values on Fig. 1 and the boiling point (b. p.) at 127° and 760 mm.,[3] the slope of this line will be proportional to the heat of evaporation according to the well-known formula $Q = R \, \mathrm{d} \ln p/\mathrm{d}(1/T)$.

From this the average heat of evaporation between -15 and $+130°$ is computed to be $Q = 8.7 \pm 0.2$ kcal.

The following table shows the relation of vapor tension to temperature, column I indicating temperature in °C., column II the tension computed on basis of $Q = 8.7$ kcal. (*i. e.*, from the mean curve), and column III the measured tension values, all in mm.

I	II	III
−15	1.75	1.9
0	4.6	4.4
11.5	8.4	8.0
19.1	13	15.5
31.1	24	28.3
40	35	42
50	55	64
60	85	93
80	175	
100	340	
(127)	(760)	(760)

The authors gratefully acknowledge financial support from "Nansenfondet."

Summary

Determination of the vapor pressure of vanadium oxytrichloride against saturated water vapor and by lower temperatures in a nitrogen current has been made. By these methods the error due to attack of vanadium oxytrichloride on manometer mercury is avoided.

The heat of evaporation has been calculated based upon the results obtained in the investigation. The fusion point of vanadium oxytrichloride has been found to be −79.5°.

TRONDHEIM, NORWAY RECEIVED JULY 22, 1937

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[3] A. Safarik and H. E. Roscoe from Mellor, ref. 1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY[1]]

The Heat Capacity of Supercooled Liquid Glycerol[1]

BY A. G. OBLAD[2] AND ROY F. NEWTON

Introduction

The heat capacity of glycerol has been determined by F. Simon[3] and by G. E. Gibson and W. F. Giauque[4] as a part of a program of critically testing the third law of thermodynamics. The results of these investigations are nearly identical, although Simon used glycerol containing about 1.2% of water. The determinations were made by a modification of the Nernst method of electrical heating in which the time from the initial temperature to the last significant temperature of a determination usually was not more than thirty minutes. According to their data the specific heat of crystalline glycerol decreases almost uniformly with decreasing temperature, while that of the supercooled liquid is somewhat greater and remains so down to about 190°K. In the neighborhood of this temperature the specific heat of the liquid rapidly approaches that of the crystals, and at still lower temperatures the specific heats become practically coincident and remain so to the lowest temperatures reached by Gibson and Giauque. These results indicate a difference of about 5 e. u.[5] between the entropy of the supercooled liquid and the crystalline solid at the absolute zero, and have led to the rather common view that the third law of thermodynamics applies only to crystalline substances, and that supercooled glasses possess a positive entropy at the absolute zero.

Otto Stern, in an unpublished communication, and F. Simon[6] have criticized these determinations on the grounds that complete equilibrium with respect to all possible forms of thermal energy may fail to be reached at low temperatures in such a short time interval as that allowed in the Nernst method. Since the determination of the heat capacities of supercooled liquids has such an

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[1] Based upon a thesis submitted by A. G. Oblad to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1937. Presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

[2] Present address: Standard Oil Company, Whiting, Indiana.

[3] F. Simon, *Ann. Physik*, **68**, 241 (1922).

[4] G. E. Gibson and W. F. Giauque, THIS JOURNAL, **45**, 93 (1923).

[5] Simon and Lange, *Z. Physik*, **38**, 227 (1926), and Ahlberg, Blanchard and Lundberg, *J. Chem. Phys.*, **5**, 539 (1937), have extended these results to 10 and 2.8°K., respectively, and have obtained a difference of 4.6 e. u. The latter authors also compared the heat capacities of two glycerol glasses which had been cooled through the congealing zone at very different rates, and found the differences to be about equal to the experimental error.

[6] F. Simon, *Z. anorg. allgem. Chem.*, **203**, 219 (1931).

important bearing on the interpretation of the third law of thermodynamics, it was considered desirable to redetermine the heat capacity of supercooled liquid glycerol by a method which would allow time for complete thermal equilibrium. Within some temperature ranges chosen for experiment the time required for equilibrium has been estimated to be several days; obviously the Nernst method is unsuited for such determinations because of the large corrections for heat leakage which would be required. To allow sufficient time for complete equilibrium and obviate large corrections for heat leakage, it was decided to use the method of mixtures, in which the material may be held at the significant temperatures as long as desired.

Description of Apparatus and Experimental Procedure

Preparation of the Glycerol.—The glycerol was prepared by distilling a quantity of Eastman best grade of glycerol under high vacuum in an atmosphere of hydrogen which had been purified by passing it over a hot chromel wire and then through concentrated sulfuric acid. The distillation took place at about 160°, and only the middle fraction was used in the determinations. During storage of the glycerol at low temperatures, spontaneous crystallization sometimes took place. This was prevented in the later runs by the addition of about 0.2% of water. The change of heat capacity due to this amount of water is well within the experimental error of the method.

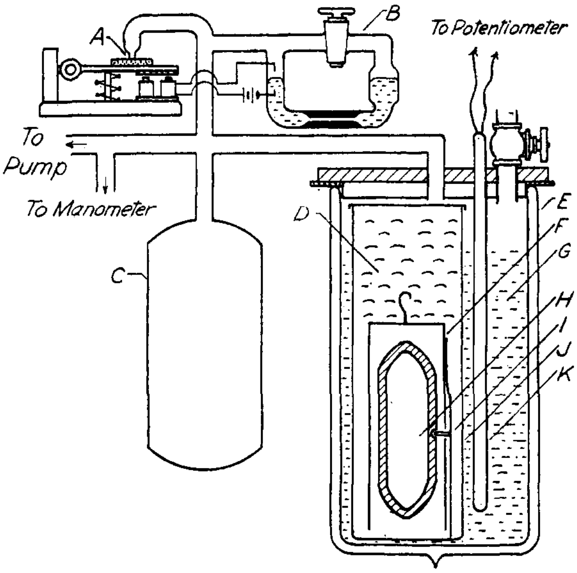

Fig. 1.—Apparatus.

Description of Apparatus.—The thermostat for holding the glycerol at constant low temperature consisted of a large Dewar flask (Fig. 1, E) about 15 cm. in diameter and about 40 cm. in depth provided with a lid which was made of a brass plate to which was fastened an insulating plug which fitted closely inside the flask. A layer of sponge rubber was placed between the lid and the top of the flask to seal the thermostat. The lid was provided with three openings, one permitted the insertion of the thermoelement (K), another connected the interior with a large gas reservoir (C), and the third was connected to a gate valve which permitted air to enter rapidly just before opening the thermostat. The bath in the flask consisted of carbon dioxide and ether (G). The temperature was controlled by regulation of the pressure by means of a large vacuum pump, pressure relay (B), and a magnetic valve (A). By this means the temperature could be maintained constant within 0.1° for nearly forty-eight hours, at which time the apparatus could be refilled with carbon dioxide rapidly enough to be sure that the sample had not undergone a significant change of temperature.

The glycerol container was made of brass tubing with copper ends which were cone-shaped to prevent splashing of the water during discharge into the calorimeter. The heat capacity of the container, which was approximately 20% of that of the glycerol, was calculated from the known weights of brass, copper, and solder used in its construction. While inside the thermostat, the glycerol container was surrounded by two jackets, an outer one (J) which served to prevent the wetting of the container by the thermostat liquid, and an inner one (F) provided with a handle and a catch (I) which held the container (H) inside the jacket during the transfer to the calorimeter. The inner jacket was removed from the thermostat with the container and served to insulate it from temperature changes while in contact with the air during transfer to the calorimeter.

The calorimeter consisted of a half-gallon Dewar flask provided with a stirrer, a thermocouple and a suitable lid. A V-shaped shield was mounted on the lid beside the opening which permitted entrance of the glycerol container, to facilitate the rapid placing of the inner jacket and container over the opening. Striking the inner jacket on the lid of the calorimeter automatically releases the catch and quickly discharges the container into the calorimeter.

The calorimeter was calibrated by holding a container filled with a known quantity of ice at the eutectic temperature of ice and potassium chloride, then quickly discharging it into the calorimeter, and measuring the temperature change of the water in the calorimeter. The amount of water used during calibrations and during all runs was 1020 g. Two thermoelements of copper–constantan were used, a twelve-junction one in the calorimeter and a ten-junction one in the thermostat. The former was compared with another thermoelement which had been calibrated by means of the steam-point and the transition-point of sodium sulfate; the latter was calibrated by means of the freezing point of mercury and the sublimation pressure of carbon dioxide.

Experimental Procedure.—The glycerol sample of about 112 g. is sealed into the container and held in the thermostat for periods of time varying from three hours to seven days. Shortly before the end of this period, water is put into the calorimeter and the temperature of the water is read every minute until the heating rate has remained constant for fifteen minutes, at which time the sample is removed from the thermostat and discharged into the calorimeter. The readings are continued every minute until after the heating rate has again become constant.

The average temperatures are calculated for the period before introducing the sample, the period immediately after its introduction, and the final period of constant rate. After the heating rates for the first and third periods have been obtained from the data of the determination, the total gain of heat from the surroundings during the second period is calculated by Newton's law of cooling. The results of these calculations and the initial and final temperatures of the second period are used to calculate the heat absorbed in raising the glycerol and its container from the low temperature T up to the final temperature of the calorimeter. All runs are corrected to an arbitrary final standard temperature T_s (292.6°K.), by use of the known heat capacities of glycerol and of the container at room temperatures.

TABLE I

RELATIVE HEAT CONTENT OF LIQUID GLYCEROL

Temp., T°K.	Cal. to warm to T_s	Heat content	Approximate time at T, hours
166.9	7558	50	24
171.4	7420	188	17
172.9	7335	253	17
174.2	7447	161	168
174.2	7376	232	6
174.2	7383	225	10
174.2	7337	271	5
174.2	7418	190	72
174.3	7404	204	28
174.3	7371	237	12
176.3	7298	310	8
176.4	7291	317	6
176.4	7318	290	14
176.5	7314	294	28
176.5	7371	237	72
176.6	7362	246	120
177.0	7284	324	13
177.2	7371	237	72
177.2	7328	280	11
177.3	7286	322	29
178.4	7238	370	6
178.8	7288	320	72
178.9	7268	340	50
180.1	7210	398	24
180.3	7176	432	27
180.5	7167	441	28
181.2	7125	483	24
182.0	7066	542	24
183.4	7010	598	24
183.7	7018	590	24
184.4	6907	701	7
185.3	6879	729	12
185.3	6879	729	26
185.5	6888	720	24
186.8	6794	814	4
186.9	6766	842	30
186.9	6766	842	72
187.0	6762	846	24
187.0	6762	846	24
188.0	6710	898	13
190.5	6562	1046	24
192.8	6440	1168	12
292.6	0	7608	(Arbitrary standard)

In a few of the runs, spontaneous crystallization of the glycerol occurred. To be certain that melting of the crystals did not contribute to the total heat absorbed, the temperature of the water in the calorimeter was so chosen as to be below the melting point of glycerol at the end of the run. When crystals are present, slight crystal growth liberates heat, but this effect is negligible because crystal growth is slow in the neighborhood of the melting point.

Discussion of Results

The results of the measurements are given in Table I and are plotted in Fig. 2, curves B and C.

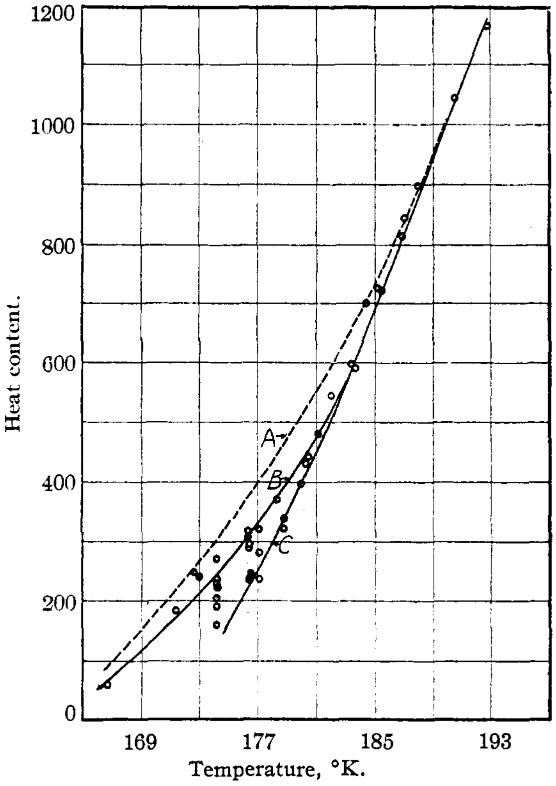

Fig. 2.

The heat contents are relative to an arbitrary standard state such that the heat content of the liquid and container is 7608 cal. at the standard temperature, T_s. Curve A is a plot calculated from the heat capacities obtained by Gibson and Giauque, curve B represents short time runs, while C represents the long time runs. The slopes of the curves represent the heat capacity of the glycerol and its container as measured in a very short time (Nernst method), short time, and long time. Within experimental error the values for the long and short times are the same down to about 183°K. and lead to an approximately constant heat capacity of about 0.45 cal./g. deg. between 183 and 190°K. Using the Nernst method, Simon, and Gibson and Giauque obtained a heat capacity from about 0.3 cal./g. deg. at the lower temperature up to about 0.45 cal./g. deg. at the higher. Below 183°K. a significant difference develops between the long and short runs, the long runs lying on a prolongation of the curve for higher temperatures, showing that complete equilibrium had been attained, while the short runs as shown by curve B, turn off sharply, giving a much smaller apparent heat capacity than the long runs. A comparison of the values from long and short runs with those by the Nernst method indicates that part of the heat capacity of the glycerol responds so slowly to changes of temperature that the Nernst method gives the complete heat capacity only for temperatures above 190°K. A few hours still suffice down to about 183°K., but from this temperature down to 177°, as high as five days may be required for complete equilibrium. It is expected that still longer times would be required for lower temperatures.

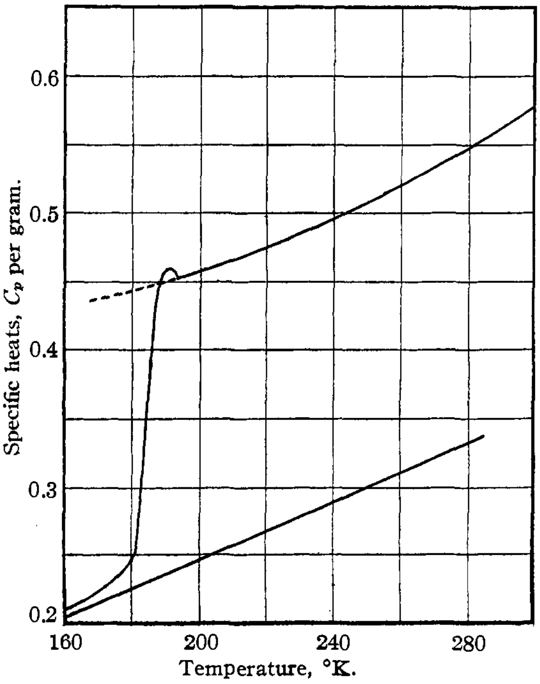

Fig. 3.

The broken line on Fig. 3 represents the heat capacity obtained by taking tangents to the curve C, which represents the measurements in which enough time is allowed for the sample to come to complete equilibrium. Within experimental error it is a prolongation of the curve obtained by Gibson and Giauque, and it would probably continue in the same general direction if very long times were allowed. Such determinations may prove difficult, for spontaneous crystallization frequently occurs during long storage at low temperature.

The persistence of a large heat capacity of supercooled glycerol to relatively low temperatures is of obvious interest in connection with the third law of thermodynamics, for it reopens the question of the entropy of glasses at the absolute zero. By making a plausible extrapolation of the heat capacity curve which has been obtained, it appears that the entropy of the glass near the absolute zero is considerably smaller than that previously obtained, and may indeed be zero.

It should be noted that our measurement of the heat capacity is not equivalent to the ordinary determination upon a thoroughly annealed glass; the annealing process is an integral part of the measurements, and measurement in the usual way of the heat capacities of glasses which have been annealed very differently, such as those carried out by Ahlberg, Blanchard and Lundberg,[5] should not produce the effect we are reporting. The calculation of entropy changes from heat capacity measurements is dependent upon the assumption that the process of heating or cooling the substance through a small temperature interval is thermodynamically reversible; our measurements lend confirmation to Simon's[6] speculations that for glasses below the congealing temperature this is true only if the heating or cooling is done extremely slowly, and hence true entropy values cannot be expected from the Nernst method.

Summary

The heat capacity of glycerol has been measured by the method of mixtures, in such a way as to ensure time for the establishment of equilibrium with respect to all forms of thermal energy of the molecules. These measurements are in disagreement with those obtained by the Nernst method for temperatures below 190°K. A nearly constant heat capacity has been found in the region in which the Nernst method gives a rapidly changing one, and a plot of these heat capacities is apparently a prolongation of the curve obtained by the Nernst method above 190°K. In the neighborhood of 175°K. about a week is required to establish complete equilibrium, and presumably at lower temperatures much greater periods will be required. The long times required indicate that some of the forms of thermal energy in very stiff

glasses are attained much too slowly to be measured by the Nernst method, and that conclusions relative to the applicability of the third law of thermodynamics to glasses cannot be based upon measurements by the Nernst method.

LAFAYETTE, INDIANA RECEIVED SEPTEMBER 1, 1937

[CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPT. OF AGRICULTURE]

Some Constituents of the Cannonball Fruit (Couroupita Guianensis, Aubl.)[1]

BY E. K. NELSON AND D. H. WHEELER

The cannonball tree, *Couroupita guianensis*, was first described and named by Fusée Aublet.[2] Descriptions of the tree and fruit have also been given by W. M. Buswell,[3] and by B. E. Dahlgren.[4]

The cannonball tree is a strictly tropical tree of the dense, humid forests of South America, but according to Buswell there is one specimen in the United States at Fort Myers, Florida, growing and fruiting apparently much as it would in its native forests.

The flowers are four to five inches in diameter, and the fruits, six to eight inches in diameter, are round and encased in a hard shell. The pulp fills the entire shell and apparently varies in color according to the degree of maturity but the odor is peculiar and disagreeable to most people. According to Dahlgren the fresh pulp is said to be used by the natives in the preparation of a cooling, medicinal drink.

The present investigation was made on two fruits sent to Washington by Atherton Lee, director of the Federal Experiment Station at Mayaguez, Puerto Rico.

The pulp from one of these weighed 1739 g.; it was mashed and distilled with steam at a slightly reduced pressure. The distillate was extracted with ether and on carefully evaporating the ether a very small quantity of volatile oil was left which had the peculiar odor of the fruit. Shaking with dilute sodium hydroxide dissolved this oil with the exception of a slight turbidity which was removed by filtration.

Carbon dioxide passed into the clear solution precipitated a phenolic substance which gave a dirty violet color in alcoholic solution with ferric chloride. The solution left after extraction of the phenol with ether was acidified and again extracted with ether, and a partly crystalline acid with an odor similar to capric acid was separated. Dried on a porous plate, the crystalline acid melted at *ca.* 130°. The amount of the volatile oil precluded further study.

The pulp magma, remaining in the still, was pressed out and the juice extracted with ether, which removed a red coloring matter which, according to Dr. C. E. Sando of the Food Research Division, gives every indication of being a carotinoid pigment, probably lycopin.

The juice was then made to a volume of 2000 cc., 10 cc. required 27.7 cc. 0.1 N sodium hydroxide to neutralize it, corresponding to 2.03% acid in the pulp, calculated as citric.

The solution was neutralized with sodium hydroxide and the acids precipitated with lead acetate. The acids were recovered from the lead precipitate and esterified by refluxing with absolute alcohol containing 2.5% of hydrochloric acid.

The esters were dissolved in ether, and the ether solution filtered and washed with dilute solution of sodium hydroxide until neutral. Fifty-seven grams of crude ethyl esters was obtained from the pulp of two fruits. Distilled at 9 mm. without a column, a small part distilled under 170° and most of it between 172 and 174°.

The hydrazide prepared from the higher boiling fraction came down at once and had the appearance of isocitric hydrazide. (Citric hydrazide crystallizes slowly and on the sides of the tube in well-formed crystals.) On filtering the hydrazide it went to a paste on the filter, showing that it was quite impure and that further fractionation was necessary.

Accordingly, the fraction boiling at 172–174° was distilled through an eight-inch (20-cm.) Widmer column at 3.5 mm. and a main fraction boiling constantly at 151° was obtained. This fraction gave the characteristic crystals of citric trihydrazide, melting at 103–105° and in the anhydrous form at 146–147°.

Optical crystallographic examination[5] showed its identity with citric trihydrazide.

The fraction boiling under 170° at 9 mm. and the residue from the redistillation of the 172–174° fraction were fractionated from a 10-cc. bulb through a Vigreux column, at 3.5 mm. From the lower boiling fraction a small amount of distillate was obtained which gave a hydrazide melting at 178–179°. Admixture with *l*-malic hydrazide gave no depression in melting point.

The residue in the flask from the main fraction was redistilled similarly, and an ester boiling at 158–160° was separated. This gave an immediate precipitate of hy-

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(1) Food Research Division Contribution No. 344.

(2) Fusée Aublet, "Histoire des plantes de la Guiane Françoise," Vol. II, 708 (1775).

(3) W. M. Buswell, *The Florida Naturalist*, n. s. II, 105 (1929); *The American Botanist*, XXXIII, 97 (1927).

(4) B. E. Dahlgren, Field Museum of Natural History, Botany Leaflet No. 6 (1924).

(5) Optical crystallographic examinations were made by G. L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture.