This analysis of the situation makes it possible to define more clearly the role played by polymerization in the volume change. A rough estimate of the extent of polymerization of pure water and of water containing dissolved urethan is attempted.

The effect of a dissolved substance on the compressibility of the solution is shown to be dependent upon the same causes which determine density. A dilute solution, even of ether, is much less compressible than pure water. Half molal solutions of three different substances in water are shown each to possess a compressibility about 3% less than that of pure water. This quantity is inevitably affected somewhat by the specific compressibility of the solute and by the internal pressures concerned.

Further investigation is planned.

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[CONTRIBUTION FROM THE CRYOGENIC RESEARCH LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

# A CRYOSTAT FOR PRECISION MEASUREMENTS AT TEMPERATURES EXTENDING TO —180°[1]

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## Introduction

For precision measurements at low temperatures it is essential that the temperature be maintained constant to ±0.01° for considerable periods of time, since the temperature scale has now been established within this limit. In this paper we describe a cryostat that maintains any desired temperature within the range 0° to —180° constant to ±0.01° for several hours at a time, with the added features of simplicity, economy and safety.

## Types of Cryostats

Among the cryostats that have been described in the literature are those of Onnes,[2] Timmermans,[3] Henning,[4] Maass,[5] Stock,[6] Henning and Stock,[7] von Siemens,[8] Cardoso,[9] Keyes[10] and Jackson.[11] All of these may be divided into five general classes: (1) boiling liquids, (2) addition of liquid air to the cryostat bath by hand, (3) regulation of the flow

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

[2] Onnes, *Leiden Communications*, Nos. 83, 94, 123 a.

[3] Timmermans, *Proc. Roy. Soc. Dublin*, **13**, 310 (1912).

[4] Henning, *Z. Instrumentenkunde*, **33**, 33 (1913).

[5] Maass and Wright, THIS JOURNAL, **43**, 1098 (1921).

[6] Stock, *Ber.*, **53**, 751 (1920).

[7] Henning and Stock, *Z. Physik*, **4**, 226 (1921).

[8] von Siemens, *Ann. Physik*, [4] **42**, 871 (1913).

[9] Cardoso, *Arch. Sci. Phys. Nat.*, **13**, 317 (1915).

[10] Keyes, Townshend and Young, *J. Math. Phys., Mass. Inst. Techn.*, **1**, No. 4, 213. Also Taylor and Smith, THIS JOURNAL, **44**, 2450 (1922).

[11] Jackson, *J. Sci. Instruments*, **2**, No. 5, 158 (1925).

of heat into a large metal block, the lower end of which is intermittently dipped into liquid air, (4) the regulation of the flow of heat from the cryostat by means of a partially evacuated Dewar tube contained in a larger surrounding Dewar tube containing liquid air and (5) the automatic cryostat.

The boiling-liquid type has been developed by Onnes[2] to a high degree of perfection. Any desired temperature below 0° may be obtained to ±0.01° for periods of an hour or more by the proper regulation of pressure on the following liquids: methyl chloride, nitrous oxide, ethylene, methane, oxygen, nitrogen, hydrogen and helium. However, such an arrangement requires a very elaborate auxiliary apparatus for purifying, compressing and liquefying the various gases and could not be reproduced without the expenditure of considerable time and money; the cost alone would prohibit its use by most laboratories.

Cryostats that depend on the regulation of heat balance in a large metal block, the lower end of which is intermittently cooled by liquid air, give satisfactory results for some types of work but great care must be exercised in placing the thermometer and experimental apparatus at identical heat gradients. Moreover, such observations as are required for specific volumes, critical phenomena, etc., are made with difficulty, if at all.

The regulation of heat flow from the thermostat bath by means of a partially exhausted Dewar tube, surrounded by liquid air contained in a second Dewar tube, has been perfected by Keyes,[10] the steadiness reaching ±0.01° for a period of 20 minutes, using hand regulation. By using the automatic regulator as described by Jackson,[11] this type of cryostat appears to be very satisfactory, the steadiness being ±0.01° with his arrangement.

There is one feature of this type, however, that appears to be quite objectionable. As the liquid air in the outer Dewar tube boils away it becomes richer in oxygen and after some time the cold bath is practically liquid oxygen. The cryostat bath must be of some highly inflammable material to remain liquid at very low temperatures, such as pentane or other hydrocarbon. Failure of the inside Dewar tube would cause a mixing of hydrocarbon and liquid oxygen in large amounts, a mixture that is highly explosive. From the standpoint of safety alone we should accept such a cryostat with considerable reserve.

## Description of Cryostat

We have modeled our cryostat after the one described by Henning.[4] He was able to maintain a steadiness of ±0.05° for 50 minutes at —22.7°, of ±0.02° for 55 minutes at —82.2° and of ±0.04° for 43 minutes at —150°. It has been our experience with this cryostat, however, that good steadiness may be maintained for several minutes and then marked fluctuations occur. With liquid air that was three days old, and hence fairly pure oxygen, we found an unsteadiness amounting to over ±0.05° over short periods of time. Moreover, there was considerable difficulty in warming the bath slightly when necessary, for there was an appreciable time lag after adjusting the controlling water head. It was also difficult to adjust the rate at which the water head should be increased, due to the warming of the liquid air and increased height through which it had to be forced over to the bath. The rate of warming of the liquid air depends entirely on the age of the air and hence varies for every lot of air used.

In our adaptation of Henning's cryostat we secure as good steadiness as possible by means of a constant addition of liquid air, then by means of a

heater operated by hand, hold the temperature slightly higher, that is, the bath always tends to become slightly colder, and the entire regulation is attained by use of the heater. In this manner we obtain a steadiness of $\pm 0.01°$ at $-150°$ for a period of three hours and of $\pm 0.015°$ at $-180°$ for a like period.

The design and method of operation will be clear by reference to Fig. 1. The Dewar vessel A of Pyrex glass,[12] inside diameter 12 cm., length 40 cm., contains casing-head gasoline for temperatures to $-140°$ and commercial butane for temperatures to $-180°$. Both of these liquids remain quite

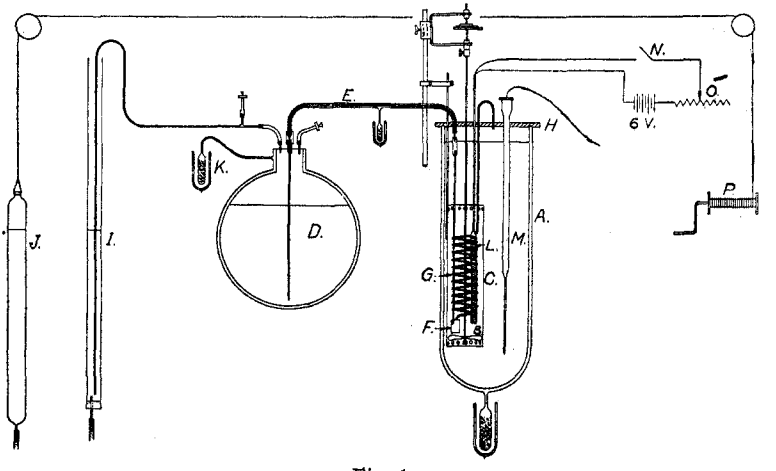


Fig. 1.

fluid to the temperatures mentioned and are very moderate in cost. The bath is vigorously stirred by the propeller B inclosed in the Monel metal or brass jacket C. The jacket prevents lateral currents of cold liquid and forces all liquid in the bath to pass the cooling and heating elements within a few seconds.

Liquid air contained in the metal Dewar bottle D is forced at a constant rate through the vacuum-jacketed tube E, of Pyrex glass.[13] It drops

[12] Pyrex is especially recommended due to its sturdiness under large temperature changes. We have used such a Dewar tube for three years without accident.

[13] The vacuum-jacketed delivery tube E, made of Pyrex glass, avoids the necessity of an expansion coil in the inner tube. Henning employed this device to prevent contraction of the inner tube sufficient to break one of the ring seals.

The method of construction of the Pyrex tube is as follows. Two tubes of the proper length, 6 and 11 mm. o. d., leaving an annular space of about 1.5 mm. when the smaller is centered within the larger, are sealed together at one end, the inner tube projecting about 5 cm. beyond the outer. The space between the two is then filled with fine, dry sand which keeps the inner tube centered when the two bends are made. After bending is effected by means of a large air-gas flame the sand is easily tapped out, and the final ring seal is made at the remaining end after the inside of the outer tube has been silvered.

into the copper cooling chamber F where it vaporizes and the vapor passes out through the copper coil G. The escaping cold air vapors, free from carbon dioxide and water, are directed by means of rubber tubing on to the surface of the bath, escaping under the asbestos lid H. The chief purpose of this procedure is to prevent condensation of carbon dioxide and water from the atmosphere in the bath liquid, causing it to become viscous and opaque.

The rate of flow of the liquid air is controlled by means of the water head I, under which the vapors from the liquid air in D escape. The metal Dewar bottle D is made of spun-copper hemispheres[14] kept evacuated by charcoal in the tube K, cooled in liquid air. Temperatures are observed by means of the platinum-resistance thermometer M, which is sensitive to 0.001°. The heater L is inside the metal jacket and is made by winding No. 26 B. and S. gage, enameled copper wire on a strip of mica, giving a total resistance of about 0.5 ohm, a storage battery furnishing the heating current.

In practice the operator observes the change of temperature of the bath by the swing of a sensitive galvanometer from the null point. Since the head of water is always adjusted so that the bath tends to cool slowly, the galvanometer is brought back to the null point by closing the heating switch N momentarily, the rate of heating being adjusted by the resistance O. This switch is located near the galvanometer telescope so that it may be operated while the galvanometer swing is being observed.

As the liquid air in D gradually boils away and becomes warmer due to enrichment in oxygen, it becomes necessary to increase the water head in I gradually. Another reason for a gradual increase in this column is the lowering of the level of liquid air in the bottle, thus increasing the height through which the liquid must be forced. The water head is raised conveniently by a cord and pulley attachment from the leveling bulb J to the reel P, located near the galvanometer and heating switch. It is necessary to increase the water head slightly every 10 to 15 minutes. It should be emphasized that only aged liquid air should be used in D, for air that has been newly made gives unexpected fluctuations in the temperature of the bath; the best results are obtained by allowing air to remain in the carafe fillers at least two days before being used.

By following the method as outlined we were able to hold the temperature to ±0.01° at —150° for three hours and to ±0.015° at —180° for a

[14] See *Report of the Oxygen Research Committee*, Dept. Sci. and Indust. Research, London, May 9, 1920.

Some difficulty was experienced in using the usual 2700 cc. (6-pint) carafe filler for the liquid-air container. Frequent breaks occurred at the neck when the rubber stopper hardened at the low temperature. The spun-copper bottle, with metal cap, in use has proved to be entirely satisfactory. The capacity of 15 liters is more than sufficient for a full day's use without the delay of refilling.

similar period of time, as mentioned above. There were considerable time intervals in these runs when the temperature did not vary over 0.001–0.002°, and when the liquid air is rich in oxygen, the control is quite simple.

The feature of safety should be emphasized, for in the event of collapse of the Pyrex Dewar vessel only a slight amount of liquid oxygen in the tube E could be mixed with the liquid hydrocarbon. The Dewar vessel should be housed on several sides, having windows for observations in the bath, in order to eliminate the possibility of the operator being sprayed with the hydrocarbon bath in event of failure of the Dewar tube. Moreover, the motor driving the stirrer should be removed to as great a distance as is practicable.

It should be added that a new temperature can be reached quickly by adding warm bath material or by cooling with liquid air in a large copper test-tube. The preliminary cooling of the bath to the desired temperature is carried out by this means, care being exercised that no boiling over of liquid air occurs to mix with the bath, especially when using commercial butane. A short portion of the copper tube bent near the top to an angle of about 45° effectively prevents this.

## Summary

Various types of cryostats are described, and the precisions, with advantages of each, discussed.

An improved cryostat is described, modeled after the Henning cryostat, which functions at any temperature from 0° to —180°. Its principal features are precision, safety and economy. Test runs showed a steadiness of ±0.01° at —150° for three hours and ±0.015° at —180° for a similar period.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, NO. 482]

# THE SOLUBILITY OF SLIGHTLY SOLUBLE CHLORIDES IN CONCENTRATED CHLORIDE SOLUTIONS

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In a previous article from this Laboratory,[1] it was predicted that the solubility of silver chloride in an aqueous solution of a second chloride MCl would increase more and more above the normal value as the radical M was made more electropositive. This prediction was based upon the general rule that the stability of an addition compound is dependent upon the differences in electro-affinity of the radicals of its components.[2] The validity of this rule for systems of the type AgCl-MCl-$H_2O$ was strikingly con-

[1] Kendall, Davidson and Adler, THIS JOURNAL, **43**, 1481 (1921).

[2] Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921).