

NONFLAMMABLE LIQUIDS FOR CRYOSTATS

By C. W. Kanolt

ABSTRACT

Several very serious accidents in laboratories have resulted from the use of flammable liquids, such as volatile petroleum distillates, or toluene, to form the bath of a cryostat. In some instances explosions have occurred, and burning liquid has been thrown upon the operator.

The purpose of the investigation has been to find liquids that will not burn, that have very low freezing points, and that are otherwise suitable for use as cryostat liquids. The materials tried were chlorine and bromine derivatives of methane, ethane, and ethylene, and mixtures of these derivatives. By mixing the substances in suitable proportions it is usually possible to obtain mixtures having lower freezing points than those of any of the constituents. The eutectic compositions and temperatures of mixtures of two, three, and four components have been determined, and some mixtures of five components have been investigated.

Some of the mixtures became very viscous at temperatures near their freezing points, and the limits of usefulness of these mixtures were determined by their viscosities rather than their freezing points. For this reason the viscosities of some of the mixtures were measured, at various temperatures. The corrosiveness of the liquids to metals was also studied.

Liquids that will not burn and are suitable for use at temperatures down to about -150° C. are described.

Apparatus is described for the determination of freezing points at low temperatures, and for the determination of viscosity at low temperatures, with special means of avoiding the presence of solid particles in the liquid.

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I. INTRODUCTION

Several very serious accidents in laboratories have resulted from the use of flammable¹ liquids, such as volatile petroleum distillates, or toluene, to form the bath of a cryostat. Some of the worst of these accidents have occurred when the bath was cooled indirectly by

¹ The American Society for Testing Materials favors the use of the word "flammable" instead of "inflammable," which is sometimes understood to mean "not flammable."

the use of liquid air. The evaporation of liquid air leaves nearly pure liquid oxygen; and if the vapor of a flammable liquid is permitted to condense into the liquid oxygen an explosive mixture is likely to be formed. Although the amount of such an explosive produced may not be very large, it may produce, if ignited, an explosion of sufficient violence to throw burning liquid upon the person using the apparatus. Another possible cause of trouble is the glass vacuum-walled vessel commonly used as a container for the bath. Such vessels may collapse during use, without any apparent cause; and the collapse of the vessel may throw the liquid about. An electric motor or other electrical apparatus may supply a spark to ignite the liquid. There is some evidence also that the collapse of such a vessel can itself produce a spark, caused, perhaps, by friction.

There are several well-known substances, such as carbon tetrachloride and aqueous solutions of calcium chloride or sodium chloride, which will not burn and which can be used without freezing at temperatures considerably below the freezing point of water, but it is often necessary to work at temperatures far below the freezing points of these liquids, and then it has been considered necessary to use some of the flammable liquids. The purpose of this work was to find new liquids which are not flammable, which have very low freezing points, and which are otherwise suitable for use in cryostats. By mixing several liquid compounds in suitable proportions it is usually possible to obtain mixtures with freezing points lower than those of any of the constituents. The work has consisted largely in the investigation of such mixtures. Freezing points, flammability, viscosity, and corrosiveness have been studied.²

II. MATERIALS

The substances used were the following halogen derivatives of methane, ethane, and ethylene: Carbon tetrachloride CCl_4 , chloroform CHCl_3 , methylene chloride CH_2Cl_2 , ethyl chloride $\text{C}_2\text{H}_5\text{Cl}$, ethyl bromide $\text{C}_2\text{H}_5\text{Br}$, trans-dichloroethylene $\text{C}_2\text{H}_2\text{Cl}_2$, and trichloroethylene C_2HCl_3 . The investigation was limited to substances which are on the market. The vapor of none of these substances is dangerously poisonous when inhaled; they are all anæsthetic, at least to some extent. All except one of them, ethyl chloride, are liquids at ordinary temperatures and atmospheric pressure. Ethyl chloride boils at 12.2°C. ; at ordinary temperatures the vapor pressure of the liquid is so little above atmospheric pressure that it is sold in glass containers.

The purest obtainable materials were purchased, but all were repurified in the laboratory before use. The use of very pure mate-

² The writer has collected for the International Critical Tables all available data relative to cryostat liquids, both flammable and nonflammable.

rial for a cryostat bath is not necessary, but since small amounts of impurity are likely to have considerable effect upon the freezing point of a liquid it was desirable to use pure materials in the investigation. Materials of commercial quality usually have lower freezing points than those reported in this paper.

Purification was accomplished by the use of a suitable dehydrating agent, usually phosphorus pentoxide, and by slow fractional distillation with a tall Hempel³ rectifying column. When ethyl chloride was distilled, the fractionating column was surrounded with circulating water maintained at such a temperature that a suitable proportion of the ethyl chloride vapor was condensed in the column.

As criteria of purity, the behavior of the substance on freezing and the reproducibility of the freezing point after repurification were observed. These criteria were found to be more sensitive than the boiling point. When the time temperature cooling curve is plotted, the portion of the curve corresponding to the process of freezing should be very nearly flat, if the substance is pure, except toward the end of the freezing process, when the accumulation of solid material prevents effective stirring and the temperature may cease to be uniform.

The chloroform purchased contained ethyl alcohol. The alcohol was removed by treatment of the chloroform with sulphuric acid, and the chloroform was further purified by fractionation with the Hempel column.

The purified liquids were stored in a dark place, to diminish oxidation; and they were used without undue delay after their purification.

III. FLAMMABILITY

Statements in the literature relative to the flammability of the less common of the substances used are in some cases in error, as the result, perhaps, of experiments upon impure material.

As a test of flammability in air a small wad of soft asbestos fiber was saturated with the liquid and laid upon a horizontal surface, and a flame from 1 to 2 cm long was applied. Air currents were avoided. If the vapor of the liquid continued to burn, even only momentarily, after the removal of the flame, the liquid was considered to be flammable. All of the liquids experimented upon in this work are so volatile that it is not necessary to heat them above ordinary room temperature in determining whether they can be ignited.

An interesting study of the behavior of different liquids under this test can be made upon a mixture of two liquid compounds, one

³ A general treatise on laboratory rectifiers will be found in Rechenberg's *Einfache und fraktionierte Destillation*, Schimmel & Co., Miltitz bei Leipzig, 1923.

flammable, the other effective in extinguishing a flame. If the mixture contains a sufficient proportion of the nonflammable constituent, its vapor extinguishes the applied flame, if the flame is a small one. If the proportion of the flammable constituent is sufficiently increased, the applied flame continues to burn without any observable ignition of the liquid. With a further increase, the applied flame becomes surrounded by a mantle of burning vapor from the liquid, which, however, does not continue to burn by itself. With a still greater increase, this vapor mantle becomes larger, until a point is reached at which it continues to burn feebly for a moment after the flame applied has been removed. The mixture is then flammable, according to the criterion adopted.

With this method of testing, it was found that carbon tetrachloride, chloroform, methylene chloride, ethyl bromide, and trichloroethylene are not flammable, while ethyl chloride and dichloroethylene are flammable. The test was also applied to various mixtures to be described later.

IV. DETERMINATION OF FREEZING POINTS

The apparatus used in the determination of freezing points is shown in Figure 1. From 12 to 15 cc of the liquid to be examined was placed in the pyrex glass vessel, *A*. Mixtures were usually prepared by weighing directly in this vessel, which is provided with three legs to permit its standing upon the pan of a balance or upon the table.

The liquid was stirred by a glass rod, *B*, carrying a horizontal loop at its lower end. This stirrer was moved up and down continually by a mechanism driven by a small electric motor. The top of the rod was connected by a wire to a rotating crank. The flexibility of this wire prevented damage to the apparatus when the downward motion of the stirrer was prevented by the freezing of the liquid. The stirrer carried a small weight, *C*, to aid in driving it downward when the liquid was viscous.

The temperature was measured by a thermocouple, *D*, inserted through a very slender glass tube. The junction of the couple projected slightly below the open end of the tube. The couple was made of copper and constantan wires about 0.13 mm in diameter. The wire was of a stock that had been carefully compared at the Bureau of Standards with a platinum resistance thermometer, which had been calibrated at the freezing point of mercury (-38.87°C.), the normal sublimation point of carbon dioxide (-78.51°C.), and the normal boiling point of oxygen (-183.00°C.)⁴.

⁴ The relation between the resistance of the thermometer and the temperature is discussed in a paper by Van Dusen, *Jour. Am. Chem. Soc.*, **47**, p. 326-332; 1925.

The motion of the stirring rod continually drove a little air into the space above the liquid, and out again. If air from the atmosphere had been permitted to enter, it would have carried in moisture, forming particles of ice in the cold liquid, which would have rendered the liquid turbid and might have influenced its freezing point. To avoid this, the top of the vessel, *A*, was constructed as shown in Figure 1, and during its use a slow current of very dry air was passed in through a rubber tube attached at *E*.

The vessel, *A*, was placed within a pyrex tube, *F*, which was inserted into an unsilvered glass vacuum-walled vessel, *G*, into which liquid air could be introduced through the funnel, *H*. The mouth of *F* was closed with cotton to prevent the entrance of moist air which would have deposited frost upon *F* and so hindered observations. The rate at which the liquid was cooled was controlled by adjusting the level of the liquid air in *G*. A vertical centimeter scale was attached to the outside of *G*, and it was learned by experience to what level on the scale the liquid air should be maintained in order to cool the liquid in *A* at a suitable rate, depending upon its freezing temperature. Liquid air was added every minute or two to keep the level constant and maintain steady conditions of cooling. It is preferable to use filtered liquid air, in order to be able to see into the apparatus clearly.

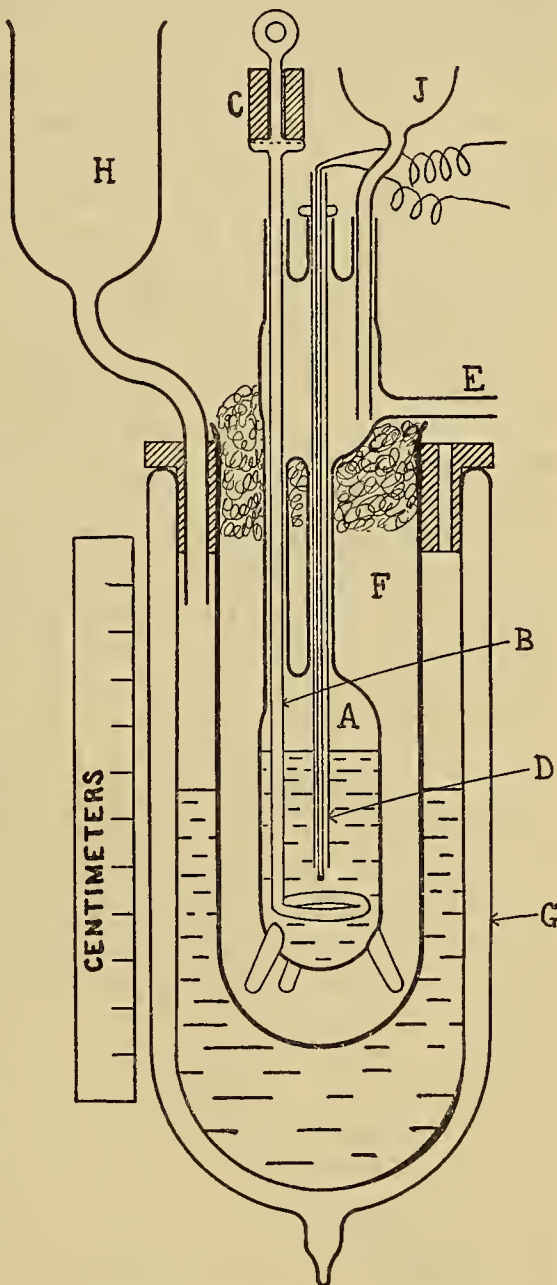


FIG. 1.—Freezing point apparatus

Most of the liquids investigated have a tendency to undercool far below their freezing points before crystallization begins. When a

mixture of several substances is being investigated this undercooling, if not prevented, would cause serious difficulty. It may, for example, cause the ingredients to crystallize in a different order relative to temperature from that corresponding to equilibrium, and so render a reliable determination of the temperature at which the first separation can occur very difficult.

The difficulty was overcome by occasionally introducing through the funnel, *J*, one or two small drops, about a millimeter in diameter, of clear liquid air. This was introduced at intervals of one to three minutes when the liquid was thought to be near its freezing point. The drops of liquid air descended readily to the surface of the liquid in *A*, and were usually very effective in starting crystallization, if the freezing point had been reached.

In the study of a series of mixtures the most important problem was usually to find the composition and the freezing point of the eutectic mixture. All observations were plotted in the form of cooling curves with time and temperature or time and thermocouple electromotive force as coordinates. When a mixture not a eutectic is cooled there is, in general, a distinct change of direction in the cooling curve as each ingredient begins to separate. The highest temperature at which any ingredient can separate is defined as the freezing point of the mixture. When the last ingredient has begun to separate the remaining liquid has the eutectic composition, and the temperature remains constant until the material is all frozen, or until so much solid is present that the material can not be stirred and uniformity of temperature can not be maintained. It is thus possible to determine the eutectic freezing point from the behavior of a mixture which has not the eutectic composition, provided its composition is not too far removed from the eutectic.

The determination of the eutectic composition is more difficult than that of the eutectic freezing point. It must be accomplished mainly by the method of trial and error; the freezing points of the mixtures already tried, with a determination of the eutectic freezing point from one of these mixtures, serve as a guide for each new estimate of the composition to be tried next. The difficulty, of course, increases with the number of constituents. The work was facilitated by the use of models in two or three dimensions, which are possible when the number of constituents is not greater than four. One 4-component eutectic composition was determined. Some measurements were made on two 5-component systems, but these liquids became so viscous near their eutectic points that the determination of freezing points was uncertain or impossible. Their viscosities set a limit to their usefulness.

Table 1 contains the values found for the freezing points of the single compounds, and presents for comparison the results of the

more recent and reliable determinations by other investigators. The determinations by Timmermanns, Van der Horst, and Kamerlingh Onnes, by Henning, and by Keyes, Townshend, and Young were made especially for the accurate establishment of the temperature scale. The agreement between the results of the writer and those of the other investigators is considered satisfactory for the purpose of the present work.

TABLE 1.—Freezing point

Substance	Present work ¹	Results of other investigators
	° C.	
CCl ₄	-23.4	{ -22.9° C., Timmermanns, Van der Horst, and Kamerlingh Onnes. ² -22.87° C., Keyes, Townshend, and Young. ³ -63.5° C., Timmermanns, Van der Horst, and Kamerlingh Onnes. ² -63.7° C., Henning. ⁴ -64.19° C., Keyes, Townshend, and Young. ³
CHCl ₃	-63.6	
CH ₂ Cl ₂	-96.0	-96.7° C., Timmermanns. ⁵
C ₂ H ₅ Cl.....	-139.4	-138.7° C., Timmermanns. ⁶
C ₂ H ₅ Br.....	-119.5	-119.0° C., Timmermanns. ⁵
C ₂ H ₂ Cl ₂ trans.....	-82.0	-80.5° C., Timmermanns. ⁶
C ₂ HCl ₃	-86.9	-86.4° C., Timmermanns. ⁶

¹ These results are not presented as a contribution to the establishment of the temperature scale.

² Timmermanns, Van der Horst, and Kamerlingh Onnes, Leiden Communication No. 157.

³ Keyes, Townshend, and Young, J. Math. Phys., Mass. Inst. Tech., **1**, 243-312; 1922.

⁴ Henning, Ann. d. Phys. (4), **43**, 282-294; 1914.

⁵ Timmermanns, Bull. Soc. Chim. Belg., **25**, 300-326; 1911.

⁶ Timmermanns, Bull. Soc. Chim. Belg., **27**, 334-343; 1913. Two values, -138.7 and -138.07° C., are given, in this paper for the freezing point of ethyl chloride. The latter value is probably a misprint.

Table 2 presents the freezing points of mixtures, with information as to their flammability in air.

The viscosity of mixture No. 39 near its freezing point is so great that the determination of the freezing point was not very accurate. At very low temperatures, mixtures Nos. 40, 41, 42, and 43 became vitreous, and no crystallization was observed at any temperature. Their freezing points are probably below -150° C. The range of temperature in which these mixtures can be used as cryostat bath liquids is limited by their viscosities rather than by their freezing points.

The freezing points of the binary mixtures of Table 2 are shown graphically in Figure 2.

None of the mixtures investigated exhibited any evidence of the formation of a compound.

The freezing curve of mixtures of ethyl chloride and ethyl bromide contains no eutectic point, indicating that these substances form solid solutions.

78988°—26†—2

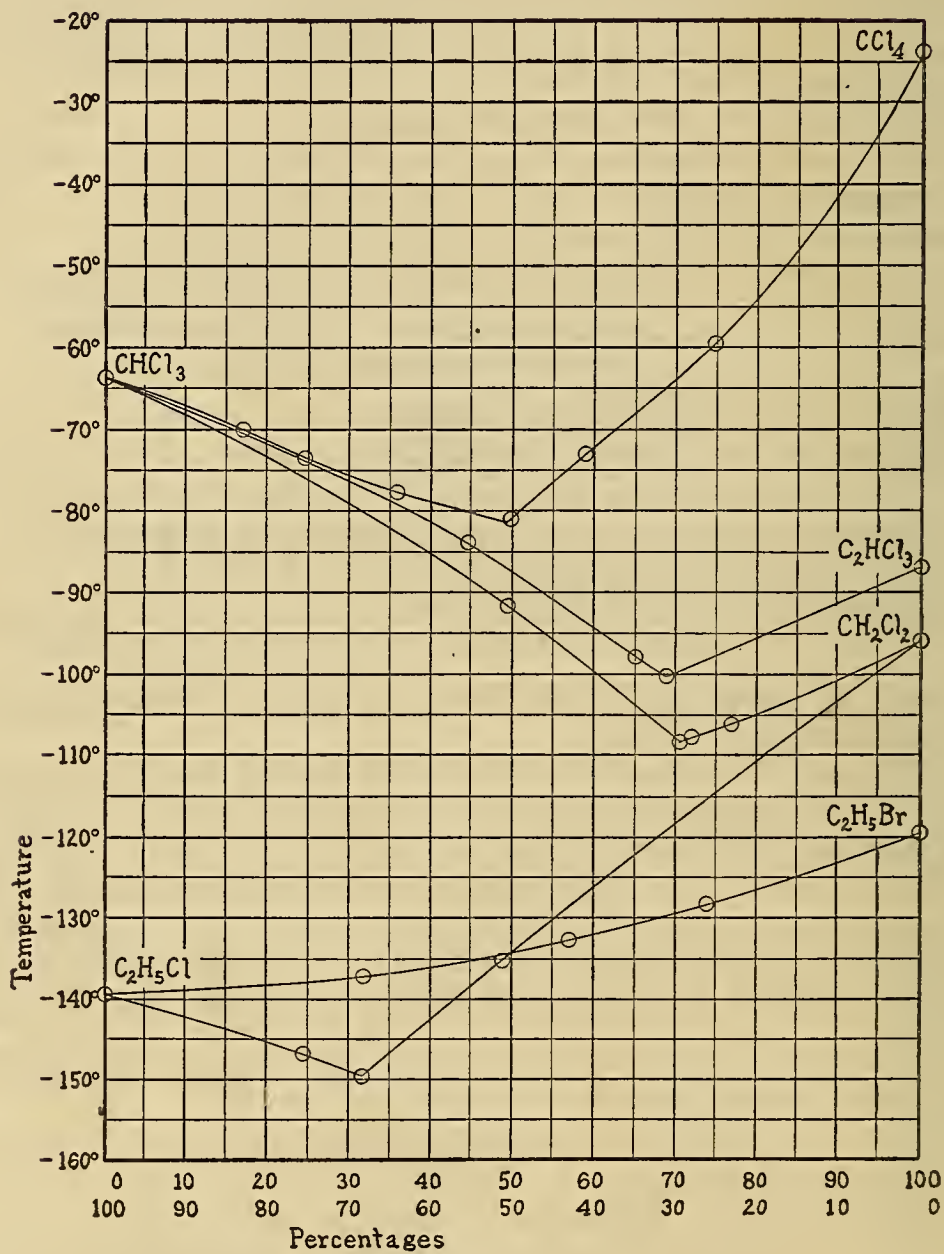


FIG. 2.—Freezing points of binary mixtures

TABLE 2.—Freezing points and flammability of mixtures

Mixture number	Percentage composition by weight							Freezing point	Flammability
	CCl ₄	CHCl ₃	CH ₂ Cl ₂	C ₂ H ₅ Cl	C ₂ H ₅ Br	C ₂ H ₂ Cl ₂ trans	C ₂ HCl ₃		
1-----	74.9	25.1						° C. -59.4	Not flamma- ble.
2-----	59.0	41.0						-73.1	Do.
3-----	49.8	50.2						-81.1	Do.
4—Eutectic ¹	49.4	50.6						-81.4	Do.
5-----	35.9	64.1						-77.2	Do.
6-----	24.7	75.3						-73.0	Do.
7-----	17.2	82.8						-70.0	Do.
8-----		50.6	49.4					-91.9	Do.
9—Eutectic		29.5	70.5					-108.4	Do.
10-----		28.1	71.9					-107.9	Do.
11-----		23.2	76.8					-106.2	Do.
12-----		55.3					44.7	-83.8	Do.
13-----		35.0					65.0	-97.8	Do.
14—Eutectic		31.2					68.8	-100.2	Do.
15-----			90.0	10.0					Limit of flam- mability.
16-----			49.0	51.0				-135.3	Flammable.
17—Eutectic			31.7	68.3				-149.7	Do.
18-----			24.4	75.6				-146.8	Do.
19-----				68.2	31.8			-137.3	Do.
20-----				42.9	57.1			-132.8	Do.
21-----				26.1	73.9			-128.4	Do.
22-----				20.0	80.0				Limit of flam- mability.
23-----	23.4	23.9	52.7					-103.0	Not flamma- ble.
24-----	20.9	16.7	62.4					-107.1	Do.
25-----	20.8	54.4	24.8					-87.2	Do.
26—Eutectic ¹	13.0	27.0	60.0					-111.4	Do.
27-----	12.8	27.0	60.2					-111.2	Do.
28-----	10.1	27.4	62.5					-110.5	Do.
29-----	10.1	24.2	65.7					-109.1	Do.
30-----	9.1	18.8	42.6				29.7	-118.9	Do.
31-----		20.0			45.4	13.4	21.2	-139.1	Do.
32—Eutectic ¹		19.7			44.9	13.8	21.6	-139.1	Do.
33-----		19.5			44.4	14.2	21.9	-139.0	Do.
34-----		16.4			39.9	23.3	20.4	-124.0	Do.
35-----		15.5			38.2	21.8	24.5	-131.5	Do.
36-----		14.1			40.3	19.5	26.1	-132.5	Do.
37-----		13.4			42.7	18.5	25.4	-132.7	Do.
38-----		12.8			41.5	17.9	27.8	-130.7	Do.
39-----		14.5	25.3		33.4	10.4	16.4	About -150.	Do.
40 ² -----		18.1		8.0	41.3	12.7	19.9	Probably below -150.	Do.
41 ² -----		17.9		9.0	40.8	12.6	19.7	Probably below -150.	Limit of flam- mability.
42 ² -----		17.9		9.3	40.7	12.5	19.6	Probably below -150.	Flammable.
43 ² -----		17.5		11.3	39.8	12.2	19.2	Probably below -150.	Do.
44 ² -----		15.8		19.9	36.0	11.0	17.3	-150.0	Do.
45 ² -----		12.4		37.0	28.3	8.7	13.6	-147.1	Do.

¹ This eutectic composition was estimated graphically from the eutectic temperature and from the freezing points of compositions differing little from the eutectic.
² These mixtures were made by adding C₂H₅Cl to No. 32.

V. MEASUREMENT OF VISCOSITY

In some cases the lowest temperature at which a liquid can be used is determined not by its freezing point, but by its viscosity, which interferes with effective stirring. The viscosity the liquid can possess without serious detriment depends somewhat upon the degree

of uniformity of temperature required. Since it is unsatisfactory to state merely that the liquids are "very viscous" or "only slightly viscous," the viscosities of some of the liquids have been quantitatively determined. For the present purpose high accuracy in this determination is not of use, and it has not been attempted.

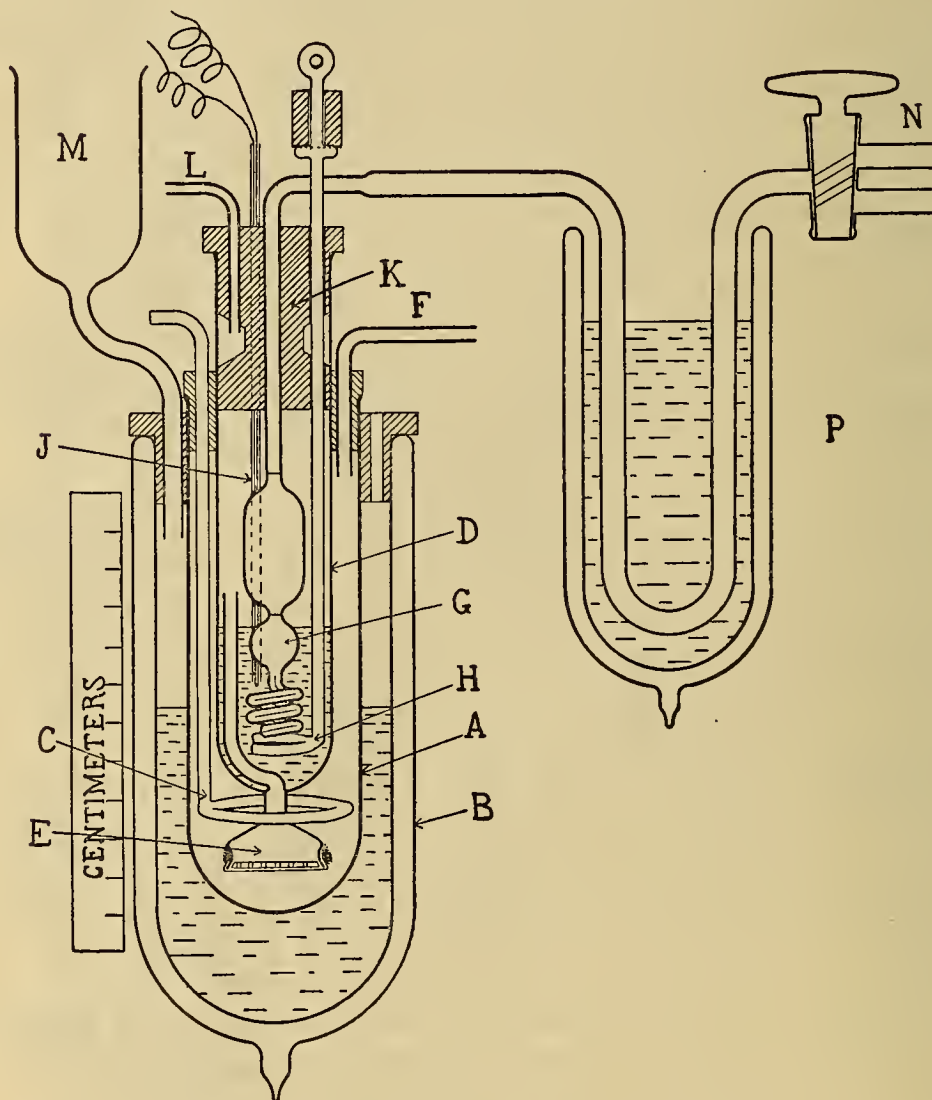


FIG. 3.—Apparatus for determining viscosity

The viscometer is shown in Figure 3. It is of the capillary-tube type. The principal problem involved in the application of an instrument of this type to work at very low temperatures is that of avoiding the presence of solid particles in the liquids. Even when the liquids have been carefully purified they sometimes become turbid at temperatures near the freezing point, as the result of the admission of moisture, which forms particles of ice, or from the presence of a trace of some other impurity. If solid particles enter

the capillary tube, they are likely to cause large errors in the measurement of viscosity. The apparatus includes means of filtering the liquid after it has been cooled, and means of avoiding the introduction of moisture after this filtering has been accomplished.

The liquid, the viscosity of which was to be determined, was first placed in the pyrex vessel, *A*. Liquid aid was introduced into the unsilvered vacuum-walled vessel, *B*, and the liquid was cooled, with agitation by the stirring rod, *C*, until its temperature was at least as low as the lowest temperature at which measurements were to be made. During this cooling, the tube, *D*, carrying at its lower end the filter, *E*, was kept drawn up so that the filter remained dry. When the liquid had been cooled, the tube, *D*, was pushed down until the filter, *E*, was near the bottom of *A*, and the liquid was driven through the filter into *D* by the application of a slight air pressure at *F*. Care was taken to stop the filtering before air could enter the filter, because this might raise the temperature, melt some of the material that had been filtered out, and permit it to pass through the filter with the last portion of the liquid.

The filter, *E*, consists of an inverted glass funnel, into the end of which is fitted a perforated porcelain plate, over which is attached a sheet of filter paper of a kind adapted to the filtering out of fine particles. The paper is folded over the edge of the funnel so that its edge enters a groove formed in the rim of the funnel; and the paper is bound down with a thick winding of thread, which completely covers the edge of the paper, preventing particles from passing under this edge.

The tube, *D*, contains the viscometer, *G*, a stirring rod, *H*, and a thermocouple, *J*. After the liquid had been introduced into *D* it was brought to the desired temperature by adjusting the level of the liquid air in *B*. This level was then adjusted every minute or two by the introduction of liquid air through *M*; and with the guidance of frequent temperature observations, the temperature in *D* could be kept constant within sufficiently narrow limits during the measurement of viscosity.

The stirrer, *H*, was driven mechanically in the same way as that of the freezing-point apparatus. To prevent the introduction of moist air by the action of the stirring rod a device was employed that is similar in principle to that in Figure 1, but is different in construction. The tube, *D*, is closed by a cork, *K*, which is cut away over a part of its length in such a way as to leave a space around the stirring rod and other glass parts, into which space a slow current of very dry air was introduced through the tube, *L*.

The viscometer, *G*, comprises a helical capillary tube, through which the liquid can be drawn into first a small bulb and then a larger bulb. The liquid was drawn through by the application at *N* of a

constant reduced pressure, and the time required for the passage of the liquid from a mark below the larger bulb to one above it was observed. The pressure difference was maintained constant by a regulator of a familiar type, in which it is determined by the height of a column of water through which air bubbles slowly. The pressure difference was measured by a water manometer.

After a measurement of viscosity had been made, the liquid was caused to run back by opening the three-way stopcock, *N*, either to the atmosphere or to a moderate air pressure. To prevent the introduction of moisture into the viscometer, the U-tube, *P*, was kept immersed in liquid air.

The viscometer was calibrated with water at 0° C., and with 40 per cent sucrose solution at 0° C., using in both cases several different pressure differences. In both the calibration and the use of the viscometer, a correction was made for the effect of the mean hydrostatic pressure of the column of liquid in the viscometer. This correction required a knowledge of the density of the liquid at the temperature of observation, but since this hydrostatic pressure was small relative to the pressure difference employed, only an approximate knowledge of the density was required. The relation between viscosity and time of flow, as found by calibration, was expressed by an equation of the usual form:

$$\mu = ApT + B\frac{\rho}{T}$$

where μ is the viscosity, T the time, p the mean pressure difference, ρ the density, and A and B are empirical constants.

The results of the measurements on each liquid were plotted with $\log \mu$ as one coordinate and $\log (t - c)$ as the other, t being the centigrade temperature, and c a constant. By a suitable choice of the constant c it was possible to obtain graphs which were very nearly straight lines, making interpolation easy. From these graphs the values in Table 3 were found by interpolation. One can gain an idea of the magnitude of the viscosities at the lower temperatures by comparison with that of olive oil, which is roughly 100 centipoises at 20° C. and that of anhydrous glycerine, which is roughly 1,000 at 20° C.

TABLE 3.—Viscosity in centipoises

Liquid	−80° C.	−90°	−100°	−110°	−120°	−130°	−140°	−145°	−150°
C ₂ H ₅ Br.....	1.81	2.25	2.89	3.86	5.6	-----	-----	-----	-----
Mixture No. 32.....	-----	3.03	4.57	7.4	13.7	29.3	81	-----	-----
Mixture No. 39.....	1.97	2.57	3.69	5.6	10.0	22.3	85	242	1,480
Mixture No. 40.....	-----	2.88	3.89	5.9	10.2	22.5	71	170	631

The viscosities of mixtures Nos. 1 to 14 are sufficiently low at all temperatures down to the freezing points, so that they are suitable in this respect for use as cryostat liquids. This may not be true of all the mixtures Nos. 16 to 21, but these are flammable, and since other mixtures having as low freezing points have been found that are not flammable, the determination of their viscosities did not appear worth while. That of the 4-component mixture No. 30 was not determined, because its freezing point is only about that of ethyl bromide, which is cheaper and possibly preferable.

VI. CORROSION

It is important that a cryostat liquid should not have too much corrosive action upon the metal parts of apparatus immersed in it. For this reason, experiments have been made on the corrosive action of some of the liquids investigated, upon the metals iron, lead, tin, copper, brass, German silver, and lead-tin solder.

When free from air and otherwise perfectly pure, the corrosive action of all the liquids used is only slight. However, some of them become oxidized by air, with the formation of very corrosive impurities, such as hydrochloric acid. Such impurities may be present in the liquids as purchased. Acid impurities can be detected by agitating some of the liquid with water, and testing the water for acid. Oxidizing impurities can be detected by agitation with a solution of potassium iodide and starch. The odor of the substance gives some indication of the presence or absence of corrosive impurities.

The removal of corrosive impurities has been accomplished by agitation with an aqueous solution of sodium carbonate. This treatment may leave water in the compound, and unless this is removed by a drying agent it may be objectionable, because it will cause the liquid to become cloudy at low temperatures. If this is not objectionable, it may be well, in the case of the liquids more subject to oxidation, to keep a layer of a carbonate solution over the top of the liquid when it is stored in a bottle. Instead of this, one may place anhydrous sodium carbonate in the stock bottle, and decant off the liquid when it is to be used. A water solution of a carbonate accidentally introduced into the cryostat may itself produce corrosion.

Pure chloroform becomes oxidized when exposed to air and light, with the formation of carbonyl chloride, which is poisonous. Commercial chloroform always contains a little ethyl alcohol, which hinders or prevents this oxidation. The alcohol need not be removed when the chloroform is to be used in a cryostat. Even in the absence of alcohol, the corrosive action was found to be rather slight.

The corrosive action of carbon tetrachloride in contact with metal for short periods is only slight, even in presence of air.

Methylene chloride, ethyl bromide, dichloroethylene, and trichloroethylene become oxidized by air with the production of corrosive compounds. This is most noticeable in the case of trichloroethylene, which proved to be from this cause the most corrosive of the substances employed. However, the corrosive impurities can be removed easily by the carbonate solution. The addition of alcohol to trichloroethylene does not prevent it from becoming corrosive, but renders it more corrosive. Of the metals tried, iron, copper, and brass were found to be more subject to corrosion than German silver, lead, tin, and lead-tin solder.

VII. RECOMMENDATIONS AND CONCLUSION

The following liquids are recommended for use at temperatures down to the limits indicated:

Liquid:	Temperature limit °C
Carbon tetrachloride.....	— 23
Chloroform.....	— 63
Mixture No. 4 (chloroform-carbon tetrachloride eutectic)	— 81
Ethyl bromide.....	— 119
Mixture No. 32.....	— 139
Mixture No. 39.....	— 145 or — 150
Mixture No. 40.....	about — 150

None of these is flammable. Some of them contain flammable ingredients (ethyl chloride and dichloroethylene), but these ingredients are sufficiently volatile so that the liquids can not become flammable by evaporation.

Because of the volatility of the liquids and the tendency of some of them to become oxidized by air, they should be kept in well-stoppered bottles when not in use. If it is desired to keep the liquids clear when used at low temperatures, it is well to filter them while cold each time they are removed from the cryostat to the stock bottle. This is conveniently accomplished by dipping into the cryostat a glass tube carrying at its lower end a filter like that shown at *E* in Figure 3, connecting this tube to the stock bottle, and drawing the liquid through the filter and into the stock bottle by mild suction. A filtering device made of metal instead of glass can be used.

At temperatures below -150° C. it will still be necessary in many cases to employ a flammable liquid, such as liquefied technical butane, which can be used at temperatures down to about -180° C.⁴ In such cases, the danger to the operator can be greatly diminished by screening the top, front, and sides of the apparatus with sheet metal. This casing should be left open at the back, so that a mild explosion can find a vent in a direction away from the operator.

⁴ Loomis and Walters, J. Am. Chem. Soc., 47, 2302; 1925.

The metal casing may have openings for observation, which can be equipped with sliding metal doors.

Over certain limited ranges of temperature one may use cryostats containing boiling liquids maintained at the desired temperature by controlling the pressure.⁵ At temperatures below about -180° C. liquid oxygen or liquid argon can be used, and, at somewhat lower temperatures, liquid nitrogen. Nitrogen, however, freezes at a higher temperature than oxygen. The use of liquid oxygen is dangerous if the apparatus immersed in the bath contains a flammable material. For the range from -180° to -150° C., in which the use of a flammable bath liquid appears unavoidable, boiling liquid methane can be used. Nitric oxide has nearly the same temperature-vapor pressure relation as methane, but its great corrosiveness renders it objectionable.

WASHINGTON, November 4, 1925.

⁵ Several papers on this subject by Kamerlingh Onnes and others are to be found in the Leiden Communications.



