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The Heat Capacities of Benzene, Methyl Alcohol and Glycerol at Very Low Temperatures¹

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The design and operation of a low temperature vacuum calorimeter which is internally cooled from 13° to 2°K is described. The principle employed is that of adiabatically expanding cooled helium gas from a small pressure chamber, located inside the calorimeter can. The heat capacities of crystalline benzene and methyl alcohol and crystalline and glassy glycerol have been measured down to 3°K. New values of the entropies of these substances at various temperatures have been calculated. Below 9°K the heat capacity of glassy glycerol is 100 percent larger than that of crystalline glycerol. The glassy form apparently has 4.64 units of entropy at the absolute zero.

INTRODUCTION

THE demonstrations by Simon and Ahlberg^{5, 6} that a thermally isolated apparatus could be effectively cooled from "hydrogen" to "helium temperatures" by the free adiabatic expansion of cold helium gas from a small pressure chamber at once suggested that the inclusion of a simple auxiliary appliance in the familiar type of low temperature vacuum calorimeter would make it possible to extend heat capacity measurements to within several degrees of the absolute zero even when liquid hydrogen was available only in moderate quantities. In connection with the development of such a calorimeter it seemed worth while to make an experimental investigation of the very low temperature heat capacities of a few organic compounds which form crystal lattices of the molecular type.

The experimental investigation of the low temperature thermal behavior of the crystalline state has been confined, for the most part, to substances forming crystal lattices of the monatomic particle type. The heat capacity of lattices composed of large molecules has, in most instances, simply been inferred from measurements at relatively high temperatures and from what was known about simpler types of structures. But in many organic substances the

vibrations of the atomic nuclei or groups of nuclei within the individual molecules begin to be appreciable factors in the total heat capacity even at "hydrogen temperatures" and at somewhat higher temperatures they become the most conspicuous factors, effectively obscuring the fine gradation in the heat capacity arising from compressional and torsional vibrations of the Debye type in the crystal lattice. It is often, therefore, only at "helium temperatures" that the observed heat capacities may be considered to give a simple, unconfused picture of the thermal behavior of a molecular crystal lattice. With an exact knowledge of the fraction of the total heat capacity which arises from lattice vibrations, it becomes possible easily to compute an experimental value for the heat capacity of the internal vibrations in the molecules. The latter information is often of great value in the interpretation of spectroscopic frequencies.

APPARATUS

General description

The calorimeter was designed primarily for measurements of heat capacity between 2° and 20°K but arrangements were also provided for continuing the measurements up to 100°K. Apart from the helium liquefaction device, the plan and operation of the calorimeter was, in principle, similar to the types of calorimeters developed by Nernst, Simon, Giauque and others. By confining the operating range of the calorimeter to temperatures below 100°K it was possible to dispense with the bulky, massive radia-

¹ A portion of the contents of this paper, including a description of the calorimeter and the measurements on benzene, was presented at the 88th Meeting of the American Chemical Society in Cleveland, O., September, 1934.

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⁵ F. Simon, *Zeits. f. ges. Kälte-Ind.* **39**, 89 (1932).

⁶ Simon and Ahlberg, *Zeits. f. Physik* **81**, 816 (1933).

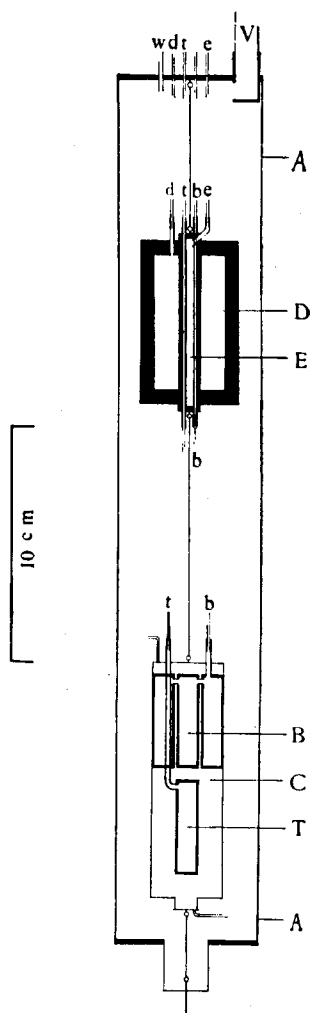


FIG. 1.

tion shield which is generally employed in vacuum calorimeters and use simply a small thermal dam to prevent heat conduction along the wires and tubes to the calorimeter can.⁷

To produce the very lowest temperatures the whole calorimeter was cooled to about 13°K by the use of liquid hydrogen. At that temperature the calorimeter can was thermally isolated and cooled to 2°K by the free expansion of cold, compressed helium from a small, capsule-like pressure chamber embedded in the calorimeter can, first to the atmosphere and then into a vacuum.

⁷ We use the term "calorimeter can" to refer specifically to the light, thermally insulated metal container in which the sample is placed and whose heat capacity is, of course, always included in the observed gross heat capacities.

Between 2° and 20°K, absolute temperatures were determined by the use of a constant volume helium gas thermometer whose bulb was imbedded in the material in the calorimeter can. Temperature intervals were measured with great accuracy by a high resistance constantan wire coil which was wound on the outside of the calorimeter can and which served both as a resistance thermometer and as the heating element. The resistance thermometer was calibrated against the gas thermometer at many temperatures during the course of every series of heat capacity measurements. Thermocouples were used for temperature measurements above 20°K.

Fig. 1 shows the vacuum compartment of the calorimeter and its contents. The liquid hydrogen cryostat (not shown) consisted of a deep glass Dewar vessel enclosed in a tight brass can which was arranged to permit boiling of the hydrogen under reduced pressure. The entire hydrogen cryostat was suspended in a deep, nickel silver vacuum container of liquid nitrogen.

Referring to Fig. 1: *A* is the vacuum compartment which was entirely immersed in liquid hydrogen when the calorimeter was in operation at low temperatures; *C* is the calorimeter can in which the materials to be investigated were sealed; *B* is the helium liquefier; *D* is an auxiliary helium liquefier and reservoir which served as a thermal dam for the control of heat leakage along the wires and tubes leading to the calorimeter can below; *T* is the bulb of the standard gas thermometer and *E* is the bulb of an auxiliary gas thermometer in the dam. To isolate *C* and *D* thermally from the liquid hydrogen bath the vacuum compartment could be evacuated to 10^{-6} mm of mercury through the tube *V*.

The helium liquefying chambers, *B* and *D* were in communication with the outside of the cryostat through small German silver tubes, indicated by *b* and *d*. The gas thermometer bulbs, *T* and *E*, connected with their respective manometers through German silver capillary tubes, indicated by *t* and *e*. All of these tubes were coiled together in a helical spiral for several turns in the space between *D* and the top of the vacuum compartment. Between *D* and *C* the tubes *b* and *t* had a length of about one meter, being coiled in a helix of ten turns. By these means the tubes

were given great length in a small space, thereby greatly reducing heat leakage along them. All of the electrical leads to the vacuum compartment were conducted inside a small copper tube, w , through the hydrogen bath to the outside of the cryostat where they emerged through a vacuum tight, plastic seal.

Calorimeter can

The calorimeter can, C , was a cylindrical container made from pure silver tube and sheet of 0.3 mm thickness. The can was 10 cm high, 3.3 cm in diameter and held about 60 cc of material. Six radial fins of silver foil, extending from the wall towards the center, were soldered into the can to promote rapid conduction of heat through the sample. For the same purpose the can was filled with a low pressure of helium gas at the time a sample was sealed in. Ordinary 60 Sn–40 Pb solder was used in the construction of the can. Suspended inside the can was the small pressure chamber, B , in which helium was liquefied and subsequently boiled under reduced pressure. The chamber consisted of several short, interconnected sections of silver tube of 1 mm wall thickness and had a total volume of 6 cc. The German silver tube, b , used for the admission and expansion of helium had an o.d. of 1.6 mm and an i.d. of 1 mm.⁸

The bulb, T , of the standard gas thermometer was permanently suspended in the center of the calorimeter can. It was made from a section of stout silver tube and had a volume of 2 cc. Leading from the bulb to the top of the cryostat was a continuous piece of German silver capillary tubing, t , which had an internal diameter of 0.22 mm.

Thermal dam

The protective helium reservoir, D , was a massive, hollow copper cylinder suspended from the top of the vacuum compartment by a stout silk fishline. The electrical wires leading to the

calorimeter can below were wound around and cemented to the cylinder while the tubes b and t passed through the cylinder. When partially filled with liquid helium this dam provided sufficient thermal insulation for the calorimeter can below to permit the latter to be held at 1.5°K for several hours. For measurements above the boiling point of helium the cylinder contained a sufficient mass of copper to enable it to serve as a thermal dam simply by virtue of the heat capacity of the metal. By means of a heating coil wound on its outside, the cylinder could be brought to approximately the temperature of the calorimeter can below. Inside the dam was a copper cylinder, E , which served as the bulb of a helium gas thermometer used for control purposes at the lowest temperatures. It was connected by a German silver tube, e (0.4 mm i.d.), to an ordinary Bourdon type vacuum gauge on the outside of the cryostat.⁹ This thermometer was filled with helium gas to a pressure of one atmosphere when the system was at 298°K. At very low temperatures this simple arrangement functioned well as a moderately sensitive thermometer.

Cooling procedure

To cool the calorimeter to "helium temperatures" compressed helium from a commercial storage cylinder was allowed to flow, first, through a high pressure purifying system, and then into the pressure chambers, B and D , while the latter were in contact with liquid hydrogen boiling under reduced pressure. Thermal contact between B and C and the boiling hydrogen, which surrounded the vacuum compartment, was established by admitting helium gas to the vacuum compartment to a pressure of 1 cm (at 298°K). After the compressed helium had cooled to the lowest temperature attainable with hydrogen (12° to 14°K in practice), the dam, D , and the calorimeter can, C , were thermally isolated by pumping the exchange gas completely out of the vacuum compartment. The cold compressed helium in the two pressure chambers was then released slowly to the atmosphere simply by loosening the coupling nuts by which the feed lines were attached to the storage cylinder. By this expansion sufficient cooling

⁸ The small diameter German silver tubes used in the construction of the calorimeter had wall thicknesses much greater than would have been necessary simply to withstand the gas pressures to which they were subjected. Experience showed that tubes with walls thinner than those finally used would, in time, develop fissures and fractures due to either or both the mechanical strains which were set up during rapid cooling of the apparatus and the slight corrosive action developed at soldered joints.

⁹ K. Mendelssohn, *Zeits. f. Physik* **73**, 494 (1932).

was produced to cool the dam, and the calorimeter can and its contents, each unit working separately, to 4°K and liquefy sufficient helium in the two chambers so that the temperature of each unit could be still further reduced to below 2°K by boiling off the liquid helium under reduced pressure.

By employing the device of placing a "micro" helium liquefier inside the calorimeter can itself, it was possible to pump the exchange gas out of the vacuum compartment as soon as the cooling with liquid hydrogen had been completed, thus eliminating the necessity for an inner vacuum compartment. It was also of considerable help in securing a high vacuum to get the exchange gas out before the lower temperatures were reached.

When it was time to begin the heat capacity measurements, whatever liquid helium was left in the helium chamber *B* was boiled out by cautiously passing an intermittent current of one milliamper through the constantan thermometer-heater until the temperature showed a slight permanent rise.

An initial helium pressure of 70 atmospheres at 12°K was usually sufficient to produce the desired cooling although pressures up to 140 atmospheres were used when they were available. It was estimated that 1 cc of liquid helium formed in the chamber *B* and 25 cc in the dam *D* when the starting pressure was 75 atmospheres. Extremely pure helium was necessary for the liquefaction operation since even the most minute traces of foreign gases, including hydrogen, proved sufficient to freeze up the small tubes through which the helium chambers were blown down. Especially carefully handled helium supplied in pressure cylinders was further purified by slow passage under high pressure over peat charcoal contained in a series of copper traps immersed in boiling nitrogen. For the satisfactory removal of hydrogen from helium by adsorption on charcoal at liquid air temperatures it was found necessary to pass the gas over the charcoal at high pressures even when the gas was to be used subsequently at low pressures as in the gas thermometer.

Gas thermometer

The fine German silver capillary tube connecting the silver bulb of the standard gas

thermometer with the outside of the cryostat was joined, at the top of the cryostat, to a somewhat larger sized tube (0.46 mm i.d.) which led over to the manometer several feet away. The use of a relatively large sized tube in the room temperature part of the connecting system was found to result in much more rapid equalization of pressure in the system without objectionably increasing the dead space correction in the cases of very low temperature measurements. The obnoxious volume in the manometer and connecting tubes amounted to 3 cc.

The manometer for the standard gas thermometer was in most respects similar to that described by Mendelssohn.⁹ It consisted of a long and a short limb of 15 mm glass tubing mounted vertically beside each other on a massive stand which could be accurately leveled. A glass manifold for the transmission of mercury connected the lower ends of the two limbs to each other and to a mercury reservoir. The top of the short limb was closed with a brass plug cemented into the end of the glass tube. The German silver tube from the thermometer bulb and another small tube used for purging and filling the bulb were soldered into holes passing through the brass plug. From the center of the underside of the plug protruded a short ivory pointer which served as the fixed reference mark for setting the mercury levels. The top of the long limb was connected to a McLeod gauge and a mercury diffusion pump. Behind the long limb was a mirror-backed, glass scale on which the height of the mercury level could be estimated directly to 0.1 mm. A careful comparison of the levels of the mercury in the two limbs when both were under zero pressure showed that surface displacements due to surface tension were equal in the two limbs.

For the measurements reported in this paper the limbs of the manometer were made from Pyrex glass. It was noted, however, that there was a substantial loss of helium from the thermometer when it was allowed to stand idle for some days with a large surface of Pyrex glass exposed to the gas. Since no ordinary leaks could be detected anywhere in the system, it was concluded that the loss was due to solution of considerable helium in the glass and diffusion through it. The amount of gas lost seemed larger

than would have been expected from the observations of several investigators who have examined this phenomenon.^{10, 11} For subsequent measurements a soft glass manometer of the same design was therefore substituted.

Inasmuch as the indications of the gas thermometer were checked against the triple and boiling points of hydrogen at the beginning and end of every series of measurements with satisfactory agreement in every instance we are satisfied that there was no significant loss of helium from either manometer during the seven or eight hours required for a series of measurements. When the manometers were in use the surface of glass exposed to the helium gas was very small.

The standard thermometer was filled with purified helium to a pressure of approximately 1 atmosphere while the bulb was at the normal boiling temperature of nitrogen. This operation was carried out conveniently while the cryostat was being precooled, preparatory to being filled with liquid hydrogen. With this amount of gas in the thermometer the pressure change per degree was roughly 1 cm of mercury at temperatures below 20°K. The constants for the gas thermometer equation were determined twice at the boiling point of hydrogen each time the calorimeter was used. The temperature scale was based on a value of 20.39°K, given by Bonehoffer and Harteck,¹² for the normal boiling point of normal hydrogen. The equation of state data for helium of Onnes, Keesom *et al.*,¹³ of F. Henning¹⁴ and of Holborn and Otto¹⁵ were used for converting pressure readings to temperatures on the thermodynamic temperature scale. By means of thermocouples and mercury thermometers, the temperatures of the various thermal zones in the connecting tubes and manometer system were continuously observed and appropriate correction terms introduced into the gas thermometer equation. The volumes of

the various parts of the thermometer system were determined by conventional methods.

Electrical measurements

For service both as resistance thermometer and heating element, a coil of No. 40 B. & S. Gauge, double silk covered constantan wire¹⁶ was wound on the outside of the calorimeter can. Prior to the winding of the wire the surface of the can was slightly roughened with fine sandpaper and painted with a moderately thick coat of Bakelite lacquer. The can was then baked at a temperature of 100°C for 10 hours. A heavy coating of lacquer was applied to the surface and also to the wire itself as the wire was wound onto the can. This lacquer was allowed to dry at room temperature for 24 hours and then was baked as before. Despite the different thermal expansions of constantan and silver, the wire remained firmly cemented to the can through repeated coolings and warmings over the period of a year that the calorimeter was in use. Measurements of the temperature head developed between the coil and the material inside the can during heating periods showed that errors introduced into the measurements due to temperature heads could not amount to more than one-tenth of one percent. The thermometer-heater had a resistance of 4800 ohms at 298°K.

Two leads of No. 40 copper wire were joined directly to each end of the constantan coil. For resistance measurements, current was supplied by a thermostated 6-volt storage battery discharging through a 300,000 ohm resistance placed in series with the thermometer. The resistance of the thermometer was measured by comparing the potential drop across the coil itself, by means of the extra set of leads, with the drop across a standardized fixed resistance placed in series with the thermometer. During the determinations of the heat capacity of benzene and of the empty calorimeter all of the potentiometric measurements were made with a White double potentiometer which had recently been checked by the makers. For measurements on the other substances reported in this paper and subsequent papers, a new low range Wenner potentiometer¹⁷ was used for the re-

¹⁰ Baxter and Starkweather, *Science* **68**, 516 (1928); **73**, 618 (1931).

¹¹ W. D. Urry, *J. Am. Chem. Soc.* **54**, 3887 (1932).

¹² Bonehoffer and Harteck, *Naturwiss.* **17**, 321 (1929).

¹³ Leiden Comm. No. 170, Suppl. 51 and 70; *Physica* **2**, 37 (1935).

¹⁴ F. Henning, *Zeits. f. ges. Kälte-Ind.* **37**, 169 (1930).

¹⁵ Holborn and Otto, *Zeits. f. Physik* **30**, 321 (1924); **38**, 365 (1926).

¹⁶ Advance brand.

¹⁷ (a) F. Wenner, *Phys. Rev.* **31**, 94 (1910); (b) L. Behr, *Rev. Sci. Inst.* **3**, 109 (1932).

sistance measurements. This instrument had been calibrated by the National Bureau of Standards for an accuracy of 0.01 percent in the ranges of voltages for which the instrument was used.

The electrical instruments were located in a special room where they were protected from sudden changes of temperature. The standard cells used with the potentiometers were frequently compared with a reference cell. All of the cells were enclosed in a cork-lined box which, in turn, was kept in a closed cupboard. The galvanometers were placed thirty feet from the scale on which the deflections were read by the displacement of a focused light beam. Switches constructed entirely of copper and lead sheathed copper wires were used in all the external electrical circuits. The potentiometers, galvanometers, the calorimeter and the connecting wires were all brought under the same shielding system.

The resistance thermometer was frequently compared with the gas thermometer during the progress of every set of heat capacity measurements. Between 2° and 20°K the resistance thermometer exhibited a smooth, continuous relationship between resistance and temperature and between the dR/dT coefficients and temperature. In this range the change in resistance was roughly 0.16 percent per degree. Between 20° and 25°K the resistance became relatively independent of temperature so that the thermometer could not be used above that region. The dR/dT coefficients of the thermometer remained practically constant during the period of a year that the thermometer was in use.

At temperatures above 20°K a single junction pair copper-constantan thermocouple, soldered to the top of the calorimeter can was used to extend the measurements to temperatures where our samples could be compared with those studied by other workers. The ice point was used as the reference junction. The calibration and behavior of this and other thermocouples that were used has been discussed by two of the authors.¹⁸

The energy used to produce the measured temperature rises was supplied to the constantan thermometer-heater by a large battery of lead

storage cells. The heating periods varied from 5 seconds at the very lowest temperatures to 14 minutes at 85°K. For the short heating periods required below 15°K the total energy input was computed by the use of the formula $\Delta H = 0.23904 \times R_{av} \times I^2 \times t$ where R and I are in international units and t is in units of 1/86400 mean solar day. The mid-time or average resistance of the heater during a heating period was computed from the thermometer readings taken just before and just after the energy input.

For the very short heating periods at temperatures below 4°K the current was determined by measuring the potential drop across a standard resistance placed in series with an accurately adjustable resistance which had been set, as nearly as possible, at the same resistance as the calorimeter heater. As soon as this measurement was completed the current was rapidly switched to the calorimeter. The battery was stabilized by allowing it to flow through the adjustable resistance for some time before the final measurement was made. The change in resistance of the constantan heater was so small and so regular over the short temperature ranges used and the thermal drift of the calorimeter was so small that energy measurements made in this way were well within the limits of the accuracy of the time measurements.

During the heating periods of several minutes duration, used between 4° and 15°K, the current was measured directly while it was flowing through the heater. During the longer heating periods, permissible above 15°K, the potential across the heater was also measured directly at the half-time by means of a volt box circuit and the total energy input calculated in the conventional manner.

The timing of the heating periods was done with two calibrated stopwatches, operated manually. The absolute error in the timing did not exceed 0.3 second.

Accuracy and remarks

The heat capacity of the empty calorimeter was determined by measurements carried out in exactly the same way as those on the substances studied. Below 20°K the heat capacity of the empty calorimeter can, including the enclosed helium liquefier and the gas thermometer bulb,

¹⁸ Ahlberg and Lundberg, *J. Am. Chem. Soc.* **57**, 2722 (1935).

was about 45 percent of the 0.60 mole sample of benzene that was studied.

Below 4°K the over-all accuracy of the data obtained was determined both by the time and the temperature difference measurements. Above 4°K the temperature difference measurements were the primary factor in determining the over-all accuracy. With the possible exception of the measurements below 5°K, the reported heat capacity values are estimated to be within 2 percent of the true values at all temperatures. On the basis of mutual consistency within the series, the measurements obtained in most of the runs were well within a 2 percent limit. At the very lowest temperatures at which measurements were obtained the heat capacity of the helium gas, which was placed in the calorimeter can to promote heat conduction, began to be an appreciable part of the total measured heat capacity and introduced an additional element of uncertainty.

When the calorimeter was designed it was intended that the thermocouples would be used only for control and comparison purposes at relatively high temperatures. But the excellent degree of thermal isolation which the calorimeter can displayed when the calorimeter was in operation led us to make complete sets of measurements up to 95°K in several cases with all of the care which the accuracy and sensitivity of the thermocouples justified.

Two to three liters of liquid hydrogen were required for a cooling of the calorimeter. In filling the cryostat the liquid hydrogen was piped through small, articulated glass "Dewar tubes" directly from the main laboratory liquefier which stood some distance from the calorimeter. The use of intermediate transfer vessels was thus eliminated to considerable advantage. About 45 liters of liquid nitrogen were required for a complete experiment which included the precooling of the calorimeter, the liquefaction of hydrogen, the purification of helium and keeping filled for twenty-four hours the nitrogen well in which the cryostat was immersed.

MATERIALS

Benzene

The benzene sample was taken from a batch of Baker's "C. P. Analyzed" material. The

freezing point of the material was determined by a time temperature experiment and found to be 4.92°C, indicating a probable purity of 99.1 mole percent. A higher degree of purity would have been of no virtue for measurements in the temperature range studied.

Methyl alcohol

This substance was supplied to us by Dr. J. C. Woodhouse of E. I. du Pont de Nemours and Company and was described as of excellent purity. The density of the material, as determined by us, was $d_4^{25}=0.78631$. If it is assumed that water was the only impurity, the material was 99.7 mole percent methyl alcohol.

In the work with benzene and methyl alcohol, care was taken to cool the calorimeter slowly through the freezing region of the substances in order to insure complete crystallization. While the cryostat was at room temperature helium gas was admitted to the vacuum compartment to a pressure of about 1 cm. Liquid nitrogen was then transferred intermittently in small portions into the hydrogen Dewar vessel which surrounded the vacuum compartment until the whole apparatus had cooled to 78°K. The nitrogen was removed from the cryostat just before the liquid hydrogen was run in. Visual observations made by plunging test tubes of benzene and methyl alcohol directly into liquid air indicated that, even with such drastic cooling rates, crystallization would proceed to completion. The observations of Kelley¹⁹ indicate that the high temperature modification of crystalline methyl alcohol does not tend to supercool.

Glycerol

Three studies were made on a single sample of this substance. A batch of Baker's "C. P." glycerol was distilled through an all glass still under a pressure of less than 1 cm of mercury at a temperature of 170°C. The sample for the heat capacity measurements was taken from the middle one of three equal fractions that were collected. The purity of the material was attested to by the fact that very little evidence of pre-melting was apparent when the sample was fused after crystallization. Two sets of measurements were made with the material in the glassy

¹⁹ K. K. Kelley, J. Am. Chem. Soc. **51**, 180 (1929).

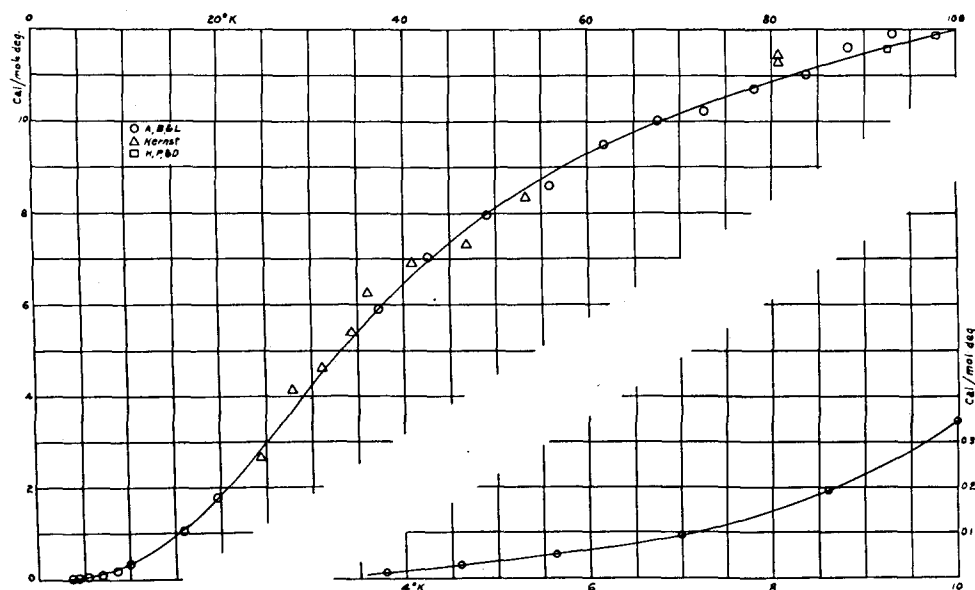


FIG. 2.

state and one with it crystallized. The chronological order of the measurements was: glass I, crystals, glass II.

Glass I was formed from material which had never been in the crystalline state, at least since it had been distilled. In order to effect rapid cooling of the sample in the calorimeter, the vacuum compartment was pumped out and the calorimeter can warmed to 300°K while the cryostat was being filled with liquid nitrogen. When the walls of the vacuum compartment had cooled the vacuum was broken by the admission of an exchange gas.

Following the measurements on glass I, the sample was crystallized, without seeding, by allowing it to warm up extremely slowly from about 200°K.²⁰ Crystallization set in at approximately 257°K. The material was remelted and recrystallized several times, always without difficulty, to insure the dependability of the procedure. Before cooling the material for the heat capacity measurements, the crystallized glycerol was held, in the calorimeter, at 283°K for several days to insure complete crystallization and then cooled slowly with liquid air.

Glass II was formed following the melting of the crystals, without, moreover, ever permitting the temperature of the glycerol to rise above

300°K. To insure complete fusion, the material was held, in the calorimeter, at 298°K for several days before the formation of the glass. In the formation of this glass the calorimeter was cooled relatively slowly by the technique used in the cases of benzene and methyl alcohol.

BENZENE AND METHYL ALCOHOL

The experimental values of the molal heat capacities of benzene at constant pressure are shown in Table I and Fig. 2. The electrical

TABLE I. Molal heat capacities of benzene. Molecular weight 78.05; moles in sample 0.6004. 0°C = 273.17°K: 1 calorie = 4.185 abs. joules.

| T °K | ΔT | C_p cal./deg./mole | C_p/T^3 |
|-------|------|-------------------------|-----------------------|
| 3.79 | 0.32 | 0.0125 | 2.30×10^{-4} |
| 4.60 | .48 | 0.0302 | 3.10×10^{-4} |
| 5.63 | 1.14 | 0.0525 | 2.94×10^{-4} |
| 7.00 | 1.40 | 0.095 | 2.77×10^{-4} |
| 8.60 | 1.64 | 0.192 | 3.02×10^{-4} |
| 10.02 | 1.64 | 0.347 | 3.45×10^{-4} |
| 15.90 | 2.28 | 1.07 | 2.66×10^{-4} |
| 19.82 | 2.42 | 1.80 | 2.31×10^{-4} |
| 37.35 | 5.13 | 5.90 | |
| 42.82 | 5.75 | 7.03 | |
| 49.01 | 6.36 | 7.96 | |
| 55.97 | 6.27 | 8.60 | |
| 61.88 | 5.64 | 9.5 | |
| 67.56 | 5.31 | 10.0 | |
| 72.71 | 5.10 | 10.2 | |
| 78.08 | 5.80 | 10.7 | |
| 83.59 | 5.60 | 11.0 | |
| 88.21 | 5.36 | 11.6 | |
| 93.16 | 5.23 | 11.9 | |

²⁰ Gibson and Giauque, J. Am. Chem. Soc. 45, 93 (1923).

energy used for heating was measured in International units and converted to calories by the use of the definition: 1 calorie = 4.1833 Int. joules. Before computing the number of mole in the samples the weights of the materials were reduced to "in vacuum" values. Below 20°K the temperature measurements were made by a joint employment of the helium gas thermometer and the constantan resistance thermometer. Above 20°K the temperatures were measured with the copper-constantan thermocouple. In the case of benzene the measurements made with the thermocouple unfortunately did not prove as consistent and satisfactory as some of those made subsequently on other substances.

In Table II are given the molal heat capacities as read off the most plausible curve through the observations (the solid curves of Fig. 2). In constructing the curve at points where there was any element of choice, due weight was given to the measurements of Nernst²¹ between 20° and 80°K and those of Huffman, Parks and Daniels²² starting at 92°K. Applications of the new heat capacity data for benzene have been made by Lord and Andrews²³ and by Lord, Andrews and Ahlberg²⁴ in papers published elsewhere.

The entropy of benzene at various temperatures is shown in Table III. The usual graphical method of integration was employed for our own heat capacity data. The value of the entropy at 3°K was approximated by the use of the conventional rule $S_T = aT^3/3$ in which the value of "a" was determined from the heat capacity measurements below 9°K and found to have the

value 2.85×10^{-4} cal./deg.⁴/mole. The new experimental value of the entropy at 90°K is 0.46 E. U. lower than the value based on extrapolation given by Huffman, Parks and Daniels.²² The entropy data of the latter authors were employed in computing the entropies given for temperatures above 90°K.

Experimental values of the molal heat capacities of methyl alcohol from 3° to 28°K are given in Table IV. The measurements were made in a manner exactly similar to those on benzene. The agreement of our values with those of Kelley¹⁹ in the interval between 16° and 30°K is satisfactory. Several of Kelley's measurements are included, in italics, in Table IV for comparison. In Table V the entropy at various temperatures has been computed. The T^3 formula was used rather arbitrarily to estimate the value of the entropy at 3.25°K. As will be noted in the last column of Table IV, the C_p/T^3 quotient is not constant below 7°K but diminishes in a rather regular manner with the temperature. A very similar but somewhat more pronounced effect was also obtained in the measurements on crystalline glycerol. The drift is larger than our estimate of the random errors in the measurements but may be due to a systematic error. Between 7° and 15°K the obedience to the T^3 law is quite satisfactory. For a practical estimation of the numerical value of the entropy at 3.25°K almost any simple function of the temperature can be made to serve almost equally well for the extrapolation of the heat capacity data.

Kelley gives a value of 0.26 E.U. for the entropy at 16.5°K, based on extrapolation, which is in agreement with our value of 0.267 E.U. based on experimental measurements

TABLE II. Molal heat capacities of benzene. Read from smooth curve through observations. Molecular weight 78.05. 0°C = 273.17°K: 1 calorie = 4.185 abs. joules.

| T °K | C_p cal./deg./mole | T °K | C_p cal./deg./mole |
|------|-------------------------|------|-------------------------|
| 4 | 0.0195 | 40 | 6.47 |
| 6 | .065 | 50 | 8.14 |
| 8 | .147 | 60 | 9.32 |
| 10 | .346 | 70 | 10.16 |
| 15 | .920 | 80 | 10.85 |
| 20 | 1.84 | 90 | 11.44 |
| 25 | 3.00 | 100 | 11.99 |
| 30 | 4.24 | | |

²¹ W. Nernst, Ann. d. Physik **36**, 395 (1911).

²² Huffman, Parks and Daniels, J. Am. Chem. Soc. **52**, 1547 (1930).

²³ Lord and Andrews, J. Phys. Chem. **41**, 149 (1937).

²⁴ Lord, Andrews and Ahlberg, to be published.

TABLE III. Entropy of benzene.

| T °K | S cal./deg./mole |
|----------------|---------------------|
| 0 | 0 |
| 3.63 | 0.0045(a) |
| 10.0 | 0.098 |
| 20.0 | 0.73 |
| 90.0 | 10.89 |
| 278.6 Crystals | 30.91(b) |
| 278.6 Liquid | 39.34 |
| 298.1 | 41.49 |

(a) By extrapolation $S = aT^3/3$ where $a = 2.85 \times 10^{-4}$.

(b) Values above 90°K based on the data of Huffman, Parks and Daniels, J. Am. Chem. Soc. **52**, 1554 (1930).

TABLE IV. Molal heat capacities of methyl alcohol. Molecular weight 32.03: moles in sample 1.426. $0^\circ\text{C}=273.17^\circ\text{K}$: 1 calorie = 4.185 abs. joules.

| $T^\circ\text{K}$ | ΔT | C_p cal./deg./mole | C_p/T^3 |
|-------------------|------------|-------------------------|-----------------------|
| 3.68 | 0.86 | 0.0067 | 1.35×10^{-4} |
| 4.65 | .90 | .0139 | 1.38 |
| 5.44 | .80 | .0252 | 1.56 |
| 6.30 | .98 | .0427 | 1.70 |
| 7.33 | 1.19 | .071 | 1.80 |
| 8.58 | 1.29 | .110 | 1.75 |
| 9.73 | 1.24 | .165 | 1.79 |
| 10.75 | 1.37 | .235 | 1.89 |
| 12.28 | 1.82 | .359 | 1.93 |
| 14.37 | 2.48 | .517 | 1.75 |
| 16.94 | 3.13 | .817 | 1.68 |
| 18.80 | | 1.11(a) | |
| 20.50 | 4.76 | 1.29 | |
| 21.55 | | 1.51(a) | |
| 23.94 | 2.92 | 1.94 | |
| 24.43 | | 1.96(a) | |
| 27.25 | | 2.29(a) | |
| 28.39 | 3.77 | 2.57 | |

(a) Measurements by K. K. Kelley, J. Am. Chem. Soc. 51, 180 (1929).

down to 3.25°K . Data by Kelley were employed in computing the value given for the entropy at 298.1°K .

GLYCEROL

It has been suggested²⁵ that glasses of the same substance formed under different conditions should display slight differences in their fundamental properties at low temperatures. For some substances, at least, it seems necessary to conclude that the liquid state is not one of complete randomness but rather that there is some slight degree of order or orientation among the particles which varies inversely as the temperature. In a viscous liquid, moreover, there must be an appreciable lag in the attainment of the degree of order corresponding to the new temperature state when the temperature is decreased rapidly through a considerable interval. Furthermore, the changes which occur when a liquid such as glycerol passes through its "congealing zone" may reasonably be assumed to involve an inhibition or extreme slowing up of the processes by which an equilibrium state of order is arrived at. These considerations made it seem not altogether inconceivable that glasses which had been cooled through their congealing zone at rapid but different rates might show significant differences in their heat capacities at very low tempera-

²⁵ F. Simon, Zeits. f. anorg. allgem. Chemie 203, 219 (1931).

tures where the heat capacity is determined wholly by the structural configuration and properties of the solid state. With these ideas in mind, the sample of glycerol was congealed twice, as described above, under circumstances as different as it was possible to make them. The measurements on the glass designated as glass I were extended from 2.3° to 85°K while those on the glass designated as glass II were only carried up to 22°K . Starting at 14°K the observed heat capacity values for glass II fall slightly below those of glass I by increasing amounts up to 22°K where the measurements on glass II were unfortunately interrupted. The best curves drawn through the two sets of measurements indicate a difference in heat capacity between the two glasses of some 0.13 calorie per mole at 18.5°K . Below 14°K the heat capacities of the two glasses differ irregularly and by amounts substantially less than the limits set by experimental uncertainty. The present data are not adequate for a decision as to the reality of this apparent difference which presumably ought to be more pronounced rather than less at the lower temperatures. It may be said, however, that the two glasses are certainly quite similar if not altogether identical in structure.

The molal heat capacities of glassy and crystalline glycerol at constant pressure are shown in Tables VI and VII, respectively, and in Figs. 3 and 4. Since it does not seem justifiable to weight the small differences observed above 14°K in the heat capacities of the two glasses, the data on both are included in Table VI. The results of the very brief series of measurements between 10° and 12°K by Simon and Lange²⁶ are included, in italics, in Tables VI and VII. The agreement with the present measurements is good, particularly so in the case of the crystalline

TABLE V. Entropy of methyl alcohol.

| $T^\circ\text{K}$ | S cal./deg./mole |
|-------------------|-----------------------|
| 0 | 0 |
| 3.26 | 0.00154(a) |
| 16.25 | 0.267 |
| 298.1 | 30.3(b) |

(a) By extrapolation.

(b) Based on the data of Kelley (reference 19) above 20°K .

²⁶ Simon and Lange, Zeits. f. Physik 38, 227 (1926).

TABLE VI. Molal heat capacities of glassy glycerol. Molecular weight 92.06; moles in sample 0.8049. $0^\circ C = 273.17^\circ K$: 1 calorie = 4.185 abs. joules.

| Glass | $T^\circ K$ | ΔT | C_p cal./deg./mole | C_p/T^3 |
|-------|-------------|------------|-------------------------|-----------------------|
| I | 2.30 | 0.20 | 0.0037 | 3.04×10^{-4} |
| I | 2.63 | 0.12 | 0.0081 | 4.45 |
| I | 3.03 | 0.21 | 0.0055 | 1.98 |
| II | 3.33 | 0.33 | 0.0122 | 3.30 |
| I | 3.43 | 0.19 | 0.0091 | 2.25 |
| I | 3.66 | 0.28 | 0.0131 | 2.67 |
| II | 4.01 | 0.67 | 0.0177 | 2.75 |
| I | 4.22 | 0.57 | 0.0211 | 2.81 |
| II | 4.75 | 0.75 | 0.0339 | 3.16 |
| I | 5.45 | 0.49 | 0.052 | 3.21 |
| II | 5.57 | 0.91 | 0.057 | 3.32 |
| I | 6.28 | 1.24 | 0.085 | 3.43 |
| II | 6.56 | 1.05 | 0.104 | 3.68 |
| I | 7.37 | 1.10 | 0.148 | 3.70 |
| II | 7.68 | 1.31 | 0.163 | 3.60 |
| I | 8.40 | 1.07 | 0.230 | 3.88 |
| II | 9.12 | 1.71 | 0.282 | 3.72 |
| I | 10.52 | 0.99 | 0.435 | 3.74 |
| (a) | 10.58 | | 0.413 | 3.50 |
| (b) | 10.84 | | 0.433 | 3.37 |
| II | 10.88 | 1.85 | 0.461 | 3.58 |
| (a) | 11.67 | | 0.524 | 3.32 |
| (b) | 12.26 | | 0.578 | 3.14 |
| I | 12.33 | 2.65 | 0.614 | 3.28 |
| (a) | 12.69 | | 0.636 | 3.11 |
| II | 13.10 | 2.62 | 0.722 | 3.21 |
| I | 14.80 | 2.33 | 1.02 | 3.15 |
| II | 15.90 | 2.90 | 1.10 | 2.74 |
| I | 17.16 | 2.37 | 1.35 | 2.67 |
| II | 18.81 | 2.91 | 1.52 | 2.28 |
| I | 19.75 | 2.79 | 1.80 | 2.33 |
| I | 22.62 | 2.92 | 2.34 | |
| I | 28.98 | 3.28 | 3.45 | |
| I | 32.05 | 2.85 | 3.86 | |
| I | 34.88 | 2.82 | 4.43 | |
| I | 37.45 | 2.44 | 5.00 | |
| I | 40.33 | 3.13 | 5.36 | |
| I | 44.14 | 4.74 | 6.03 | |
| I | 51.19 | 5.69 | 7.05 | |
| I | 57.37 | 6.65 | 8.02 | |
| I | 63.65 | 5.94 | 8.99 | |
| I | 69.37 | 5.51 | 9.65 | |
| I | 74.37 | 5.22 | 10.17 | |
| I | 79.68 | 5.60 | 11.23 | |
| I | 85.12 | 5.28 | 12.00 | |
| I | 90.12 | 5.14 | 12.29 | |
| I | 94.89 | 4.87 | 13.12 | |

(a) Measurement of Simon and Lange, Series I.
(b) Id.; Series II, Zeits. f. Physik 38, 227 (1926).

form. Above $80^\circ K$ our measurements tie in well with those of Gibson and Giauque.²⁷

In Table VIII, column I is a tabulation of the entropies of the crystalline state at various temperatures, assuming that the crystalline form obeys the so-called third law of thermodynamics. The value of 9.05 E.U. for the entropy at $90^\circ K$ is 0.8 E.U. lower than the value given by

²⁷ Gibson and Giauque, J. Am. Chem. Soc. 45, 93 (1923).

TABLE VII. Molal heat capacities of crystalline glycerol. Molecular weight 92.06; moles in sample 0.8049. $0^\circ C = 273.17^\circ K$: 1 calorie = 4.185 abs. joules.

| $T^\circ K$ | ΔT | C_p cal./deg./mole | C_p/T^3 |
|-------------|------------|-------------------------|-----------------------|
| 3.08 | 0.59 | 0.0051 | 1.74×10^{-4} |
| 3.86 | 0.77 | 0.0093 | 1.62 |
| 5.03 | 1.57 | 0.0193 | 1.52 |
| 6.30 | 1.31 | 0.0414 | 1.66 |
| 7.44 | 1.27 | 0.070 | 1.70 |
| 8.51 | 1.19 | 0.116 | 1.88 |
| 9.66 | 1.33 | 0.172 | 1.91 |
| 10.57 | | 0.242(a) | 2.06 |
| 10.67 | | 0.239(b) | 1.97 |
| 10.98 | 1.62 | 0.266 | 2.01 |
| 11.96 | | 0.353(a) | 2.07 |
| 12.47 | 1.83 | 0.413 | 2.13 |
| 12.83 | | 0.438(b) | 2.07 |
| 12.91 | | 0.438(a) | 2.04 |
| 14.58 | 2.39 | 0.629 | 2.03 |
| 17.45 | 3.03 | 0.983 | 1.85 |
| 19.54 | 1.22 | 1.282 | 1.72 |
| 21.89 | 3.42 | 1.621 | 1.54 |
| 25.25 | 3.65 | 2.19 | |
| 29.55 | 5.03 | 2.88 | |
| 35.36 | 6.17 | 3.82 | |
| 42.96 | 8.00 | 5.17 | |
| 49.19 | 4.14 | 6.32 | |
| 54.57 | 6.02 | 7.22 | |
| 61.00 | 5.15 | 8.13 | |
| 66.81 | 5.53 | 9.12 | |
| 72.34 | 5.12 | 9.86 | |
| 77.45 | 4.78 | 10.62 | |
| 82.33 | 4.53 | 11.21 | |
| 86.92 | 4.31 | 11.90 | |

(a) Measurements of Simon and Lange, Series I.
(b) Id., Series II; Zeits. f. Physik 38, 227 (1926).

Parks, Kelley and Huffman²⁸ who extrapolated the data of Gibson and Giauque²⁷ and of Simon and Lange.²⁶ The data of Gibson and Giauque were employed in computing the values given for temperatures above $90^\circ K$. Column II of Table VIII gives values of the integral $\int_0^T C_p d \ln T$ for the glassy form.

If it is assumed, in the absence of conclusive evidence to the contrary, that the liquid ordinarily resulting from the melting of a glycerol crystal and the liquid resulting from the softening of a glycerol glass are thermodynamically identical and therefore possess identical entropy, the following equality will, by thermodynamics, hold for the liquids at the melting point of the crystal.

$$S_{(l)}^{291} = \int_0^{291} [C_{p(cry.)} d \ln T] + \Delta S_f + S_{(cry.)}^0 \\ = \int_0^{291} [C_{p(g.l.)} d \ln T] + S_{(g.l.)}^0$$

²⁸ Parks, Kelley and Huffman, J. Am. Chem. Soc. 51, 1969 (1929).

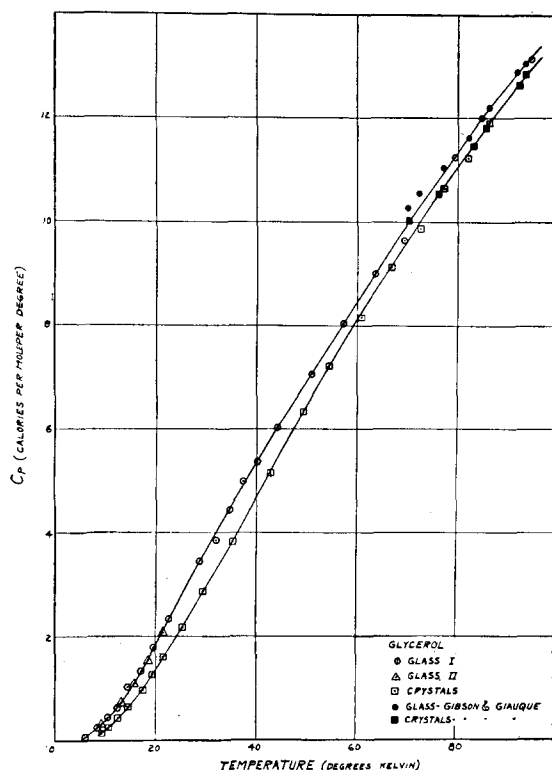


FIG. 3.

where ΔS_f is the entropy change involved in the melting of the crystal form at 291°K; $S^0_{(cr.)}$ has the value zero according to the third law, and $S^0_{(gl.)}$ is the apparent entropy of the glassy form at 0°K. The entropy difference between the two forms at any temperature below the melting point is therefore given by

$$\Delta S_{(gl.-cr.)} = \Delta S_f$$

$$- \int_T^{T_{MP}} [C_{p(gl.)} - C_{p(cr.)}] d \ln T, \quad (I)$$

while $S^0_{(gl.)}$ is obviously obtained by setting the lower limit of the integral at zero. The values of the entropy differences between the two forms at various temperatures as given by this equation are shown in column III of Table VIII. The accuracy with which $S^0_{gl.}$ can now be given is limited by the experimental accuracy of the heat of fusion and the high temperature heat capacities. An appraisal of the existing high temperature data indicates that the value of $S^0_{gl.}$ is 4.64 ± 0.04 E.U. In order to take advantage of

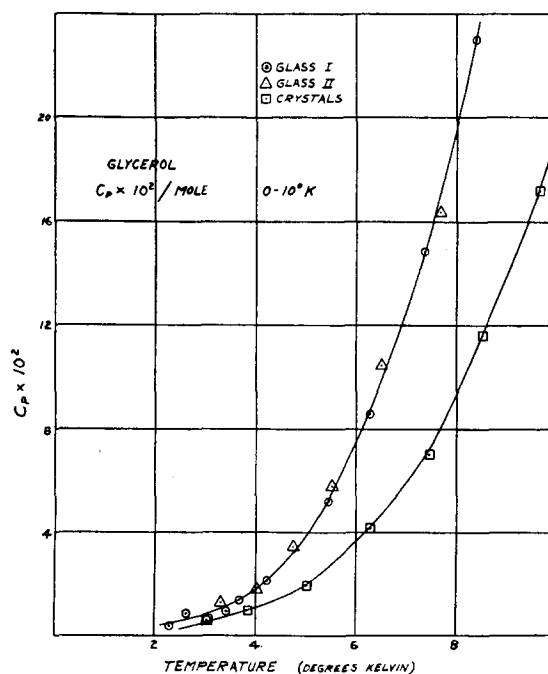


FIG. 4.

the accuracy of our low temperature measurements for showing the temperature trend of the entropy differences between the crystalline and glassy forms of the substance, the values of

$$\int_0^T [C_p d \ln T]_{(gl.)} - S_{T(cr.)}$$

are given in column IV.

The importance of heat capacity data at very low temperatures for a correct picture of the solid state of "soft" substances is illustrated by Figs. 3 and 4. At liquid-air temperatures the heat capacity curves of crystalline and glassy glycerol are very close together and appear to run practically parallel to each other. Proceeding downward, the curves begin to diverge in no uncertain manner at about 50°K as differences in heat capacity due to differences between the structure of the crystalline and glassy states begin to have measurable effect on the total observed heat capacities. In Fig. 4 the curves appear to be converging rapidly but this is an effect due to the rapidly diminishing absolute values of the two sets of heat capacities. At 18°K the heat capacity of the glass is larger than that of the crystal by 40 percent of the latter, at 12° by 55 percent and

between 9° and 5° by 100 percent. As column IV of Table VIII shows, this divergence of the heat capacity curves is sufficient to produce an error of +1 E.U. if an attempt is made to evaluate S_{gi}^0 by extrapolating the high temperature heat capacity data.

The present measurements confirm the conclusions and predictions of Simon and Lange²⁶ about the behavior and significance of the low temperature heat capacities of crystalline and

glassy glycerol and little need be added here to their discussion. They predicted an entropy for the glass at the absolute zero of 4.6 ± 0.3 E.U. which is in agreement with our value of $4.64 \pm .04$ E.U. Unless decidedly *ad hoc* assumptions as to the behavior of the heat capacity below 3°K are to be admitted, it seems safe to conclude that the four glasses which have been studied at very low temperatures (two by Simon and Lange and two in this investigation) retain 4.6 units of entropy at the absolute zero. This, however, is undoubtedly the residual entropy of a frozen-in state which is an equilibrium state of the glass only at or above the congealing temperature (180°K) rather than the entropy of an "ideal glass" at the absolute zero. Amorphous states formed by a cooling path radically different from those which can be obtained in the types of vacuum calorimeters that have been employed might well show a measurably different entropy at the absolute zero.

The authors are indebted to the United States Navy Department and especially to Mr. C. E. Earle for the trouble taken in supplying pure helium gas for use in the liquefier. To Professor D. H. Andrews the authors are most grateful for his part in putting the equipment of the Cryogenic Laboratory at their disposal and to Messrs. W. T. Ziegler and C. F. Squire for assistance in the calculations and graphical work.

TABLE VIII. Entropies of crystalline and glassy glycerol.

I. Entropies of crystalline glycerol at the indicated temperatures and, above 291°K, of liquid glycerol. II. Values of the integral $\int_0^T C_p d \ln T$ for the glassy state and super-cooled liquid. III. Entropy differences between the glassy and crystalline forms, $S_{gl} - S_{cry}$, as computed by Eq. (I). IV. Values of $\int_0^T (C_p d \ln T)_{gl} - S_{T(cry)}$.

| T °K | I cal./deg./mole | II cal./deg./mole | III cal./deg./mole | IV cal./deg./mole |
|--------|---------------------|----------------------|-----------------------|----------------------|
| 0.0 | 0.0 | — | 4.64(a) | — |
| 2.20 | 0.00058(b) | 0.00088(b) | 4.64 | 0.0003 |
| 2.79 | 0.0012(b) | 0.0018 | 4.64 | 0.0006 |
| 10.00 | 0.0472 | 0.119 | 4.71 | 0.072 |
| 20.00 | 0.505 | 0.784 | 4.92 | 0.279 |
| 70.00 | 6.307 | 7.290 | 5.62 | 0.983 |
| 90.00 | 9.052 | 10.118 | 5.71 | 1.066 |
| 291.00 | 32.58(c) | 42.96(c) | 15.02(c) | |

Liquefaction, $-S_{fusion} = 15.02(c)$

291.00 47.60

298.10 48.87

(a) ± 0.04 E.U.

(b) By extrapolation.

(c) Computed using the data of Gibson and Giauque for temperatures above 90°K. (J. Am. Chem. Soc. 45, 93 (1923); see also Parks, Kelley and Huffman, J. Am. Chem. Soc. 51, 1971 (1929).)