

POLYMORPHISM IN MONOBROMOACETIC ACID AND THE
DIAGRAM OF STATE OF DICHLOROACETIC ACID AT
ELEVATED PRESSURES

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ABSTRACT

Piezometric measurements to 5000 atmospheres have shown that dichloroacetic acid occurs in only one crystalline form; monobromoacetic acid exists in three forms with triple points at about 50.5°C and 120 kg/cm² (liq, C I, C II) and 53°C and 260 kg/cm² (liq, C II, C III). The transitions C I to C II and C II to C III have negative temperature-pressure coefficients (dT/dP) and occur only at elevated pressures. No example has been previously reported of an organic compound which has two successive solid transitions with negative dT/dP coefficients such as were observed for monobromoacetic acid.

Values of dT/dP , ΔH , and ΔS , calculated from the piezometric data are given for the fusion of dichloroacetic acid and for the two solid transitions and the fusion (C III, liq) of monobromoacetic acid. An evaluation of purity of the acids from time-pressure data is discussed.

1. INTRODUCTION

This report is one of two papers [1] (4) resulting from an investigation conducted at the Université Libre de Bruxelles on the polymorphism of halogenated acetic acids. In this investigation, monobromo- and

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(4) Numbers in brackets refer to literature references at the end of this paper.

dichloroacetic acids were studied at pressures to 5000 atmospheres. The only previous study of a halogenated acid under pressure was by BRIDGMAN [3], who obtained the stable form and one of the metastable modifications (mp 50°C at 1 atm.) of monochloroacetic acid, but observed no solid-solid transitions.

Interest in these acids arose from a comparison of the melting points, at atmospheric pressure, of the halogenated fatty acids. The mono-, di-, and tri-halogen derivatives of an acid in which halogen atoms are substituted for hydrogens at the same carbon atom show a regularity in the melting point, with the iodine derivative melting higher than the bromine derivative, which in turn melts higher than the chlorine derivative [1, 2]. An exception to this rule is that monochloroacetic acid melts higher than monobromoacetic acid. A search was undertaken for an additional solid form of this acid with a melting point, at atmospheric pressure, higher than that of monochloroacetic acid.

In the high-pressure experiments described here, the phase diagrams to 2500 atmospheres in the region 10° to 90°C were established for monobromo- and dichloroacetic acids. Two additional forms of monobromoacetic acid were obtained which exist only under pressure. These two forms are of especial interest as they have negative temperature-pressure coefficients. This is the first organic compound reported to have two successive solid transitions with negative temperature-pressure coefficients.

2. PIEZOMETRIC METHOD

The name "piezometric" was proposed by TIMMERMANS [4] to describe the method for the determination of phase equilibria in which the substance is maintained at a constant temperature while the volume of the system is slowly increased and the resulting pressures are observed. During a phase transition the pressure remains constant because the change in volume of the substance compensates for the change in volume in the system. From the ΔV and P data thus obtained, the T - P phase diagram for the substance and the changes in enthalpy and entropy during solid-solid and liquid-solid transitions may be calculated.

Deffet, in a series of papers from the Université Libre [5, 9], starting in 1935, described the application of the piezometric method to compounds and mixtures. The present apparatus and procedure are essentially those described by Trappeniers[10], except as discussed below.

2.1. *Filling the Glass Vessel for Piezometric Measurements*

The procedure [5,10] used previously for filling glass vessels with samples for piezometric analysis was considered inadequate for the hygroscopic acids used in this work. Traces of water introduced during filling would accelerate the reaction of the acid with the mercury used to separate the sample from the hydraulic oil. In the altered procedure used here, the degassed substance was vacuum distilled into the vessel. The entire vessel, including a ground glass joint, was weighed and attached by the joint to the vacuum transfer system. The acid was distilled into the vessel and the narrow connection between the vessel and the joint fused. Reweighing the vessel plus sample and the detached ground joint gave the weight of substance. For the piezometric analysis, the acid was frozen at -78°C and the vessel then inverted with the tip under dry mercury. The tip was broken and the mercury allowed to fill the free volume. This vessel with the narrow neck at the bottom was then placed in a steel cylinder containing mercury. A small hole in the cap of this cylinder allowed excess mercury to escape. This hole also allowed pressure to be transmitted by the mercury without oil coming in contact with the sample. For further details see [10,11].

This method of filling also permitted the sample to be kept sealed in the vessel under anhydrous conditions and out of contact with mercury until needed for piezometric analysis. Since the procedures for degassing a substance and for drying the internal walls of a glass system are lengthy, considerable time is saved when degassed samples are transferred in vacuo, especially when several portions are sealed at one time.

2.2 *Apparatus and Procedure*

The sample in a small steel cylinder, 4 (figure 1), is maintained at a constant temperature in a thermostated bath. The mercury in this cylinder fills the space not occupied by the sample in the piezometric glass vessel. The hand pump, 1, is used to obtain hydraulic pressures to 500 kg/cm^2 (Gage P); reservoir R contains the hydraulic oil. In cylinder 2, the pressure is amplified to a maximum of about 7000 kg/cm^2 by a differential piston with a BRIDGMAN mobile joint. The amplified pressure in the block distributor, 3, is then directed to the Bourdon gage, B, and to the laboratory cylinder, 4, containing the sample. Openings

at F, G, H, I, and J contain valves for controlling or releasing the pressure at these points. An oil manometer, V, at atmospheric pressure, connects through an opening, S, with a channel whose volume is confined by the differential piston. Changes in the volume of this channel as read on the manometer permit observations of the movement of this piston. Detailed descriptions are given in [10].

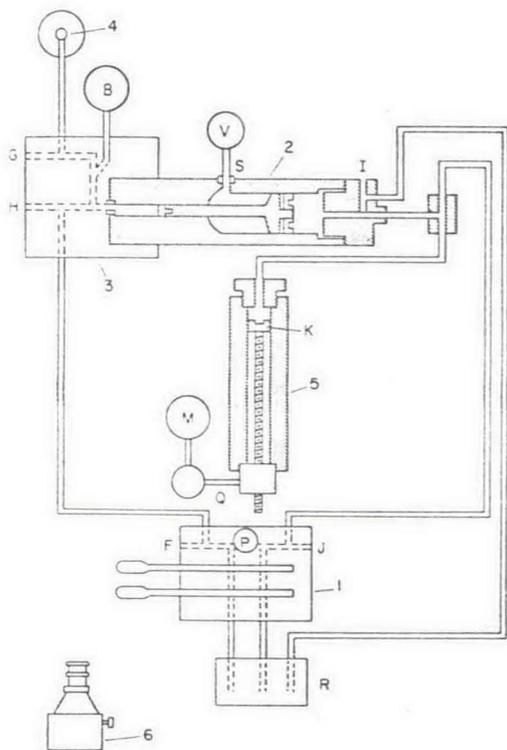


Fig. 1 -- Schematic drawing of the high-pressure apparatus.

After crystallization and temperature equilibration of the sample at a high pressure, the pressure in the system is reduced slowly by a decompression cylinder, 5⁽³⁾. The volume of the system is increased at

⁽³⁾ A detailed drawing of this cylinder, which was installed prior to the present investigation, may be obtained from Marcel Beckers at the Université Libre de Bruxelles.

a constant rate ⁽⁶⁾ as the piston, K, is withdrawn in the precision bore of this cylinder, 5, by the constant-speed motor, M, and reduction gears, Q. A pressure seal for the piston was made with a washer of specially formulated rubber ⁽⁷⁾ which was locked in position by a steel ring at the upper end of the piston. Washers of this material operated as pressure seals without leaking and were in good condition after 600 hours of use.

The camera, 6, is automatically operated by a synchronous clock motor so that a picture of the Bourdon gage and of a spring-driven watch is made every ten minutes. The watch provided a convenient way of assuring that the photograph was taken every ten minutes and that the electric current to the apparatus was uninterrupted. The maximum variation in a 10-minute interval was 3 seconds. Sufficient film was used for about 20 hours of continuous operation. Since the decompression rate and the thermostated bath were also automatically controlled, the apparatus could be run at night and over weekends without attention. About 4000 individual pictures from the pressure experiments on these acids were thus made. The pressure readings were plotted as a function of time. Phase transitions were represented as nearly horizontal portions of the curves. As the samples became more impure due to decomposition, these plateaus for the solid-liquid transitions became less distinct and exhibited increased curvature. These curves were analysed as described below to obtain the volume changes and sample purities.

3. EVALUATION OF SAMPLE PURITY

The time-pressure curve in the fusion region may be used to evaluate the impurity of the sample in procedures similar to those used for

⁽⁶⁾ With cylinder 5 operating, the volume increase in the system at 4 was determined from calibration experiments to be $3.99 \times 10^{-3} \text{ cm}^3$ per minute. These calibration experiments with benzene in the sample container were performed prior to this research.

⁽⁷⁾ The Rubber Section at the National Bureau of Standards supplied this rubber after a request to replace the polyvinylchloride [10] with a more elastic type of material. The greater elasticity was to overcome small imperfections (such as longitudinal scratches) in the bore of the decompression cylinder, which had become damaged on prior usage and leaked with polyvinyl chloride washers. The authors are indebted to Frank L. Roth for this special oil-resistant Neoprene rubber which was formulated in parts by weight as follows: 100, Neoprene; 20-30, carbon black; 5, zinc oxide; and 5, magnesium oxide.

time-temperature freezing curves [12, 13]. The observed high-pressure data are plotted with pressure and time decreasing, so that the time-pressure plot resembles a time-temperature freezing curve at ordinary pressures. The duration of the fusion is obtained by extrapolating the time-pressure lines for the liquid and for the solid until they intersect the pressure at which an infinitesimal amount of solid is in equilibrium with the liquid.

For a pure substance with solid and liquid phases in equilibrium, the pressure during the fusion period will lie on a horizontal line. Impurities in the sample of the type that do not form solid solutions with the substance will cause the time-pressure line to depart from a straight line; for liquid-soluble, solid-insoluble impurities which form ideal solutions, the change in the curve will be proportional to the concentration of the impurity in the liquid phase. The purities of the acids were evaluated from the difference in the pressures when the sample was one-half solid and all liquid. The increase in pressure between these two conditions, in which the original impurity is doubled, is the same as the pressure change that would be caused by adding a like amount of impurity to the pure material.

In the piezometric experiments at high pressures, the increasingly higher pressures that are required for the solid-liquid equilibrium as the liquid phase becomes more and more impure are quite analogous to the decreasingly lower temperatures that are required under similar conditions in the thermometric or calorimetric experiments at constant pressure.

In piezometric analysis at constant temperature, pressure and volume are measured to obtain values of the volume change on fusion, ΔV ; in calorimetric measurements at constant pressure, heat and temperature are measured to obtain values of the heat of fusion, ΔH .

For dilute solutions or nearly pure substances, in which the impurity forms an ideal solution, the simplified equations for determining the impurity from piezometric and calorimetric measurements are, respectively :

$$N_2^* = (\Delta V_0/RT') (P-P_0), \quad (1)$$

$$N_2^* = (\Delta H_0/RT_0^2) (T_0-T), \quad (2)$$

where N_2^* = mole fraction of impurity in liquid phase,

ΔV_0 = molar volume of liquid minus that of solid for the pure substance at constant temperature T' and pressure P_0 .

ΔH_0 molar heat of fusion for the pure substance at constant pressure P' and temperature T_0 .

- R = gas constant per mole,
 T = observed absolute temperature of equilibrium, at a fixed pressure P' ,
 T_0 = absolute temperature of the freezing point of the pure substance at fixed pressure P' ,
 P = observed equilibrium pressure at fixed temperature T' ,
 P_0 = equilibrium pressure of pure substance at T' .

The heat of fusion is a function of temperature and pressure; at ordinary pressures the effects of changes in pressure are usually negligible. The temperature dependence may be included by incorporating terms involving the specific heats of the two phases, as below. In a similar manner, ΔV is a function of temperature and pressure. However, the effects of both temperature and pressure are significant, especially at higher pressures. These effects may be included with terms involving the compressibility and the thermal expansion coefficient; if these are not available, the values of ΔV must be measured at each temperature of interest.

In the evaluation of purity from thermometric data, the change in the temperature of the liquid-solid transition, as the substance becomes more impure is more adequately expressed [14,15] as :

$$\begin{aligned}
 -\ln N_1 &= (\Delta H_0/RT_0^2) \Delta T \left[1 + \left(1/T_0 - \frac{\Delta C_{P_0}}{2\Delta H_0} \right) \Delta T + \dots \right], \quad (3) \\
 &= A\Delta T [1 + B\Delta T + \dots], \quad (3a)
 \end{aligned}$$

where

- N_1 = mole fraction of substance in the liquid phase,
 ΔT = $(T_0 - T)$
 ΔC_{P_0} = molar heat capacity of liquid less that of solid for the pure substance at T_0 ,
 A = $\Delta H_0/RT_0^2$, main cryoscopic constant,
 B = $(1/T_0 - \Delta C_{P_0}/2\Delta H_0)$, secondary cryoscopic constant.

Equation 3 takes into account the change in the heat of fusion with temperature. Taylor and Rossini, by making certain assumptions, were able to express [16] equation 3 as a rectangular hyperbola; this was used to extrapolate the time-temperature data from freezing and melting point measurements to obtain values for the freezing points of the sample and the pure material. Saylor [17] has recently used an optical method of fitting a skewed hyperbola to such data.

A similar development may be applied to the piezometric data to obtain the expanded form ⁽⁹⁾:

$$\begin{aligned}
 -\ln N_1 &= (\Delta V_0/RT) (P-P_0) \left\{ (1 + 1/2\Delta V_0) [(dV/dP)_l - (dV/dP)_c] (P-P_0) \right\}, \quad (4) \\
 &= A'\Delta P [1 + B'\Delta P], \quad (4a)
 \end{aligned}$$

where

$$A' = \Delta V_0/RT$$

$$B' = (1/2\Delta V_0) [(dV/dP)_l - (dV/dP)_c]$$

(dV/dP) = molar compressibility coefficient of the liquid (*l*) or solid (*c*) phase at the pressure P_0 and temperature T .

Equation 4 takes into account the change in volumes of the solid and liquid phases during the changing pressure of the fusion. The similarity of the forms of equation 3 and 4 seemed to justify the extrapolation of the time-pressure data by hyperbolic equations similar to those used for the time-temperature data.

The pressure, P , and time, t_a , at which an infinitesimal amount of solid is in equilibrium with liquid were obtained by fitting the values in the liquid-solid region to a curve and extrapolating to the intersection with the time-pressure curve for the liquid. The time, t_b , when the sample would have been completely solid, if pure, was obtained by extrapolating the time-pressure curve for the solid to the pressure, P . The interval $(t_a - t_b)$ was taken as the duration of the transition and was used to calculate ΔV_0 (the volume change for the transition).

⁽⁹⁾ A derivation of this equation follows:

The basic differential equation at constant temperature is:

$$-d\ln N_1 = \left(\frac{V_l - V_c}{RT} \right) dp = (\Delta V/RT) dp \quad (a)$$

$$\text{Let: } \Delta V = \Delta V_0 + (k_l - k_c) (P - P_0), \quad (b)$$

where: P_0 is the pressure when $N_1 = 1$; P is the pressure when $N_1 = N_1$; and k is dV/dP for each phase.

Substitute for ΔV into equation (a):

$$-d\ln N_1 = \frac{\Delta V_0 + (k_l - k_c) (P - P_0)}{RT} dP. \quad (c)$$

$$\text{Integrate: } -\ln N_1 = \frac{\Delta V_0}{RT} (P - P_0) + \frac{(k_l - k_c) (P - P_0)^2}{2RT}.$$

Rearrange and substitute for k :

$$\begin{aligned}
 -\ln N_1 &= (\Delta V_0/RT) (P - P_0) \\
 &\quad \left\{ 1 + (1/2\Delta V_0) [(dV/dP)_l - (dV/dP)_c] (P - P_0) \right\}. \quad (d)
 \end{aligned}$$

The pressure, $P_{1/2}$, at which the sample is one-half solid, was obtained by drawing a line from the point $1/2 (t_a + t_b)$, on the horizontal P line, with a slope equal to the average of those for the liquid and solid curves.

The intersection of this line with the experimental liquid-solid curve gives $P_{1/2}$. The difference, $(P_{1/2} - P)$, is assumed to be the same as the pressure change, $(P - P_0)$, that would be caused by adding a like amount of impurity to the pure substance, P_0 . Equation 1 was then used to calculate the amount of impurity.

4. MATERIALS AND PIEZOMETRIC DATA

4.1. Dichloroacetic Acid

The preparation of the sample of dichloroacetic acid used in this work has been described previously [1]; its purity had been determined cryoscopically to be 99.8 mole percent. It was alternately melted and frozen at least four times under high vacuum to remove dissolved gases before transfer to the piezometric vessel as described in 2.1. Before the sample was transferred, the piezometric vessel was heated for 16 hours at a pressure of 10^{-5} mm Hg to remove adsorbed water. Despite these precautions, some reaction occurred during the high pressure experiments. To minimize this reaction, the experiments were made at the lower temperatures first. The reaction was accelerated when the sample was heated to 60°C.

Eleven piezometric experiments were performed: five experiments at 15°C and two each at 30°, 45°, and 60°C. In experiments at 15°, 45°, and 60°, a search was made for solid-solid transitions at pressures to about 4900 kg/cm². No transitions below this pressure were observed for this compound other than fusion. A summary of the piezometric data for dichloroacetic acid is given in table 1. From the data of experiment 11, an impurity of about 0.35 mole percent was calculated, in reasonable agreement with the value of 0.2 mole percent from the cryoscopic measurements on the original sample. Calculations for succeeding experiments at 30° and 60°C indicated that the impurity had increased to 0.6 and 1.7 mole percent, respectively; no calculation of purity was made for experiments 17 and 18, at 45°C, because of the much larger pressure changes during fusion.

The temperature-pressure phase diagram for dichloroacetic acid obtained from the data in table 1 is shown in figure 2. The open circles

TABLE I
Summary of Piezometric Data for Dichloroacetic Acid (*)

Exp.	T °C	Equil. (a) time hrs	Decomp. (b) time hrs	Pressure (c) range kg/cm ²	P (d) kg/cm ²	P ₀ (e) kg/cm/	ΔP (f) kg/cm ²	Fusion time min.	ΔV (g) cm ³ / g × 10 ⁻³	N ₂ (h) mole %
8	15.2	4	41	4860- 150	—	—	—	—	—	—
9	15.0	4	8	2455-1545	—	—	—	—	—	—
10	15.2	3	4	365- 300	—	—	—	—	—	—
11	15.2	4	12	285- 35	100	92.5	7.5	(260) (i)	(86)	0.35
12	30.1	3	23-1/2	1970- 265	695	680	15	235	79	0.6
13	30.5	5	9	975- 500	695	—	—	—	—	—
14	59.4	5	26	4960-1535	2200	2120	80	(135)	(46)	1.7
15	59.4	4	6-1/2	2790-2260	—	—	—	—	—	—
16	15.1	4	8-1/2	870- 320	—	—	—	—	—	—
17	45.0	16	30	4840-1070	1510	1400	110	—	—	—
18	45.0	4	13	2495-1225	1605	1480	125	—	—	—

(*) Original purity 99.8 mole percent [1]; weight of sample 11.9728 g.

(a) Time sample allowed to come to equilibrium at high pressure before decompressing.

(b) Time of continuous experimental decompression of sample.

(c) Pressure range of experiment.

(d) Observed pressure for solid-liquid transition.

(e) Approximate pressure, corrected for impurity in sample.

(f) Pressure difference when sample is one-half solid and all liquid.

(g) Volume change for transition of solid to liquid.

(e) Approximate impurity calculated from $(\Delta V_0/RT)\Delta P$

(i) Values in parentheses have larger uncertainties because of erratic pressure pattern.

represent measurements uncorrected for impurity; the solid points have been corrected for impurity with equation 1. In drawing the curve, the points at 45°C were given little weight because the experimental data showed a large pressure range for the fusion, due to the increased amount of impurity.

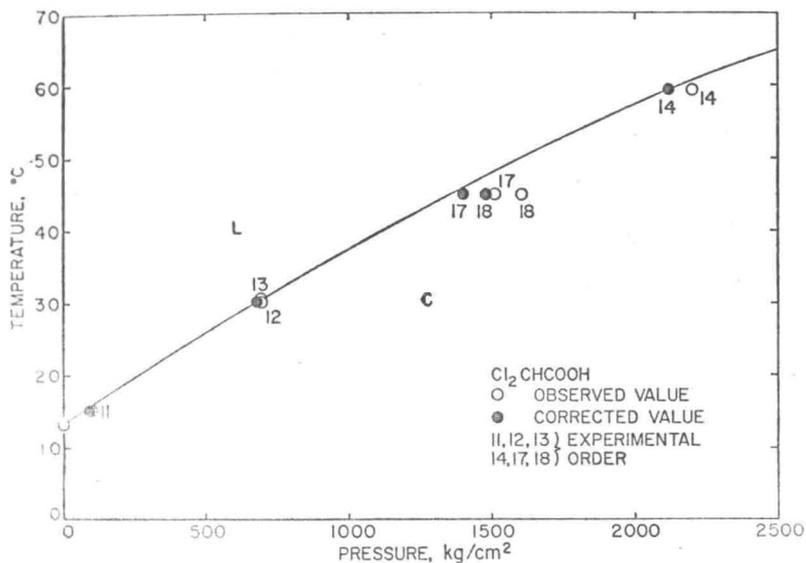


Fig. 2 — Phase diagram for dichloroacetic acid at elevated pressures.

4.2. Monobromoacetic Acid

The purification of the monobromoacetic acid used has been described previously [1]; its purity had been determined cryoscopically to be 99.97 mole percent. The sample was introduced into the piezometric vessel by the procedure described in section 2. As the rate of the reaction between mercury and monobromoacetic acid would be expected to be greater at the higher temperatures, where the acid would be liquid, it was decided to look first for any solid-solid transitions, keeping the acid solid at all times.

A total of 20 experiments was made with this acid to obtain the data shown in figure 3. The experimental conditions during the piezometric experiments on the solid are given in table 2; resulting data for the solid-solid transitions are summarized in tables 3 and 4. The experimental conditions and data for the fusion are given in table 5.

TABLE II

Experimental Conditions in Piezometric Experiments with Monobromoacetic Acid for Solid-Solid Transitions ()*

Experiment	Temp. °C	Equilibrium Time hrs.	Decompression Time hrs.	Pressure Range kg/cm ²
1	15.1	4-1/2	39	4800-260
2	15.2	3	36	4880-435
3	15.2	4	22-1/2	2010-380
4	15.2	2	13-1/2	1020-230
5	15.2	1-1/2	5-1/2	800-485
6	30.1	1-1/2	40-1/2	4650-365
7	30.2	3	23-1/2	3010-500
8	30.1	11	33	3490-180
9	30.1	10	24-1/2	2025-575
10	30.1	2	22	2100-230
11	30.0	4-1/2	18	2015-340
12	30.0	4	14	1515-255
13	30.0	11-1/2	14-1/2	1510-145
14	30.0	5	17	1500- 85
15	45.1	5	16	1480- 80
16	45.0	7	16-1/2	1500- 90

(*) Original purity 99.97 mole percent [1]; weight of sample 19.6198 g.

TABLE III

Summary of Piezometric Data on Monobromoacetic Acid for Transition C II to C I

Experiment (a)	Temperature °C	P kg/cm ²	Transition Time min.	ΔV cm/g $\times 10^{-3}$
1	15.1	560	(20) (b)	(4.0)
3	15.2	530	(20)	(4.0)
4	15.2	570	(20)	(4.0)
5	15.2	560	(20)	(4.0)
8	30.1	400	(20)	4.1
14	30.0	390	20	4.1
15	45.1	200	20	4.1
16	45.0	200	20	4.1

(a) Experiments 2, 6 and 11 did not extend to low enough pressures to define the liquid curve; in experiments 10, 12, and 13 the time-pressure data were very irregular. The results of these experiments are in substantial agreement with those tabulated.

(b) Values in parentheses have larger uncertainties because of erratic pressure pattern.

TABLE IV

Summary of Piezometric Data on Monobromoacetic Acid for Transition C III to C II

Experiment (a)	Temperature °C	P kg/cm ²	Transition Time min.	ΔV cm ³ /g $\times 10^{-3}$
2	15.2	1650	16	3.2
3	15.2	1650	16	3.2
6	30.1	1000	16	3.3
7	30.2	1000	16	3.3
8	30.1	990	15	3.1
9	30.1	980	(10) (b)	—
10	30.1	980	(12)	—
11	30.0	990	(12)	—
12	30.0	980	16	3.3
13	30.0	(990)	(10)	—
14	30.0	(1000)	(8)	—
15	45.1	495	15	3.1
16	45.0	505	(8)	—

(a) In experiment 1, the recording camera failed in the transition region; extrapolation from higher and lower pressures gives values in agreement with those from experiments 2 and 3.

(b) Values in parentheses have larger uncertainties because of erratic pressure pattern.

The solid-solid transitions showed small volume changes. A larger number of experiments were performed to prove that such changes were real and not due to malfunctioning of the apparatus. The agreement among the results of the replicate experiments at the same temperature (table 4) is satisfactory. The phase diagram derived from these measurements is shown in figure 3.

Values for the impurity N₂ were calculated from the time-pressure curves with equation 1. The small impurity (0.22 mole percent) found for experiment 17 indicates that little reaction had taken place during the preceding experiments. However, the amount of impurity progressively increased during experiments 18, 19, and 20, in which the sample was melted at higher temperatures.

TABLE V

Summary of Piezometric Data on Monobromoacetic Acid for CIII to Liquid Transition

Exp.	T °C	Equil. (a) time hrs	Decomp. (b) time hrs	Pressure (c) range kg/cm ²	P (d) kg/cm ²	P ₀ (e) kg/cm ²	ΔP (f) kg/cm ²	Fusion time min.	ΔV (g) cm ³ / g × 10 ⁻³	N ₂ (h) mole %
17	60.0	6-1/2	14	1000- 100	570	555	15	150	31.2	0.22
18	54.8	10-1/2	14	1000- 115	335	315	20	185	38.4	0.38
19	74.8	5	14-1/2	2200- 735	1370	1330	40	125	26.0	0.48
20	89.8	7	15-1/2	2925-1320	2265	2205	60	105	22.0	0.60

(a) Time sample allowed to come to equilibrium at the high pressure before decompressing.

(b) Time of continuous experimental decompression of sample.

(c) Pressure range of experiment.

(d) Observed pressure for solid-liquid transition.

(e) Approximate pressure, corrected for impurity in sample.

(f) Pressure difference when sample is one-half solid and all liquid.

(g) Volume change for transition of solid to liquid.

(h) Approximate impurity calculated from $(\Delta V_0/RT)\Delta P$.

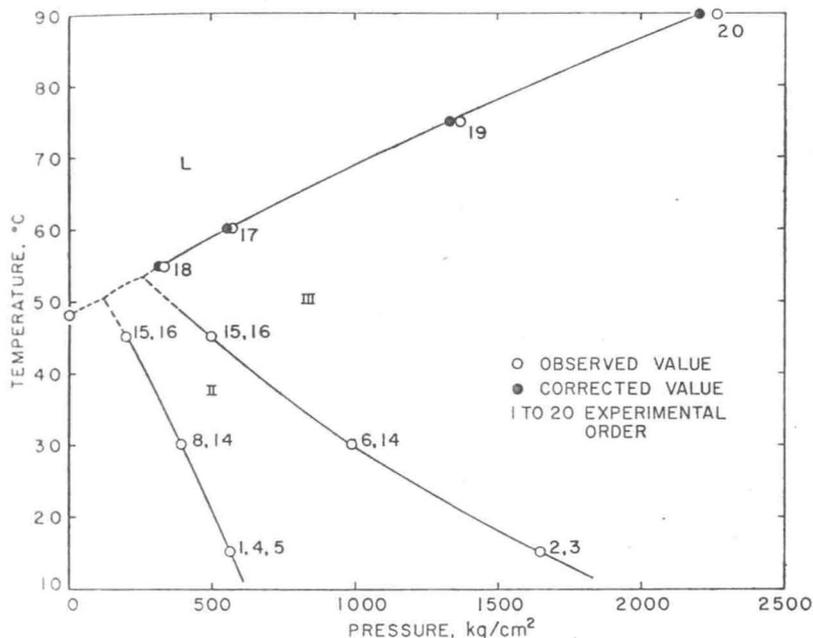


Fig. 3 Phase diagram for monobromoacetic acid at elevated pressures.

5. THERMODYNAMIC PROPERTIES FROM HIGH-PRESSURE DATA

5.1. Dichloroacetic Acid

The temperature-pressure coefficients and molar heats and entropies of fusion calculated at three different temperatures and pressures for the equilibrium between liquid and solid dichloroacetic acid are given in table 6. No values were calculated from the data at 45°C because of the large amounts of impurity present during these experiments. The heat of fusion calculated from the high-pressure data is in good agreement with the more precise value of 2950 ± 30 cal/mole at the triple point (13.39°C) determined calorimetrically [1] on another portion of the same sample of acid. The values reported previously [18,19] for the heat of fusion (1830 cal/mole) and melting point (10.8°C) are significantly different.

TABLE VI

Heat of Fusion, Entropy, and Temperature-Pressure Coefficient Calculated from High-Pressure Data

Dichloroacetic Acid
Solid to Liquid

Temp. °C	Press. kg/cm ²	ΔV cm ³ /kg	dT/dP °C/kg cm ⁻²	ΔH_m cal/mole	ΔS_m cal/deg./mole
15.2	100	86	.026 ₆	2830	9.8
30.1	695	79	.023 ₄	3040	10.
59.4	2200	46	.016 ₆	2870	8.6

TABLE VII

Latent Heats, Entropies, and Temperature-Pressure Coefficients Calculated from High-Pressure Data

Monobromoacetic Acid

Temp. °C	Press. kg/cm ²	ΔV cm ³ /kg	dT/dP °C/kg cm ⁻²	ΔH_t cal/mole	ΔS_t cal/deg/mol
C III to Liquid					
54.8	335	38	.023 ₄	1750	5.3
60.0	570	31	.021 ₀	1600	4.6
74.8	1370	26	.017 ₄	1690	6.1
89.8	2265	22	.016 ₄	1580	4.4
C I to C II					
15.2	563	-4.0	-.095	40	0.14
30.1	395	-4.1	-.083	49	0.16
45.1	200	-4.1	-.071	60	0.19
C II to C III					
15.2	1650	-3.2	-.018	167	0.58
30.1	990	-3.2	-.027	123	0.39
45.1	500	-3.1	-.034	94	0.30

Triple points: (1) L, C I, C II approx. 50.5°C and 120 kg/cm²
(2) L, C II, C III approx. 53°C and 260 kg/cm²

5.2. *Monobromoacetic Acid*

The temperature-pressure coefficients and heats and entropies of phase change in monobromoacetic acid, calculated from the high-pressure data, are given in table 7 for the fusion of C III, and for the transitions C I to C II and C II to C III. Although reaction occurred when this sample was melted and subjected to high pressures, it is felt, from an analysis of the piezometric data, that the acid retained its purity during the experiments at 45°C and below. No previous high-pressure studies on this compound have been reported.

6. POLYMORPHIC FORMS OF MONOBROMOACETIC ACID UNDER PRESSURE

It will be noted in table 7 that the solid transitions of monobromoacetic acid occurred at increasingly lower pressures as the temperature was increased. Such negative temperature-pressure coefficients are unusual. BRIDGMAN [19, 20] did not find any organic compound in which negative temperature-pressure coefficients occurred for two consecutive crystal transitions. Crystalline transitions with negative coefficients occur infrequently; examples are found in the transitions between forms I and II of urethane, ethylurethane, acetamide, benzene, and ammonium thiocyanate. Inorganic compounds have been reported which have several crystalline transitions with negative temperature-pressure coefficients; i.e., the potassium acid sulfate transitions C II to C III, C II to C IV, and C III to C IV.

In related polymorphic studies at ordinary pressures [1], monobromoacetic acid was obtained in only one crystalline form, although monochloroacetic acid exists in at least three. Although three forms of the monochloro acid exist at ordinary pressure and three forms of the monobromo acid at elevated pressures, no comparison of the phase diagrams of the solid forms of these acids can be made on the basis of corresponding states. This is because two of the three crystalline forms of monobromoacetic acid at the elevated pressures cannot exist in equilibrium with liquid at ordinary pressures. No polymorph of monobromoacetic acid was observed which would have melted at a higher temperature at atmospheric pressure.

The comparatively low pressures associated with the solid transitions in monobromoacetic acid suggest the possibility of x-ray or neutron diffraction studies of the crystal structure of the high-pressure forms.

Information on the structures of these polymorphs is necessary before an explanation of the differences in the phase behavior among the various halogen-substituted acetic acids is possible.

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