant wt.	3	no	[288]
Parks & Huffman	1930	c(93–290)	isoperibol	C	high grade commercial sample, recrystallized twice from water			[51]
Satoh & Sogabe	1939	c(273–372)	drop	H	Kahlbaum sample	1	no	[289]
Vanderzee & Westrum	1970	c(5–323)	adiabatic	C	reagent grade sample, recrystallized 4 times from water, crystals finely ground and dried 25 hrs. at 102–118° C, then formed to pellets and dried 48–72 hrs. in a dessicator	89	I–68	[71]

TABLE 111. Reported Phase Transition Data for 1,4-Butanedioic Acid

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Phelps & Hubbard	1907	c,I⇌l	455.45	mp			[301]
Viseur	1926	c,I⇌l	455.85	mp			[302]
Dupre la Tour	1932	c,II⇌c,I	410				[296]
		c,I⇌l	460	mp			
McNeight & Smyth	1936	c,I⇌l	455.95	mp			[231]
Wilhoit & Shiao	1964	c,I⇌l	460.66	mp			[297]
Weintraub, Vitcha & Limon	1965	c,I⇌l	457.15–458.15	mp			[303]
Usol'tseva, Kobenina & Pobedinskaya	1973	c,I⇌l			53100.	c	[298]
SELECTED VALUES		c,II⇌c,I	410.±2				
		c,I⇌l	461.0±0.3				

TABLE 112. Parameters for Heat Capacity of 1,4–Butanedioic Acid

Phase	c	c	c	c	c	c
Data Points						
Number	13	13	14	49	89(11)	7(1)
Temp./K	5.2 – 13.8	14.9 – 44.7	48.7 –100.7	107.0 –322.9	5.2 –322.9	323.0* – 423.2‡
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 – 14.0	14.0 – 45.0	45.0 –105.0	105.0 –325.0	0 –325.0	325.0 – 420.0
a_i		4.252	–26.650	4.65		–239.9
b_i x 10		–9.1047	15.710	8.9391		20.71
c_i x 10^3		67.299	–6.610	–3.4827		–2.510
d_i x 10^5	90.51	–97.103	–0.603	1.05092		
e_i x 10^7	–70.3	47.449	1.027	–0.11010		
Deviations						
Average, d	–0.004	0.000	0.000	0.000	0.000	0.000
R.M.S., $r(\sigma)$	0.017	0.017	0.059	0.100	0.042(0.046)	1.51
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.02	0.03	0.08	0.2		3.0
$\delta(H–H_0)$	0.2	0.9	29.	53.		305.
$\delta(S)$	0.020	0.04	0.18	0.29		0.9
$\delta(G–H_0)/T$	0.007	0.016	0.11	0.14		0.17

*Lower temperature for enthalpy measurement.

‡Upper temperature for enthalpy measurement.

TABLE 113. Thermodynamic Functions of 1,4-Butanedioic Acid
$C_4H_6O_4$ M = 118.089

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.000	0.000
4	-0.005	0.014	0.06	0.019	0.056
5	-0.009	0.027	0.14	0.037	0.109
6	-0.016	0.047	0.28	0.063	0.186
8	-0.037	0.110	0.88	0.147	0.435
10	-0.072	0.212	2.12	0.284	0.835
15	-0.237	0.693	10.39	0.929	2.700
20	-0.547	1.575	31.50	2.122	5.953
25	-1.030	2.865	71.63	3.895	10.233
30	-1.692	4.50	134.86	6.187	15.133
35	-2.523	6.38	223.42	8.907	20.314
40	-3.509	8.45	338.03	11.960	25.513
45	-4.630	10.63	478.25	15.257	30.533
50	-5.864	12.86	642.9	18.722	35.263
60	-8.604	17.32	1039.3	25.927	43.843
70	-11.602	21.66	1516.1	33.260	51.329
80	-14.766	25.78	2062.7	40.550	57.845
90	-18.030	29.67	2670.2	47.699	63.541
100	-21.347	33.31	3331.3	54.660	68.59
110	-24.684	36.73	4040.6	61.416	73.22
120	-28.019	39.96	4795.0	67.98	77.65
130	-31.340	43.02	5593.1	74.36	81.94
140	-34.64	45.95	6433.6	80.59	86.14
150	-37.90	48.77	7315.7	86.67	90.27
160	-41.14	51.49	8238.8	92.63	94.35
170	-44.34	54.13	9202.6	98.47	98.40
180	-47.51	56.70	10206.8	104.21	102.45
190	-50.64	59.22	11251.6	109.86	106.50
200	-53.74	61.68	12337.	115.43	110.58
210	-56.81	64.11	13463.	120.92	114.70
220	-59.85	66.50	14631.	126.35	118.86
230	-62.86	68.87	15841.	131.73	123.07
240	-65.84	71.22	17093.	137.06	127.34
250	-68.79	73.55	18388.	142.34	131.66
260	-71.72	75.87	19726.	147.59	136.03
270	-74.63	78.18	21108.	152.81	140.46
280	-77.51	80.48	22535.	158.00	144.93
290	-80.38	82.78	24007.	163.16	149.43
298.15	-82.70	84.65	25240.	167.35	153.11
300	-83.22	85.08	25524.	168.30	153.95
310	-86.05	87.37	27086.	173.42	158.47
320	-88.86	89.67	28693.	178.53	163.0
330	-91.65	92.00	30360.	183.65	170.2
340	-94.44	94.36	32081.	188.79	174.1
350	-97.20	96.68	33840.	193.89	177.5
360	-99.96	99.0	35629.	198.9	180.4
370	-102.70	101.2	37445.	203.9	182.8
380	-105.4	103.4	39282.	208.8	184.6
390	-108.1	105.5	41136.	213.6	186.
400	-110.8	107.5	43001.	218.3	187.
410	-113.5	109.4	44873.	223.0	187.
420	-116.2	111.3	46745.	227.5	187.

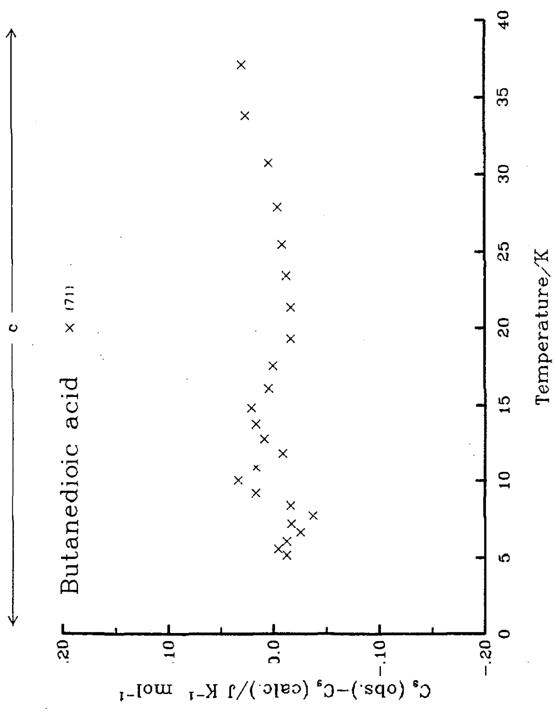

FIG. 88. Deviation plot for butanedioic acid (succinic acid), c, 0–40 K.

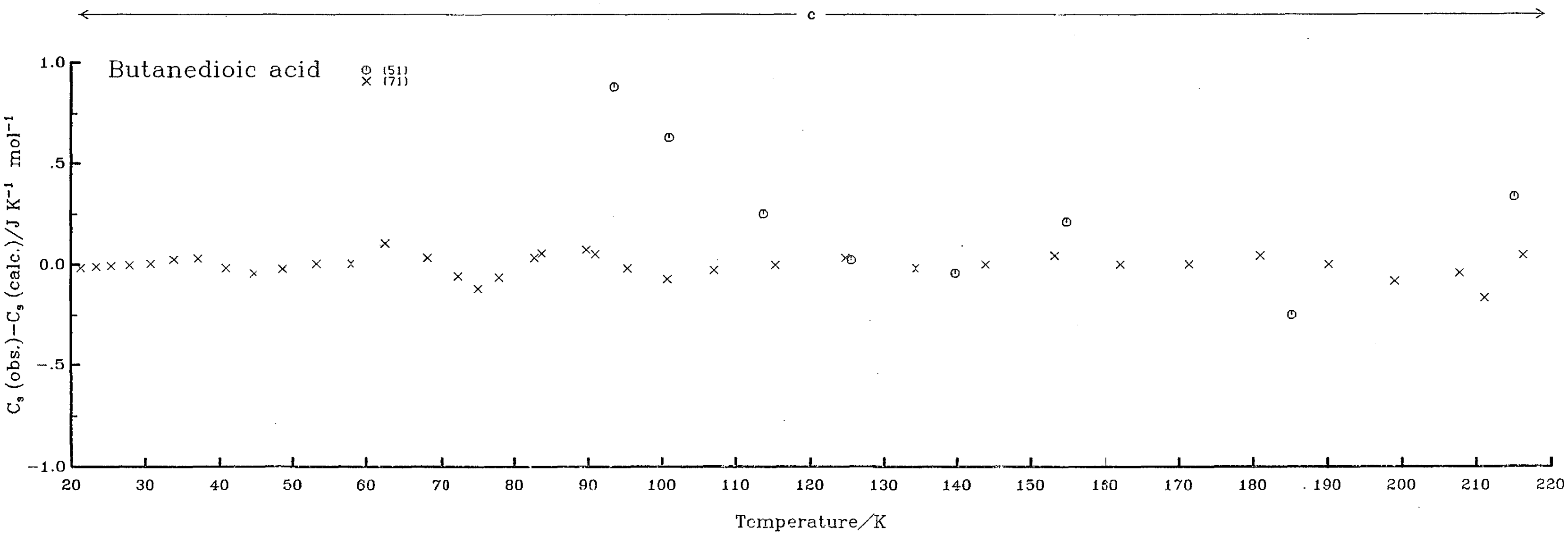

FIG. 89. Deviation plot for butanedioic acid (succinic acid), c, 20–220 K.

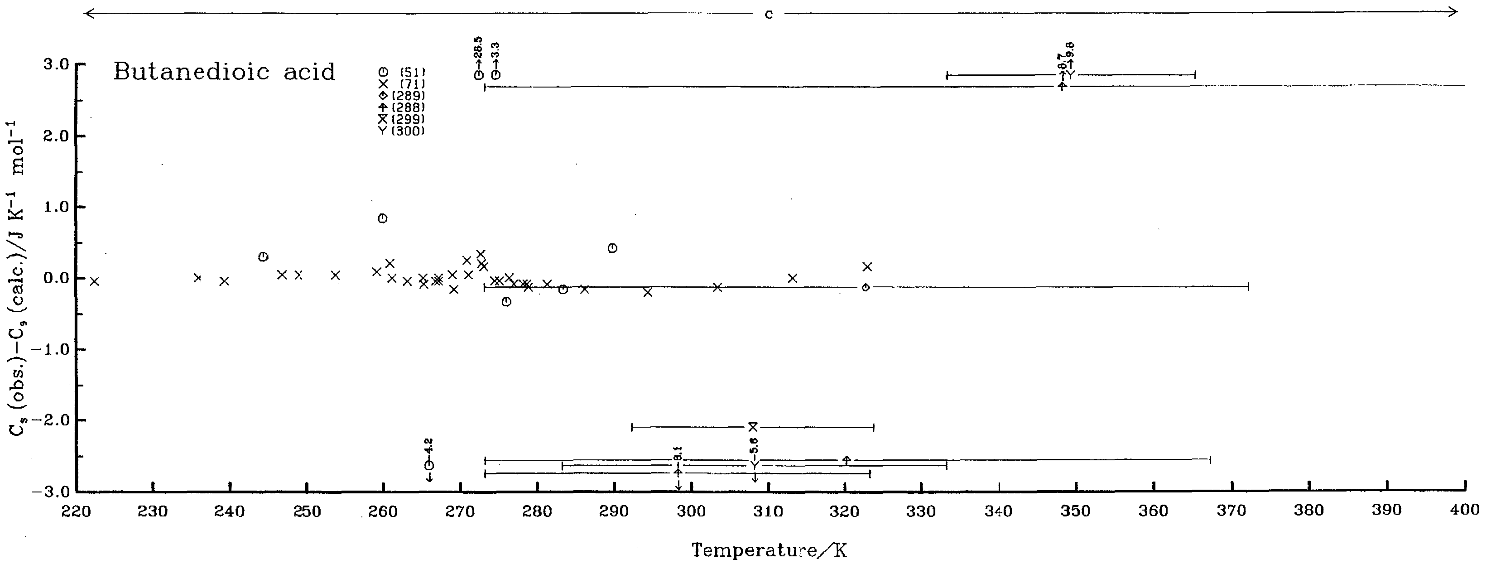

FIG. 90. Deviation plot for butanedioic acid (succinic acid), c, 220–320 K.

28. trans-Butenedioic Acid(Fumaric Acid)

The only source of heat capacity data is Parks and Huffman [51]. Wilhoit and Shiao [297] reported a melting point of 562.4 to 562.8 K for a carefully purified and dried sample. It was probably accompanied by some decomposition. The enthalpy and entropy given in Table 116 were estimated by the use of equations (4) and (5) of section 1.2.b. This leads to an entropy of 168.0 J K^{-1} mol^{-1} at 298.15 K. Kelley, Parks and Huffman [7] estimated the entropy at 90 K to be 51.5 J K^{-1} mol^{-1} and then calculated the value 166.1 J K^{-1} mol^{-1} at 298.15 K using the experimental data.

TABLE 114. Sources of Heat Capacity Data for Butenedioic Acids

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
			trans-Butenedioic Acid					
Parks & Huffman	1930	c(91–297)	isoperibol	C	sample prepared by J.B.Conant purified by recrystallization from water 3–4 times	16	no	[51]
			cis-Butenedioic Acid					
Parks & Huffman	1930	c(91–294)	isoperibol	C	redistill maleic anhydride,then recrystallized from water by evaporation in vacuum	16	no	[51]

TABLE 115. Parameters for Heat Capacity of trans-Butenedioic Acid

Phase	c	c	c
Data Points			
Number	9	7	16(6)
Temp./K	91.3 -184.9	193.5 -297.1	91.3 -297.1
Parameters for	C_s	C_s	C_s
Temp./K	90.0 -190.0	190.0 -300.0	90.0 -300.0
a_i	-8.08	-22.2	
b_i x 10	11.271	10.174	
c_i x 10^3	-4.849	-2.519	
d_i x 10^5	1.037	0.3203	
Deviations			
Average, d	0.025	-0.050	0.000
R.M.S., $r(\sigma)$	0.251	0.301	0.277(0.326)
Estimated Uncertainty in Tabulated Values			
$\delta(C)$	1.0	2.0	
$\delta(H-H_0)$	316.	385.	
$\delta(S)$	3.1	3.2	
$\delta(G-H_0)/T$	0.4	0.4	

TABLE 116. Thermodynamic Functions of trans-Butenedioic Acid
$C_4H_4O_4$ M = 116.073

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
			Crystal		
90	-22.1	31.4	2824.	53.5	61.6
100	-25.6	34.7	3465.	60.2	66.5
110	-29.0	37.8	4153.	66.8	71.0
120	-32.5	40.7	4885.	73.2	75.3
130	-35.8	43.5	5658.	79.4	79.3
140	-39.2	46.2	6470.	85.4	83.1
150	-42.4	48.8	7320.	91.2	86.9
160	-45.7	51.3	8207.	97.0	90.6
170	-48.8	53.7	9132.	102.6	94.3
180	-52.0	56.1	10094.	108.1	98.2
190	-55.1	58.4	11096.	113.5	102.1
200	-58.1	60.7	12137.	118.8	106.
210	-61.1	62.9	13218.	124.1	110.
220	-64.1	65.2	14338.	129.3	114.
230	-67.1	67.4	15494.	134.4	118.
240	-70.0	69.5	16688.	139.5	121.
250	-72.9	71.7	17917.	144.5	125.
260	-75.7	73.8	19183.	149.5	128.
270	-78.5	75.9	20484.	154.4	132.
280	-81.3	77.9	21821.	159.3	135.
290	-84.1	80.0	23194.	164.1	139.
298.15	-86.3	81.6	24340.	168.0	142.
300	-86.9	82.0	24603.	168.9	143.

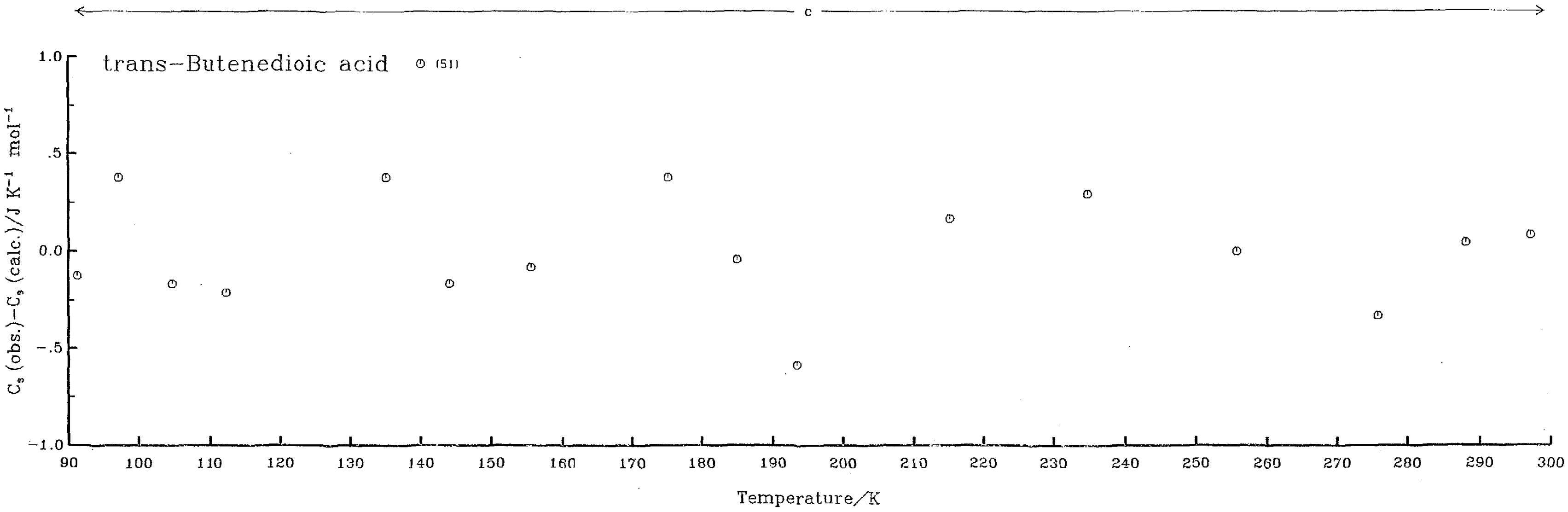

FIG. 91. Deviation plot for trans-butenedioic acid (fumaric acid), c, 90–300 K.

29. cis-Butenedioic Acid (Maleic Acid)

The only source of heat capacity data is Parks and Huffman [51]. Wilhoit and Shiao [297] reported a melting point of 403.5 to 404.2 K for a carefully purified and dried sample contained in a sealed tube. The enthalpy and entropy at 90 K given in Table 118 were estimated by the group contribution method of section 1.2.b. This leads to an entropy of 160.8 J K^{-1} mol^{-1} at 298.15 K. Kelley, Parks and Huffman [7] estimated the entropy at 90 K to be 50.6 J K^{-1} mol^{-1} and calculated the entropy at 298.15 of 159.4 J K^{-1} mol^{-1} using the experimental data.

TABLE 117. Parameters for Heat Capacity of cis-Butenedioic Acid

Phase	c	c	c
Data Points			
Number	9	7	16(6)
Temp./K	91.3 -184.9	193.5 -297.1	91.3 -297.1
Parameters for	C_s	C_s	C_s
Temp./K	90.0 -190.0	190.0 -300.0	90.0 -300.0
a_i	-8.08	-22.2	
$b_i \times 10$	11.271	10.174	
$c_i \times 10^3$	-4.849	-2.519	
$d_i \times 10^5$	1.037	0.3203	
Deviations			
Average, d	0.025	-0.050	0.000
R.M.S., $r(\sigma)$	0.251	0.301	0.277(0.326)
Estimated Uncertainty in Tabulated Values			
$\delta(C)$	1.0	2.0	
$\delta(H-H_0)$	316.	385.	
$\delta(S)$	3.1	3.2	
$\delta(G-H_0)/T$	0.4	0.4	

TABLE 118. Thermodynamic Functions of cis-Butenedioic Acid
$C_4H_4O_4$ M = 116.073

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
90	-21.5	30.5	2746.	52.0	59.9
100	-24.9	33.6	3365.	58.5	63.9
110	-28.2	36.6	4023.	64.8	67.8
120	-31.5	39.3	4720.	70.9	71.6
130	-34.8	42.0	5454.	76.7	75.3
140	-38.0	44.5	6225.	82.4	78.9
150	-41.1	46.9	7032.	88.0	82.5
160	-44.2	49.2	7874.	93.4	86.0
170	-47.3	51.5	8753.	98.8	89.6
180	-50.3	53.7	9667.	104.0	93.2
190	-53.2	55.9	10617.	109.1	96.8
200	-56.2	58.0	11603.	114.2	100.
210	-59.0	60.1	12625.	119.2	104.
220	-61.9	62.2	13683.	124.1	107.
230	-64.7	64.2	14775.	128.9	111.
240	-67.5	66.3	15901.	133.7	114.
250	-70.2	68.3	17063.	138.5	118.
260	-72.9	70.2	18261.	143.2	122.
270	-75.6	72.2	19496.	147.8	125.
280	-78.3	74.2	20770.	152.5	129.
290	-80.9	76.2	22084.	157.1	133.
298.15	-83.1	77.8	23186.	160.8	137.
300	-83.5	78.1	23440.	161.7	138.

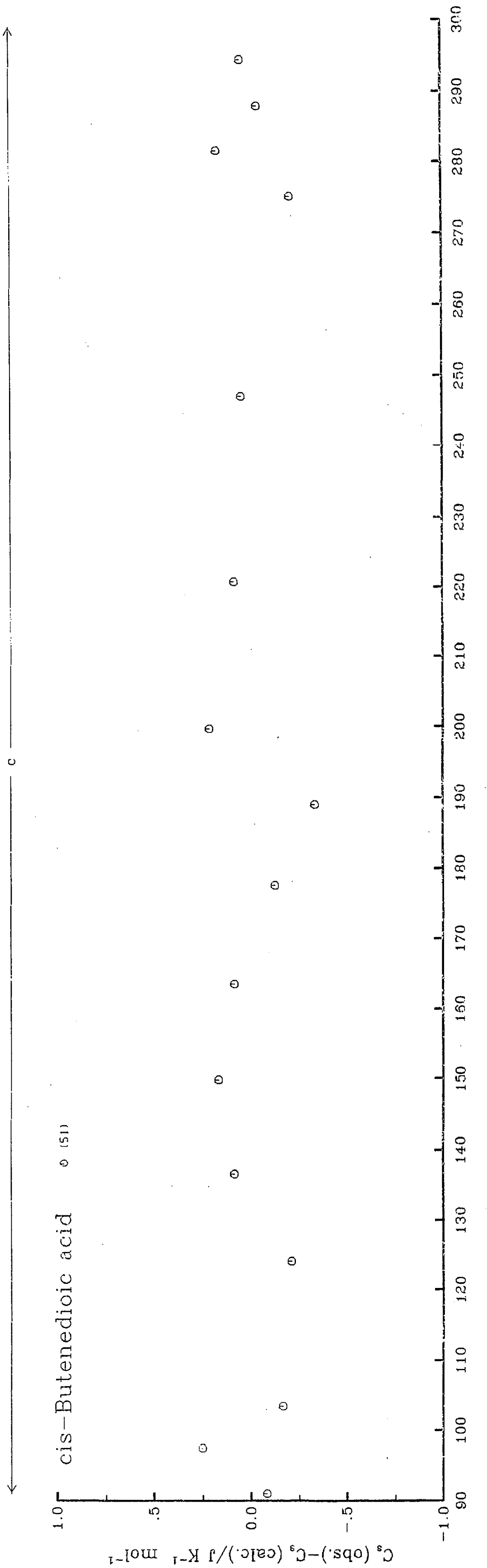

FIG. 92. Deviation plot for cis-butenedioic acid (maleic acid), c, 90–300 K.

30. 2-Hydroxypropanoic Acid (Lactic Acid)

Lactic acid contains an asymmetric carbon atom and thus exists in two optically active, D(–)- and L(+)-, forms. Both the commercial racemic and optically active lactic acid syrups consist of about 50% 2-hydroxypropanoic acid monomer. The remainder is a more or less equilibrium mixture of water, a cyclic (ethylene oxide) form, the anhydride, a bimolecular cyclic ester (lactide), and a varity of polymeric chain and ring esters.

Borsook, Huffman, and Liu [304] published a procedure for preparing pure crystalline D(–)and L(+)-2-hydroxypropanoic acids by a series of fractional crystallizations of the commercial syrup. They found the melting point of the pure optically active isomers to be 326.0 K. A synthetic 50-50 mixture of D(–)- and L(+)- isomers melted at 290.0 K. Lockwood, Yoder, and Zienty [305] reported the melting point of the optically active form as 327 K and of a synthetic racemic mixture as 301 - 306 K.

On standing at temperatures above 268 K pure 2-hydroxypropanoic acid spontaneously reverts to the mixture of the free acid in equilibrium with water and various anhydro derivatives. The conversion is complete within a few hours at room temperature.

Parks, Thomas, and Light [56] measured the heat capacity of a sample of racemic 2-hydroxypropanoic acid in a Nernst type calorimeter. The composition of the initial material is given in Table 119. Three series of measurements were made. The first series was made after cooling the sample to around 90 K. It then consisted of a mixture of crystalline and amorphous forms. Next, the melt obtained after the first series was cooled rapidly in liquid air to form a completely glassy material. The second series of measurements was made on this sample. At the end of these runs the sample was held for forty-eight hours at 343 K, and the third series of measurements was made on this material which consisted of the equilibrium mixture of 2-hydroxypropanoic acid, water, and anhydro forms. Data from the third series were not used here.

The heat capacities obtained from the first two series of measurements showed the rapid increase in the transition region, 200–210 K, typical of a glass. The glass transition temperature obtained from the second series was 204 K. The parameters in Table 120 for the glass and liquid phases were obtained from a least squares fit to the data from the second series. A satisfactory fit could not be obtained when the usual constraints for continuity at the boundaries were maintained. The requirement for continuity in the temperature derivative of heat capacity was removed for 208.3 K. The comparison of observed and calculated values is made in Figure 94.

By comparing the increase in heat capacity near the glass transition temperature observed in the second series of measurements with that seen in the first series, Parks et al. estimated that the original sample consisted of 12.2% crystals and 87.8% glass. The subtraction of the heat capacity of the glass portion from the values obtained in the first series gave, they assumed, the heat capacity of the pure crystals.

The parameters in Table 120 for the crystal phase were obtained by a least squares fit to the values calculated in this way by Parks et al. They also measured a heat of fusion of 11340 J mol^{-1}. Smoothed values of the thermodynamic properties of crystal and liquid calculated from these data are given in Table 121. The reference state for enthalpy and entropy in this table is 90 K. The corresponding properties for the glass are given in Table 122 and the enthalpy and entropy are given relative to those of the crystal at 90 K.

Parks et al. estimated the entropy of crystalline 2-hydroxypropanoic acid at 90 K to be 48.2 J K^{-1} mol^{-1} and also gave the value of 192.4 J K^{-1} mol^{-1} for the entropy at 298.15 K.

TABLE 119. Sources of Heat Capacity Data for 2-Hydroxypropanoic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
			DL-2-Hydroxypropanoic Acid					
Parks, Thomas & Light	1936	c(90–280),l(294–303) gl(104–227)	isoperibol	C	fract. distillation of commercial syrup, final sample contains 98.4% monomer,1.4% lactide & 0.2% water by titration	32	no	[56]
			D(–)- and L(+)-2-Hydroxypropanoic Acid					
Huffman, Ellis & Borsook	1940	c(84–311)	isoperibol	C	fract. crystillization of commercial syrup	39	no	[306]

TABLE 120. Parameters for Heat Capacity of DL-2-Hydroxypropanoic Acid

Phase	c	c	c	gl	gl	gl	gl,l
Data Points							
Number	6	5	11(6)	10	4	14(8)	7(4)
Temp./K	90.0 -180.0	190.0 -280.0	90.0 -280.0	103.5 -187.9	193.5 -212.5	103.5 -212.5	204.2 -303.0
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	90.0 -180.0	180.0 -290.0	90.0 -290.0	90.0 -190.0	190.0 -208.3	90.0 -208.3	208.3 -310.0
a_i	13.81	8.3		462.75	-1942591.4		-3191.3
$b_i \times 10$	5.801	5.658		-124.868	387697.127		539.587
$c_i \times 10^3$	-1.594	-0.920		138.260	-289645.558		-320.864
$d_i \times 10^5$	0.364	0.1290		-65.2221	95994.763		84.0172
$e_i \times 10^7$				11.4007	-11906.2665		-8.1373
Deviations							
Average, d	-0.001	0.002	0.000	-0.017	0.184	0.000	-0.121
R.M.S., $r(\sigma)$	0.063	0.071	0.071(0.096)	0.310	0.62	0.352(0.54)	0.59(0.83)
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.6	1.0		0.6	1.0		1.0
$\delta(H-H_{90})$	54.	123.		169.	168.		147.
$\delta(S-S_{90})$	0.4	0.6		0.7	0.7		0.7

Huffman, Ellis, and Borsook [306] prepared samples of the optically active D(-) and L(+) 2-hydroxypropanoic acid by the method of Borsook, Huffman, and Liu [304]. They contained 99.7% 2-hydroxypropanoic acid monomer as determined by titration. They measured the heat capacities of the two crystalline forms in a Nernst type calorimeter. The temperature was measured by a copper-constantan thermocouple calibrated against a thermocouple described by Giauque, Johnston, and Kelley [307]. Since no accurate comparison of this scale with IPTS-68 can be made at this time, no temperature scale corrections were applied to their data.

Although the D(-) and L(+) forms were run separately, no significant difference could be seen between them, as would be expected. They were,

TABLE 121. Thermodynamic Functions of DL-2-Hydroxypropanoic Acid
$C_3H_6O_3$ $M = 90.079$

T/K	$H-H_{90}$ J mol^{-1}	$S-S_{90}$	C_s J K^{-1} mol^{-1}
	Crystal		
90	0.	0.0	55.8
100	576.	6.1	59.5
120	1840.	17.6	66.8
140	3245.	28.4	73.8
160	4790.	38.7	80.7
180	6475.	48.6	87.8
200	8304.	58.2	95.
220	10274.	67.6	102.
240	12383.	76.8	109.
260	14631.	85.8	116.
280	17019.	94.6	123.
290.0	18266.	99.0	126.
	Liquid		
290.0	29609.	138.1	208.
298.15	31316.	143.9	211.
300	31707.	145.2	212.
310	33846.	152.2	215.

TABLE 122. Thermodynamic Functions of DL-2-Hydroxypropanoic Acid
$C_3H_6O_3$ $M = 90.079$

T/K	$H-H_{90}$ J mol^{-1}	$S-S_{90}$	C_s J K^{-1} mol^{-1}
	Glass and Liquid		
90	4247.	10.3	58.2
100	4828.	16.4	58.5
110	5423.	22.0	61.0
120	6051.	27.5	64.6
130	6718.	32.8	68.7
140	7426.	38.1	72.8
150	8172.	43.2	76.5
160	8955.	48.3	80.0
170	9772.	53.2	83.5
180	10628.	58.1	87.8
190	11533.	63.0	93.6
198	12290.	66.9	99.1
200	12496.	68.0	107.2
202	12722.	69.1	119.9
204	12979.	70.3	137.2
206	13274.	71.8	158.8
208	13616.	73.4	184.0
210	13992.	75.2	188.2
212	14368.	77.0	188.6
220	15882.	84.0	189.7
240	19697.	100.6	192.
260	23568.	116.1	196.
280	27554.	130.9	203.
290	29608.	138.1	208.

therefore, combined into one set of data for the least squares calculation of the parameters. The enthalpy and entropy at 90 K in Table 124 were estimated by the group additivity method of section 1.2.b. Huffman et al. estimated the entropy of D(–)-2-hydroxypropanoic acid to be 43.6 J K^{-1} mol^{-1} and of L(+)-2-hydroxypropanoic acid to be 42.9 J K^{-1} mol^{-1} at 90 K.

Huffman et al. also obtained 16.86 kJ mol^{-1} for the enthalpy of fusion of D(–)-2-hydroxypropanoic acid. However, since the melting was accompanied by the formation of some anhydro derivatives, this result cannot be considered as reliable.

TABLE 123. Parameters for Heat Capacity of D(–)-2-Hydroxypropanoic Acid

Phase	c	c	c	c
Data Points				
Number	14	10	15	39(8)
Temp./K	84.1 –149.5	157.2 –243.2	254.8 –311.2	84.1 –311.2
Parameters for	C_s	C_s	C_s	C_s
Temp./K	80.0 –150.0	150.0 –250.0	250.0 –315.0	80.0 –315.0
a_i	5.21	23.71	–773.2	
b_i x 10	6.450	3.560	95.265	
c_i x 10^3	–1.4947	–0.1082	–35.2204	
d_i x 10^5	0.2124	0.0244	4.4967	
Deviations				
Average, d	–0.007	0.020	–0.005	0.000
R.M.S., $r(\sigma)$	0.159	0.268	0.289	0.230(0.259)
Estimated Uncertainty in Tabulated Values				
$\delta(C)$	0.3	0.4	0.5	
$\delta(H-H_0)$	151.	157.	160.	
$\delta(S)$	1.2	1.2	1.2	
$\delta(G-H_0)/T$	0.2	0.2	0.2	

TABLE 124. Thermodynamic Functions of D- and L-2-Hydroxypropanoic Acid

$C_3H_6O_3$ $M = 90.079$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
		Crystal			
80	–13.62	21.63	1730.7	35.25	48.33
90	–16.36	24.84	2236.0	41.20	52.70
100	–19.13	27.84	2784.1	46.97	56.89
110	–21.91	30.66	3373.2	52.58	60.90
120	–24.69	33.35	4001.6	58.04	64.76
130	–27.47	35.91	4667.8	63.38	68.47
140	–30.22	38.36	5370.5	68.58	72.04
150	–32.95	40.72	6108.3	73.67	75.50
160	–35.65	43.00	6880.3	78.65	78.90
170	–38.33	45.21	7686.3	83.54	82.30
180	–40.97	47.37	8526.3	88.34	85.71
190	–43.58	49.48	9400.4	93.06	89.12
200	–46.18	51.54	10309.	97.72	92.53
210	–48.74	53.58	11251.	102.32	95.96
220	–51.28	55.6	12228.	106.86	99.39
230	–53.79	57.6	13239.	111.35	102.83
240	–56.28	59.5	14285.	115.80	106.3
250	–58.74	61.5	15365.	120.2	109.8
260	–61.22	63.4	16479.	124.6	113.1
270	–63.61	65.3	17627.	128.9	116.5
280	–66.02	67.2	18810.	133.2	120.1
290	–68.43	69.1	20030.	137.5	124.1
298.15	–70.37	70.6	21058.	141.0	128.1
300	–70.82	71.0	21295.	141.8	129.0
310	–73.15	72.9	22614.	146.1	134.9

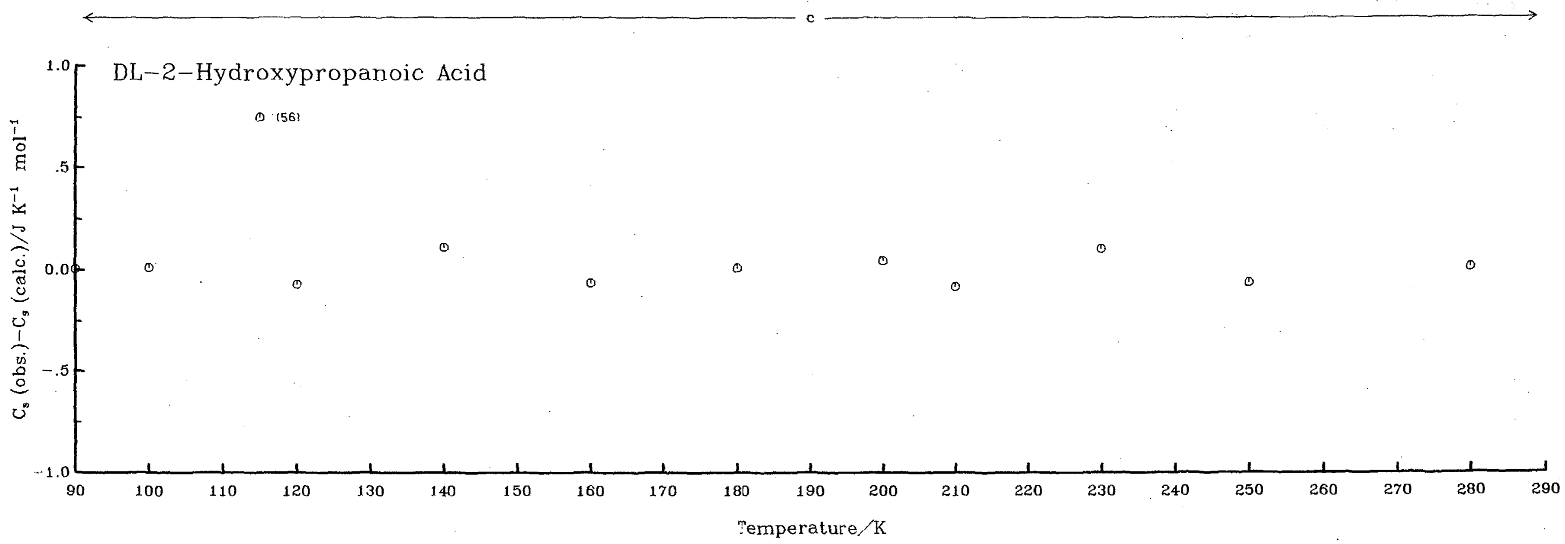

FIG. 93. Deviation plot for DL-2-hydroxypropanoic acid (lactic acid), c, 90–280 K.

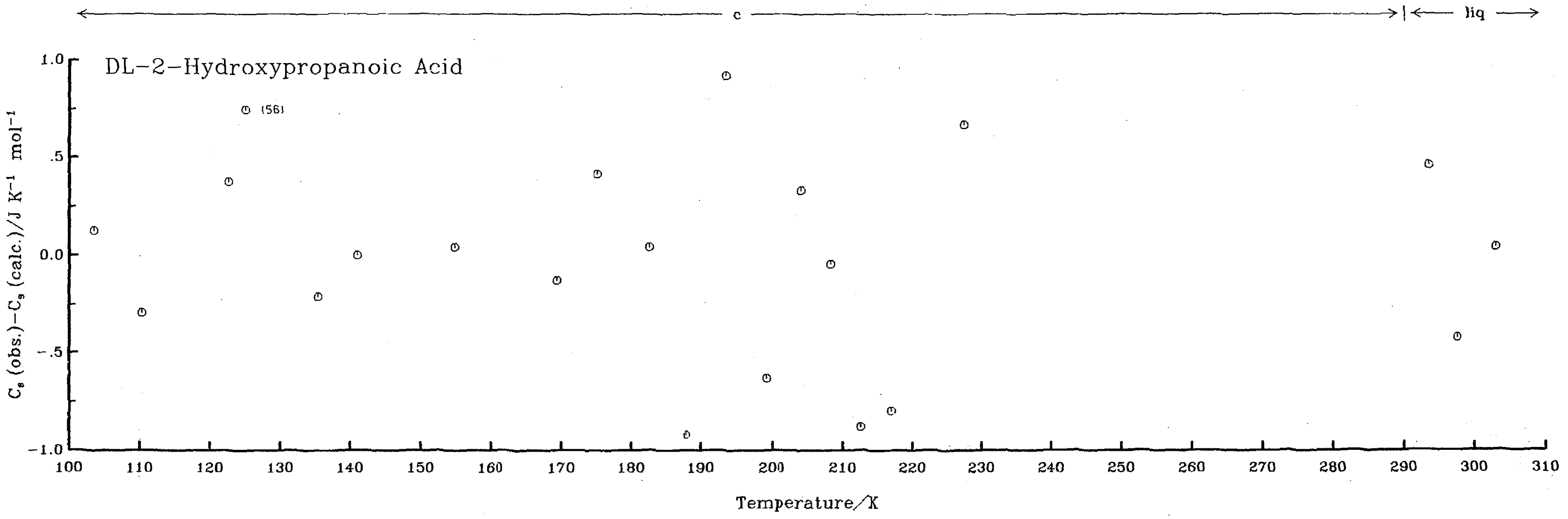

FIG. 94. Deviation plot for DL-2-hydroxypropanoic acid (lactic acid), gl, l, 100–300 K.

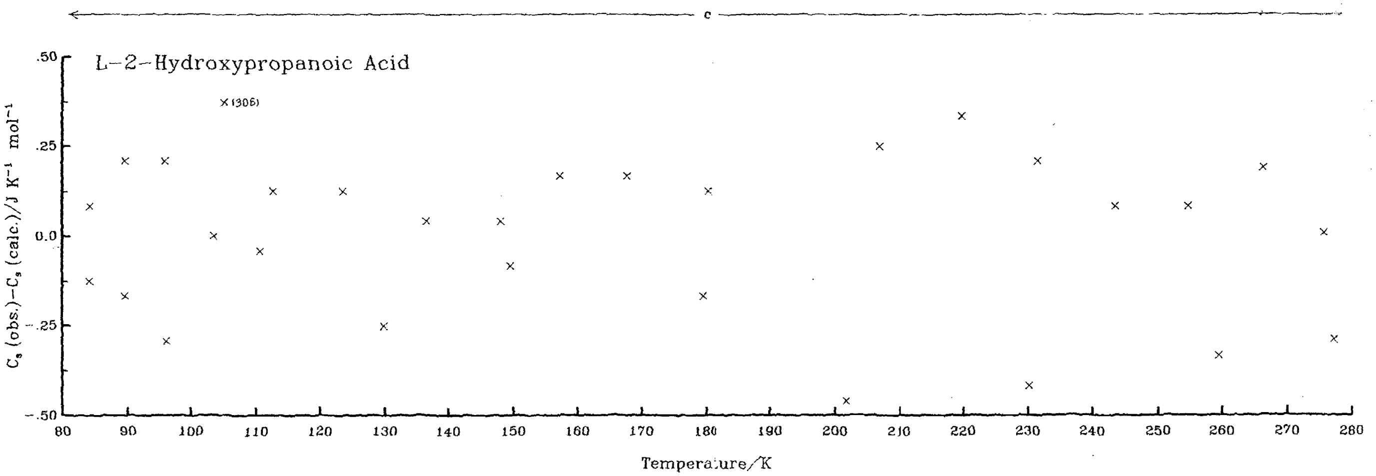

FIG. 95. Deviation plot for L-2-hydroxypropanoic acid (lactic acid), c, 90–380 K.

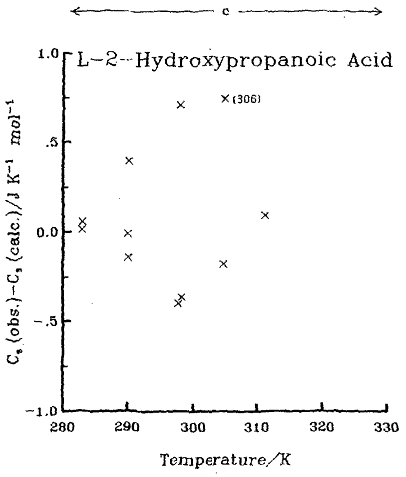

FIG. 96. Deviation plot for L-2-hydroxypropanoic acid (lactic acid), c, 280–310 K.

31. 2,3-Dihydroxybutanedioic Acid (Tartaric Acid)

2,3-Dihydroxybutanedioic acid has two symmetrically arranged asymmetric carbon atoms. It has two diastereoisomeric forms: a meso form and a pair of optically active forms. In the crystal phase, the optically active forms normally occur as either an anhydrous L–isomer, or as a racemic monohydrate.

A few scattered measurements of mean heat capacities of both types of crystals made in drop calorimeters have been reported. These are not sufficient as a basis for a complete thermodynamic table. However, they were fit to linear and quadratic functions of temperature and used to calculate the heat capacity and enthalpy in Tables 127 and 128.

The $\bar{C}_s$ of DL–2,3–dihydroxybutanedioic acid monohydrate reported by Kopp [299] differed considerably from those of Ewald [308]. The selected values were calculated from Ewald's data only. Although he made six measurements they were grouped into only three different temperature increments. They did not lie on a straight line, and so they are represented by a quadratic function of temperature.

TABLE 125. Sources of Heat Capacity Data for 2,3-Dihydroxybutanedioic Acid

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
			Anhydrous L–2,3–Dihydroxybutanedioic Acid					
Kopp	1865	c(294–324)	drop	H	not stated	1	no	[299]
Forch & Nordmeyer	1906	c(81–287)	drop	H	not stated	1	no	[309]
Satoh & Sogabe	1939	c(273–372)	drop	H	Kahlbaum sample	1	no	[289]
			DL–2,3–Dihydroxybutanedioic Acid Monohydrate					
Kopp	1865	c(292–324)	drop	H	not stated	1	no	[299]
Ewald	1914	c(82–329)	drop	H	Kahlbaum sample	6	no	[308]

TABLE 126. Parameters for Heat Capacity of 2,3-Dihydroxybutanedioic Acid

	Anhydrous(L)	Monohydrate(DL)
Phase	c	c
Data Points		
Number	3(2)	6(3)
Temp./K	81.0 -372.0	82.0 -328.2
Parameters for	C_s	C_s
Temp./K	80.0 -370.0	80.0 -325.0
a_i	30.7	61.5
$b_i \times 10$	4.817	-1.25
$c_i \times 10^3$		2.515
Deviations		
Average, d	0.00	0.00
R.M.S., $r(\sigma)$	0.50(0.84)	0.38(0.54)
Estimated Uncertainty in Tabulated Values		
$\delta(C)$	2.0	4.0
$\delta(H-H_{80})$	600.	980.
$\delta(S-S_{80})$	3.1	5.6

TABLE 127. Thermodynamic Functions of L–2,3–Dihydroxybutanedioic Acid
$C_4H_6O_6$ M = 150.088

T/K	$H-H_{90}$ J mol^{-1}	$S-S_{90}$ J K^{-1} mol^{-1}	C_s
	Crystal		
80	0.	0.	69.
100	1481.	16.	79.
120	3155.	32.	89.
140	5021.	46.	98.
160	7080.	60.	108.
180	9332.	73.	117.
200	11777.	86.	127.
220	14414.	98.	137.
240	17244.	111.	146.
260	20266.	123.	156.
280	23481.	135.	166.
298.15	26566.	145.	174.
300	26889.	147.	175.
320	30490.	158.	185.
340	34283.	170.	194.
360	38269.	181.	204.

TABLE 128. Thermodynamic Functions of DL-2,3-Dihydroxybutanedioic Acid, Hydrate $C_4H_6O_6 \cdot H_2O$ $M = 168.103$

T/K	$H-H_{90}$ J mol^{-1}	$S-S_{90}$	C_s J K^{-1} mol^{-1}
	Crystal		
80	0.	0.	68.
100	1414.	16.	74.
120	2979.	30.	83.
140	4736.	44.	93.
160	6725.	57.	106.
180	8985.	70.	120.
200	11557.	84.	137.
220	14482.	98.	156.
240	17800.	112.	176.
260	21550.	127.	199.
280	25774.	143.	224.
298.15	30050.	157.	248.
300	30511.	159.	250.
320	35801.	176.	279.

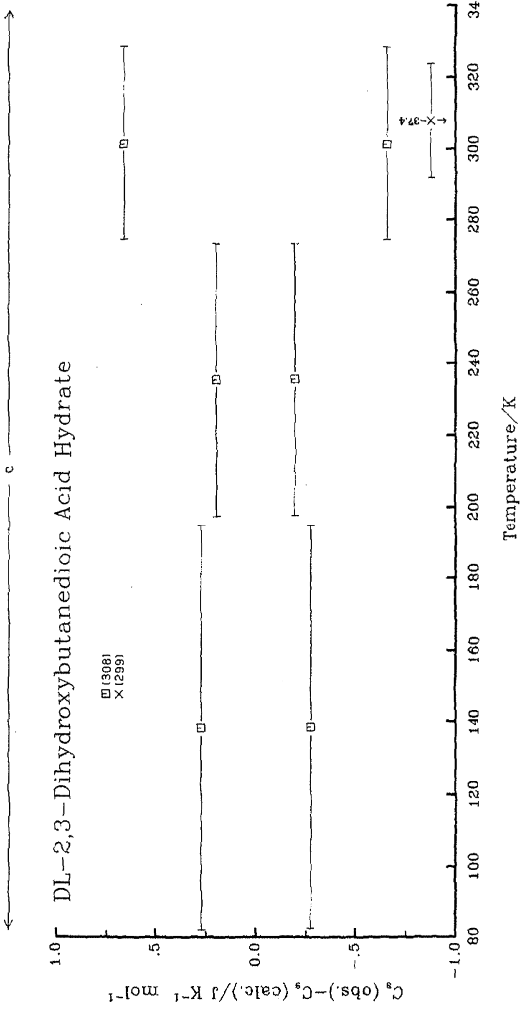

FIG. 97. Deviation plot for DL-2,3-dihydroxybutane-dioic acid (tartaric acid), hydrate, c, 80–320 K.

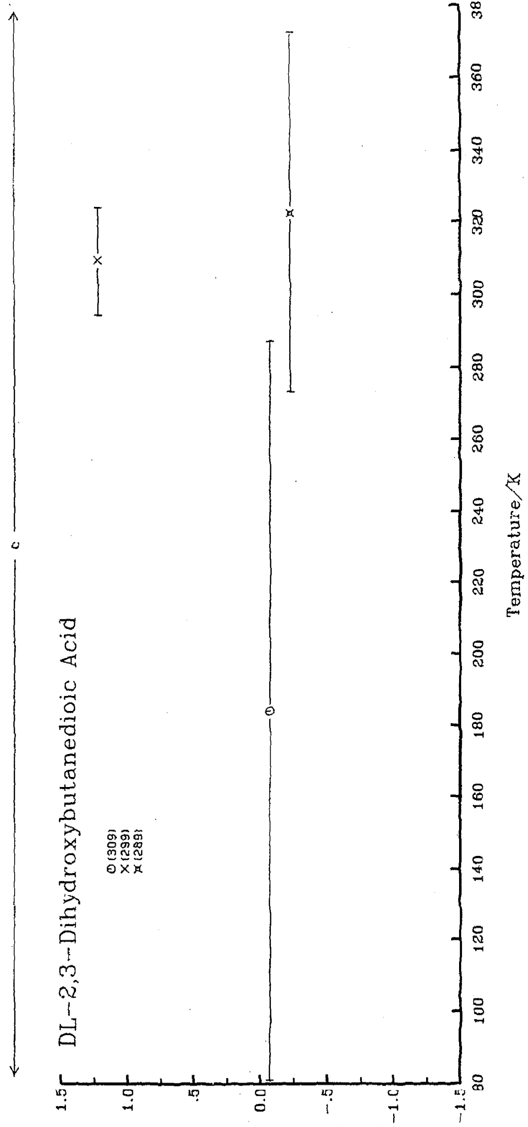

FIG. 98. Deviation plot for L-2,3-dihydroxybutane-dioic acid (tartaric acid), c, 80–380 K.

32. Ethyl Ethanoate (Ethyl Acetate)

Table 129 identifies three sources of heat capacity but Parks, Huffman and Barmore [52] are the only source for the crystal phase. They also obtained 189.40 K for the triple point. However, the value 189.30 K, reported by Dreisbach and Martin [151] was selected. This temperature was corrected for the presence of impurity in the sample, as established by analysis of the cooling curve. It is a melting point however, rather than a true triple point. Sapgir [150] measured a (cryoscopic) enthalpy of fusion of 9548 J mol^{-1} at 198.4 K, while Parks, Huffman and Barmore obtained 10519 J mol^{-1}. The latter value was selected for the final table.

By extrapolation of their heat capacity data from 90 to 0 K, Parks, Huffman, and Barmore estimated the entropy of the crystal to be 62.80 J K^{-1} mol^{-1} at 90 K. The value in Table 131 was calculated by the correlation of section 1.2.b.

TABLE 129. Sources of Heat Capacity Data for Ethyl Ethanoate

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Favre & Silbermann	1846	l(290–350)	drop	H	not stated			[223]
Schiff	1886	l(282–338)	drop	H	not stated	4	no	[16]
Parks, Huffman & Barmore	1933	c(92–167),l(196–294)	isoperibol	C	sample prepared by J. Timmermans	23	no	[52]
Kurnakov & Voskresenskaya	1936							[227]
Zhadanov	1945	l(280–355)	drop	H				[167]
Roux, Perron & Desnoyers	1978	l(283–303)	flow	C	A.C.S. grade, > 99.8%^{c}			[247]
Fuchs	1979	l(298)	Dewar flask	C	commercial sample, >99 wt%			[310]

TABLE 130. Parameters for Heat Capacity of Ethyl Ethanoate

Phase	c	l
Data Points		
Number	15(4)	12(4)
Temp./K	92.2 -167.3	195.7 -337.4
Parameters for	C_s	C_s
Temp./K	90.0 -189.22	189.22-330.0
a_i	-49.36	180.31
b_i x 10	25.036	-0.734
c_i x 10^3	-16.726	-0.6935
d_i x 10^5	4.3495	0.2785
Deviations		
Average, d	0.000	0.000
R.M.S., $r(\sigma)$	0.205(0.239)	0.184(0.226)
Estimated Uncertainty in Tabulated Values		
$\delta(C)$	0.4	0.5
$\delta(H-H_0)$	106.	135.
$\delta(S)$	2.0	2.0
$\delta(G-H_0)/T$	0.8	0.8

TABLE 131. Thermodynamic Functions of Ethyl Ethanoate
$C_4H_8O_2$ M = 88.106

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
			Crystal		
90	-23.7	36.8	3310.0	60.5	72.19
100	-27.8	40.6	4057.9	68.37	77.23
110	-31.8	44.1	4852.2	75.94	81.54
120	-35.8	47.4	5687.	83.2	85.4
130	-39.7	50.5	6559.	90.2	89.0
140	-43.6	53.3	7467.	96.9	92.7
150	-47.3	56.1	8413.	103.4	96.6
160	-51.1	58.8	9402.	109.8	101.2
170	-54.7	61.4	10440.	116.1	106.6
180	-58.3	64.1	11537.	122.4	113.0
189.30	-61.5	66.6	12621.	128.2	120.2
			Liquid		
189.30	-61.5	122.2	23118.	183.8	160.5
190	-62.0	122.4	23255.	184.4	160.4
200	-68.4	124.3	24858.	192.7	160.2
210	-74.5	126.0	26459.	200.5	160.1
220	-80.4	127.5	28061.	207.9	160.3
230	-86.1	129.0	29665.	215.1	160.6
240	-91.6	130.3	31274.	221.9	161.2
250	-96.9	131.6	32891.	228.5	162.1
260	-102.1	132.8	34518.	234.9	163.3
270	-107.2	133.9	36158.	241.1	164.8
280	-112.1	135.0	37814.	247.1	166.5
290	-116.8	136.2	39489.	253.0	168.6
298.15	-120.6	137.1	40871.	257.7	170.6
300	-121.4	137.3	41187.	258.7	171.1
310	-126.0	138.4	42912.	264.4	173.9
320	-130.4	139.6	44666.	270.0	177.1
330	-134.7	140.8	46454.	275.5	180.7

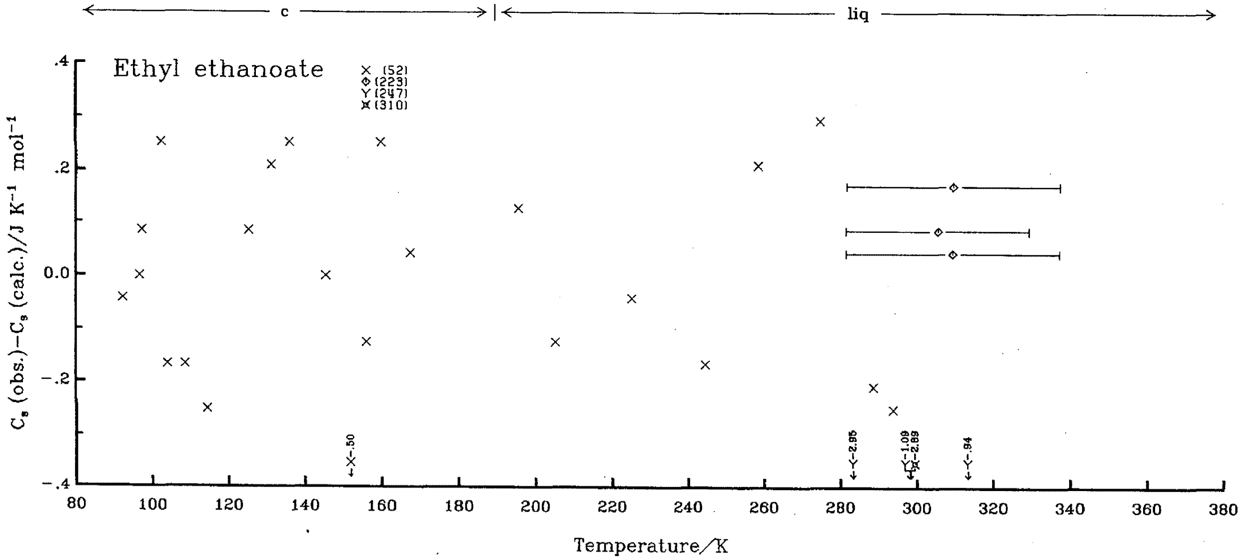

FIG. 99. Deviation plot for ethyl ethanoate, c, 1, 90–340 K.

33. Epoxyethane (Ethylene Oxide)

All of the experimental data used to generate Tables 134 and 135 were taken from Giauque and Gordon [40]. They used an elaborate procedure to insure sample purity. The measurements were made with the isoperibol calorimeter designated as Gold Calorimeter II. In these measurements, the absolute temperatures were measured by a laboratory standard thermocouple, while the temperature increments were measured by a gold wire resistance thermometer. The calibration of these thermometers has been described in earlier reports from this laboratory. The temperatures reported for the epoxyethane data were corrected to an ice point of 273.16 K. However, there was no direct link between their scale and IPTS-68. Thus no temperature scale corrections were applied to their data. The authors did make corrections for vaporization of the sample into the gas space in the calorimeter.

Melting points of epoxyethane have also been reported by Maas and Boomer [219], Timmermans and Hennaut-Roland [311], and McDonald, Shrader, and Stull [312]. They range from 0 to 1.2 K higher than the selected value.

The two heat capacity values for 146.19 and 151.40 K showed some effect for pre-melting and were not included in the least squares fit of the parameters. Giauque and Gordon estimated the entropy of crystalline epoxyethane at 15 K by the usual Debye extrapolation. They then calculated the entropy of the solid and liquid at the triple point and of the liquid at the boiling point by a graphical integration of the measured C_s/T. Their results (converted to joules) are compared with the values obtained from an analytical integration of the parameters of Table 134 in Table 132.

NBS Technical Note 270-3 gives values for the entropy and heat capacity of the liquid at 298.15 K. They are 153.85 J K^{-1} mol^{-1} and 87.95 J K^{-1} mol^{-1}, respectively.

Deviations between observed and calculated heat capacities in Figures 101 and 102 do not appear systematic.

TABLE 132. Entropy of Epoxyethane at the Triple Point

T/K	state	S/ J K^{-1} mol^{-1} from Ref.[40]	S/ J K^{-1} mol^{-1} from Table 134
15	c	0.92	0.604
160.65	c	69.24	70.05
283.60	1	148.53	149.31

TABLE 133. Sources of Heat Capacity Data for 1,2-Epoxyethane

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Giauque & Gordon	1949	c(15–151),1(166–284)	isoperibol	C	Matheson Chemical Co.sample dried with P_2O_5, repeated freezing & thawing to degas, then distilled, 99.98^c mol%	49	no	[40]

TABLE 134. Parameters for Heat Capacity of Epoxyethane

Phase	c	c	c	c	c	l
Data Points						
Number	2	8	5	12	27(8)	22(4)
Temp./K	15.3 - 17.7	20.0 - 44.0	48.8 - 67.7	72.8 -140.6	15.3 -140.6	166.0 -283.9
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 18.0	18.0 - 45.0	45.0 - 70.0	70.0 -160.65	0 -160.65	160.65-285.0
a_i		-3.828	4.857	-16.87		144.59
b_i x 10		1.279	0.389	13.9498		-7.5698
c_i x 10^3		23.146	14.233	-11.2073		2.8165
d_i x 10^5	87.10	25.951	-11.282	3.7222		-0.30483
e_i x 10^7	-59.0					
Deviations						
Average, d	-0.046	0.013	-0.008	0.000	0.000	0.000
R.M.S., $r(\sigma)$	0.067	0.067	0.054	0.076	0.076(0.080)	0.096(0.105)
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.06	0.08	0.10	0.15		0.2
$\delta(H-H_0)$	0.2	2.2	3.3	14.		45.
$\delta(S)$	0.017	0.08	0.09	0.15		0.23
$\delta(G-H_0)/T$	0.009	0.03	0.03	0.05		0.06

TABLE 135. Thermodynamic Functions of Epoxyethane
C_2H_4O $M = 44.053$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
			Crystal		
0	0.000	0.000	0.00	0.000	0.000
10	-0.070	0.206	2.06	0.276	0.812
15	-0.164	0.440	6.60	0.604	2.423
20	-0.406	1.362	27.24	1.768	5.912
25	-0.843	2.654	66.36	3.497	9.781
30	-1.459	4.179	125.4	5.637	13.83
35	-2.227	5.85	204.7	8.075	17.88
40	-3.121	7.59	303.8	10.72	21.71
45	-4.118	9.36	421.1	13.48	25.15
50	-5.194	11.10	554.8	16.29	28.28
60	-7.52	14.45	867.2	21.97	34.06
70	-9.98	17.60	1231.9	27.58	38.62
80	-12.52	20.45	1635.8	32.97	42.06
90	-15.08	23.02	2071.6	38.10	45.03
100	-17.63	25.36	2535.7	42.99	47.78
110	-20.15	27.52	3027.1	47.67	50.51
120	-22.63	29.56	3546.7	52.19	53.46
130	-25.08	31.52	4097.8	56.60	56.85
140	-27.48	33.47	4685.9	60.95	60.90
150	-29.86	35.46	5318.8	65.32	65.84
160	-32.21	37.54	6006.4	69.75	71.88
160.65	-32.37	37.68	6053.2	70.05	72.32
			Liquid		
160.65	-32.37	69.88	11226.2	102.25	83.03
170	-36.34	70.58	11999.1	106.92	82.32
180	-40.39	71.22	12819.6	111.61	81.81
190	-44.26	71.77	13636.	116.03	81.53
200	-47.95	72.25	14451.	120.21	81.47
210	-51.49	72.70	15266.	124.18	81.60
220	-54.88	73.11	16084.	127.99	81.91
230	-58.14	73.5	16905.	131.64	82.39
240	-61.27	73.9	17732.	135.16	83.01
250	-64.30	74.3	18565.	138.6	83.75
260	-67.22	74.6	19407.	141.9	84.59
270	-70.04	75.0	20258.	145.1	85.53
280	-72.78	75.4	21118.	148.2	86.53

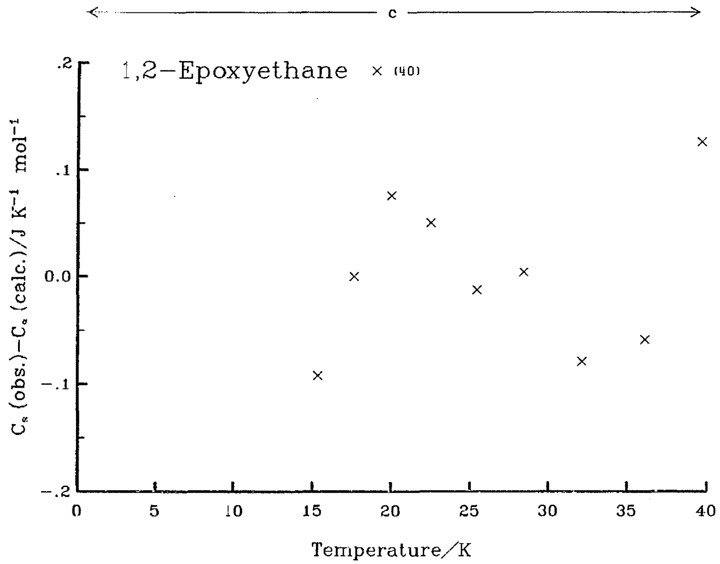

FIG. 100. Deviation plot for 1,2-epoxyethane, c, 0–40 K.

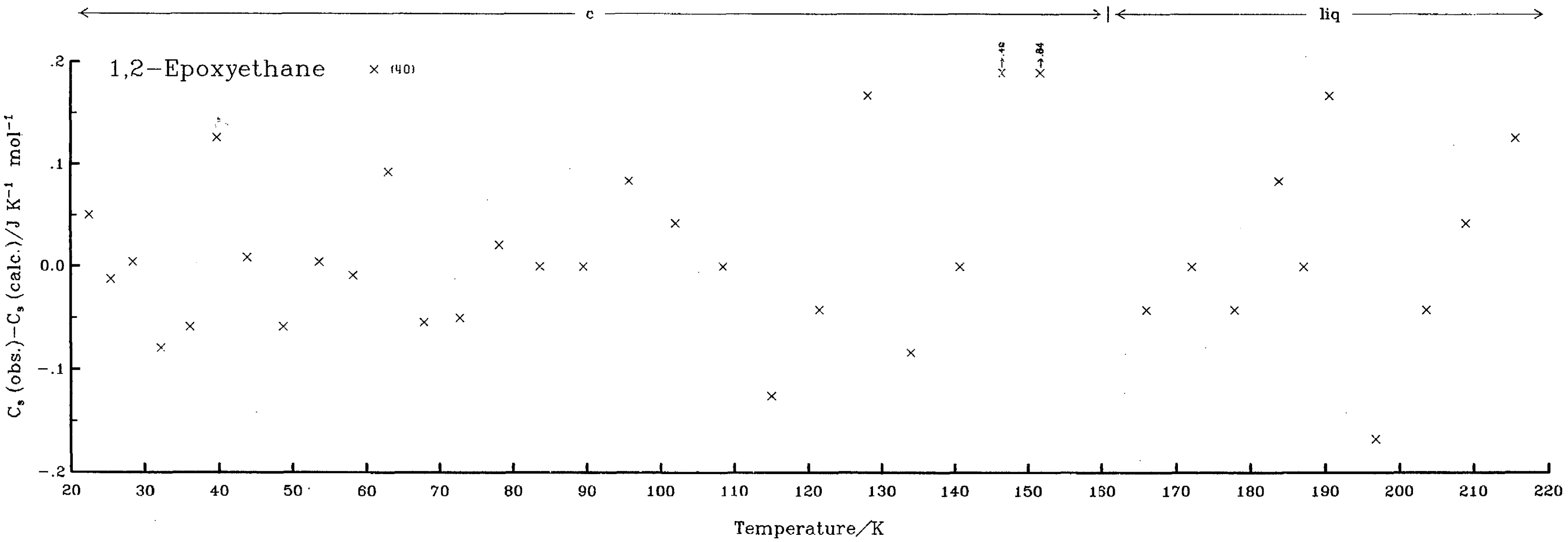

FIG. 101. Deviation plot for 1,2-epoxyethane, c, l, 20–220 K.

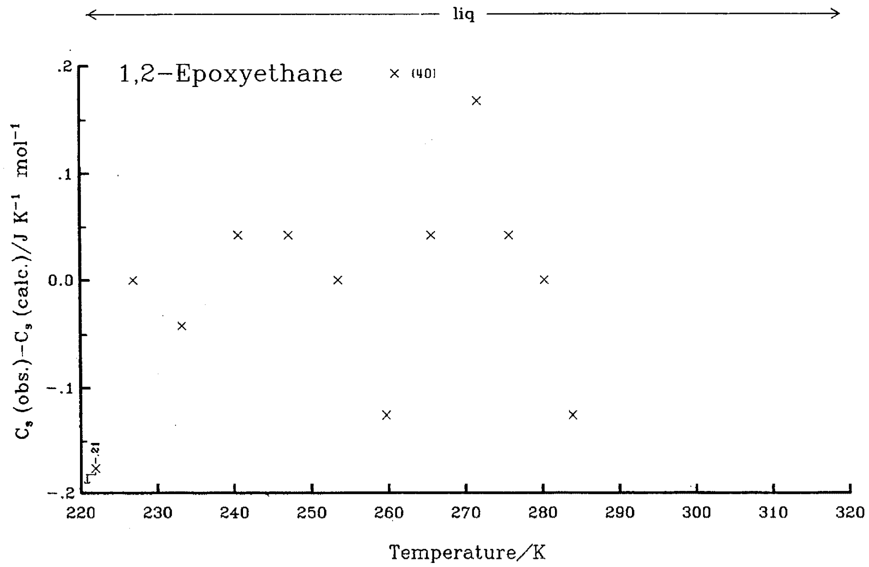

FIG. 102. Deviation plot for 1,2-epoxyethane, 1, 220–290 K.

34. 1,2-Epoxypropane (Propylene Oxide)

Table 136 identifies two sources of heat capacity data for 1,2-epoxypropane. Both sets of data were measured with adiabatic calorimeters. The apparatus used by Oetting [63] had previously been described by Stull [313], Hildenbrand, Kramer, McDonald, and Stull [314], Oetting and McDonald [315], and Oetting [62]. Beaumont, Clegg, Gee, Herbert, Marks, Roberts, and Sims [316] reported heat capacity values and several derived properties for several polymers of epoxyethane and epoxypropane in addition to those of epoxypropane monomer. They listed only the smoothed values at multiples of 10 K.

Oetting obtained the triple point of 161.22 ± 0.05 K and the enthalpy of fusion of 6533 ± 7 J mol^{-1}, while Beaumont et al. found 161.25 K and 6585 ± 20 J mol^{-1}, respectively. The heat capacity values of Beaumont et al., in the range of overlap, ran 2 to 5 J K^{-1} mol^{-1} higher than those of Oetting. Beaumont et al. rounded their tabulated heat capacity values to about 1 J K^{-1} mol^{-1}, but the systematic difference between the two sets of data is probably larger than the calorimetric errors. The origin of the discrepancy must therefore lie in the samples used. The data of Oetting [63] were adopted for Tables 137 and 138. Both sets of investigators found large pre-melting effects and so points above 144.86 K were not used in the least squares fit. The thermometer used by Beaumont et al. was calibrated in terms of the IPTS-48. Oetting did not specify his temperature scale, and therefore no scale corrections were applied to his data.

The 1,2-epoxypropane molecule has an asymmetric carbon atom. Both sets of reported heat capacities refer to the racemic combination. There is no direct evidence on the nature of the interaction between D- and L-isomers in the crystal. In order to obtain agreement between the third law entropy and the entropy calculated from the partition function of the perfect gas, Oetting found it necessary to add $R \ln 2$ to the value calculated from the calorimetric data. This implies that the crystal at 0 K is a random solution of the optically active forms. The $R \ln 2$ term was retained for the entropy listed in Table 138.

Beaumont et al. did not carry out measurements below 90 K. They estimated 48.5 J K^{-1} mol^{-1} for the entropy of epoxypropane at 90 K by the method of Kelley, Parks, and Huffman [7] taking epoxyethane as the standard. The addition of $R \ln 2$ gives 54.3 J K^{-1} mol^{-1}. S_{90} from Table 138 is 52.61 J K^{-1} mol^{-1}.

TABLE 136. Sources of Heat Capacity Data for 1,2-Epoxypropane

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Oetting	1964	c(11–154),l(166–301)	adiabatic	C	sample from Dow Chemical Co., dried with Drierite, then fract. distill, 99.94$^{c\#}$mol%	127	no	[63]
Beaumont, Clegg, Gee, Herbert, Marks, Roberts & Sims	1966	c(90–160),l(170–300)	adiabatic	C	dried with CaH_2, fract. distill, >99.9 mol%			[316]

TABLE 137. Parameters for Heat Capacity of DL-1,2-Epoxypropane

Phase	c	c	c	c	c	l
Data Points						
Number	14	20	9	22	65(8)	62(4)
Temp./K	11.2 - 22.7	24.0 - 57.2	62.5 - 89.9	92.5 -144.9	11.2 -144.9	166.4 -301.4
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 - 23.0	23.0 - 60.0	60.0 - 95.0	95.0 -161.22	0 -161.22	161.22-305.0
a_i		-16.432	25.70	54.65		168.05
b_i x 10		13.179	-0.619	-5.581		-6.986
c_i x 10^3		-3.827	7.060	7.8815		2.4593
d_i x 10^5	169.54	-4.367	-3.688	-2.4313		-0.2187
e_i x 10^7	-332.5					
Deviations						
Average, d	0.000	-0.092	0.075	-0.004	0.000	0.000
R.M.S., $r(\sigma)$	0.272	0.389	0.251	0.109	0.293(0.314)	0.134(0.138)
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.15	0.25	0.25	0.20		0.35
$\delta(H-H_0)$	1.8	9.	13.	18.		57.
$\delta(S)$	0.11	0.3	0.3	0.3		0.4
$\delta(G-H_0)/T$	0.04	0.09	0.10	0.10		0.11

TABLE 138. Thermodynamic Functions of DL–1,2–Epoxypropane C_3H_6O $M = 58.080$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	-5.763	0.000	0.00	5.76	0.00
10	-5.888	0.357	3.57	6.24	1.36
15	-6.156	1.094	16.41	7.25	4.04
20	-6.627	2.327	46.5	8.95	8.24
25	-7.321	4.02	100.6	11.34	13.44
30	-8.228	6.02	180.5	14.24	18.48
35	-9.31	8.14	284.8	17.45	23.13
40	-10.54	10.28	411.2	20.82	27.37
45	-11.87	12.39	557.7	24.26	31.14
50	-13.28	14.44	721.8	27.72	34.44
60	-16.26	18.22	1093.0	34.47	39.43
70	-19.32	21.53	1506.8	40.84	43.31
80	-22.39	24.48	1958.8	46.87	47.05
90	-25.43	27.18	2446.6	52.61	50.43
100	-28.42	29.66	2965.6	58.08	53.34
110	-31.36	31.94	3513.6	63.30	56.26
120	-34.23	34.09	4090.8	68.32	59.16
130	-37.04	36.12	4696.2	73.17	61.88
140	-39.79	38.05	5327.3	77.84	64.28
150	-42.48	39.87	5980.2	82.35	66.21
160	-45.11	41.56	6649.5	86.67	67.53
161.22	-45.42	41.76	6732.0	87.83	67.65
		Liquid			
161.22	-45.42	82.28	13265.0	127.70	110.18
170	-49.82	83.70	14229.7	133.53	109.62
180	-54.65	85.1	15323.7	139.78	109.23
190	-59.29	86.4	16415.	145.68	109.10
200	-63.75	87.5	17506.	151.28	109.21
210	-68.04	88.6	18600.	156.62	109.55
220	-72.19	89.5	19698.	161.72	110.10
230	-76.19	90.4	20803.	166.63	110.86
240	-80.05	91.3	21916.	171.37	111.81
250	-83.80	92.2	23040.	175.96	112.93
260	-87.43	93.0	24175.	180.5	114.22
270	-90.95	93.8	25324.	184.8	115.66
280	-94.38	94.6	26489.	189.0	117.24
290	-97.71	95.4	27670.	193.2	118.94
298.15	-100.37	96.1	28645.	196.5	120.41
300	-100.96	96.2	28868.	197.2	120.76

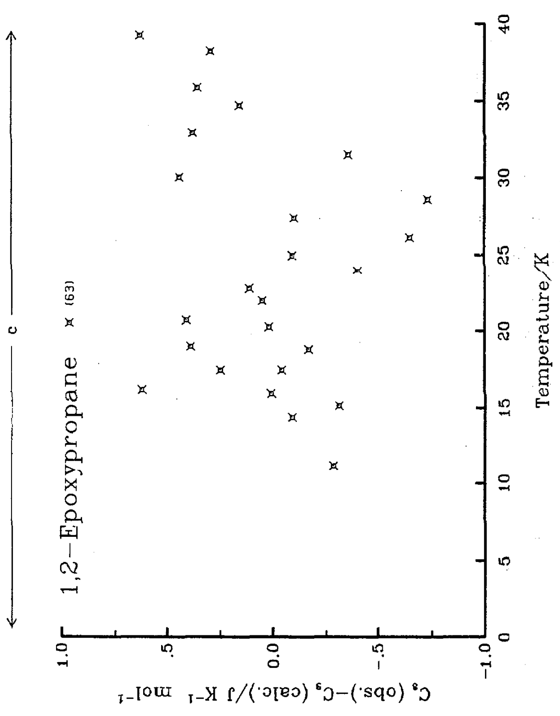

FIG. 103. Deviation plot for 1,2-epoxypropane, c, 0–40 K.

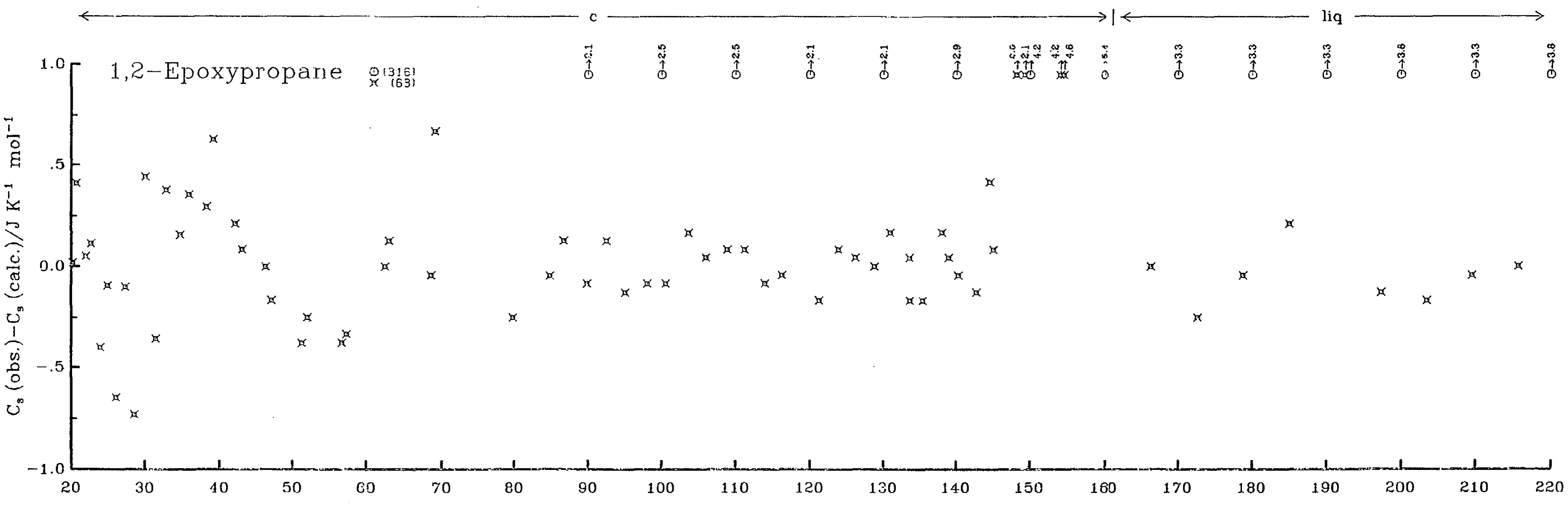

FIG. 104. Deviation plot for 1,2-epoxypropane, c, l, 20–220 K.

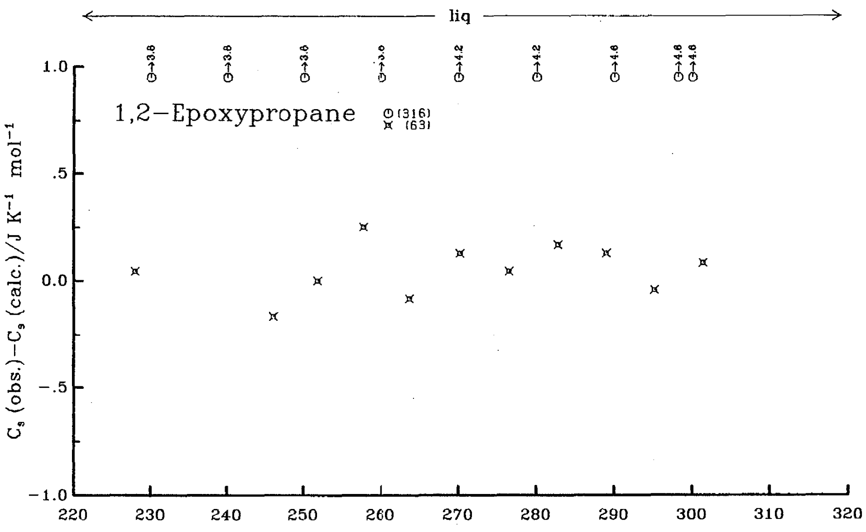

FIG. 105. Deviation plot for 1,2-epoxypropane, l, 220–300 K.

35. 1,2-Epoxybutane (Butylene Oxide)

All data for this compound were taken from Douslin, Good, Finke, Messerly, Osborn, Harrison, and Moore [81]. Their sample was purified by means of a preparative-scale gas chromatograph. The work was done at the Bartlesville Energy Research Center and the thermal measurements were made with a modern adiabatic calorimeter of high accuracy. Corrections were made for the vaporization of the sample into the gas space in the calorimeter.

All of the reported heat capacity values, except one, were used in the least squares fit of the parameters. The highest measured temperature for the crystal was 134.85 K which is about 9 K below the triple point. The thermodynamic properties in Table 141 which were calculated from the parameters in Table 140 were close to those given in the table of smoothed values in the Bartlesville report, except in the region between 130 K and the triple point. At 143.87 K, for example, the heat capacity of the crystal is given as 78.63 J K^{-1} mol^{-1} in the report and as 82.39 J K^{-1} mol^{-1} in Table 135. The values for both tables in this region are based on an extrapolation of lower temperature data. Douslin et al. stated that corrections for the effect of pre-melting had been applied to their smoothed values.

They reported an enthalpy of fusion of 6714.1±0.2 J mol^{-1} at the triple point. They used their extrapolated heat capacity data for the crystal in converting the measured heat input to enthalpy of fusion in equation (56). The use of the heat capacity values from Table 141 gives 6695. J mol^{-1} for the enthalpy of fusion. This was therefore used in Table 141 for internal consistency with the measured data.

TABLE 139. Sources of Heat Capacity Data for 1,2-Epoxybutane

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Douslin, Good, Finke, Messerly, Osborn Harrison & Moore	1973	c(12–235),l(137–322)	adiabatic	C	commercial sample, specially purified, 99.997^{g} mol%, 99.93^{c} mole%	65	I–68	[81]

TABLE 140. Parameters for Heat Capacity of DL–1,2–Epoxybutane

Phase	c	c	c	c	c	l
Data Points						
Number	5	16	11	9	41(11)	24(5)
Temp./K	11.7 – 14.7	15.2 – 45.6	50.2 – 98.9	102.2 –134.8	11.7 –134.8	136.8 –322.5
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 – 15.0	15.0 – 50.0	50.0 –100.0	100.0 –143.87	0 –143.87	143.87–325.0
a_i		0.559	–45.378	626.291		163.86
b_i x 10		–4.9611	31.1745	–216.3934		–3.2284
c_i x 10^3		76.063	–42.1588	301.2331		0.42934
d_i x 10^5	262.95	–155.955	30.3010	–182.4465		0.29356
e_i x 10^7	–665.0	106.706	–8.5053	41.2513		–0.04629
Deviations						
Average, d	0.002	–0.002	0.000	0.003	0.000	0.000
R.M.S., $r(\sigma)$	0.013	0.025	0.025	0.017	0.021(0.025)	0.038(0.042)
Estimated Uncertainty in Tabulated Values						
$\delta(C)$	0.02	0.03	0.04	0.06		0.10
$\delta(H-H_0)$	0.1	1.1	2.3	3.5		19.
$\delta(S)$	0.007	0.04	0.05	0.05		0.1
$\delta(G-H_0)/T$	0.003	0.015	0.017	0.019		0.03

TABLE 141. Thermodynamic Functions of DL-1,2-Epoxybutane C_4H_8O $M = 72.107$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
		Crystal			
0	0.000	0.000	0.00	0.000	0.000
10	-0.186	0.524	5.24	0.710	1.964
15	-0.571	1.545	23.18	2.117	5.508
20	-1.220	3.120	62.39	4.340	10.293
25	-2.121	5.072	126.80	7.192	15.496
30	-3.235	7.243	217.3	10.478	20.668
35	-4.521	9.512	332.9	14.034	25.519
40	-5.940	11.793	471.7	17.734	29.921
45	-7.459	14.03	631.4	21.491	33.904
50	-9.051	16.21	810.4	25.258	37.658
60	-12.377	20.36	1221.6	32.737	44.325
70	-15.807	24.18	1692.8	39.991	49.777
80	-19.268	27.68	2214.7	46.952	54.505
90	22.718	30.91	2781.5	53.623	58.797
100	-26.130	33.89	3389.5	60.025	62.74
110	-29.493	36.69	4035.7	66.181	66.48
120	-32.800	39.32	4718.4	72.119	70.04
130	-36.046	41.82	5437.1	77.871	73.84
140	-39.236	44.29	6200.8	83.527	79.33
143.87	-40.457	45.27	6513.5	85.730	82.39
		Liquid			
143.87	-40.457	91.81	13208.5	132.27	133.06
150	-44.328	93.49	14022.8	137.81	132.66
160	-50.449	95.92	15346.9	146.36	132.19
170	-56.336	98.04	16667.3	154.36	131.94
180	-62.00	99.93	17986.5	161.90	131.92
190	-67.45	101.61	19306.5	169.04	132.12
200	-72.71	103.15	20630.	175.82	132.54
210	-77.78	104.56	21958.	182.31	133.18
220	-82.68	105.88	23294.	188.52	134.03
230	-87.42	107.13	24639.	194.50	135.08
240	-92.01	108.32	25996.	200.28	136.33
250	-96.46	109.47	27367.	205.87	137.77
260	-100.78	110.58	28752.	211.30	139.39
270	-104.97	111.69	30155.	216.60	141.17
280	-109.06	112.77	31576.	221.77	143.11
290	-113.03	113.86	33018.	226.82	145.20
298.15	-116.20	114.73	34208.	230.87	147.00
300	-116.91	114.94	34481.	231.78	147.41
310	-120.70	116.0	35966.	236.66	149.74
320	-124.41	117.1	37476.	241.45	152.17

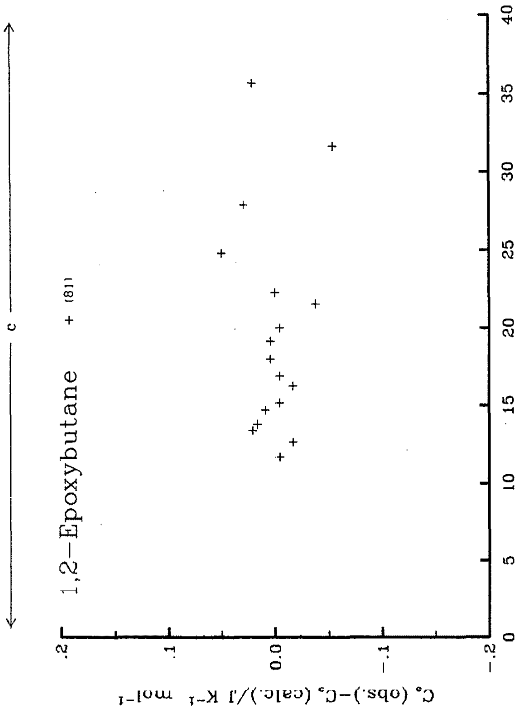

FIG. 106. Deviation plot for 1,2-epoxybutane, c, 0–40 K.

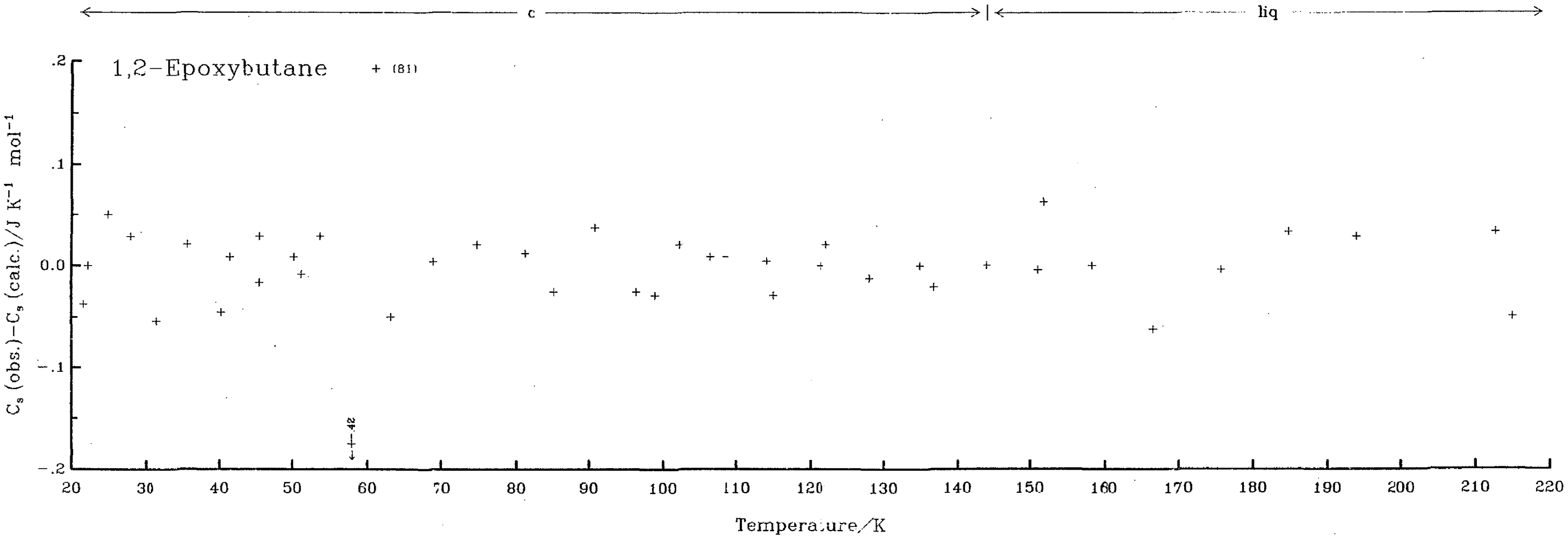

FIG. 107. Deviation plot for 1,2-epoxybutane, c, 1, 20–220 K.

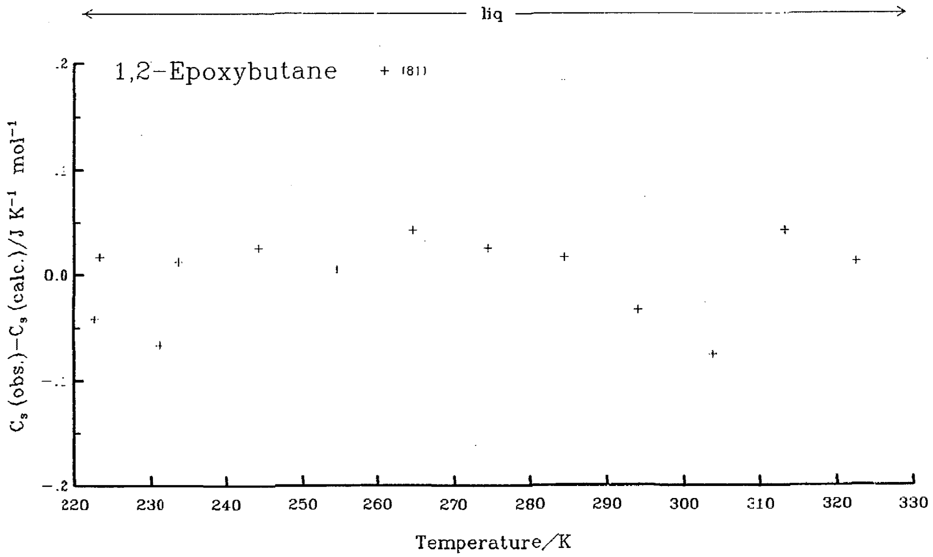

FIG. 108. Deviation plot for 1,2-epoxybutane, 1, 220–300 K.

36. Furan (Oxole)

All data used for this compound were taken from Guthrie, Scott, Hubbard, Katz, McCullough, Gross, Williams, and Waddington [82] of the Bureau of Mines Petroleum Experiment Station in Bartlesville. The original measurements were made in terms of the NBS–39 temperature scale below 90 K and of the IPTS–68 above 90 K. Their data were converted to IPTS–68 before calculating the parameters in the heat capacity equations.

Guthrie et al. found a small lambda point between 50 and 60 K and a crystal phase transition at 150.0 K. The observed heat capacity in the region from 80 to 160 K showed some dependence on the thermal history of the sample. The reported values were obtained after conditioning the sample by cooling it slowly through the transition region for periods of greater than one day. All auxiliary data needed to convert C_s to C_p were also taken from Guthrie et al.

Guthrie et al. measured the heat of fusion and obtained 3802 J mol^{-1}. Brooks and Pilcher [232] obtained 187 K for the triple point and 3720–400 J mol^{-1} for the enthalpy of fusion with a calorimeter designed to test sample purity. Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan [317] reported a melting point of 187.6 K.

The presence of a solid phase transition about 30 K below the triple point and the low entropy of fusion of c,I confirm that furan is a plastic crystal.

TABLE 142. Sources of Heat Capacity Data for Furan

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Guthrie, Scott, Hubbard, Katz, McCullough, Gross, Williamson & Waddington	1952	c(12–184),l(191–299)	adiabatic	C	fract. distilled in N_2 atm., then distilled in absence of other gases, 99.98^c mol%	97	corr	[82]

TABLE 143. Parameters for Heat Capacity of Furan

Phase	c,II	c,II	c,II	c,II	c,II	c,I	c,I
Data Points							
Number	7	28	9	14	58(8)	10	6
Temp./K	11.7 – 16.9	17.7 – 59.0	59.2 – 89.0	93.8 –142.2	11.7 –142.2	153.3 –163.8	166.8 –183.8
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0 – 17.0	17.0 – 59.1	59.1 – 90.0	90.0 –150.0	0 –150.0	150.0 –165.0	165.0 –187.54
a_i		–9.23	30.08	14.87		–9041.85	–12676.60
b_i x 10		10.995	–1.590	6.636		1717.113	2243.007
c_i x 10^3		–1.104	7.716	–4.926		–1079.361	–1316.285
d_i x 10^5	370.5	–6.36	–4.303	1.677		226.393	257.731
e_i x 10^7	–1122.						
Deviations							
Average, d	0.019	–0.011	0.022	–0.046	0.000	0.010	–0.016
R.M.S., $r(\sigma)$	0.054	0.059	0.100	0.059	0.059(0.063)	0.054	0.205
Estimated Uncertainty in Tabulated Values							
$\delta(C)$	0.10	0.2	0.3	0.5		0.6	0.8
$\delta(H-H_0)$	0.5	8.4	13.	33.		34.	39.
$\delta(S)$	0.04	0.25	0.3	0.4		0.4	0.4
$\delta(G-H_0)/T$	0.017	0.11	0.11	0.12		0.12	0.12

Phase	c,I	l	l
Data Points			
Number	16(6)	23(4)	23(4)
Temp./K	153.3 –183.8	191.0 –299.1	191.0 –299.1
Parameters for	C_s	C_s	C_p
Temp./K	150.0 –187.54	187.54–300.0	187.54–300.0
a_i		140.30	138.35
b_i x 10		–5.442	–5.164
c_i x 10^3		2.0979	1.9674
d_i x 10^5		–0.18826	–0.16794
Deviations			
Average, d	0.000	0.000	0.000
R.M.S., $r(\sigma)$	0.134(0.167)	0.033(0.034)	0.029(0.033)
Estimated Uncertainty in Tabulated Values			
$\delta(C)$		0.4	0.4
$\delta(H-H_0)$		60.	60.
$\delta(S)$		0.44	0.44
$\delta(G-H_0)/T$		0.13	0.13

TABLE 144. Thermodynamic Functions of Furan

C_4H_4O $M = 68.075$

T/K	$(G-H_0)/T$	$(H-H_0)/T$	$H-H_0$	S	C_s	C_p
	J K^{-1} mol^{-1}		J mol^{-1}		J K^{-1} mol^{-1}	
			Crystal II			
0	0.000	0.000	0.00	0.000	0.000	0.000
10	-0.253	0.704	7.04	0.957	2.593	2.593
15	-0.761	2.000	30.00	2.760	6.874	6.874
20	-1.579	3.838	76.8	5.417	11.81	11.81
25	-2.656	5.913	147.8	8.569	16.57	16.57
30	-3.924	8.07	242.0	11.99	21.04	21.04
35	-5.329	10.22	357.7	15.55	25.17	25.17
40	-6.832	12.33	493.1	19.16	28.91	28.91
45	-8.402	14.36	646.1	22.76	32.22	32.22
50	-10.016	16.29	814.4	26.31	35.03	35.03
60	-13.303	19.78	1186.7	33.08	39.02	39.02
70	-16.580	22.74	1591.9	39.32	42.00	42.00
80	-19.789	25.32	2025.8	45.11	44.71	44.71
90	-22.906	27.60	2484.4	50.51	46.90	46.90
100	-25.921	29.63	2962.7	55.55	48.74	48.74
110	-28.831	31.45	3459.3	60.28	50.58	50.58
120	-31.640	33.12	3974.8	64.76	52.55	52.55
130	-34.354	34.70	4511.	69.05	54.73	54.73
140	-36.98	36.22	5070.	73.20	57.24	57.24
150.0	-39.53	37.71	5657.	77.25	60.17	60.17
			Crystal I			
150.0	-39.53	51.36	7704.	90.89	69.99	69.99
160	-42.89	52.66	8425.	95.55	73.37	73.37
170	-46.12	53.96	9173.	100.08	76.2	76.2
180	-49.24	55.29	9952.	104.53	80.8	80.8
187.54	-51.53	56.53	10601.	108.06	93.3	93.3
			Liquid			
187.54	-51.53	76.80	14403.	128.33	99.6	99.6
190	-52.54	77.09	14648.	129.63	99.72	99.74
200	-56.52	78.24	15648.	134.76	100.32	100.33
210	-60.36	79.31	16655.	139.67	101.10	101.12
220	-64.08	80.32	17671.	144.40	102.07	102.08
230	-67.67	81.29	18697.	148.96	103.21	103.22
240	-71.15	82.23	19735.	153.38	104.51	104.52
250	-74.52	83.1	20787.	157.67	105.95	105.97
260	-77.80	84.1	21855.	161.86	107.54	107.57
270	-80.99	85.0	22939.	165.95	109.25	109.29
280	-84.10	85.9	24040.	170.0	111.07	111.14
290	-87.13	86.8	25160.	173.9	113.00	113.09
298.15	-89.54	87.5	26088.	177.0	114.64	114.76
300	-90.08	87.7	26300.	177.8	115.02	115.15

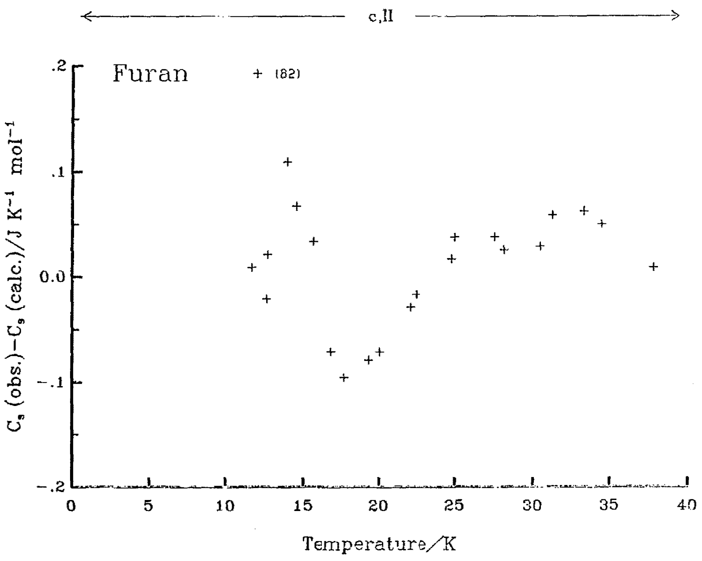

FIG. 109. Deviation plot for furan, c,II, 0–30 K.

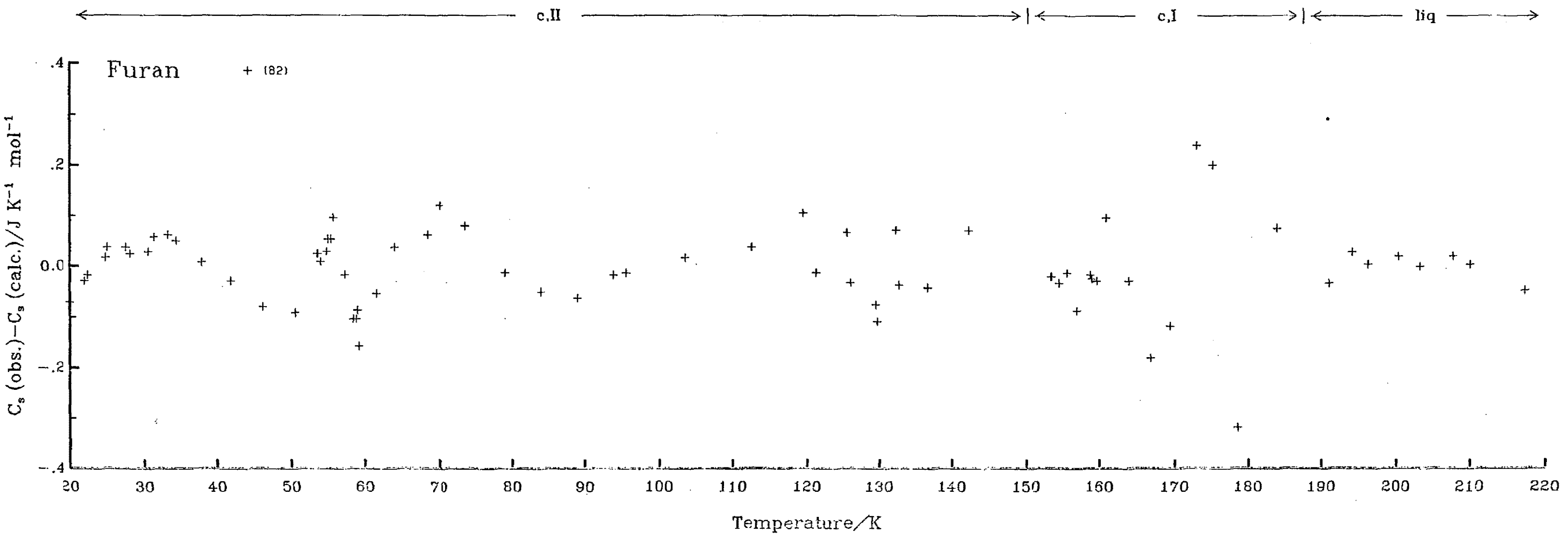

FIG. 110. Deviation plot for furan, c,II, c,I, l, 20–220 K.

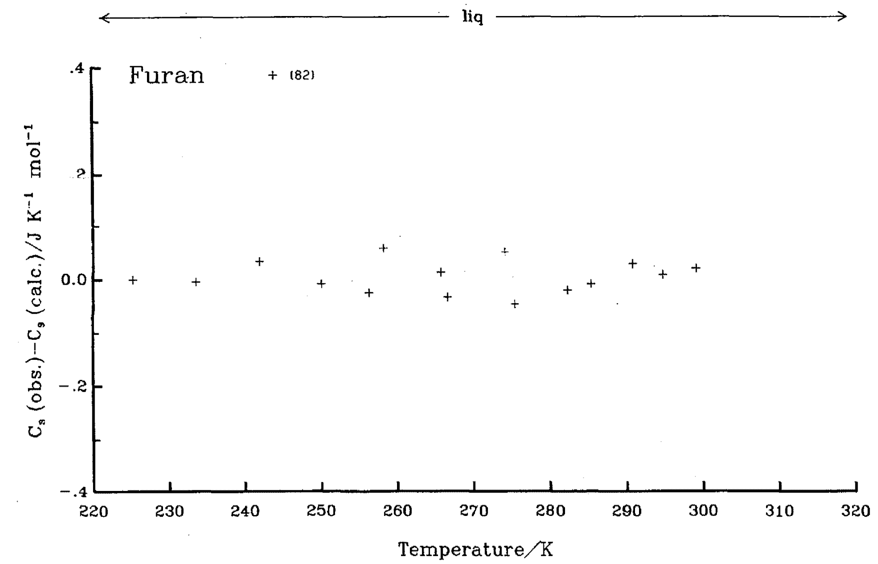

FIG. 111. Deviation plot for furan, 1, 270–300 K.

37. Tetrahydrofuran

All data were taken from the work of Lebedev, Rabinovich, Milov, and Lityagov [318]. These were obtained with modern techniques on a high purity sample. An attempt was made to prepare the glass form of tetrahydrofuran, but it was not successful.

Lebedev et al. gave a table of smoothed thermodynamic properties derived from these measurements. The heat capacities were read from a graph drawn through the experimental points and the other properties were calculated by numerical integration. Their values were within the experimental uncertainties of those in Table 147. A large pre-melting effect was observed starting about 4 degrees below the triple point.

Extrapolation from 9 to 0 K was made with a Debye function having a characteristic temperature of 143.6 K. This gave an entropy of 0.3009 J K^{-1} mol^{-1} at 10 K, compared to 0.319 J K^{-1} mol^{-1} from Table 147.

Using their thermal data in combination with other auxiliary data, Lebedev et al. calculated the third law entropy of tetrahydrofuran in the perfect gas state at 298.15 K to be 288 J K^{-1} mol^{-1}. Previously Scott [320] calculated the entropy to be 302 J K^{-1} mol^{-1} from the molecular energy states. They could not provide an explanation of the discrepancy. If neither calculation contains a significant error it must be caused by some randomness in molecular arrangement in the crystal at 0 K.

TABLE 145. Sources of Heat Capacity Data for Tetrahydrofuran

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Kurnakov & Voskresenskaya	1936							[227]
Conti, Gianni, Matteoli & Mengheri	1976	l(298)	Calvet	C	not stated			[172]
Lebedev,Rabinovich, Milov & Lityagov	1978	c(9–164),l(165–323)	adiabatic	C	synthesized, treated with Na–K and distilled, 99.80^c mol%	102	I–68	[318]
Kiyohara, D'Arcy & Benson	1979	l(298)	flow	C	commercial sample, purified by glc, dried with molecular sieve			[319]

TABLE 146. Parameters for Heat Capacity of Tetrahydrofuran

Phase	c	c	c	c	c	l
Data Points						
Number	8	16	22	6*	52*(11)	18
Temp./K	8.8- 14.8	16.1- 53.2	55.7–119.7	120.9–164.76	8.8–164.76	161.6–197.4
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	0- 16.0	16.0- 55.0	55.0–120.0	120.0–164.76	0–164.76	161.0–200.0
a_i		1.915	-80.933	-149.69		322.07
b_i x 10		-7.4577	45.9141	64.240		-32.402
c_i x 10^3		72.9404	-65.6739	-77.048		16.041
d_i x 10^5	96.31	-128.518	45.4103	42.106		-2.604
e_i x 10^7	-7.95	76.497	-11.761	-8.398		
Deviations						
Average, d	0.014	–0.012	0.005	0.024	0.000	–0.005
R.M.S.,r(δ)	0.037	0.095	0.119	0.257	0.091(0.103)	0.063
Estimated Uncertainties in Tabulated Values						
$\delta(C)$	0.02	0.05	0.1	0.8		0.15
$\delta(H\text{-}H_0)$	0.3	2.0	7.0	36.		50.
$\delta(S)$	0.02	0.07	0.1	0.3		0.5
$\delta(G\text{-}H_0)/T$	0.01	0.03	0.04	0.05		0.06

Phase	l	l
Data Points		
Number	32	50(6)
Temp./K	200.3-322.6	161.6–322.6
Parameters for	C_s	C_s
Temp./K	200.0–320.0	161.0–320.0
a_i	185.21	
b_i x 10	-9.632	
c_i x 10^3	3.536	
d_i x 10^5	-0.3328	
Deviations		
Average, d	0.005	0.000
R.M.S.,r(δ)	0.144	0.112(0.120)
Estimated Uncertainty in Tabulated Values		
$\delta(C)$	0.2	
$\delta(H\text{-}H_0)$	60.	
$\delta(S)$	0.6	
$\delta(G\text{-}H_0)/T$	0.08	

*Includes five extrapolated values from 130 to 164.76 K.

TABLE 147. Thermodynamic Functions of Tetrahydrofuran

C_4H_8O $M = 72.107$

T/K	$(G-H_0)/T$ J K^{-1} mol^{-1}	$(H-H_0)/T$ J K^{-1} mol^{-1}	$H-H_0$ J mol^{-1}	S J K^{-1} mol^{-1}	C_s J K^{-1} mol^{-1}
		Crystal			
0	0.000	0.000	0.00	0.000	0.000
5	-0.010	0.030	0.15	0.040	0.120
10	-0.080	0.239	2.39	0.319	0.955
15	-0.269	0.805	12.07	1.073	3.210
20	-0.634	1.87	37.44	2.51	7.118
25	-1.21	3.38	84.45	4.58	11.766
30	-1.98	5.18	155.54	7.16	16.685
35	-2.93	7.18	251.19	10.10	21.542
40	-4.02	9.26	370.5	13.28	26.12
50	-6.54	13.46	673.0	20.00	34.14
60	-9.35	17.49	1049.7	26.85	40.97
70	-12.34	21.24	1486.6	33.57	46.18
80	-15.40	24.63	1970.0	40.02	50.39
90	-18.48	27.70	2493.2	46.18	54.21
100	-21.54	30.54	3054.1	52.09	57.96
110	-24.58	33.20	3652.4	57.79	61.69
120	-27.58	35.72	4287.0	63.30	65.15
130	-30.53	38.12	4955.1	68.65	68.5
140	-33.44	40.4	5659.0	73.87	72.3
150	-36.31	42.7	6402.	79.0	76.3
160	-39.14	44.9	7184.	84.0	80.0
164.76	-40.47	45.9	7568.	86.4	81.6
		Liquid			
164.76	-40.47	97.8	16108.4	138.24	107.21
170	-43.53	98.1	16669.3	141.59	106.90
180	-49.15	98.5	17737.0	147.69	106.71
190	-54.49	99.0	18804.9	153.46	106.92
200	-59.58	99.4	19876.2	159.0	107.4
210	-64.44	99.8	20953.0	164.2	108.0
220	-69.09	100.2	22038.	169.3	109.0
230	-73.55	100.6	23134.	174.1	110.2
240	-77.84	101.0	24243.	178.9	111.7
250	-81.97	101.5	25368.	183.4	113.4
260	-85.96	102.0	26511.	187.9	115.3
270	-89.82	102.5	27675.	192.3	117.4
280	-93.56	103.1	28860.	196.6	119.7
290	-97.18	103.7	30068.	200.9	122.1
298.15	-100.07	104.2	31071.	204.3	124.1
300	-100.71	104.3	31301.	205.0	124.6
310	-104.14	105.0	32561.	209.2	127.2
320	-107.49	105.8	33847.	213.3	130.0

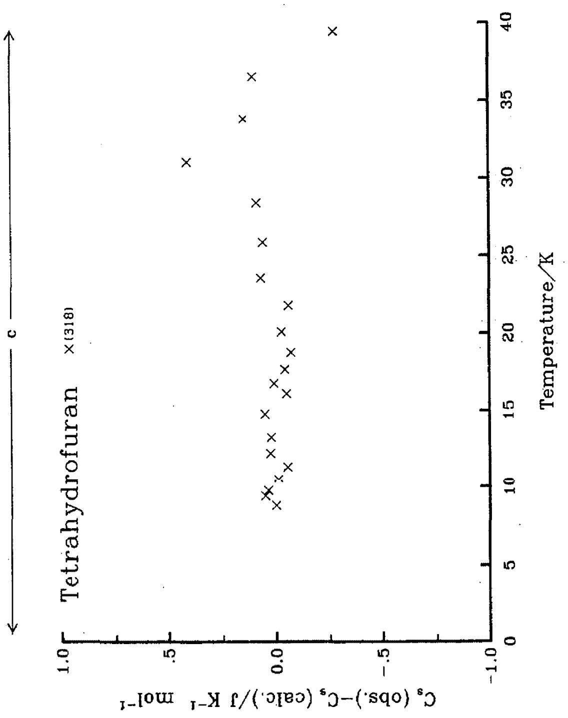

FIG. 112. Deviation plot for tetrahydrofuran, c, 0–40 K.

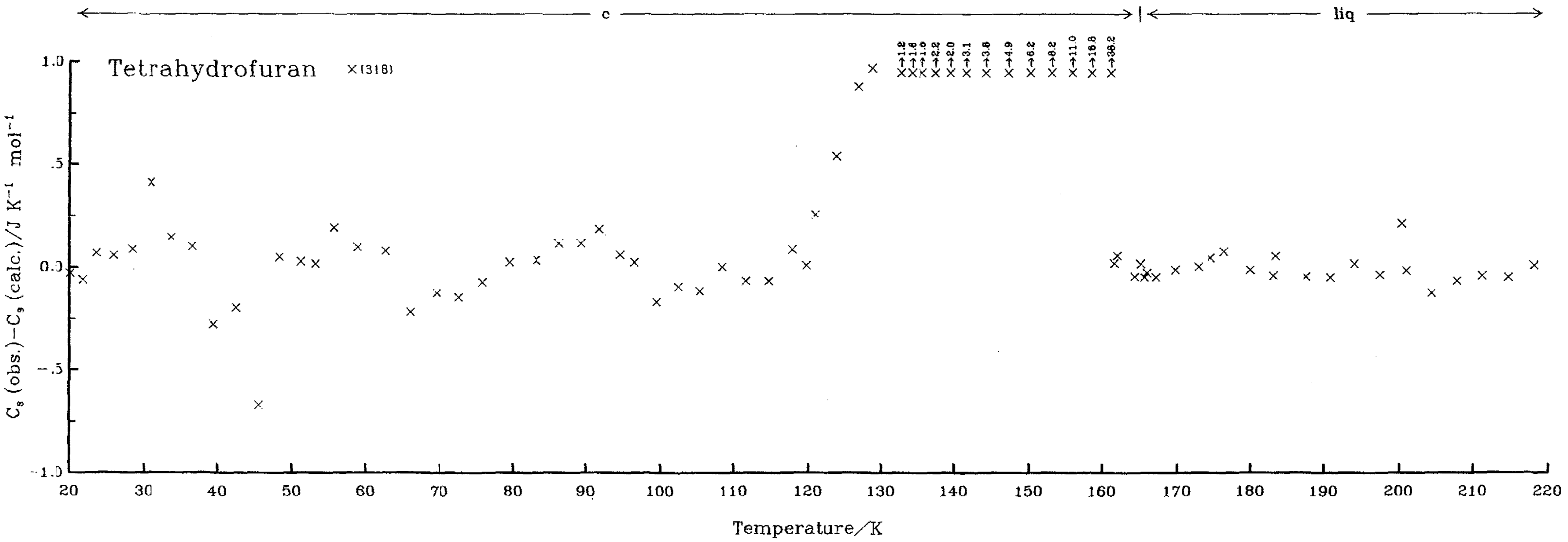

FIG. 113. Deviation plot for tetrahydrofuran, c, 1, 20–220 K.

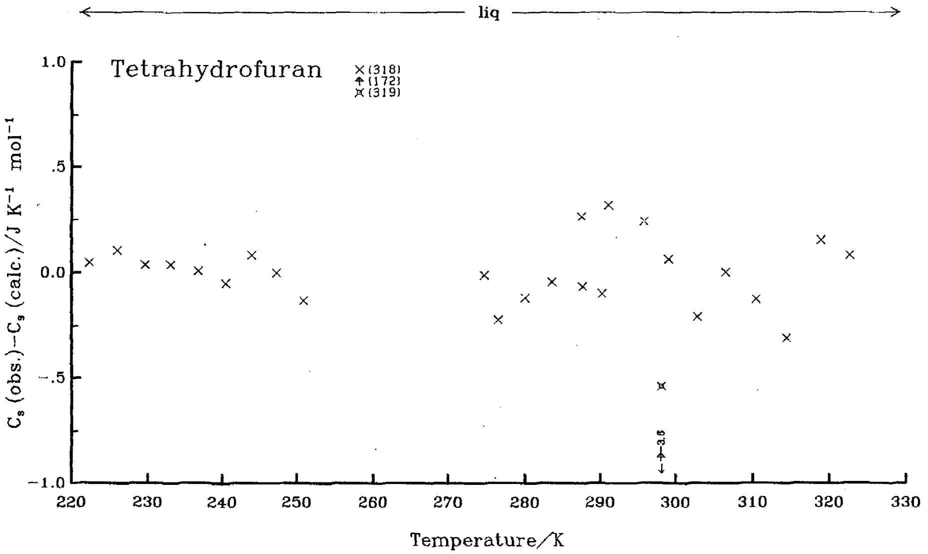

FIG. 114. Deviation plot for tetrahydrofuran, 1, 270–330 K.

38. 1,4-Dioxane

Selected properties of the crystal were based on the heat capacity data of Jacobs and Parks [47]. The data of Jacobs and Parks, Roth and Meyer [321] and Deshpande and Bhatgadde [117] were combined for the liquid phase.

Jacobs and Parks [47] found a solid phase transition at 272.9 K. They concluded that pre-melting effects caused the observed heat capacities for c,I to be too high. They suggested that the value 147 J K^{-1} mol^{-1} was better. Roth and Meyer [321] measured several values of the mean heat capacity in the range of 273 to 284 K. These ran 14 to 30% higher than the value recommended by Jacobs and Parks. The Jacobs and Parks value was adopted for Table 151.

The entropy and enthalpy of the crystal at 90 K were calculated by equations (4) and (5) of section 1.2.b. Jacobs and Parks estimated the entropy at 90 K to be 46.5 J K^{-1} mol^{-1} using the method of Kelley, Parks, and Huffman [7].

The molecular symmetry and existence of a phase transition 12 degrees below the c–l triple point suggests a plastic crystal for 1,4-dioxane. However, the entropy of fusion of 45.1 J K^{-1} mol^{-1} seems too large for this conclusion.

TABLE 148. Sources of Heat Capacity Data for 1,4–Dioxane

Author	Year	State(Temperature Range)	Type of Calorimeter	Type of Meas.	Preparation and Purity of Sample	Number of Points	Temp. Scale	Reference
Herz & Lorentz	1929	l(296)	drop	H	not stated			[322]
Roth & Meyer	1933	c(273–284), l(281–301)	drop	H		9	no	[321]
Jacobs & Parks	1934	c(93–276),l(289–298)	isoperibol	C	Eastman Kodak sample, fract. crystallized 8 times	20	no	[47]
Stallard & Amis	1952	l(313)	Dewar flask	C	not stated			[323]
Hyder Kahn & Subrahmanyam	1971	l(298,313)	Dewar flask	C	analytical grade, purified by "standard method"			[324]
Deshpande & Bhatgadde	1971	l(295–315)	adiabatic	C	distilled	3	no	[117]
Conti, Gianni, Matteoli & Mengheri	1976	l(298)	Calvet	C	not stated			[172]

TABLE 149. Reported Phase Transition Data for 1,4–Dioxane

Author	Year	Transition	T	Type	Enthalpy ΔH J mol^{-1}	Method	Reference
Anschutz & Broeker	1926	c,I⇌l	284.2	mp	11920.	t	[325]
Herz & Lorentz	1929	c,I⇌l			11880.	t	[322]
Roth & Meyer	1933	c,I⇌l	284.2	mp	12470.	c	[321]
Kraus & Vingee	1934	c,I⇌l	284.93	mp	10510.	t	[326]
Jacobs & Parks	1934	c,II⇌c,I	272.9	tp	23510.	c	[47]
		c,I⇌l	284.1	tp	12840.	c	
Gallaugher & Hilbert	1936	c,I⇌l	284.2	mp			[197]
SELECTED VALUES		c,II⇌c,I	272.9±0.2		23510.±100		
		c,I⇌l	284.93±0.05		12840.±80		

TABLE 150. Parameters for Heat Capacity of 1,4–Dioxane

Phase	c,II	c,II	c,II	c,II	c,I	l
Data Points						
Number	6	5	6	17(8)	1*	15(3)
Temp./K	92.5 –126.2	156.4 –198.0	224.6 –357.2	92.5 –257.2		288.7 –318.2
Parameters for	C_s	C_s	C_s	C_s	C_s	C_s
Temp./K	90.0 –150.0	150.0 –200.0	200.0 –272.9	90.0 –272.9	272.9 –284.93	284.93–320.0
a_i	30.23	–23.40	–614.2		147.3	949.6
b_i x 10	0.491	12.287	90.703			–55.137
c_i x 10^3	2.453	–6.125	–40.228			9.539
d_i x 10^5	–0.698	1.3668	6.1998			
Deviations						
Average, d	0.004	–0.007	0.000	0.000		0.000
R.M.S., $r(\sigma)$	0.176	0.117	0.398	0.255(0.352)		2.43(2.62)
Estimated Uncertainty in Tabulated Values						
δ(C)	0.5	0.6	1.0		10.	2.5
$\delta(H\text{–}H_0)$	301.	303.	312.		400.	425.
$\delta(S)$	3.0	3.0	3.0		3.1	3.2
$\delta(G\text{–}H_0)/T$	1.0	1.0	1.0		1.0	1.0

*Estimated value.

TABLE 151. Thermodynamic Functions of 1,4–Dioxane

$C_4H_8O_2$ $M = 88.106$

T/K	$(G\text{–}H_0)/T$	$(H\text{–}H_0)/T$	$H\text{–}H_0$	S	C_s
	J K^{-1} mol^{-1}		J mol^{-1}	J K^{-1} mol^{-1}	
		Crystal II			
90	–16.8	25.2	2270.	42.0	49.43
100	–19.6	27.8	2780.5	47.38	52.69
110	–22.3	30.2	3324.0	52.55	56.02
120	–25.1	32.5	3901.1	57.57	59.38
130	–27.8	34.7	4512.	62.5	62.73
140	–30.4	36.8	5156.	67.2	66.03
150	–33.0	38.9	5832.	71.9	69.23
160	–35.6	40.9	6540.	76.5	72.38
170	–38.1	42.8	7280.	80.9	75.62
180	–40.6	44.7	8053.	85.4	79.0
190	–43.1	46.6	8861.	89.7	82.7
200	–45.5	48.5	9708.	94.1	86.7
210	–48.0	50.5	10595.	98.4	90.7
220	–50.3	52.4	11520.	102.7	94.4
230	–52.7	54.3	12483.	107.0	98.2
240	–55.1	56.2	13487.	111.3	102.6
250	–57.4	58.2	14538.	115.5	107.8
260	–59.7	60.2	15648.	119.9	114.3
270	–62.0	62.3	16830.	124.4	122.5
272.9	–62.7	63.0	17189.	125.7	125.2
		Crystal I			
272.9	–62.7	149.2	40703.	211.8	147.
280	–66.5	149.1	41749.	215.6	147.
284.93	69.1	149.1	42475.	218.2	147.
		Liquid			
284.93	–69.1	194.2	55320.	263.3	153.0
290	–72.5	193.4	56096.	266.0	152.9
298.15	–77.9	192.3	57344.	270.2	153.6
300	–79.1	192.1	57628.	271.2	154.0
310	–85.4	190.9	59182.	276.3	157.
320	–91.4	189.9	60776.	281.3	162.

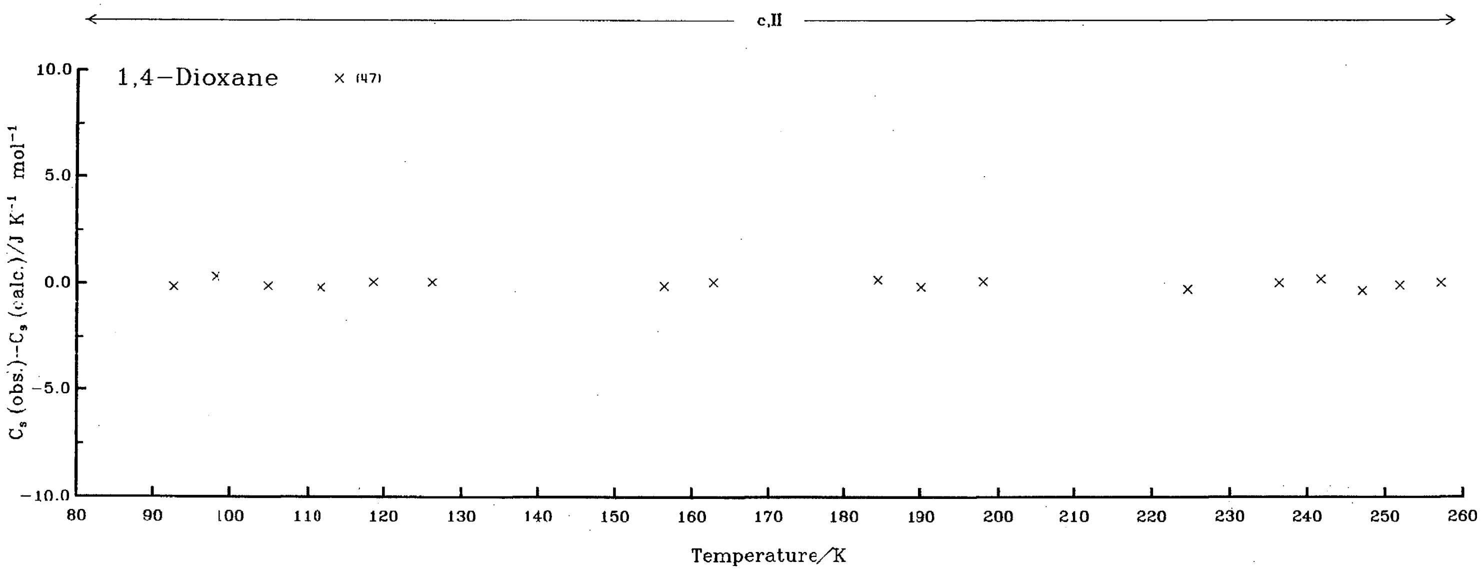

FIG. 115. Deviation plot for 1,4-dioxane, c, II, 90–260 K.

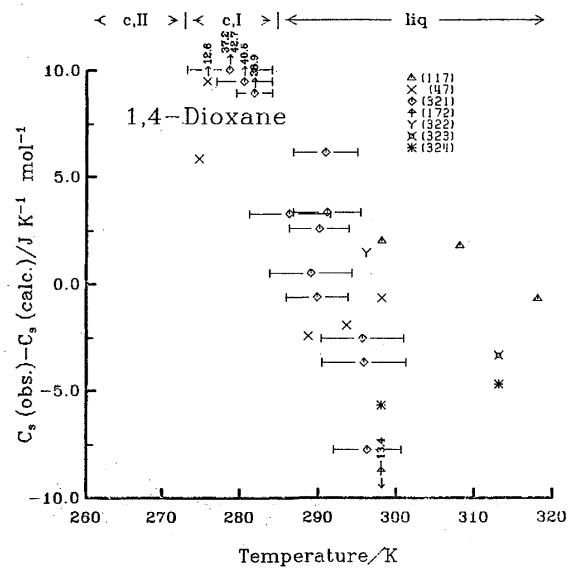

FIG. 116. Deviation plot for 1,4-dioxane, c,I, 1, 260–320 K.

39. Acknowledgment

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