

# APPLICATION OF LOW TEMPERATURES TO CHEMICAL RESEARCH<sup>1</sup>

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The important physical-chemical investigations which have been carried out at temperatures below 0°C. are reviewed from the point of view of special methods involved, and in order to facilitate reference to the literature. An extensive bibliography is given.

The work has been arranged under the following headings:—the measurement of temperature; cryostats; crystallization and distillation at low temperatures; boiling point; melting point; density; dielectric constant; heat capacity; heats of fusion, transition, and vaporization; phase equilibria; adsorption of gases on solids; other physical properties.

## I. INTRODUCTION

Many fields of physical chemistry have been advanced by studies made below the melting point of ice. The investigations have sufficient in common to make it desirable to review them together. This has been done briefly in the present article, mainly with the object of acquainting the reader with the special methods employed and facilitating reference to the literature by those commencing investigations at temperatures below 0°C.

In some cases it has been necessary to include elementary or well-known theory in order to make clear the object of certain studies,—for example, those on dielectric constant.

While the literature has been covered up to December, 1944, no attempt has been made to make the bibliography complete.

## II. THE MEASUREMENT OF TEMPERATURE

### *A. Gas thermometer*

It goes without saying that the fundamental method of measuring low temperatures is by gas thermometry. This subject has been discussed thoroughly by Keesom and Tuyn (117), and many convenient gas thermometers have been described (19, 23, 30, 73, 102, 115, 119, 126).

Fortunately, it is never necessary to use the gas thermometer to measure temperature directly. Instead, the readings of a secondary thermometer are standardized against a gas thermometer and the calibrated instrument is used in subsequent work.

### *B. Vapor-pressure thermometer*

The vapor pressure of a substance is a highly sensitive temperature indicator. In the case of oxygen near its boiling point the vapor pressure increases 1 mm.

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per 0.013° rise in temperature. For a substance which boils below room temperature it is merely necessary to introduce it (sufficient to be sure that there is liquid) into an evacuated bulb connected to a manometer (94, 123). The bulb must be the coldest part of the system. As a check on the purity it is advisable to take the vapor pressure after various fractions of the liquid have been distilled off.

It is necessary that the tube leading to the vapor-pressure bulb be protected from the surface of the cryostat if there be any chance of its being colder than the vapor-pressure bulb. This can be accomplished best by surrounding the tube with a vacuum jacket (94).

A small compact vapor-pressure thermometer has been described by Farkas and Farkas (65).

The vapor pressures of hydrogen, oxygen, and carbon dioxide are the basis of reproducible fixed points on the temperature scale. It is customary to take readings near the normal boiling point of the substances and to calculate from them and report the normal boiling point (the temperature where the vapor pressure would be 760 international millimeters of mercury). (See, for example, reference 94.)

#### *C. Liquid-in-glass thermometer*

This type of thermometer has been extensively used and was developed by Timmermans (243) for work on the properties of organic compounds at low temperatures. If properly constructed of strain-free glass such thermometers are reliable to 0.1°. Toluene can be used as the liquid down to  $-95.1^{\circ}\text{C}$ ., while normal pentane can be used down to  $-131.5^{\circ}\text{C}$ . and isopentane down to  $-159.7^{\circ}\text{C}$ . Such thermometers are usually calibrated against a secondary standard such as a platinum resistance thermometer.

#### *D. Thermocouple*

The most commonly used thermocouple for temperatures down to  $-260^{\circ}\text{C}$ . is copper-constantan. For the so-called Advance (constantan) wire of Driver-Harris against copper, reference tables have been given (19, 73, 202, 225).

For work down to liquid-air temperatures, if an accuracy of only 0.2° is required, it is sufficient to calibrate such a thermocouple against the boiling point of oxygen and the sublimation point of solid carbon dioxide (202). The condition for such a method to be valid is that the deviation in microvolts from the reference tables be nearly proportional to the electromotive force of the couple. This condition is generally fulfilled, so that temperatures can be calculated from the reference tables and a deviation graph. For more accurate work, comparison against a resistance thermometer or directly against a gas thermometer is advisable. At liquid-air temperatures, and above, such thermocouples retain their original calibration to a few hundredths of a degree (18).

For work below liquid-air temperatures direct calibration against a gas thermometer is advisable, and the original calibration should be frequently checked against fixed points (e.g., triple and boiling point of hydrogen, first transition

and melting point of oxygen). Deviations from the original calibration of  $0.4^\circ$  at the hydrogen triple point have been known to develop after extended use (18). If such deviations are detected and a correction applied, the copper-constantan thermocouple is a satisfactory thermometer down to the triple point of hydrogen.

#### *E. Resistance thermometer*

Resistance thermometers of platinum (35), platinum-rhodium (30, 228), and gold (116) with a trace of silver added (76) have been used from room temperature down to liquid-hydrogen temperatures. Copper resistance thermometers have also been used (77). Below  $-245^\circ\text{C}$ . constantan (118) and below  $-265^\circ\text{C}$ . phosphor-bronze (113) are suitable for resistance thermometers. For accurate work it is necessary to calibrate such instruments against a gas thermometer, with one single exception—the platinum resistance thermometer which is the basis of the international temperature scale (35).

A resistance thermometer of pure platinum between  $0^\circ\text{C}$ . and  $-183^\circ\text{C}$ . obeys the equation

$$R_t/R_0 = 1 + At + Bt^2 + C(t - 100)^3 \quad (1)$$

where  $R_t/R_0$  is the ratio of the resistance at the Centigrade temperature  $t$  to that at the ice point, while  $A$ ,  $B$ , and  $C$  are constants. The international temperature scale below  $0^\circ\text{C}$ . is defined by assigning values to the boiling point of oxygen ( $-182.970^\circ\text{C}$ .) and the boiling point of sulfur ( $444.60^\circ\text{C}$ .), which were the best available values on the perfect gas scale. The freezing point and boiling point of water are respectively taken as  $0^\circ$  and  $100^\circ\text{C}$ . The constants  $A$  and  $B$  are evaluated by measuring  $R_t/R_0$  at the boiling points of sulfur and water (for technique see references 21, 22, and 114). In defining the temperature scale in the range of  $0$ – $444.60^\circ\text{C}$ ., the last term of equation 1 is not included but the same constants are retained. Therefore, the last term is omitted during the solution for  $A$  and  $B$ . The constant  $C$  is obtained by taking readings in a bath of boiling oxygen (for technique see references 115 and 202).

If it is not convenient to heat the thermometer above the ice point, the sublimation point of carbon dioxide and the freezing point of mercury may be used to replace the steam and sulfur points. These points have been established as secondary points on the international temperature scale (see reference 94). Once the constants have been obtained for a pure platinum thermometer, equation 1 yields temperatures on the international scale. The object was to have the international scale agree with that of a perfect gas.

Measurements at Leiden (115) and at the Reichsanstalt (95) indicate that the international temperature scale lies below the thermodynamic Centigrade scale by a maximum of  $0.04^\circ$  at  $-80^\circ\text{C}$ ., while at the boiling point of oxygen the two coincide to within the experimental error ( $0.01^\circ$ ). No value of the ice point on the absolute scale was recommended for converting international temperature to absolute temperatures. To convert the international temperature scale to the absolute thermodynamic scale as used in a particular laboratory, it is best to solve for  $C$  of the resistance thermometer equation, using the Centigrade

temperature for the boiling point of oxygen on the scale of that laboratory. To the temperature calculated using this value of  $C$ , the value of the absolute thermodynamic temperature of the ice point (on the scale of that laboratory) should then be added.

In defining the international temperature scale it was specified that the entire section of the thermometer at the measured temperature be of pure platinum and that the wire be wrapped in such a way as to eliminate strain. Furthermore, it is stipulated that:

$$R_{100^{\circ}\text{C.}}/R_{0^{\circ}\text{C.}} > 1.39, \quad R_{444.60^{\circ}\text{C.}}/R_{0^{\circ}\text{C.}} > 2.645, \quad R_{-183^{\circ}\text{C.}}/R_{0^{\circ}\text{C.}} < 0.25$$

Suitable platinum resistance thermometers are now supplied by several instrument makers (for their construction see references 114, 131, and 211) and a

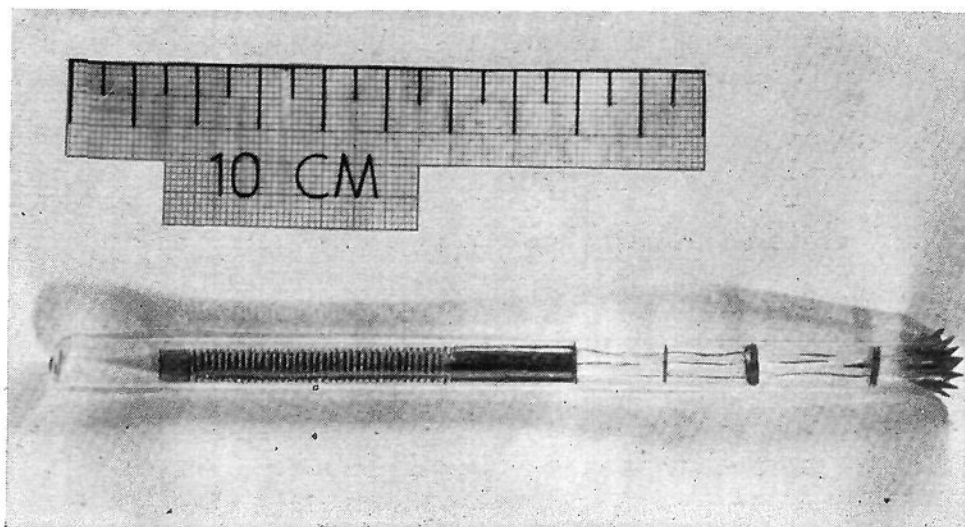


FIG. 1. Resistance thermometer

highly convenient resistance thermometer of the strain-free type has been designed by Meyers (159), the over-all dimensions of which are 5 mm. x 2 cm. Such thermometers can be put in a glass tube the size of an ordinary mercury thermometer or inside a short platinum case (5 x 45 mm.) (see reference 228) and the leads taken through a soft-glass cap. Such a thermometer, typical of several in use in this laboratory, is shown in figure 1. In this figure the cross with the platinum wire wrapped on is shown inside a glass case.

For the calibration to be permanent any of the resistance thermometers mentioned above should be so constructed that the wire is wrapped free from strain. Occasionally, it is necessary to wrap resistance thermometers directly on the outside of a calorimeter, but in this case they should be calibrated during each run against a thermocouple (76) or a strain-free resistance thermometer.

### III. CRYOSTATS

For physical measurements at low temperature it is necessary to have some device to keep the temperature constant. A list of the most important types of cryostat with a brief description follows:

- (a) A stirred bath of some liquid with a very low freezing point, for example,

pentane, is kept in a Dewar. The pentane is cooled by the addition of liquid air, or some other refrigerant. The liquid air should never be added directly, as explosions are almost certain, but rather to a copper vessel dipping into the pentane. Stock (231) has devised an ingenious apparatus for this purpose, which consists of a heavy ring of copper with a chamber for liquid air forming a segment of the ring. The ring fits closely around the upper part of the Dewar and has two loops of copper strip fastened to it which hug the sides of the Dewar (see figure 2). The whole is submerged in the bath liquid, which can be stirred.

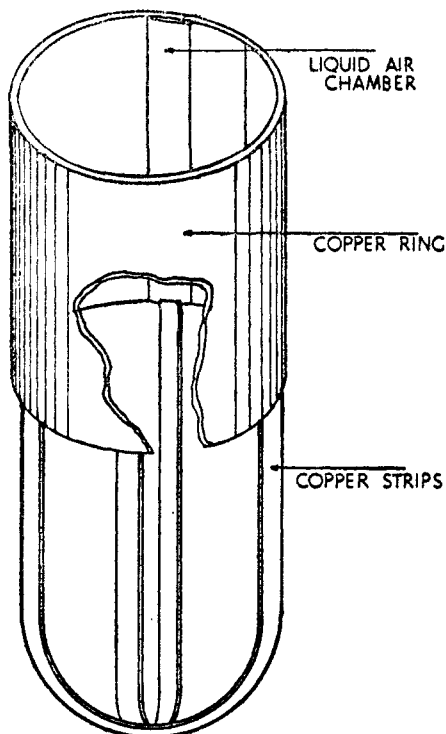


FIG. 2. Type *a* cryostat

Such cryostats have, of course, a slowly rising temperature but measurements good to a few tenths of a degree may be obtained with them.

(*b*) If a temperature range is not required, a series of liquids in equilibrium with the solid at the freezing point may be used in the cryostat of type *a* and thus very constant temperatures may be attained.

(*c*) In a somewhat more elaborate form of the liquid cryostat, capable of maintaining temperatures constant to  $0.01^\circ$ , the liquid is contained in a Dewar vessel with a stopcock connection to the vacuum space which allows the pressure in this space to be controlled (242). This Dewar is immersed in a second Dewar which contains the refrigerant (generally liquid air). The cryostat liquid is mechanically stirred. Its temperature may be controlled by adjusting the pressure be-

tween the walls of the inner Dewar. In some cryostats of this type, the pressure is kept sufficiently high to produce a general tendency to cool which is balanced by a heater in the bath (236). Such a cryostat is shown in figure 3. The heater can be operated manually, but more often it is automatically regulated. For automatic regulation bimetallic regulators have been used (108, 123), or a photoelectric regulation device is attached (225) to the galvanometer of a poten-

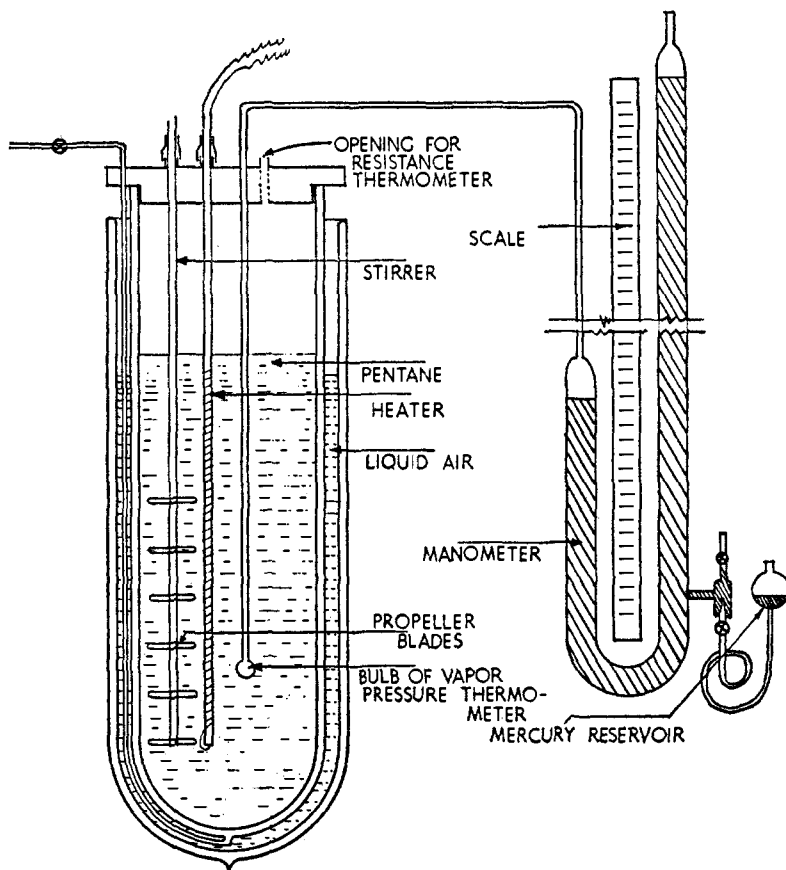


FIG. 3. Type *c* cryostat

tiometer. The potentiometer balances the electromotive force of a sensitive thermocouple (generally copper-constantan), or that across a resistance thermometer, with a constant current, which registers the bath temperature. If this rises, the galvanometer mirror directs a beam of light onto the photoelectric cell whose current then shuts off the heater. When a resistance thermometer is used, the galvanometer is sometimes placed in a bridge circuit containing the thermometer in one arm. A cryostat based on these principles has been designed by Scott and Brickvedde to give a constancy of  $0.002^\circ$  (115, 203). The particular feature of this cryostat is a very efficient system of stirring.

When liquid air is used there is the danger that breaking of the inner Dewar may let the pentane into the liquid air, thus producing an explosive mixture. Southard and Andrews (225) use a copper tube to contain the pentane, and their heater is wrapped around the outside of this tube, which fits the Dewar closely. A convenient modification of this cryostat (126, 127) automatically controls the vacuum in the walls of the Dewar between the refrigerant and the bath by means of a solenoid valve controlled by a reversible Telechron motor operated by the same relay which shuts the intermittent heater on and off.

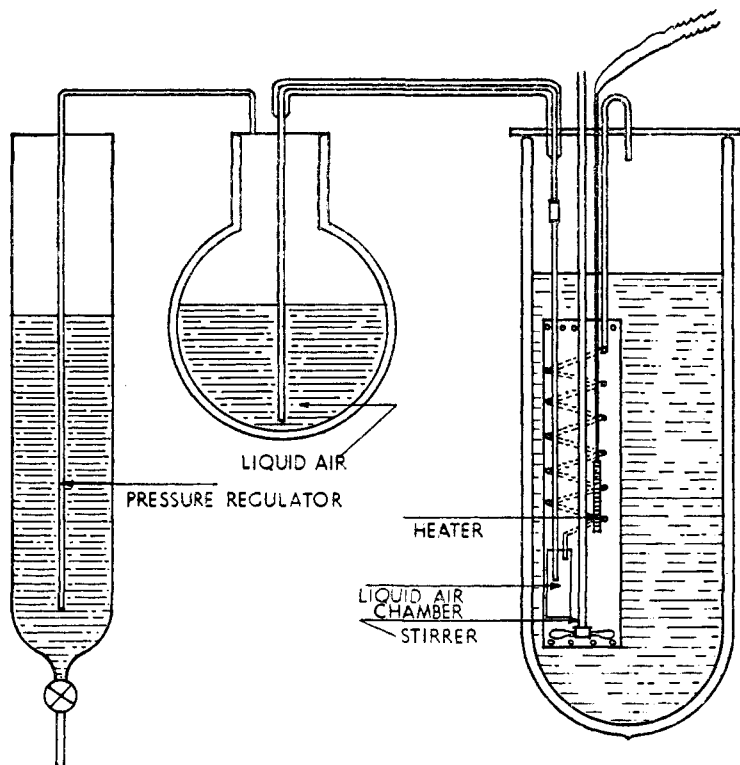


FIG. 4. Type *d* cryostat

(*d*) Liquid cryostats can also be maintained at constant temperature by controlling the amount of refrigerant supplied (146). Pentane or some other low-freezing liquid is contained in a Dewar. Liquid air is added slowly to a small copper vessel. The evaporation of the liquid air keeps the pentane cool. By controlling the rate of addition of liquid air and stirring, temperatures constant to  $0.1^\circ$  can be obtained.

Walters and Loomis (274) have brought such a cryostat to a high degree of precision. Their apparatus is shown in figure 4. They use good mechanical stirring and force the liquid air into the chamber through a vacuum-jacketed tube by pressure in the storage vessel. The pressure is controlled, by passing the evaporated air through a column of water (91), so as to supply enough liquid

air to produce a general tendency to cool. This cooling is balanced by a hand-regulated electrical heater. A constant temperature of  $0.01^\circ$  for 3 hr. can be obtained using this cryostat. Instead of using the electrical heater it is possible to control automatically the supply of liquid air to obtain a constancy of  $0.02$ – $0.05^\circ$ . The regulator is a vapor-pressure thermometer with a manometer which makes an electrical contact at a fixed pressure. Thus a solenoid escape valve is closed in the compressed-air supply to the liquid-air storage vessel. Pressure can

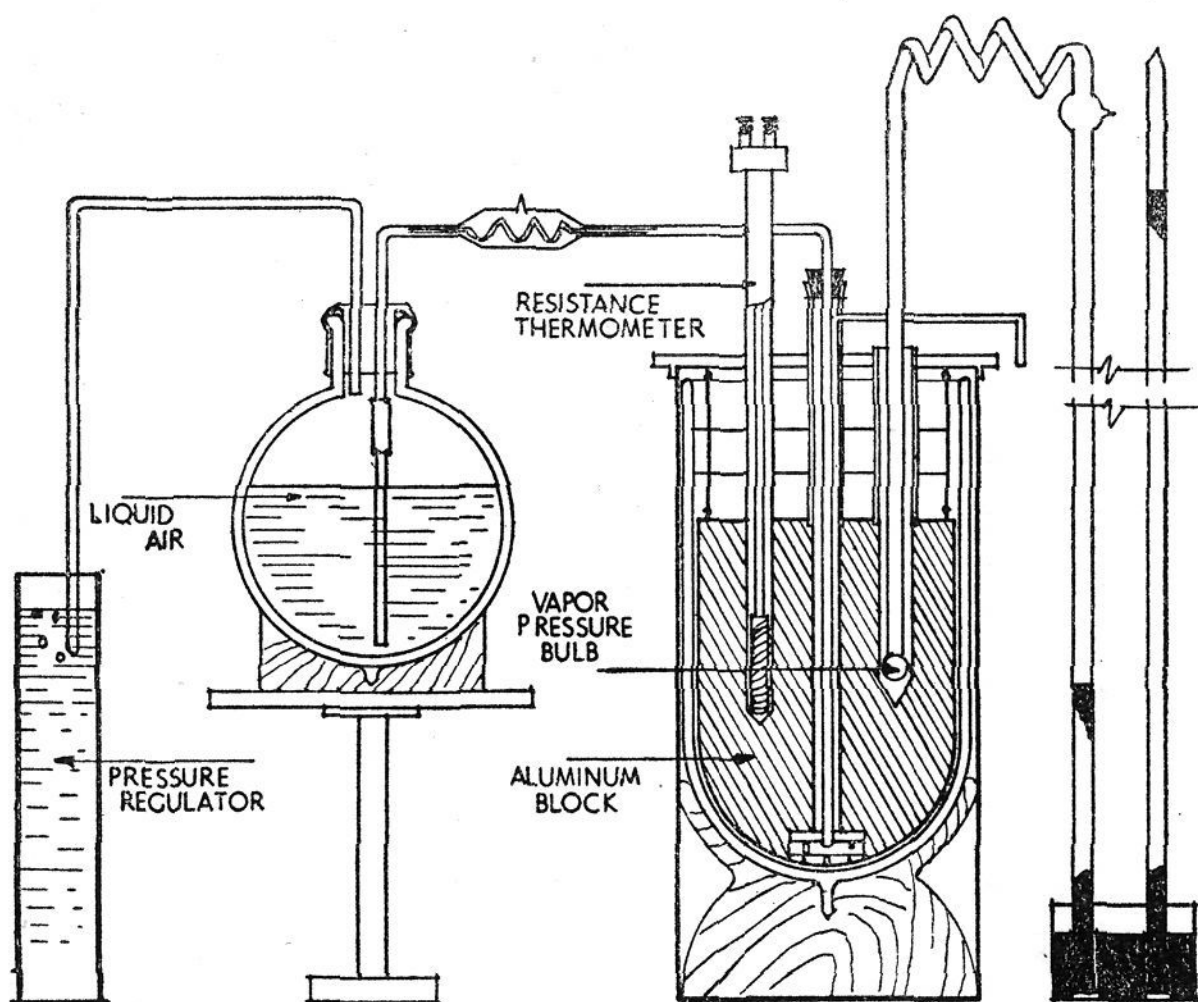


FIG. 5. Type *e* cryostat

thus build up and blow liquid air into the cooling chamber of the cryostat (144, 287). A regulated stream of cold air passing through coils in the cryostat can be used *instead of liquid air*. The air is cooled by passing through liquid air and its temperature regulated by combining with a stream of warmer air (51, 187). The air after cooling can be heated by an electric furnace regulated by a thermoregulator (68).

(*e*) A cryostat primarily for use in vapor-pressure measurements has been designed by Henning and Stock (92). It consists of an aluminum block machined to fit inside a Dewar vessel. Holes are drilled for two vapor-pressure bulbs and two resistance thermometers. A vacuum-jacketed tube leads from a liquid-air reservoir to a hole down the center of the block. The temperature of the block is regulated by controlling the rate of addition of liquid air to the



hole. This is accomplished by regulating the pressure on the liquid-air storage Dewar by evaporation through a column of water. The apparatus is illustrated in figure 5. The vapor-pressure bulbs can be easily exchanged. Temperature can be maintained constant to  $0.02^\circ$  for half an hour.

In connection with low-freezing liquids for cryostats it is worth noting that a mixture of 5.8 cc. *n*-pentane, 2.2 cc. methylcyclohexane, and 1 cc. normal propyl alcohol is liquid and fairly fluid down to  $-180^\circ\text{C}$ . (24).

#### IV. CRYSTALLIZATION AND DISTILLATION AT LOW TEMPERATURE

Purification of simple organic compounds which are gases at ordinary temperature and for which no chemical method is available must be effected by means of low-temperature fractional crystallization or distillation, while the purification of substances which are liquids at ordinary temperatures by recrystallization requires low-temperature technique.

The methods of fractional crystallization at low temperatures have been sadly neglected until recently. Indeed, it is for this reason that substances which are liquid at ordinary temperatures, and which seem to be pure as indicated by a constant temperature of distillation, yield such a variety of values for their freezing points as determined by different investigators. Such compounds have usually been purified by distillation which, in general, is not as satisfactory as recrystallization.

It is hoped that in the near future the subject of crystallization below room temperatures will be given more attention. Already the group at the National Bureau of Standards, while working on the isolation of the hydrocarbons from a midcontinent petroleum (275), has developed methods for the crystallization of hydrocarbons from mixtures. Miss Hicks (96) completely froze solutions of the hydrocarbon mixtures and placed the solid in vacuum-jacketed funnels. As the solid melted, with stirring, the liquid was drawn off from time to time.

Leslie and Schicktanz (139) froze the liquid mixture to a slush with vigorous stirring in a cylindrical funnel with a gauze bottom covered by a plate. Carbon dioxide snow and ether or liquid air were used as external baths for cooling. After freezing, the plate covering the gauze was removed and the unfrozen liquid drawn off by suction. In another apparatus the gauze bottom was omitted and the liquid removed by suction through a tube dipping to the bottom of the vessel and fitted with a filter plate at its lower end.

Hicks-Bruun and Bruun (97) have developed a low-temperature centrifuge which was used to purify heptane and methylcyclohexane obtained from gasoline. In this case, the material was completely frozen with vigorous stirring in a cylindrical vessel. The mush was transferred to the centrifuge by a method which eliminated moisture. The centrifuge was a rotating drum with perforated walls lined with fine linen. The liquid centrifuged out through the cloth collected in an outer housing which was surrounded by a bath of carbon dioxide slush. The liquid could be drawn off from the housing.

Leslie (138) has developed an apparatus for the crystallization of hydrocarbon mixtures by pouring their propane solutions into liquid methane. The crystals

are separated by the use of a low-temperature centrifuge. For details of the ingenious apparatus the original paper should be consulted.

It is also worthwhile to mention the solvent dewaxing of lubricating oils at temperatures below 0°F. (110, 151). The oil is dissolved in a solvent such as naphtha, ethylene dichloride, trichloroethylene, propane, or benzene-acetone mixtures and chilled to -20°F. The waxes which separate are removed either by filtering or by centrifuging.

Fractional distillation through a column below room temperature differs from that above room temperature in the respect that it is more difficult to make a column adiabatic when heat has to be kept out than when it has to be kept in. Heat can be kept in by an easily controlled heated jacket at the same temperature as the column, whereas a cooled jacket is required to keep heat out—and this is not easy to control. The difficulty is solved by entirely vacuum jacketing the apparatus, and this procedure is followed in most modern columns.

The literature on low-temperature columns has been reviewed by Podbielniak (176) and by Rose (186). Podbielniak (177) has discussed thoroughly the effect of packing on column efficiency as well as the design and efficiency of vacuum jackets and Dewar vessels.

Low-temperature distillation has been used for analysis (169, 177, 178, 206, 209, 283) of low-boiling petroleum fractions as well as for their separation (31). Sometimes the column is surrounded by a separate and closely fitting vacuum jacket and sometimes it is sealed into a vacuum jacket. A reflux condenser at the top of the column keeps the column wet and supplies refrigeration.

Columns have been operated on total and partial reflux. In the former case, where the gas is withdrawn below the reflux condenser, the pressure can be kept constant by leaving the top of the column open to the air or open to a gas holder of hydrogen. In the case of partial reflux the gas is taken off at the top of the condenser and the entire apparatus is filled with the vapors of the substance being distilled. The coldest part of the apparatus controls the pressure, so that it is necessary to adjust the temperature of the condenser according to the rate at which gas is being withdrawn at the top of the column. This is done by adjusting the supply of refrigerant. When the refrigerant is liquid air, this can be done automatically (178). A manometer is attached to the top of the column. When the pressure gets too high the mercury in the manometer makes contact in a circuit which opens a solenoid valve and applies air pressure to the liquid-air container. Liquid air is blown into the condenser until the pressure falls and contact is broken. An alternative procedure is to cool the condenser with a stream of cold air passing through coils. The solenoid valve allows the current of cold air to pass or shuts it off. Either procedure can be applied to a total reflux column where an inert gas is not used. Figure 6 shows a diagram of our laboratory low-temperature column which operates on this principle. This column is packed with glass helices. It is used for the purification of simple organic compounds which boil below room temperature and whose physical properties are being studied.

Simons has described simple columns for the same purpose (209).

In connection with the separation of the chemical individuals from a mid-continent petroleum oil (see above), methods have been worked out for continuous counter-current extraction with low-boiling solvents (137). One apparatus is of glass and another of metal.

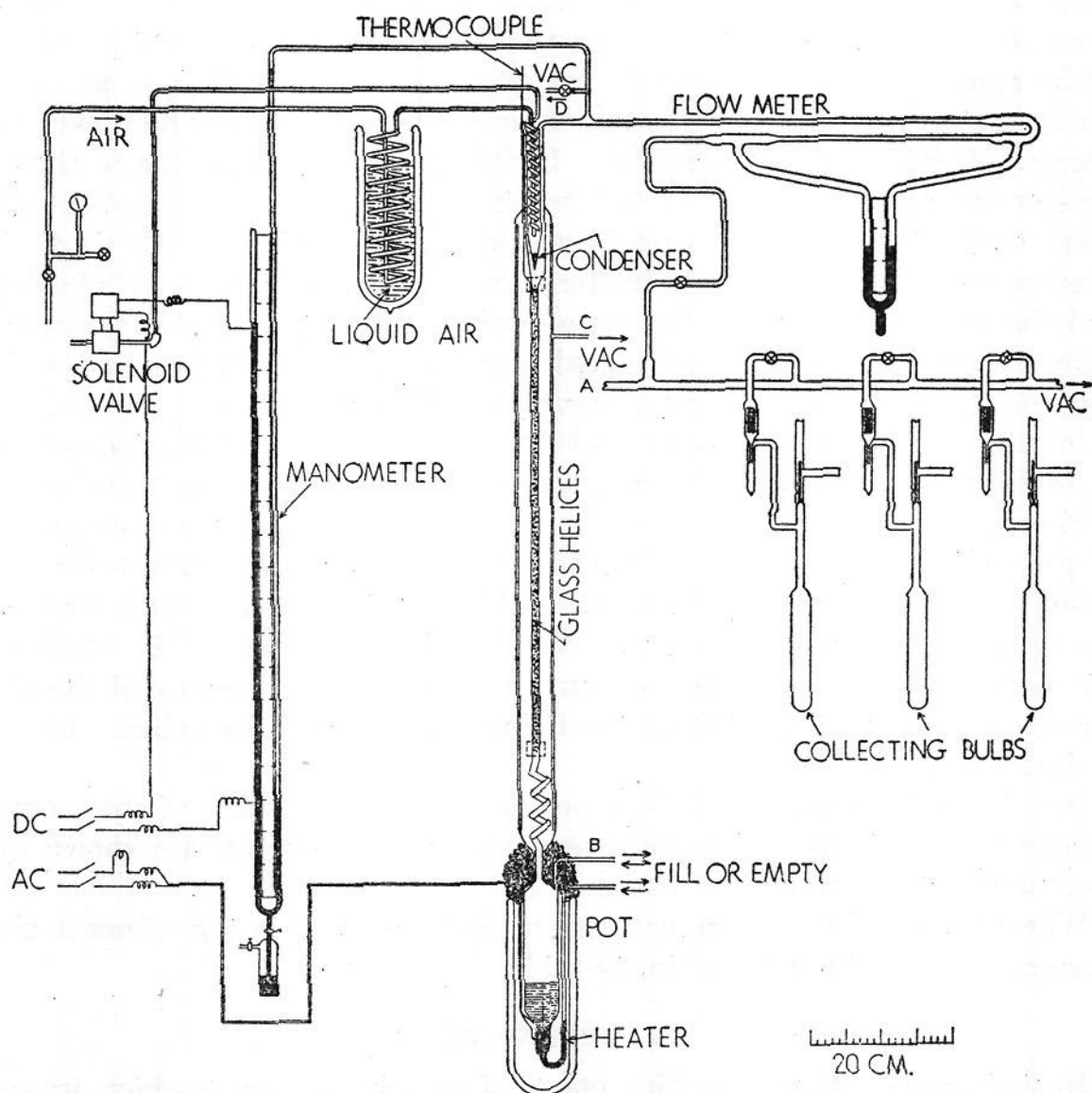


FIG. 6. Low-temperature column

#### V. BOILING POINT

For substances boiling below room temperature the accurate determination of boiling point is greatly simplified. The substance is placed in the bulb of a vapor-pressure thermometer as described above (94, 123). The vapor-pressure measurements are usually made against a thermocouple or resistance thermometer. A cryostat of type *c* (see figure 3) (123, 236) or type *d* is generally used (see figure 4) (146, 147, 274). In figure 5 the bulb of a vapor-pressure thermometer is located in the cryostat and shown connected to a manometer. With such an arrangement, it is possible to obtain results with an accuracy in temperature of  $0.01^\circ$ . From the results the normal boiling point can be calculated.

In recent calorimetric investigations on condensed gases and low-boiling liquids

which will be discussed presently (Section IX), a tube from a manometer leads to the calorimeter so that the vapor pressure of the substance within can be measured. Either a thermocouple or a resistance thermometer fastened to the calorimeter measures the temperature. The calorimeter is surrounded by a radiation shield whose temperature can be controlled so that there is no heat transfer by radiation across the high vacuum in the chamber which holds the entire apparatus. The tube to the calorimeter makes an intimate contact with the top of the radiation shield, whose temperature is kept a few hundredths of a degree hotter than the calorimeter. In this way the temperature of the calorimeter never drifts more than  $0.01^\circ$  during a vapor-pressure measurement which takes about 10 min. This drift is a continuous function of the time. The average temperature of the calorimeter is known to a few thousandths of a degree and the average pressure to the same degree of accuracy. If the substance is pure, boiling points may be calculated from the vapor pressures to a few thousandths of a degree, providing the accuracy of the temperature scale warrants it. It is believed that this method at least rivals any other in precision and accuracy.

An extremely ingenious apparatus for determining vapor pressures has been devised by Francis and Robbins (71) for the determination of the vapor pressures of propane and propylene. It consists of a capillary-tube manometer whose closed end contains air and whose open end is attached to a small bulb containing the sample, confined by mercury. The bulb is easily filled. The readings of the manometer give the vapor pressure, after adding the pressure of the air on the closed side (calculated from the filling pressure and the volume not filled with mercury).

In table 1 are given the boiling points and melting points of some organic compounds which boil below room temperature; these points are known to an accuracy of a few tenths of a degree.

Where the previous determinations are discussed fully in the reference given, these are not usually included in the table.

#### VI. MELTING POINT

In the determination of melting points of organic substances which are solids only at low temperatures, Timmermans has been a pioneer. For his early work (243, 245, 246) he used pentane thermometers which had been previously calibrated against a platinum resistance thermometer. His method was that used in determining freezing points by the Beckmann method. About 10 g. of the material was partly solidified to a mush of crystals and liquid by slow cooling with vigorous stirring in a tube immersed in an air bath surrounded by the refrigerant (solid carbon dioxide and acetone or liquid air). The temperature of the stirred equilibrium mixture was then read on the pentane thermometer (of suitable range) and a stem correction made. This method (hereafter referred to as method I) has been claimed to yield results accurate to  $0.1^\circ$ , but this claim has not been substantiated.

When only a small quantity of material was available, a little was sealed in a capillary tube and frozen by liquid air. The tube was then attached to a pen-

TABLE 1  
*Melting and boiling points of simple organic compounds*

COMPOUND	MELTING OR TRIPLE POINT	REFERENCE	NORMAL BOILING POINT	REFERENCE
	°C.		°C.	
Methane.....	-182.5	(39)	-161.37	(92)
	-182.47	(72)	-161.61	(123)
	-182.6	(63)		
Ethane.....	-183.23	(281)	-89.0	(281)
Propane.....	-187.65	(121)	-42.06	(121)
Butane.....	-138.29	(15)	-0.50	(15)
Propene.....	-189.9	(147)	-47.8	(51)
	-184.9	(106)	-47.0	(147)
			-47.5	(262)
			-47.64	(7)
			-47.76	(128)
			-47.8	(36, 38)
	-185.24	(180)	-47.74	(180)
Acetylene.....	-81.8	(147)	-84.0	(37, 38)
Methyl chloride.....	-97.72	(157)	-24.22	(157)
Methyl bromide.....	-93.66	(58)	3.56	(58)
Cyclopropane.....	-127.56	(189)	-32.77	(7)
			-32.80	(189)
	-12.7	(261)	-34.2	(261)
Ethylacetylene.....	-122.5	(166)	8.6	(166)
Methylacetylene.....	-101.5	(166)	-23.3	(166)
			-23.1	(88)
Methylamine.....	-93.46	(17)	-6.32	(17)
Dimethylamine.....	-92.19	(10)	6.88	(10)
Trimethylamine.....	-117.08	(16)	2.87	(16)
Tetramethylmethane.....	-16.63	(14)	9.45	(14)
Isobutane.....	-159.42	(13)	-11.72	(13)
1-Butene.....	-185.34	(11)	-6.25	(11)
2-Butene ( <i>trans</i> and <i>cis</i> ).....	-127	(40)	1.0	(40)

TABLE 1—*Continued*

COMPOUND	MELTING OR TRIPLE POINT	REFERENCE	NORMAL BOILING POINT	REFERENCE
	°C.		°C.	
2-Butene ( <i>trans</i> ).....	-105.55	(84)	0.88	(85)
2-Butene ( <i>cis</i> ).....	-139.3*	(128)	3.73	(128)
	-136.3	(254)	3.53	(130)
	-138.90	(204)	3.72	(204)
Isobutene.....	-146.8	(40)	-6.6	(40)
	-140.7	(128)	-6.97	(128)
	-140.7	(254)	-7.12	(130)
	-139	(248)		
Allene.....			-35.0	(143)
Fluoroform.....	-160	(191)	-82.2	(89)
			-84.4	(191)
Cyanogen.....	-27.90	(175)	-21.17	(175)
Dimethyl ether.....	-138.0	(145)	-24.9	(145)
	-141.50	(122)	-24.82	(122)
Ethylene oxide.....	-111.3	(145)	10.73	(145)
Carbon tetrafluoride.....	-183.6	(156)	-128.00	(156)
	-183.69	(64)		

\* Impurity 0.1 per cent as determined by Todd and Parks.

tane thermometer and placed in a cold bath of acetone and petroleum ether which was allowed to warm up at about 1° per minute until melting occurred (the conventional method of the organic chemist). This method, hereafter referred to as method II, yields results accurate to 1° or so but with modifications can be made more accurate.

Later (248, 250) a platinum resistance thermometer replaced the pentane thermometer in Timmermans' more accurate measurements by method I. Curves were plotted of the temperatures of the well-stirred mixture during slow cooling, and the melting point was obtained from the temperature of the flat portion. This procedure (method I) with platinum resistance thermometer or thermocouple has been used by other investigators (98, 149, 185).

The rate of cooling can be controlled by placing the sample in a Dewar vessel and varying the vacuum between the walls (149, 213). Roper (185), while obtaining cooling curves by method I, takes particular pains to have the temperature of the outer cooling bath falling at a constant known rate. He used a cryostat of type *c* (225) for this purpose. Thus the rate of cooling of the sample was practically equal to that of the bath until the freezing point was reached, and the cooling curves were more easily interpreted. Such a procedure is to be

recommended. It has been used previously by others with somewhat less precision (4, 181, 238).

Taylor and Rossini (237) have developed a method for the theoretical analysis of certain time-temperature freezing and melting curves as applied to hydrocarbons. Their method is a further refinement of the method used by Mair, Glasgow, and Rossini (150), who showed that in dealing with time-temperature freezing and melting curves obtained on hydrocarbons, when significant undercooling occurs on freezing, the observation can be analyzed to yield, in proper relation to the subsequent equilibrium part of the curve, the time at which crystallization would have begun in the absence of undercooling. Mair, Glasgow, and Rossini employed a visual extrapolation of the equilibrium curve to zero time, while Taylor and Rossini developed a method, which may be used analytically or graphically, for extrapolating the equilibrium part of a time-temperature freezing or melting curve to give the freezing or melting point of the substance under study.

They also describe a method for deducing, within certain wide limits, from the same observations on the substance under study the freezing point for zero impurity which, together with the freezing point of the sample and its molar heat of fusion, enables one to calculate the amount of liquid-soluble, solid-insoluble impurity. By proper calibration of the instrument, it is possible to obtain heats of fusion directly.

Skau (210) has developed an apparatus in which only 0.5 to 0.7 g. of material is required to obtain cooling curves. In principle his method is the same as that of Roper.

Method II has been used by Maass and his collaborators (40, 147). The accuracy was improved by using a larger bulb of the substance and holding the temperature at the melting point for several minutes.

The most accurate method for measuring melting points is to carry out the determination in a vacuum-jacketed calorimeter of one of the types discussed in connection with the paragraphs on specific heats which follow. This will be referred to as method III. If there are any impurities, as the melting point of the sample is approached a small fraction of the solid melts to a solution which contains the impurities (premelting). The heat necessary for this melting causes an obvious abnormal rise in the specific heat. Finally, at the freezing point all the heat put into the calorimeter is absorbed in fusion, and for a highly purified compound only very slight temperature increases (a few thousandths of a degree) result from the input of sufficient energy to melt the remaining 90 per cent of the material. Thus the melting point is easily ascertained. The more impurity is present, the lower is the temperature at which obvious premelting is encountered. From the fraction melted at any temperature below the freezing point, the percentage of impurity in the sample can readily be calculated, assuming the laws of perfect solution (109). The fraction melted is calculated from the energy input above that due to the specific heat, using an approximate heat of fusion. By freezing point is meant the equilibrium temperature in the calorimeter when the amount of crystals is negligibly small. This value can then be corrected

for the lowering caused by the impurity to obtain the melting point of the pure material.

Aston, Fink, Tooke, and Cines (12) describe a melting-point calorimeter whose basic design is similar to that of a precision adiabatic calorimeter, described in Section IX, in which some accuracy is sacrificed for speed. The sample is poured into the calorimeter, thereby greatly facilitating filling, and the operation of the calorimeter has been simplified to enable operation by one person.

A further advantage of the calorimetric determinations of purity over the freezing-point determinations of purity is that it is possible to detect solid solution simultaneously with the purity determination by comparing the impurity calculated from premelting heat capacities with that calculated from the fusion temperatures. This method has been described by Aston, Cines, and Fink (8).

A simple heat-conductivity calorimeter for melting-point determinations been described by Fischl (70). This method is advantageous as compared to method I in cases where excessive supercooling occurs, as has been noticed in high-molecular-weight hydrocarbons.

The calorimeter consists of a copper ampoule, with a thermocouple attached, in which the sample under study is placed, suspended from a heavy copper shield. The shield is kept at about  $2-3^{\circ}$  above that of the ampoule, and time-temperature readings of the shield and ampoule are recorded until the entire sample is molten. The results obtained with this apparatus are less precise than those obtained with the electrically heated adiabatic melting-point calorimeter.

It is important to realize that measurements can be taken, by method III, when almost all of the material is melted, whereas other methods require a mush of crystals and consequent concentration of impurities by freezing.

In the course of the work of the Bureau International (247) on the physical properties of organic compounds, Timmermans has measured the freezing points of a large number of organic compounds by method I with an accuracy depending on the purity of the organic compounds.

A number of investigations have been made to determine the freezing points or triple points of certain pure organic compounds with sufficient accuracy (about  $0.02^{\circ}$ ) so that they could serve as fixed points on the temperature scale. The freezing points were measured against a resistance thermometer or thermocouple that had been compared directly with a gas thermometer. For such an investigation, Keyes, Townshend, and Young at the Massachusetts Institute of Technology (124) placed the organic liquid in the inner Dewar of a small cryostat of type *c* from which the heater was omitted. Stirring was accomplished by air. The cooling was effected by liquid air in the outer Dewar, and its rate controlled by adjusting the vacuum between the walls of the inner Dewar. A thermocouple previously calibrated against a nitrogen thermometer was used to read the temperature of the solid-liquid equilibrium mixture. The results are recorded in table 2 (column 4).

In a similar investigation by Timmermans, van der Horst, and Kamerlingh Onnes (251), a well-stirred tube of the liquid was cooled by a current of cold air whose temperature was adjusted to give the required rate of cooling. A platinum



resistance thermometer which had been previously compared with a helium thermometer was used to read the equilibrium temperature of the well-stirred solid-liquid mush at the freezing point. The values obtained have been revised by Timmermans (249). The revised results are summarized in table 2 (column 2).

Similarly, the melting points of several organic compounds have been determined by Henning at the Reichsanstalt by method I, using a platinum resistance thermometer which had been calibrated against a helium thermometer (90). The fixed points thus obtained appear in column 3 of table 2.

Timmermans (249) has discussed these three sets of fixed points and concludes that the differences are due to impurities in the Reichsanstalt and the M.I.T. compounds.

TABLE 2  
*Melting points of organic compounds*

COMPOUNDS	LEIDEN: TIMMER- MANS, VAN DER HORST, AND KAMER- LINGH ONNES (249,251)	REICHSANSTALT: HENNING (90)	MASSACHUSETTS INSTITUTE OF TECHNOLOGY: KEYES, TOWNSHEND, AND YOUNG (124)	*CALIFORNIA (120) (TRIPLE POINT); **PENNSYLVANIA STATE (157) (TRIPLE POINT); ***INTER- NATIONAL (185) (ROPER)
	°C.	°C.	°C.	°C.
Carbon tetrachloride.....	-22.85		-22.87	
Chloroform.....	-63.7	-63.6	-64.19	
Chlorobenzene.....	-45.35	-45.5	-45.58	
Ethyl acetate.....	-83.6			
Toluene.....	-95.0		-95.70	
Carbon bisulfide.....	-111.8	-112.0	-112.97	
Diethyl ether:				
Stable.....	-116.3		-115.9	
Unstable.....	-123.3	-123.6	-123.40	
Methyl chloride.....			-98.39	-97.72**
Methyl alcohol.....			-98.54	-97.88* -97.68***

In column 5 of table 2 are recorded the melting points of any of these substances which have been determined against the temperature scale of other laboratories.

Transition points can be determined in exactly the same way as melting points. In this case the superiority of method III is quite evident.

Table 1 lists melting points for some organic substances which boil below room temperature.

Phase (freezing-point) diagrams have been constructed for binary liquids at low temperatures. Mixtures of certain chloro compounds have been studied by Timmermans and Vesselovsky (252). 1,2-Dichloroethane and 1,1,2,2-tetrachloroethane form an equimolecular compound melting at  $-32^{\circ}\text{C}$ . The melting point for the compound of the corresponding bromo compounds is  $-8.25^{\circ}\text{C}$ . (non-congruent). The dichloroethane forms an equimolecular compound with the tetrabromoethane (non-congruent m.p.  $-28.5^{\circ}\text{C}$ .); so also does the dibromoethane with the tetrachloroethane (non-congruent m.p.  $-35^{\circ}\text{C}$ .).

Huelting and Smyth (105) find no compound formation between 1,2-dichloroethane and benzene, but the former forms a compound with diethyl ether (m.p.  $-103^{\circ}\text{C}$ ). A freezing-point study of a number of pure hydrocarbons and their binary mixtures (213) reveals that as a rule solutions of the hydrocarbons behave ideally, but *n*-octane-*n*-nonane and 2,2,3-trimethylbutane-2,2,3,3-tetramethylbutane are systems which yield mixed crystals.

#### VII. DENSITY

The measurement of densities of liquids below room temperature has been made for four main reasons: (1) because physical properties of low members of homologous series are of particular interest and these are liquids only at low temperatures; (2) to verify the law of rectilinear diameters, which states that the mean of the densities of a liquid and its saturated vapor lie on a straight line passing through the critical temperature; (3) to obtain density for the purpose of calculating molecular refractions and polarizations (221); and (4) to be used in calculating thermodynamic properties. The results can be used to verify the results of the law of corresponding states,—that the ratio of the densities of two liquids at the same corresponding temperature is a constant (147, 172). For one reason or another a large number of simple organic compounds have been investigated.

The pycnometers (or dilatometers) employed can be either a bulb with a long graduated capillary (147) or the U-shaped pycnometer (123) commonly used at ordinary temperatures. If the former is used, a single weight of liquid serves for several temperatures, as the increasing volume is read by the position of the meniscus in the capillary. Low-boiling liquids such as dimethyl ether, whose vapor pressure is less than 10 atm. at room temperature, can be weighed directly in the pycnometer (147) or weighed in glass bulbs after distillation from the pycnometer (172). The weight of lower boiling liquids must be measured by taking a known volume of gas and calculating the weight from the density of the gas (123, 179). In any case, for temperatures where the vapor pressure is appreciable the weight of vapor above the liquid must be subtracted from the total weight. Constant temperatures are best obtained by cryostats of types *c* or *d*.

The liquid densities of methane have been determined by Keyes, Taylor, and Smith (123) as part of an investigation on the thermodynamic properties of methane made in connection with the recovery of helium from natural gas. Porter (179) has studied the densities of liquid ethane at low temperatures as part of the program on hydrocarbon research at the U. S. Bureau of Mines. The densities of liquid ethylene at low temperatures have been measured by Mathias, Crommelin, and Watts (152, 153), who showed that this gas obeys the law of rectilinear diameters only approximately.

Maass and his coworkers have made measurements on the density of the lower hydrocarbons in most cases down to near their melting point. Their work has included ethane, propane, ethylene, acetylene, propylene (147), isobutylene (41), butane and isobutane (40), methyl- and ethyl-acetylenes (166), dimethyl- and *n*-propylacetylenes (167). The work was done as part of a study of the general physical properties of these lower hydrocarbons.

The densities of liquid and gaseous propane, butane, and isobutane have been determined by Dana, Jenkins, Burdick, and Timm as part of an investigation of their thermodynamic properties (51). Timmermans has determined liquid densities on pentane and isopentane (244).

Certain simple fluorinated hydrocarbons have recently been prepared in a relatively pure state by Ruff and his coworkers, who have reported liquid densities at low temperatures on fluoroform (191) and carbon tetrafluoride (192), tetrafluoromethane and hexafluoroethane (190), and chlorotrifluoromethane, dichlorodifluoromethane, and trichlorofluoromethane (193).

Early work by Timmermans on liquid densities down to near the melting point was carried out to test the law of rectilinear diameters in the region of low gas densities. The compounds investigated were methyl and ethyl alcohols, ether, acetone, isobutyric acid, ethyl acetate, acetonitrile, ethyl bromide, chloroform, isopentane, toluene, chlorobenzene, and pyridine (241), and ethyl acetate (242). Acetone has more recently been studied down to  $-90^{\circ}\text{C}$ . (5, 69).

As part of a study of the thermodynamic properties of diethyl ether, Taylor and Smith (236) have made a thorough study of the densities of the liquid at low temperatures. Dimethyl ether and ethylene oxide have been investigated as part of a study of their physical properties (145).

Smyth and his coworkers have made studies of liquid densities at low temperatures for the purpose of calculating values of the polarization from the dielectric-constant measurements (57, 214, 221, 222, 223). Morgan and Lowry have carried out similar work on other compounds (168). The compounds studied in both cases are listed in table 3 in the section on dielectric constants.

As part of a general study on physical properties, Tonomura (256) has measured the liquid densities down to  $-100^{\circ}\text{C}$ . of isopropyl, *n*-butyl, and allyl alcohols, toluene, and methyl ethyl ketone. Mitsukuri and Kitano have studied propyl and isobutyl alcohols (161).

Schaufelberger (200) has determined the densities of low-boiling liquids by condensing them in an unsilvered Dewar. The density is then read by a hydrometer.

An important investigation has been carried out by Heuse (93) on the densities of certain solid organic compounds at liquid-hydrogen temperatures. The purpose of the investigation was a comparison of the molecular volumes at the absolute zero with those calculated from the volumes of the constituent atoms by Kopp's Law. The volume of the solid hydrocarbon was measured by ascertaining the free volume in the container. This was done by expanding helium from the container into a known volume. From the initial and final pressures the original volume occupied by the gas could be calculated. The aromatic hydrocarbons (benzene, toluene, *m*-xylene, ethylbenzene, propylbenzene, mesitylene, and naphthalene) had molecular volumes within experimental error of those calculated using Kopp's Law. So did ethylene. On the other hand, the normal saturated hydrocarbons from ethane to nonane, isopentane, and cyclohexane had molecular volumes lower than those calculated by Kopp's Law. For methane the reverse was true. It does not seem that data on molecular volumes at low

temperatures possess any marked advantage from the standpoint of the use of additivity relations in determining structure.

The change of molecular volume with temperature in the neighborhood of the transition point where rotation sets in has been studied for solid *d*-camphor and camphor (278).

#### VIII. DIELECTRIC CONSTANT

As is well known, the average electric moment of a molecule can be calculated from dielectric-constant measurements of solutions in a non-polar solvent (54). Briefly, the polarization ( $P$ ) is first calculated from the dielectric constant ( $\epsilon$ ) using the relation

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_1 N_1 + M_2 N_2}{\rho} \quad (2)$$

where  $\rho$  is the density and  $M_1$  and  $M_2$  are, respectively, the molecular weights of the non-polar solvent and of the solute whose electric moment is to be found. The respective mole fractions are  $N_1$  and  $N_2$ .

The polarization,  $P_2$ , of the solute can be calculated from the relation

$$P_{12} = P_1 N_1 + P_2 N_2 \quad (3)$$

if  $P_1$ , the polarization of the pure solvent, is known. Such measurements yield values of  $P_2$  dependent on the concentration. From a plot of  $P_2$  against  $N_2$  the value of  $P_2$  at zero concentration can be obtained; it is characteristic of the free polar molecule if there is no interaction with the solvent. This limiting value of  $P_2$  will be denoted by  $P_0$  and can be considered as being due to (a)  $P_E$ , the electronic polarization due to electronic shifts, (b)  $P_A$ , the atomic polarization due to the shift of atoms or radicals, and (c)  $P_M$ , which is due to the orientation of molecules of electric moment  $\mu$  in the field. So that

$$P_0 = P_E + P_A + P_M \quad (4)$$

if  $P_0$  be plotted against  $1/T$  from data over a range of temperatures, a straight line is obtained.

$$P_0 = a + b/T \quad (5)$$

where  $a = P_E + P_A$  and  $b = 4\pi N \mu^2 / 9k = P_M T$ . ( $N$  is the Avogadro number and  $k$  is the Boltzmann gas constant.) This same equation obviously applies to the polarization of a pure gas at zero pressure.

For most non-polar solvents (e.g., hexane, benzene, carbon tetrachloride) it is necessary, because of low boiling points, to go to low temperatures (i.e., to just above the freezing point) to obtain a suitable range of values for accurate calculation of  $b$  (and hence of  $\mu$ ) from the slope of the  $P_0$  vs.  $1/T$  plot.

It is well known that to obtain  $\epsilon$  one obtains the ratio of the capacity of a condenser, filled with the solution, to that of air.

The work of Smyth and Morgan (221), who obtained the electric moments of ethyl bromide, chloroform, and chlorobenzene from such measurements in

hexane, is illustrative of the methods used. They made measurements from  $-90^{\circ}\text{C.}$  to  $+60^{\circ}\text{C.}$  and employed a cell consisting of three concentric platinum cylinders encased between two glass cylinders sealed together at the top and bottom so as to hold the liquid between them. Constant temperatures in the low range were obtained by use of a cryostat of type *d*. Temperatures were measured by using a platinum resistance thermometer placed inside the hollow ring of the cell. The results of such measurements by several investigators are given in table 3.

The moment of ethyl iodide was obtained from measurements in heptane solution down to  $-100^{\circ}\text{C.}$  Ethyl alcohol was studied down to  $-110^{\circ}\text{C.}$  in hexane and heptane; *n*-butyl alcohol in heptane (down to  $-90^{\circ}\text{C.}$ ); *n*-octyl alcohol in heptane (only to  $-30^{\circ}\text{C.}$ ) (223). Butyl chloride, bromide, and iodide as well as heptyl bromide and ethylene dibromide have been measured in heptane; diiodomethane, bromoform, and iodoform were studied in benzene (222), some down to  $-90^{\circ}\text{C.}$  In order to study the change of electric moment with temperature ethyl acetate, ethylene dichloride, and ethylene chlorobromide were measured in heptane down to low temperatures (214).

A thorough study of the dielectric constants and densities of all the normal saturated hydrocarbons from pentane to dodecane at temperatures covering the entire liquid range has been made (57). The polarization did not change with temperature, indicating a vanishingly small electric moment. The investigations of dielectric constants of gaseous methane extended down to  $-154^{\circ}\text{C.}$  (184) and of gaseous ethane and propane down to  $-80^{\circ}\text{C.}$  (224, 277) and showed no moment. Measurements of dielectric constant on the gases down to  $-80^{\circ}\text{C.}$  also showed ethylene, acetylene (224, 276), and carbon tetrafluoride (224, 277) to have no moment. On the other hand, similar measurements have shown propene (276) to have a small moment ( $0.37 \times 10^{-18}$ ). While the range of investigation did not extend below  $0^{\circ}\text{C.}$ , temperature coefficients of the dielectric constants of butene, 2-methylpropene ("isobutene"), and methylacetylene show small moments (224, 277) in the order  $0.30 \times 10^{-18}$ ,  $0.49 \times 10^{-18}$ ,  $0.72 \times 10^{-18}$ . It is curious that allene also shows a moment.

From table 3 it is noticed that the moment of ethylene dichloride and of ethylene chlorobromide changes with temperature. This has been interpreted (158, 214) to mean that the repulsive effect of the dipoles favors the *trans* position. If the potential associated with the effect is of the order of 2000 cal. and causes most of the molecules to oscillate about the *trans* position in a way that may be treated as a classical vibration (214), such an assumption explains the temperature effect.

Just as the dielectric constant decreases with rise in temperature it will decrease with frequency if the medium is sufficiently viscous. In this case, the time of the relaxation of the system is too long to allow the dipole orientation to follow the alternation in current. The higher the viscosity the lower the frequency at which this change with frequency (anomalous dispersion) can be observed.

By working at low temperatures (down to  $-90^{\circ}\text{C.}$ ) the change with frequency

TABLE 3  
*Electric moments obtained from low-temperature dielectric-constant measurements  
 in solution*

COMPOUND	SOLVENT	TEMPERATURE RANGE °C.	MOMENT $\mu \times 10^{18}$	REFERENCE
<i>n</i> -Hexane	None	-90 to +60	0	(221)
Ethyl bromide	<i>n</i> -Hexane	-90 to +60	1.86	(221)
Chloroform	<i>n</i> -Hexane	-90 to +60	1.05	(221)
Chlorobenzene	<i>n</i> -Hexane	-80 to +60	1.52	(221)
Ethyl iodide	<i>n</i> -Heptane	-100 to +70	1.66	(223)
Ethyl alcohol	<i>n</i> -Hexane	-90 to +60	Association	(223)
Ethyl alcohol	<i>n</i> -Heptane	-110 to +60	Association	(223)
<i>n</i> -Butyl alcohol	<i>n</i> -Heptane	-90 to +90	Association	(223)
<i>n</i> -Octyl alcohol	<i>n</i> -Heptane	-30 to +60	Association	(223)
Ethylene dichloride	a. <i>n</i> -Heptane	-90 to +70	1.16 at -50°C.	(100, 214)
	b. <i>n</i> -Amylene		1.41 at +30°C.	(164)
Ethylene dichloride	<i>n</i> -Hexane	-71 to +40.9	2.4 at $1/T = 0$	(101, 158)
Ethylene chlorobromide	a. <i>n</i> -Heptane	-50 to +90	0.92 at -50°C.	(214)
	b. <i>n</i> -Hexane		1.19 at +30°C.	(214)
Ethyl acetate	<i>n</i> -Heptane	-90 to +70	1.57 at all °T.	(214)
Ethylene dibromide	a. <i>n</i> -Heptane		0.57 at -50°C.	(101, 218)
	b. <i>n</i> -Hexane	-40 to +90	0.92 at +50°C.	
	c. Benzene			
Trimethylene bromide	<i>n</i> -Heptane	-30 to +70	2.19 at +50°C.	(218)
Pentamethylene bromide	<i>n</i> -Heptane	-40 to +90	2.47 at +40°C.	(218)
Ethyl alcohol	Diethyl ether	-60 to +25	1.79	(99)
Ethylene glycol	Diethyl ether	-60 to +20	1.2 at -60°	(99)
			2.4 at +20°	
			0.72 at -60°	
Acetic acid	Diethyl ether	-60 to +25	1.23 at +25°	(99)
<i>n</i> -Butyl chloride	Heptane	-90 to +70	1.88	(222)
<i>n</i> -Butyl iodide	Heptane	-80 to +80	1.59	(222)
<i>n</i> -Butyl bromide	Heptane	-90 to +90	1.81	(222)
<i>n</i> -Heptyl bromide	Heptane	-70 to +90	1.83	(222)
Pentane	None	-90 to +30	0.0	(57)
Hexane	None	-90 to +50	0.0	(57)
Heptane	None	-90 to +90	0.0	(57)
Octane	None	-50 to +50	0.0	(57)
Nonane	None	-50 to +50	0.0	(57)
Decane	None	-30 to +170	0.0	(57)
Undecane	None	-10 to +190	0.0	(57)
Dodecane	None	-10 to +210	0.0	(57)
Methyl chloride*	Carbon tetra- chloride	-46 to +18	1.56	(168)
Methyl chloride*	Hexane	-106.2 to +42.2	1.65	(168)
Dichloromethane*	Carbon tetra- chloride	-89 to +40.5	1.48	(168)
Methyl bromide*	Hexane	-103.4 to +37	1.45	(168)
Methyl iodide*	Hexane	-87 to +33.7	1.35	(168)

\* Investigation also carried out on the solid.

has been observed at 1 kilocycle for a series of glycols, whereas at ordinary temperatures there is no change with frequency until the frequency is greater than 100 kilocycles (280).

The dielectric constants of simple crystalline organic compounds which melt considerably below room temperatures are of considerable interest, because in certain cases they yield evidence concerning the rotation of molecules in crystals.

If the molecule is held rigidly in the crystal, the polarization is due only to electronic and atomic displacements; that is,

$$P = P_E + P_A \quad (6)$$

As a result the dielectric constant is low. Furthermore, the apparent dielectric constant measured (with a constant weight of crystals between the plates of the condenser) is almost independent of temperature and frequency. A very slight temperature and frequency dependence is due to the increased opportunity for atomic polarization as the structure becomes slightly more open with rising temperature. There have been very few substances found for which the dielectric constant of the solid has been found to behave otherwise. 1-Octanol (219) is typical of the usual solid with a dielectric constant of 2.32 at 87.3°K., 2.34 at 179.1°K., and 2.77 at 251.3°K. These values were determined at a frequency of 50 kilocycles. Dielectric-constant measurements have been made in the liquid and solid states for oxygen, chlorine, and hydrogen chloride (112). The last of these does not follow equation 6 since, apparently, there is a rotation in the crystal below the melting point.

The dielectric constants of solid hydrogen chloride, hydrogen bromide, and hydrogen iodide, which have been studied down to  $-190^{\circ}\text{C}$ . (216), below the melting point increase rapidly as the temperature decreases. The same can be said of the polarizations. This behavior is due to the rotation of the molecules in the solid state. All three molecules exhibit transitions. Hydrogen chloride exhibits one such transition. Between this transition and the melting point the polarization obeys equation 5, indicating dipole orientation in the solid state, but below this transition the dielectric constant drops to such a low value that there is evidently little possibility of dipole orientation. The behavior of the other hydrogen halides is similar, but for these there is more than one transition and the behavior of the dielectric constant and polarization between them is complicated. These studies have been extended to hydrogen cyanide, hydrogen selenide, and arsine (220). In the last case, measurements were made down to liquid-hydrogen temperatures (20°K.). Hydrogen selenide rotates freely in the solid state down to  $-190^{\circ}\text{C}$ ., but hydrogen cyanide does not rotate at all. Arsine rotates freely down to 32.1°K., where a transition sets in.

Methyl alcohol (217, 219) in the solid state exhibits an abnormally high dielectric constant which increases with temperature. Its value for 5 kilocycles is 3.28 at 108.4°K. and rises to 4.66 at 159.9°K., where there is a transition to a form whose dielectric constant is 5.65 at the same temperature and 9.00 at 169°K. (6.4° below the melting point). These results point to freedom of the methyl

alcohol to turn in the crystal with the field above the transition temperature. They point against actual rotation in the crystal in the absence of the field, because such a situation would give rise to a dielectric constant rising as the temperature fell, as is the case for the solid hydrogen halides (216). Moreover, as other alcohols (219) behave like 1-octanol, it must be the whole molecule which can orient itself with the field and not the OH group alone. Dimethyl sulfate (215) in the solid state at 60 kilocycles shows abnormally high values of the dielectric constant, which decrease with rising temperatures as for the hydrogen halides. This is to be attributed to rotation of the methoxyl group for several molecules in the crystal in the absence of the field. Information on other methoxyl compounds would be interesting, although solid anisole and hydroquinone dimethyl ether do not show this behavior (111).

In view of the result with methyl alcohol it is surprising that methylamine (155) shows the dielectric-constant values of the ordinary solid. Diethyl ether, acetone, benzophenone, and succinic acid (155), the methyl halides, methylene chloride, and chloroform (168) also show no evidence of orientation or rotation in the solid. The dielectric-constant measurements, however, show nothing about the rotation of the methyl group about its axis, as this group has no electric moment and therefore does not contribute to the dielectric constant.

Measurements of the dielectric constant of ethylene cyanide have been made from  $-190^{\circ}$  to  $78.2^{\circ}\text{C}$ . (279). The polarization suffers no sharp change at the freezing point ( $54.2^{\circ}\text{C}$ .). The discontinuity in the polarization at about  $-40^{\circ}\text{C}$ . accompanies a transition, and it is probably only below this that rotation about any axis is restricted in the solid. Below this point, there is probably no rotation in the solid. Similar measurements on ethylene dichloride, ethylene dibromide, ethylene thiocyanate, and ethylenediamine show that there is no dipole rotation in these solids (279).

Isobutyl chloride, isoamyl chloride, tertiary amyl chloride, and 1,2-dichloro-2-methylpropane do not rotate in the solid state (263). Low-temperature dielectric-constant measurements on *d*-camphor, *dl*-camphor, and bornyl chloride show dipole rotation above transition points which occur at about  $-40^{\circ}$ ,  $-60^{\circ}$ , and  $-110^{\circ}\text{C}$ ., respectively (284). Studies of the change of heat capacity and molecular volume at the transition and of the entropy of fusion confirm this conclusion (278).

A thorough study of the effect of pressure and temperature on the dielectric constants of hydrogen, deuterium, helium, oxygen, air, and carbon monoxide has been made by van Itterbeek and Spaepen (266). They made measurements between  $20^{\circ}\text{K}$ . and room temperature and found the dipole moment of carbon monoxide to be  $0.11 \times 10^{-18}$ . The same authors have made measurements on liquid deuterium (265). Measurements on liquid and solid hydrogen (82) and on nitrogen (81) have been made by Guillien and on helium I and II by Wolfke (282). Conner and Smyth (44) have used dielectric-constant measurements to study the solid-liquid equilibrium diagram of the system carbon tetrachloride-*tert*-butyl chloride.



## IX. HEAT CAPACITY, HEAT OF FUSION, HEAT OF TRANSITION, AND HEAT OF VAPORIZATION

The object of most low-temperature heat-capacity determinations is either the determination of the entropy or the procurement of data for comparison with results calculated on the basis of the theory of the solid or gaseous state.

To obtain the entropy the following equation is used:

$$S - S_0 = \int_0^{12} C_p d \ln T + \int_{12}^{T_t} C_p d \ln T + \frac{\Delta H_t}{T_t} + \int_{T_t}^{T_m} C_p d \ln T + \frac{\Delta H_m}{T} + \int_{T_m}^{T_v} C_p d \ln T + \frac{\Delta H_v}{T} + \int_{T_v}^T C_p d \ln T$$

where the first integral represents an extrapolation below 12°K., and  $T_t$ ,  $T_m$ , and  $T_v$  are temperatures of transition, melting, and vaporization, while  $\Delta H_t$ ,  $\Delta H_m$ , and  $\Delta H_v$  are the corresponding molal heat effects associated with these changes.  $C_p$  is the molal heat capacity of the phase. Temperatures down to 10°K. are obtained by pumping on solid hydrogen.

Most of the heat-capacity determinations at low temperatures have been performed using the technique originally devised by Nernst (170) and Eucken (62). In the earliest measurements of specific heats of metals at low temperatures, the substance itself acted as the calorimeter. A block of the material was suspended inside of a jacket of very large heat capacity which in turn was placed in a Dewar flask containing the refrigerant. The jacket was evacuated to provide thermal isolation, the calorimeter was heated by supplying a known amount of electrical energy, and the rise in temperature was observed by a thermocouple or resistance thermometer. Corrections had to be applied for radiation and other heat leaks. At temperatures below that of the boiling point of liquid air these corrections were quite small, but at higher temperatures they were so large as to make the results quite inaccurate.

This difficulty has been corrected somewhat by Nernst and Schwers (171), Gibson and coworkers (77, 78), Giaque and coworkers (74, 75, 76), and others (1, 3, 14, 85, 134, 135, 160, 173) by using shields of various types which keep the temperatures of the surroundings very near to that of the calorimeter. Although this method is a vast improvement over the original technique, the necessity of correcting for thermal leakage (usually of the order of 0.05 to 1.0 per cent) still remained, which as a rule decreased the accuracy of the final results. Obviously, the ideal condition is to keep the temperature of the shield at all times exactly equal to that of the calorimeter. This situation is approximated very closely in the so-called adiabatic calorimeter. The calculation of results is thus much simpler, as there are no corrections to be made for heat leaks, radiation, etc.

The first adiabatic calorimeter was employed by Lange (132) and later further developed by Southard and Andrews (226), Southard and Brickwedde (227), Aston and Eidinoff (9), Yost *et al.* (285), Ruehrwein and Huffman (188), and Scott and Brickwedde (204, 205).

A less precise apparatus (1–3 per cent) for measuring heat capacity at low temperatures has been developed by Andrews and coworkers (2, 87, 212, 232, 286). This is called the calibrated heat-conductivity calorimeter. The calorimeter is heated by conduction and radiation from a surrounding jacket by means of a constant thermal head. The rate of temperature rise of the calorimeter under these conditions is compared with the rate of rise obtained under the same conditions when the calorimeter contains a standard substance of known heat capacity.

The most accurate heats of fusion and transition are obtained in the adiabatic calorimeter discussed above, which is also used to measure heat capacities. The heat necessary to raise the temperature of a known amount of substance from slightly below its melting point to slightly above its melting point is measured, and appropriate corrections are applied as described in the references mentioned. Heats of fusion and transition may also be obtained in the calibrated heat-conductivity calorimeter.

Heats of vaporization of pure substances may be determined in either the Nernst type or the adiabatic type of calorimeter. The only important additions are a filling tube through which the material is vaporized and a means of measuring the amount of liquid vaporized. With low-boiling substances, the vaporized material may be collected in the gas state and its volume measured, or it can sometimes be absorbed chemically. The vapor may be condensed at a low temperature, or at a regulated temperature slightly below that of the calorimeter.

Heats of vaporization of binary mixtures present many difficulties. According to the conditions under which the mixture is evaporated, different values may be obtained. In a static system, the liquid and vapor composition will vary during the experiment and the final results obtained are for averaged vapor and liquid composition. Using a dynamic method, Dana (50) succeeded in measuring heats of vaporization at constant pressure and composition for mixtures of oxygen and nitrogen at atmospheric pressure. With an electrical heating coil, liquid mixtures of oxygen and nitrogen were evaporated from an insulated glass vessel, liquid of constant composition being continuously introduced into the calorimeter. In the stationary state, the vapor leaving the apparatus must have the same composition as the liquid introduced. At the same time, the liquid in the calorimeter will be enriched with oxygen, so as to be in equilibrium with the escaping vapor. But this liquid does not enter into the process. From the quantity of heat introduced and the amount of vapor leaving the apparatus in a given time, the heat of vaporization is obtained for the composition of the escaping vapor.

For the determination of heat capacities of gases at low temperatures the conventional flow method is only applicable in a limited number of cases, since the pressure at which most substances condense is considerably below 1 atm.

The most widely used method is the "hot wire" method of Eucken and Weigert, which is essentially a thermal conductivity method (64). This method can be used at pressures as low as  $10^{-3}$  mm. of mercury. The apparatus can be maintained at low temperatures in cryostats of types *a*, *b*, *c*, and *d*. The method has been used to study the heat capacity of ethane down to 94°K. (107, 125, 127).

## X. PHASE EQUILIBRIA

A. *Liquid-vapor equilibrium*

An excellent review of the methods of obtaining data on liquid-vapor equilibrium is presented by Ruhemann (195) in his book entitled *The Separation of Gases*; certain sections below are quoted almost directly from his book. Only the low-temperature techniques are presented.

Ruhemann has divided the methods for obtaining liquid-vapor equilibrium roughly into four groups: (1) dew- and boiling-point method; (2) static method; (3) flow method; (4) circulation method. These methods will be discussed independently.

In the dew- and boiling-point method a gas of known composition is introduced into the equilibrium vessel at constant temperature, and the pressures at which condensation starts and is completed are observed. This method has been used by Holst and Hamburger (103) on argon-nitrogen mixtures, by Bourbo and Ischkin (32) on argon-oxygen mixtures, and by Steckel (229) on nitrogen-carbon monoxide mixtures; Sage and Lacey (197, 198) have used it for light hydrocarbon mixtures. The advantage of this method is that the phases need not be analyzed as mixtures may be composed arbitrarily, but great care must be used if accurate results are to be obtained.

In the static method a mixture is confined in the equilibrium vessel at constant temperature and pressure and the compositions of the liquid and vapor phases in equilibrium are determined. Baly (20) first used the static method to determine the equilibrium of oxygen-nitrogen mixtures. The static method was also used by Verschoyle (267) for nitrogen-hydrogen, carbon monoxide-hydrogen, and nitrogen-carbon monoxide-hydrogen, by Freeth and Verschoyle (72) for hydrogen-methane mixtures, by Fedoritenko and Ruhemann (67) for mixtures of nitrogen and helium, and by Torocheshnikov and Ershova (260) for argon-oxygen-nitrogen mixtures. The main disadvantage of this method is that equilibrium may be destroyed when samples are drawn for analysis. Thus the method is more reliable at high pressure than at low pressure.

In the flow method, the gas is passed slowly and continuously at constant pressure through an apparatus which is constructed to ensure good thermal contact. The gaseous phase flows into a gasometer, and the liquid phase collects in the equilibrium vessel. The gas and liquid may be analyzed either during the measurement or at the end of the measurement. This method has been used by Steckel and Zinn (230) for hydrogen-nitrogen-methane mixtures, by Ruhemann and Zinn (196) with hydrogen-nitrogen-carbon monoxide mixtures, by Fedoritenko and Ruhemann (67) for nitrogen-helium mixtures, by Ruhemann (194) for methane-ethane mixtures, and by Guter, Newitt, and Ruhemann (83) for methane-ethylene mixtures. The disadvantage of this method is that the equilibrium vessel may become too full of liquid because of too rapid condensation, thereby upsetting the equilibrium.

In the circulation method, the gas is circulated through the liquid in the equilibrium vessel at constant temperature and pressure until equilibrium is established. This is ascertained by continuous analysis of the liquid and vapor states

until constant analyses are obtained. This method was developed by Dodge and Dunbar (56) for studies of mixtures of oxygen and nitrogen. It has also been used by Torocheshnikov (259) for mixtures of carbon monoxide and nitrogen. This method is probably the most accurate and reliable of all existing methods but demands a rather elaborate and complicated equipment. Cryostats of types *a*, *b*, *c*, and *d* can be used to maintain the necessary temperatures.

### *B. Solid-liquid equilibrium*

The methods of obtaining solid-liquid equilibrium have been discussed in the section dealing with melting points.

## XI. ADSORPTION OF GASES ON SOLIDS

An advanced discussion of the theory and methods of physical adsorption has been presented by Brunauer (33) in his book *Physical Adsorption*. For methods of desorption and the proper preparation of the surface of the adsorbent, the reader is referred to this treatise.

### *A. Determination of adsorption isotherms*

The determination of the amount of gas adsorbed on a solid may be determined by the following method: The adsorbent is separated from the measuring apparatus during evacuation by a stopcock and immersed during measurements in a proper thermostat. Prior to adsorption the volume and pressure of the gas are measured, and then the stopcock is opened to the evacuated adsorbent. After adsorption, the volume and pressure of the gas are again measured. Part of the gas is adsorbed and part fills the dead space in the adsorbent. To determine this dead space, a non-adsorbing gas such as helium usually is employed in the same apparatus. Relatively simple apparatus for these determinations has been described by Homfray (104), Titoff (253), Richardson (183), and Pease (174).

A somewhat more complicated apparatus has been described by Coolidge (45) for the adsorption of vapors by charcoal. One of the main features is that it contains no stopcocks, thereby eliminating the possibility of the adsorption of stopcock grease. Mercury cut-off valves are used in place of the stopcocks.

The methods mentioned above measure the adsorption at constant volume. Occasionally, as in rate measurements, it is desired to measure the adsorption at constant pressure. Taylor and Strother (235) describe such an apparatus. The pressure control is made by raising the mercury level in a reservoir to a height at which the contact between the meniscus of the mercury in the manometer and a tungsten electrode is broken. As the gas is adsorbed, the pressure decreases, and the mercury makes contact with the tungsten electrode. This closes an electric circuit which sends current through an electrolytic cell. The gas generated exerts a pressure on the surface of the mercury reservoir, forcing the gas into a buret and building up the pressure inside, which results in breaking the contact between the tungsten electrode and the meniscus.

The type of data obtained in determining adsorption isotherms is exemplified

by the results of Emmett and Brunauer (61) for nitrogen adsorbed on an iron catalyst for ammonia synthesis between  $-195.8^{\circ}$  and  $-183^{\circ}\text{C}$ . The curve obtained was the typical S-shaped adsorption isotherm. At low pressures the isotherms are concave, at the higher pressures convex toward the pressure axis. In using such an isotherm in measuring the surface area of the catalyst it is necessary to select the point on the curve corresponding to the completion of a monolayer of adsorbed molecules and to assign a value for the average area covered by each adsorbed molecule. In assigning a value to the average area occupied by an adsorbed molecule, Emmett and Brunauer calculated the diameter of the adsorbed molecules from the densities of the liquefied or of the solidified adsorbate. If the physically adsorbed molecules are close-packed on the surface, the following equation for the average area per molecule is used:

$$\text{Area per molecule} = 4(0.866) \left( \frac{M}{4\sqrt{2}N\rho} \right)^{2/3}$$

where  $M$  is the molecular weight of the gas,  $N$  is the Avogadro number, and  $\rho$  is the density of the solidified or liquefied gas. This equation was derived on the assumption that the molecules are hexagonally close-packed in the solidified or liquefied gas.

Emmett and Brunauer also determined the adsorption isotherms for nitrogen, carbon monoxide, oxygen, carbon dioxide, and butane at temperatures between  $-195.8^{\circ}$  and  $0^{\circ}\text{C}$ . for ten different samples of iron catalysts for ammonia synthesis and discuss the method of obtaining the point corresponding to a monolayer. Brunauer (33) and Emmett (60) in Kraemer's *Advances in Colloid Science* present excellent discussions of the theories involved.

### B. Determination of heats of adsorption

In the direct determination of the heat of adsorption both isothermal and adiabatic calorimeters have been employed. In the isothermal calorimeter the heat is allowed to escape from the system and is utilized to produce a phase change such as, for example, the melting of mercury or the evaporation of liquid. The system remains at a constant temperature, and the heat developed is calculated from the amount of solid melted. In the adiabatic calorimeter, the heat is kept in the system, and the amount evolved is calculated from the temperature rise.

Favre (66) was the first to measure heats of adsorption quantitatively, using the isothermal method with mercury as the calorimeter substance. Dewar (55) determined the heats of adsorption of gases on charcoal at  $-185^{\circ}\text{C}$ . with the help of a liquid-air calorimeter.

Adiabatic calorimeters have found more favor for the investigation of heats of adsorption in recent years, because they do not restrict the adsorption to one particular temperature. One type of adiabatic calorimeter for low temperature has a platinum resistance thermometer (234) in the center. The adsorbent is in a ring-shaped space surrounding the thermometer. The calorimeter proper is wound with a platinum heating coil used for calibration purposes and is pro-

ected by a layer of mica. The calorimeter is placed in a vacuum jacket which is completely immersed in ice. Several similar calorimeters have been described by others (27, 29, 148).

The great drawback of this type of adiabatic calorimeter is that the temperature rise of the thermometer is largely dependent upon the thermal conductivity of the adsorbent and the adsorbate. Since porous substances and gases at low pressures are poor conductors, erroneous values are likely to be obtained for the heats of adsorption of gases at low pressures. This situation has been discussed by Bull, Hall, and Garner (34) and by Schwab and Brennecke (201).

This difficulty has been partly eliminated in calorimeters described by Beebe and coworkers (25, 26, 28). A filling tube for introduction of the gaseous adsorbate reaches to the bottom of the calorimeter and is perforated with many small holes to bring as much of the gas in contact with the adsorbent as possible, in order to prevent formation of hot spots and temperature gradients. To further insure rapid heat distribution, six vertical vanes of perforated copper foil are placed in the calorimeter and copper sheet is intermixed with the adsorbent.

Determination of the specific heat of the adsorbate supplies further interesting information about the state of adsorbed matter. Simon (207) has determined the specific heat of hydrogen adsorbed on chabasite. He found the heat capacity between 20° and 35°K. to be about 3 cal. per mole and independent of temperature. Simon concluded, from the specific heats, that the adsorbate behaves as a free gas.

Simon and Swain (208) have determined the specific heats of argon and hydrogen on charcoal at very low temperatures. The results with hydrogen were ambiguous, because the determination was complicated by the simultaneous occurrence of the ortho-para conversion. The results with argon, however, were clear-cut. The specific heat of the adsorbate is much smaller than that of solid argon,—namely, 2 cal. per degree between 60° and 80°K. Since each translational degree of freedom of a perfect gas contributes  $R/2$  cal. to the specific heat, Simon and Swain believed that the result indicated free motion of the argon atoms over the surface in two dimensions.

## XII. OTHER PHYSICAL PROPERTIES

### A. Surface tension

The surface tension of simple organic liquids, and its change with temperature, yield evidence concerning their structure. In order to cover a sufficient temperature range, it is necessary to go to low temperatures.

Two quantities which can be calculated from the surface tension are of interest. The molecular surface energy is given by the equation of Ramsay and Shields

$$\gamma(V_M)^{2/3} = K(T_c - T - 6) \quad (7)$$

(where  $\gamma$  is the surface tension,  $V_M$  the molecular volume, and  $T_c$  the critical temperature) from which it is seen that the molecular surface energy is proportional to the temperature. The proportionality constant  $K$  is about 2 for non-associated liquids, which have little surface orientation; for associated liquids,

$K$  is lower. Where there is orientation of a chain in a direction normal to the surface (producing a surface area less than  $V_M^{2/3}$ ),  $K$  is higher than 2.

The total free surface energy per unit area is given by equation 8

$$\gamma_0 = \frac{\partial E}{\partial \sigma} = \gamma - T \frac{\partial \gamma}{\partial T} \quad (8)$$

where  $\gamma_0$  is the total free surface energy per unit area,  $E$  is the total energy of the surface, and  $\sigma$  is the surface area.

For simple hydrocarbon molecules, Langmuir (133) had deduced that this quantity should be about 47 ergs per square centimeter, because in every case

TABLE 4

*Surface energy and Ramsay and Shields constant from low-temperature surface-tension data*

COMPOUND	$\gamma_0$	$K$ (RAMSAY AND SHIELDS)	REFERENCE
Ethane.....	45.7	1.98	(147)
Propane.....	50.3	2.15	(147)
<i>n</i> -Butane.....	47.8	2.21	(40)
Isobutane.....	47.2	2.23	(40)
Ethylene.....	47.7	2.14	(147)
Propylene.....	49.7	2.12	(147)
$\alpha$ -Butylene.....	51.1	2.21	(40)
$\beta$ -Butylene.....	51.2	2.14	(40)
$\gamma$ -Butylene.....	49.8	2.15	(41)
Acetylene.....	56.0	2.02	(147)
Methylacetylene.....	59.4	1.99	(167)
Ethylacetylene.....	53.5	1.96	(166, 167)
Dimethylacetylene.....	51.8	1.75	(167)
Propylacetylene.....	53.3	2.12	(167)
Ethylene oxide.....	73.1	1.79	(145)
Dimethyl ether.....	55.1	2.00	(145)
Acetaldehyde.....	56.6	1.41	(145)

the methyl groups form the surface layer. Methyl groups occupy the surface when this is the least active group in the molecule.

The method of measuring surface tension at low temperatures has been essentially the method of capillary rise, used at ordinary temperatures (182) with the exception that for volatile compounds provision is made to distill the compound into the evacuated apparatus and seal it off from the filling line (147). Cryostats of type *c* or *d* are used. Maass and his coworkers studied the hydrocarbons and other simple compounds at low temperatures (146). Table 4 gives a summary of the results obtained. An example of work at low temperatures is the determination of the surface tension of liquid deuterium by van Itterbeek (264), using the capillary rise method at liquid-hydrogen temperatures. The value found was 1.7 times that of liquid hydrogen.

The lower saturated hydrocarbons behave as non-polar liquids, with the same total surface energy (methyl group at the surface). The Ramsay and Shields

constant shows no association for the olefins, but the total surface energy is evidence for slightly higher surface forces. For the acetylenes, no association is manifested and the surface forces are even greater than the olefins. This indication of polarity in simple olefins and acetylenes is borne out by other properties. The temperature coefficient of the dielectric constant has been seen to yield a small permanent molecular moment for unsymmetrically substituted olefins and acetylenes.

Table 4 shows also results obtained with simple oxygenated compounds. Dimethyl ether is the most nearly normal.

Other surface-tension measurements, at low temperatures, have been made by Tonomura and coworkers on toluene, acetone, ethyl ether, methyl alcohol (257), ethyl alcohol, and carbon disulfide (258).

TABLE 5  
*Temperature range of certain investigations of viscosity at low temperatures*

SUBSTANCE	TEMPERATURE RANGE	REFERENCE
Methane	-162 to -183°C.	(187)
Ethylene	-104 to -163°C.	(187)
Ethyl ether, acetone; methyl, ethyl, <i>n</i> -propyl, isopropyl, <i>n</i> -butyl, iso-butyl alcohols	Room temperature to freezing point	(162, 163, 255, 256)
Acetone	Room temperature to -90°C.	(5)
Diethyl ether	Room temperature to -109.8°C.	(6)
Ethylene oxide	Room temperature to -50°C.	(145)

### *B. Viscosity of liquids*

An Ostwald viscosimeter is used. Constant temperatures are secured by use of cryostats of type *c* or *d*. Tonomura (256) uses a viscosimeter with pairs of platinum points at the top and at the bottom as reference marks. He measures the capacity between the points by the method of heterodyne beats and notes when the liquid passes the points by the change of note in the ear phones of the capacity apparatus. In other work, the liquid level is observed through un-silvered strips in the cryostat Dewar.

Table 5 summarizes the compounds which have been studied by various investigators with the temperature range.

### *C. Spectroscopic measurements*

Eisman has described an excellent apparatus for investigation of the absorption spectra of gases and liquids at low temperatures up to pressures of 500 atm. (59).



Methane was found to be transparent in the visible and quartz ultraviolet under all conditions, indicating no association. Ashdown, Harris, and Armstrong have found continuous absorption in the ultraviolet for liquid propylene and cyclopropane at  $-78^{\circ}\text{C}$ . (7, 86).

Methods have been worked out for the study of the Raman spectra of liquids boiling below room temperature (80, 129, 233). The liquid is kept below the boiling point in a tube immersed in a simple cryostat, with arrangements for letting the light from the mercury tube be incident on the sides of the tube and for observing the light scattered in the direction of its axis. Oxygen (199), hydrogen chloride (136), ethane, propane, and ethylene (52, 53, 79), methyl chloride and bromide (46, 48), and dimethyl ether (47, 49) have been investigated under these conditions. Harris, Ashdown, and Armstrong have measured the Raman spectrum of liquid cyclopropane (86) at liquid-ammonia temperatures and describe an ingenious apparatus for the purpose.

Conn, Lee, and Sutherland (43) describe an infrared spectrometer to study the change in spectrum with a change in state at a transition point. The infrared-absorption spectrum of hydrogen chloride at liquid-nitrogen temperatures (136) was determined along with the Raman spectrum.

Conant and Crawford (42) have shown that the absorption bands of the porphyrins in the visible are split into finer ones at liquid-air temperatures, owing to reduction of the number of molecules in higher energy states.

Terenin, Yakovkin, and Volobuyev (240) have found that benzaldehyde exhibits fluorescence at  $-180^{\circ}\text{C}$ .

The study of absorption spectra of dyes at low temperatures, because of the simpler nature of the spectra, affords evidence concerning the nature of the energy levels in dyes (140, 141, 142). Such evidence is confirmed by a study of the spectrum of the fluorescent light emitted on illumination at temperatures attained with solid carbon dioxide, liquid air, and liquid hydrogen. Terenin (239) has conducted a spectral investigation of the association and photochemical reactions of aromatic compounds at the temperature of liquid air. A convenient apparatus for low-temperature absorption-spectrum measurements has been perfected by Beck (24).

#### *D. Crystal properties*

The birefringence of a series of organic substances, including all the simple hydrocarbons, has been investigated by Wahl down to liquid-hydrogen temperatures (268, 269, 270, 271, 272, 273). Wahl has detected crystal transition in many cases. This beautiful work is useful in forecasting transitions which will appear in systematic low-temperature specific-heat measurements on simple organic compounds.

X-ray measurements have been made on solid acetylene by Mooy (165). A preliminary interpretation indicates a possible cubic structure with two molecules per cell.

Similar measurements by McLennan and Plummer (154) have been made on methane, indicating a face-centered cubic structure with four molecules per cell (the hydrogen atoms could not be detected).

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