[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE THIRD LAW OF THERMODYNAMICS. EVIDENCE FROM THE SPECIFIC HEATS OF GLYCEROL THAT THE ENTROPY OF A GLASS EXCEEDS THAT OF A CRYSTAL AT THE ABSOLUTE ZERO

BY G. E. GIBSON AND W. F. GIAUQUE

Received November 6, 1922

In a recent paper[1] reasons were given for believing that the third law of thermodynamics, like the second, contains the statement of an inequality as well as an equality of entropy. Regarded from the point of view of the laws of chance, the statement that the entropy of a perfect crystal is zero at the absolute zero corresponds to the perfect order of the arrangement of the atoms in the crystal. The statement that the entropy of a non-crystalline system may be greater but can never be less than zero corresponds to the fact that the arrangement of the parts of a system may be more but can never be less random than in a perfect crystal at the absolute zero.

The experimental evidence is now amply sufficient to establish the third law in so far as it applies to crystalline substances.[2] This, however, cannot be said of the experimental evidence in favor of the inequality contained in the third law. The only experiments published hitherto which have any bearing on this question are those on the specific and latent heats of crystalline and amorphous alcohol[3] and silica,[4] and on the specific heats of ethyl and propyl alcohols[3] and their equimolal mixture. Wietzel, in testing the third law for fused and crystalline silica, came to the conclusion that the entropy of the fused form is appreciably greater than that of the crystals at liquid hydrogen temperatures. The uncertainties in the specific-heat measurements at high temperatures, and still more in the measurements of heats of transition and inversion, are very great, so that this perhaps can hardly be regarded as a decisive confirmation of the existence of an entropy difference at the absolute zero.

The data on the heat of fusion of ethyl alcohol and the specific heats of the crystalline and supercooled forms seem to show that the entropy of the supercooled form is the greater at the absolute zero. However, considering the difficulty in preventing crystallization, and the assumptions made in extrapolating heat capacities below liquid air temperatures, this cannot be regarded as completely established.

The data on the entropy of mixing of ethyl and propyl alcohols appear to show that the entropy of the mixture is the greater at the absolute

[1] Lewis and Gibson, THIS JOURNAL, **42**, 1529 (1920).

[2] Lewis, Gibson and Latimer, *ibid.*, **44**, 1008 (1922).

[3] Gibson, Parks and Latimer, *ibid.*, **42**, 1542 (1920).

[4] R. Wietzel, *Z. anorg. Chem.*, **116**, 71 (1921).

zero. The difficulties which we have already mentioned in the determination with ethyl alcohol leave some uncertainty in this conclusion also.

In the present investigation the specific heats of crystalline and supercooled glycerol have been determined from the melting point, 291° K., to 70° K. The heat of fusion has also been determined. A detailed description of the measurements will be found in the next section of this paper. Glycerol was chosen for reasons which were fully justified by the results. It can readily be obtained in either the crystalline or supercooled form at all temperatures below the melting point. The data on alcohol and other glasses show that the specific heat of the glass approaches closely that of the crystalline form at low temperatures. In the case of alcohol, the specific heat of the glass is still 10% higher than that of the crystals at liquid air temperature. It seemed likely, as was found to be the case, that on account of the higher melting point of glycerol the specific heats of the 2 forms would become practically coincident above liquid air temperature and thus reduce the uncertainty of the extrapolation. The difficulty of calorimetric determinations increases greatly with the temperature, owing mainly to the increased radiation. The melting point of glycerol is, however, sufficiently low to permit the determination of the heat of fusion with the required accuracy.

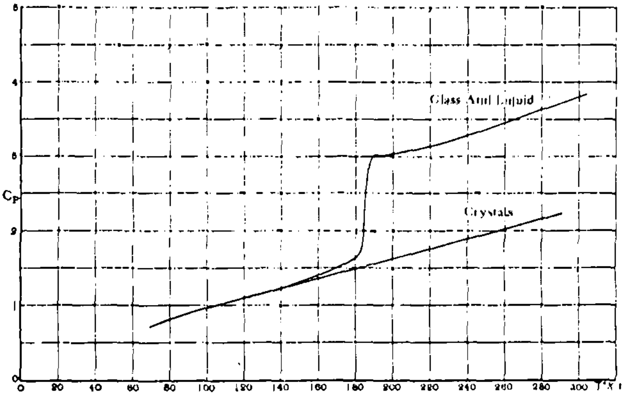

Fig. 1.—Heat capacity of glycerol per mean gram atom.

In Fig. 1 the heat capacities per mean gram atom for supercooled and crystalline glycerol are plotted against the absolute temperature. The data from which these curves were plotted are given in Tables I and II, pages 106, 107. The curve of the supercooled liquid has the same characteristic form which was found for ethyl and propyl alcohols. The sudden change of properties which occurs about 190° K. is even more abrupt than in the case of the alcohols. The maximum just after the sudden rise is probably due to a belated emission of heat, and might not have appeared if more time had been allowed to elapse between measurements.

The measurements were made at intervals of about 1 hour, but the establishment of equilibrium is very slow in the region where the specific heat is changing rapidly. For this reason too much stress cannot be laid on the actual values obtained for the specific heats in this region. It is possible that this change in the character of a supercooled liquid as it passes through the region in which the specific heat changes rapidly may be a true liquefaction. The gradual appearance of the change may be due to a kind of strain depending on the previous treatment of the glass, so that if it were possible to obtain a glass free from strain at all temperatures, the liquefaction would occur at a definite temperature with a definite heat of liquefaction. We should then be justified in speaking of the "liquefaction point" of a glass, as we speak of the melting point of a crystal. Since we are more interested in the entropy change than in the values of the heat capacity, the measurements were carried out in such a way as to give the total heat absorbed throughout the whole region of rapid change. A curve was then drawn so as to make the area under the curve equal to the actually determined energy input. The uncertainty in the value of the entropy due to this method of calculation is entirely negligible.

The specific heats and the heat of fusion were determined with the same sample in the same calorimeter. Thus the determination of the difference in entropy between the two forms is more accurate than the absolute specific-heat determinations, since uncertainties in the heat capacity of the empty calorimeter cancel one another by subtraction.

Calculation of Entropy

The entropy difference between supercooled liquid and crystalline glycerol at any temperature, T, is given by the equation,

$$\Delta S = \frac{\Delta H_{(\text{fusion})}}{T_{\text{M.P.}}} - \int_{T}^{T_{\text{M.P.}}} [C_p \text{ (glass)} - C_p \text{ (crystals)}]\, d\, ln\, T.$$

The integral was evaluated graphically by taking the area on a plot of C_p against $ln\ T$. The value of ΔS decreases rapidly with decreasing temperature until 190° K. is reached. Starting at this temperature, C_p (supercooled) decreases rapidly almost to equality with C_p (crystals), and they remain nearly equal at the lowest temperature of measurement. Thus ΔS remains practically constant during the 100° interval above 70° K., and it seems very improbable that it should do otherwise for the remaining 70° to the absolute zero. The heat of fusion was found to be 4370 calories per mole at the melting point, 291.0° K. The first term in the above equation is thus $4370/291.0 = 15.02$ cal./deg. The value of the integral between 70° K. and the melting point was found to be 9.39 cal./deg. Hence $\Delta S_{70°} = 15.02 - 9.39 = 5.6 \pm 0.1$ cal./deg. per mole, or 0.40 ± 0.01 cal./deg. per mean gram atom. We may say with confidence that this difference of 5.6 cal./deg. between the 2 forms will persist without great change to the absolute zero.[4]

In endeavoring to account for the excess of the entropy of fused-over crystalline silica, as calculated by Wietzel,[4] Nernst[5] suggests that the specific heat of the glass may diminish much more slowly than that of the crystals at temperatures below 1° K. In order to account in this way for the difference of 5.6 cal./deg. which we have found in the case of glycerol, we should have to assume that the specific heat of the glass remained appreciable down to improbably low temperatures. Thus, if we make the assumption that the specific heat of glycerol glass remains constant at the improbably high value of 0.25 cal./deg. from 1° K. to 1×10^{-10} ° K. we should just be able to account for the observed 5.6 cal./deg. difference. The evidence furnished by glycerol is, therefore, strongly in favor of the interpretation of the third law given by Lewis and Gibson.

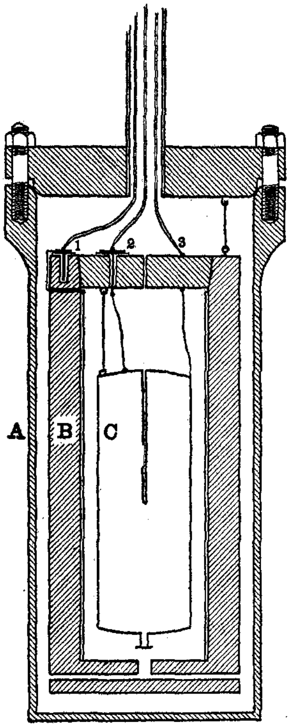

Fig. 2.

Experimental

The assembled apparatus is shown in Fig. 2. The cylindrical copper calorimeter, C, was constructed of tubing, the wall of which was turned down in a lathe to 0.5 mm. The height was 10 cm. and the diameter 3.5 cm. Eight radial vanes, 0.1 mm. in thickness, were placed inside to secure rapid distribution of heat. Extending down from the top to the center was a small tube in which a thermocouple could be placed if desired. The glycerol was introduced through a small opening in the bottom, over which a cap was soldered.

Following Eucken,[6] Nernst and others, a combined resistance thermometer-heater was used for measuring temperature and introducing energy. This was made of copper[7] since it was to be wound on the copper calorimeter, thus minimizing strain due to temperature change. The construction was as follows. The side of the calorimeter was coated with Bake-

---

[5] Since this paper was written, a paper by F. Simon [*Ann. Physik*, **68**, 241 (1922)] has come to hand. Simon has measured the specific heats of amorphous glycerol from 18.8° K. to 294.4° K. For the most part his results agree fairly well with our own, but unfortunately the sample used by Simon contained 1.3% of water, the effect of which shows decidedly in the results below the liquefaction point. It is of interest to note that his data lead to approximately the same value for the total energy input in going through the liquefaction range as do our own. His specific heats at room temperature are, however, about 2% too high.

[6] Eucken, *Physik. Z.*, **10**, 586 (1909).

[7] K. Onnes and Holst, *Comm. Phys. Lab. Leiden*, No. **142A** (1914). Meissner *Verh. deut. physik. Ges.*, **16**, 262 (1914).

lite lacquer which was baked on. Then double silk-covered copper wire of diameter 0.08 mm. (B. and S. No. 40) was wound on, 50 turns to the cm., for the full length. Another coat of lacquer, which thoroughly impregnated the silk insulation, was applied and baked. It was desirable to have as poor a radiating surface as possible, so the wire was covered by gold leaf attacked by another coat of lacquer. Gold leaf was used because it could be easily applied, added very little to the heat capacity and, of more importance, the temperature of the surface during energy input was more accurately that indicated by the thermometer than would have been the case had a heavier, less closely adhering radiating surface been used.

The calorimeter was suspended from the cover of a massive hollow copper cylinder, shown as B in Fig. 2, by 3 fine silk threads 2.5 cm. in length. The inner wall of the cylinder was a piece of copper tubing on which was wound a thermometer-heater of the same resistance and description as that on the calorimeter, except that no gold leaf was necessary, the wire being enclosed between the tubing and the cylinder. The wire was wound in a spiral groove so that the tube could be fitted tightly into place. Since the calorimeter was to be suspended in a vacuum, several holes were drilled in the bottom of the cylinder, a 90° turn preventing the passage of radiation. The cylinder weighed 2.3 kilograms.

The thermometer terminals shown at 1 and 2 were shaped like rivets with flat heads of large diameter, to insure good thermal contact with the top of the cylinder. These were insulated electrically from the cylinder, by Bakelite. This was found to be sufficient protection of the thermometers from heat conduction along the leads. Certain practical advantages were gained by the proper choice of electrical connections. The cylinder itself was made the common terminal of the calorimeter and cylinder thermometers, and the calorimeter itself the other terminal of its own thermometer. Thus accidental contact of the calorimeter and the cylinder was indicated by nearly zero resistance across the calorimeter thermometer terminals. These connections were also the most advantageous for protecting the thermometers from heat conduction along the leads.

To each of the terminals, 1, 2 and 3, were attached a current and a potential lead. The resistance of each thermometer was determined by comparison of the potential drop with that across a standard resistance in the circuit. Since the two thermometers could be put in series, one reading with the standard resistance sufficed for both measurements. An extremely constant thermometer current was obtained by the use of 8 Edison storage cells connected in series and discharging continuously through 80,000 ohms. The thermometers were put in circuit when desired. With 80,000 ohms in the circuit, slight changes in the thermometers produce a negligible effect on the total resistance, and the thermometer current remains practically constant. One current reading was found to be sufficient during a determination of the rate of heating or cooling; thus the accuracy of the current reading had no effect on the correction for heat interchange with the surroundings, which was the measurement requiring the greatest accuracy. The current used was about 0.00013 amp., and as this produced a negligible heating effect in the thermometer wire it was allowed to flow through the thermometer continuously, except when energy was being added to the calorimeter.

The size and design of the thermometers prevented any direct calibration, so it was necessary to use a thermocouple as an intermediate. This does not mean that the greater sensitivity of the thermometers over that of single thermocouples was sacrificed, because it is in the differential and rate measurements that high accuracy is most necessary. Before calibration the thermometers were seasoned by alternately cooling in liquid air and heating to room temperature about 25 times. The 4-element copper-constantan couple of Eastman and Rodebush[8] was used as a standard. The calibration

---

[8] Eastman and Rodebush, This Journal, **40**, 489 (1918).

was made with glycerol in the calorimeter and under the same conditions as in the specific-heat measurements. The thermometer had a resistance of 175 ohms at 273° K., and with the current used the sensitivity was about 100 microvolts per degree at all the temperatures of measurement.

The electrical energy for heating the calorimeter was supplied by a battery of Edison storage cells, which were brought to a steady state by a preliminary discharge through a resistance approximately equal to that of the heater.

As shown in Fig. 2, the potential leads are taken off at 2 and 3 instead of from the ends of the coil on the calorimeter. In calculating energy input a correction, which amounted to 0.05%, was made to allow for the heat generated in the No. 40 (B. and S.) copper leads between the cylinder and the calorimeter. In making this correction, it was assumed that the calorimeter received $^1/_2$ of the heat, since the average temperature difference between cylinder and calorimeter during energy input was nearly zero. Had the potential leads been taken from the calorimeter itself, the correction would still have been necessary, and the heat leak between the calorimeter and its surroundings would have been increased.

A resistance of approximately 10,000 ohms was connected in parallel with the calorimeter heater, and the voltage drop across a small known fraction of this resistance was measured, as the total potential drop was too great to be measured on the potentiometer. A correction was made for the fraction of the heating current which passed through the resistance. The parallel resistance was disconnected during temperature measurements. All electrical measurements were made on a White double potentiometer of special design, and of 100,000 microvolts range. The sensitivity was 0.04 microvolt.

The cylinder was suspended, by means of stout threads, from the top of a vacuum tight container, as shown at A in Fig. 2. The container was constructed from 10cm. hydraulic cold-drawn steel tubing with a 12mm. wall. It was turned down in a lathe to the form indicated. The bottom was welded in. The ball-V joint at the top was a highly satisfactory vacuum-tight joint[9] even when suddenly immersed in liquid air, and remained tight even after having been taken apart and put together repeatedly. The pressure was maintained below 0.00001 mm. of mercury. A soldered joint in a brass container of this size failed at liquid-air temperatures, although soldered joints have proved fairly satisfactory in smaller sizes. The top was fastened on by means of 8 vanadium steel 6mm. stud screws and nuts, which were screwed on tightly enough to mash the joint slightly at the point of contact.

The steel tube leading up from the top of the container was used to evacuate the apparatus, carry the leads and serve as a means of support. It was joined to a glass vacuum line by means of de Khotinsky cement through which the leads were taken out.

Vacuum was obtained by use of a mercury diffusion pump supported by a small 3-stage oil pump. Vacuum was measured by means of a 500cc. McLeod gage, accurate to 0.00001 mm. of mercury. A trap immersed in liquid air protected the copper apparatus from the diffusion of mercury vapor.

The steel container was surrounded by a silvered Pyrex glass Dewar tube of 11cm. inside diameter and 53cm. depth. The baths used were as follows. For measurements between 70° and 160° K., liquid air was used, the great heat capacity of the copper cylinder causing its temperature to remain practically constant even at 160° K. under these conditions. The lower temperature was obtained by evaporating the liquid air under reduced pressure. Between 160° and 200° K. carbon dioxide in ether was used, the lower temperature in this range being obtained by first cooling the apparatus with liquid air. From 200° to 270° K., carbon tetrachloride was used. It has a transition

---

[9] The use of a ball-V joint was suggested by Mr. G. F. Nelson who was responsible for the excellent mechanical construction of the apparatus.

at 224.6° K., melts at 249° K., and forms a satisfactory liquid bath from its melting point to the ice point. From 270° to 300° K. a water-bath was used.

Specific-heat Measurement.—Having cooled the apparatus to the desired temperature, the container was evacuated. Current was then passed through the cylinder heater until the cylinder temperature was approximately 2.5° above that of the calorimeter. The heating rate of the calorimeter was taken. About 0.1 ampere was then passed through the calorimeter heater for from 10 to 15 minutes, producing a temperature rise of about 4°. Since the temperature of the cylinder remained practically constant, the calorimeter was 1.5° above cylinder temperature after the energy input. The cooling rate was then measured for 15 or 20 minutes. A constant rate was attained in from 5 to 10 minutes, indicating that equilibrium had been reached. The energy input was timed to within 0.02% with a calibrated stop-watch.

Newton's law of cooling, which is that the heat transfer is proportional to the temperature difference, was used in calculating the heat interchange between cylinder and calorimeter. This involved knowing the temperatures of both at all times during a measurement. The energy measurements furnished sufficient data for obtaining the external temperature of the calorimeter during the energy input. It was found that the temperature could be considered to increase linearly within the limits of necessary accuracy. This was due to two causes, first, the energy was put in rather slowly, and second, by using over 50 meters of wire in the thermometer-heater, a very small amount of energy was developed per unit length which was almost instantaneously delivered to the calorimeter. The correction for heat interchange between the calorimeter and its surroundings was only a few tenths of 1% in nearly all cases, but this value rose to about 2% in the case of a few measurements at room temperature.

The resistance of a combined thermometer-heater increases while energy is being introduced. This causes a continuous drop in current if the applied voltage is kept constant. In order to avoid a tedious graphical process the following method was devised for obtaining the average value of the current. The change of current with time was found to be nearly constant, and the current could be represented very accurately as a quadratic function of time.

$$I = \mathrm{A} + \mathrm{B}t + \mathrm{C}t^2$$

Let I_1 be the current after t_1 seconds; I_2, the current after t_2 seconds; $I_{\mathrm{av.}}$ the average value of the current, and t_3 the total time of energy input.

$$\text{Make } t_1 + t_2 = t_3, \text{ and } \frac{I_1 + I_2}{2} = I_{\mathrm{av.}}$$

$$\text{Then } I_{\mathrm{av.}}\, t_3 = \int_0^{t_3} I\,dt = \mathrm{A}t_3 + \frac{\mathrm{B}t_3^2}{2} + \frac{\mathrm{C}}{3} t_3^3;\ I_{\mathrm{av.}} = \mathrm{A} + \frac{\mathrm{B}}{2} t_3 + \frac{\mathrm{C}}{3} t_3^2.$$

$$\text{Also } I_{\mathrm{av.}} = \frac{I_1 + I_2}{2} = \mathrm{A} + \frac{\mathrm{B}}{2}(t_1 + t_2) + \frac{\mathrm{C}}{2}(t_1^2 + t_2^2).$$

Equating the two values of $I_{\text{av.}}$ we have, $\frac{t_3^2}{3} = \frac{1}{2}(t_1^2 + t_2^2) = \frac{1}{2}(t_3^2 - 2t_3t_2 + 2t_2^2)$;

$$\text{and } 6t_2^2 - 6t_3t_2 + t_3^2 = 0.$$

$$t_2 = t_3\left(\frac{1 \pm \sqrt{\frac{1}{3}}}{2}\right) = 0.79\ t_3;\quad t_1 = 0.21\ t_3.$$

This method was particularly valuable in that it did not involve the use of initial and final readings which in most cases were not conveniently obtainable. Current readings were taken at 0.21 and 0.79 of the predetermined heating interval. Frequent readings were always taken in addition to these, but only as a precaution. By keeping the resistance between the storage battery and the heater as low as possible, the voltage at the heater terminals remained practically constant during the heating interval.

TABLE I

SPECIFIC HEATS

Glycerol: Glass and liquid

Temperature °K.	C_p per g.	C_p per mean g. atom	Temperature °K.	C_p per g.	C_p per mean g. atom
70.2	0.1116	0.734	159.3	0.2111	1.388
72.5	0.1148	0.755	165.0	0.2181	1.434
73.9	0.1166	0.767	167.9	0.2222	1.461
77.3	0.1204	0.792	173.4	0.2338	1.537
82.1	0.1260	0.829	179.8	0.2467	1.622
83.3	0.1279	0.841	187.4	0.4325	2.844
86.6	0.1325	0.871	191.6	0.4603	3.027
87.4	0.1335	0.878	192.6	0.4556	2.996
92.3	0.1403	0.923	195.6	0.4578	3.010
93.9	0.1420	0.934	201.0	0.4615	3.035
102.0	0.1522	1.001	203.7	0.4633	3.047
104.1	0.1542	1.014	206.4	0.4661	3.065
111.2	0.1616	1.063	209.6	0.4700	3.090
115.3	0.1644	1.081	218.7	0.4775	3.140
122.0	0.1708	1.123	227.1	0.4874	3.205
125.6	0.1730	1.138	240.1	0.5026	3.305
135.9	0.1834	1.206	257.9	0.5218	3.431
144.9	0.1917	1.261	275.4	0.5431	3.571
148.8	0.1981	1.303	282.2	0.5537	3.641
153.1	0.2032	1.336	291.4	0.5658	3.721
...	....	...	299.4	0.5795	3.811

The following data and calculation of one of the runs on glycerol glass are given as a typical example.

Voltage at heater terminals = 5.26966 volts.

$$I_{\text{av.}} = \frac{I_1 + I_2}{2} = \frac{0.093892 + 0.091360}{2} = 0.092626 \text{ amp.}$$

Time = 719.6 sec.

Energy supplied to calorimeter plus the resistance in parallel = 5.26966 × 0.092626 × 719.6 × 0.2391 = 83.982 cal.

Energy lost in the resistance in parallel $= \frac{(5.26966)^2}{10010.4} \times 719.6 \times 0.2391 = 0.478$ cal.

Making the 0.05% correction for energy lost in the leads between the terminals on the cylinder and the calorimeter heater.

Energy supplied to calorimeter = $(83.982 - 0.478) \times 0.9995 = 83.462$ cal.

Final resistance of thermometer	58.4515 ohms.
Initial resistance of thermometer	55.5716 ohms.
Difference	2.8799 ohms.
Correction due to heat interchange	—0.0114 ohms.
Effective increase in resistance	2.8685 ohms.

Average T obtained from average R, 115.3° K.

dR/dT at 115.3° K., 0.7760 ohms./deg.

Heat capacity of calorimeter plus glycerol, $83.462 \times \frac{0.7760}{2.8685} = 22.58$

Heat capacity of empty calorimeter at 115.3° K.	4.89
Heat capacity of glycerol	17.69

Weight of glycerol, 107.58 g.

C_p of glycerol per g.	0.1644 cal./deg.
C_p per mean gram atom (6.576 g.)	1.081 cal./deg.

The mean deviation of the results from the best curve drawn through the points is within 0.2%. The maximum deviation, which occurred only in two cases, was 0.5%.

TABLE II

SPECIFIC HEATS

Glycerol: Crystalline

Temperature ° K.	C_p per g.	C_p per mean g. atom	Temperature ° K.	C_p per g.	C_p per mean g. atom
69.9	0.1087	0.714	138.1	0.1846	1.214
70.3	0.1091	0.717	148.7	0.1945	1.279
71.3	0.1106	0.728	161.8	0.2081	1.368
76.1	0.1159	0.762	173.6	0.2193	1.442
76.2	0.1154	0.759	183.5	0.2290	1.506
80.7	0.1223	0.804	193.7	0.2390	1.572
81.4	0.1234	0.811	204.1	0.2497	1.642
83.1	0.1249	0.821	205.1	0.2493	1.640
85.9	0.1289	0.848	215.6	0.2599	1.709
86.0	0.1291	0.849	218.1	0.2618	1.721
88.7	0.1321	0.869	226.7	0.2622	1.785
92.6	0.1374	0.904	245.3	0.2922	1.922
93.9	0.1399	0.920	249.3	0.2944	1.936
98.1	0.1453	0.956	259.7	0.3095	2.035
104.7	0.1524	1.002	269.9	0.3232	2.125
115.7	0.1632	1.073	280.0	0.3778	2.464
127.8	0.1742	1.145	...	....	...

The values of heat capacity per mean gram atom are shown on a plot in Fig. 1. In the case of the supercooled liquid a sudden decrease in C_p occurs about 190° K. The change in slope of cooling curves showed that this decrease occurred at the same point on cooling as it did when heat was being introduced for C_p measurements. It was found impossible to obtain equilibrium when the temperature rise ended at about 187° K., so the point which is given in Table II at 187.4° is the mean result of energy input during a 5.51° interval.

Heat of Fusion.—After starting crystallization (by a method to be mentioned later) the apparatus was kept in ice for several days to insure completion. The apparatus was then surrounded by a water-bath at 292° K. and current was passed through the cylinder heater until the cylinder temperature was a few tenths of a degree above the melting point of glycerol, and through the calorimeter until its temperature was about 6° below the melting point. A current of 0.1 ampere was then passed through the calorimeter heater. This soon raised the temperature to the melting point and caused fusion to begin. The time required for fusion was about 4 hours. The completion of fusion was noted by the falling off in current as the heat introduced began to heat the liquid above the melting point, thus increasing the resistance of the heater.

The slight amount of impurity caused some pre-melting, and the amount of this up to the temperature where the heat of fusion determination commenced was obtained by separate measurements.

Heat of Fusion of Glycerol at the Melting Point 291.00° K.—First determination, 47.73 cal./g. Second determination, 47.26 cal./g. Third determination, 47.42 cal./g. Mean value, 47.50 cal./g. or 4370 cal./mole.

The entropy of fusion is 15.02 cal./deg. per mole or 1.073 cal./deg. per mean gram atom. The average deviation from the mean is 0.055 cal./deg. per mole, or 0.004 cal./deg. per mean gram atom.

Preparation and Properties of Glycerol.—The glycerol used was an imported sample and was distilled under reduced pressure at a temperature of 170°. The distillation was aided by glass beads and a stream of purified hydrogen emerging from a capillary tip. The middle fraction was used.

The problem of crystallizing glycerol proved to be of some interest. A tube of glycerol was kept with one end in liquid air, the other at room temperature, for a period of several weeks without results. Seeding with various organic crystals of similar structure was also tried. In fact the artifices ordinarily used for starting crystallization in the absence of seed crystals were all tried without success.

The few references in the literature indicated that glycerol has only been obtained in the crystalline form by chance. Inquiry among places storing large quantities of glycerol finally revealed some crystals at the plant of the Giant Powder Company at Nanoose Bay, B. C.

After the seed crystals had arrived it was found that crystallization practically always occurred when amounts of 100 g. of any laboratory sample were slowly warmed over a period of a day, after cooling to liquid-air temperatures. This occurred even when great precautions were taken to exclude the presence of seeds. However, it was found readily possible, by temperature manipulation alone, to produce crystalline or supercooled glycerol at will. The calorimeter was never opened, or altered in any way during the entire investigation. To obtain the supercooled form, the calorimeter was heated to about 320° K. for 24 hours. The apparatus, which had been filled with hydrogen to increase the rapidity of cooling, was immersed in liquid air. The temperature dropped from the melting point, 291° K., to 190° K. in 50 minutes. At this temperature the extremely viscous liquid underwent a rather abrupt change in properties and solidified to a transparent glass.

The rate of crystallization of seeded glycerol is very slow even at 273° K. and extremely slow in the viscous liquid at 190° K., while the rate after the formation of the glass is negligible. The start of crystallization could easily be detected by the rise in temperature due to the heat of crystallization. A rate of 0.1 g. crystallizing per hour in the 107.58 g. used was unmistakable. When crystals were desired they were either obtained by chance, or the calorimeter was cooled below 190° K. and allowed to warm during a period of 1 or 2 days. The slow warming was effected by keeping the apparatus evacuated and surrounded by an ice-bath.

Purity of Glycerol.—By means of the heat effect associated with pre-melting, and the assumption that the impurity formed a perfect solution with glycerol, it was possible to calculate the mole percentage of impurity. At the point chosen for the calculation the concentration of impurity in the small amount of liquid resulting from the pre-melting was about 7 mole per cent. For small amounts of impurities the method is sensitive to a few hundreths of a mole per cent. The purity as estimated by this method was 99.67 mole per cent., which corresponds to 0.06% water impurity.

Melting-point Determination.—The melting point was determined by adding successive amounts of energy to the calorimeter full of crystals, until the further addition of energy produced no effect on the temperature obtained after standing until equilibrium was reached. It was necessary to melt a considerable amount of glycerol before the temperature became constant to 0.001°. The value obtained was 291.00° K.

Summary

An improved calorimetric apparatus has been devised for determinations at low temperatures.

Measurements of the specific heat of supercooled glycerol and of the specific heat and heat of fusion of the crystals are described.

The specific heats of the glass and of the crystals approach one another as the temperature is lowered and are almost identical below 140° K. The entropy of supercooled liquid glycerol exceeds that of crystalline glycerol

by 5.6 ± 0.1 cal./deg. per mole at 70° K., and it is concluded that this value will not be appreciably different at the absolute zero.

We wish to express our thanks to the Giant Powder Company for supplying us with crystalline glycerol.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE EXPLOSIVES LABORATORY, CHEMICAL DIVISION OF THE PITTSBURGH EXPERIMENT STATION, UNITED STATES BUREAU OF MINES]

THE SOLUBILITY OF TRINITRO-PHENYLMETHYL-NITRAMINE (TETRYL) IN ORGANIC SOLVENTS[1]

BY C. A. TAYLOR[2] AND WM. H. RINKENBACH[3]

Received November 10, 1922

Introduction

Work on this subject was undertaken as the logical continuation of work previously done on the solubility of trinitrotoluene in organic solvents. Tetryl is one of the newer high explosives, and as it is now used to a considerable extent, to have its fundamental data available is important. A search of the literature showed that its solubility in the common solvents was expressed in a qualitative rather than a quantitative manner. Accordingly, quantitative measurements of the solubility of this substance in a number of the common organic solvents at different temperatures were made, and solubility curves were derived from the data so obtained.

Materials

Tetryl.—A good grade of commercial tetryl was purified by recrystallization from hot benzene after filtration to separate any insoluble matter. The crystals were dried in air to remove benzene held mechanically. They were then recrystallized from boiling 95% ethanol, redissolved in hot 95% ethanol, and the solution was poured into about 2 volumes of cold distilled water. The mixture was allowed to stand in a dark place for several hours to cool for complete crystallization. The crystals were caught on a Büchner funnel, washed several times with cold distilled water, and given a final rinsing with cold 95% ethanol in order to facilitate drying. The mass of crystals was dried on filter paper, and kept in desiccators over sulfuric acid in a dark place.

Efforts to obtain colorless tetryl proved unsuccessful. The material precipitated from the hot ethanol by water appeared colorless, but as soon as it was filtered a faint yellow color developed, even when the work was carried out in a dark room.

The final product of this purification was a mass of very light, flaky crystals of a very faint yellow tint. The setting point was found to be 128.72°.

Solvents.—The solvents used in this work were the same lots of purified solvents used in the study of the solubility of trinitrotoluene.[4] For a list of the physical constants and methods of purification, see that paper.

---

[1] Published by permission of the Director, United States Bureau of Mines.

[2] Explosives Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Assistant Explosives Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[4] THIS JOURNAL, 45, 44 (1923).