method shows that the former gives slightly lower results. This is largely due to the zinc which was carried down in the ferric hydroxide precipitate and was not subsequently recovered by reprecipitation.

Bromine and hydrogen sulfide must be completely removed by boiling, as they destroy the indicator. The use of sodium sulfite, sometimes recommended to remove the last traces of hydrogen sulfide, also affects the indicator. Our experience has been that the boiling alone is generally sufficient to remove the hydrogen sulfide. While small amounts of undecomposed potassium chlorate do not affect the blue color produced, its oxidizing action on the potassium ferrocyanide causes high results.

The authors wish to express their appreciation for the suggestions given by Professor C. L. von Ende and Professor J. A. Kostalek during the progress of this work.

Summary

1. Diphenylbenzidine, a new internal indicator for the titration of zinc by the ferrocyanide method, gives more satisfactory results than those obtained by the use of uranium nitrate.

2. The use of diphenylbenzidine permits back-titration.

3. No blank correction is required.

4. The time required for the titration is very much reduced.

5. Diphenylamine may also be used as the indicator, but it has the slight disadvantage that the amount of indicator affects the titration. This effect is slight and may be obviated by using a fixed amount of indicator.

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[Contribution from the Laboratory of Physical Chemistry, McGill University]

AN AUTOMATIC LOW-TEMPERATURE THERMOSTAT

By O. Maass and W. H. Barnes

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Introduction

In a previous paper[1] a method was described for maintaining cooling-baths at any low temperature between —78.5° and that of liquid air. Owing to the inconvenience of adding small amounts of liquid air by hand, an automatic device has been developed for regulating the temperature and is described in the present paper.

Description of Apparatus

The apparatus (not drawn to scale) is shown in Fig. 1. A current of air passes through a mercury pressure regulator A, two calcium chloride towers B and a large volume bottle C to a glass tap D. The head of this tap is mounted on the axle of a light metal wheel E of about 41 cm. radius.

[1] Maass and Barnes, *Proc. Roy. Soc.*, **111A**, 227 (1926).

By means of a motor the wheel can be rotated, thus alternately opening and closing the tap and allowing the passage of an intermittent supply of air. By means of another glass tap F a fine adjustment can be made of this air supply. The air is sent into the top of a 2-liter Dewar flask G and forces liquid air into the cooling bulb H.

The bulb H is made of thin copper foil closed at one end and fastened to a short piece of glass tubing at the other. Liquid air is allowed to evaporate in the bulb and the thin copper foil enables rapid heat conduction from the bath to take place.

The bath I consists of an open one-half-liter Dewar flask filled with the first distillate of petroleum ether. Stirring is effected by means of the excess of air (from the pressure regulator A) which bubbles out of the tube J. This air is dried by passage through two sulfuric acid bubblers K.

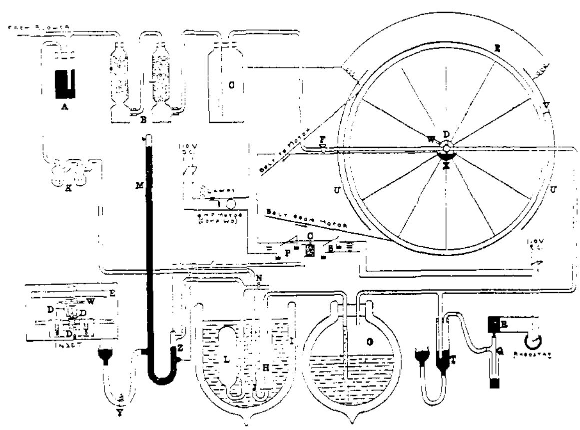

Fig. 1.

The temperature of the bath I is controlled by a bulb of air L having a capacity of about 25 cc. This bulb is connected by means of capillary tubing with one end of a closed mercury manometer M. The dead space above the mercury at Z is small enough so that variations in room temperature do not affect the setting of the control. By means of a tap N and Stopcock Y, the air bulb and manometer can be closed from the atmosphere. This prevents fluctuations in barometric pressure from altering the setting of the mercury contact at Z.

To set the control, the bath is cooled to the required temperature by blowing liquid air into the bulb H. When the required temperature is reached, the mercury level in the arm Z of the manometer is adjusted so that contact with the platinum wire is just made. Tap N and Stopcock Y are then closed. Contact at Z allows a current to flow in the small coil O thus closing the circuits at P and S.

Contacts at P and S are made between nichrome wires and mercury cups. In order to reduce sparking, the mercury in the cups is covered with a layer of glycerol and the condensers are placed across P and S as shown. The condenser across P is the usual mica and tin-foil plate type and has a capacity of 1 microfarad. A water condenser containing a few drops of hydrochloric acid is connected across the circuit at S and appreciably diminishes sparking, although a current of about 5 amps. is being made and broken there.

When contact is made at P, a short circuit is thrown across the armature of the compound-wound motor which turns the wheel E. This cuts out the current through the parallel field winding and through the armature, and the motor stops. In order that the wheel E will cease revolving only when the tap D is closed, two brass strips U,U, each about 76 cm. long and of the same curvature as the wheel, are mounted just outside the rim. These strips are connected by a wire to one of the armature brushes of the motor. A metal brush V is soldered to the rim of the wheel so as to make contact with the strips along their entire length. By means of a brass disk W (screwed to the axle of the wheel and rotating in a mercury cup X) contact is made between the brush and one of the mercury cups at P. In this way, even if contact at P is made, the armature of the motor is not short-circuited unless the brush V is in contact with one of the brass strips U,U, and in this position the tap D is closed.

In order to decrease the time necessary to build up sufficient pressure in the container G for liquid air to be forced into H, a small mercury column T is adjusted with a leveling bulb so that a column of liquid air is always kept in the outlet tube from G.

Furthermore, since the liquid air in the container G is slowly evaporating and building up a pressure inside G, a back-pressure valve Q is provided so that liquid air will not be forced into H when Tap D is closed. When the short circuit is made at P and the motor stops, contact is also made at S; this allows a current to flow through the solenoid R and raises an iron plunger to which the glass tube Q is attached. This draws the end of the tube Q out of a mercury seal and leaves open a way of escape to the liquid air evaporating in G. When Contacts P and S are broken and the motor is running, Q drops back into the seal.

The tap D is fastened to the end of the axle of Wheel E as shown in the inset. A brass cap D_1 fits over the end of the axle. Into a groove across the front of this cap is placed the head of the tap D in a rubber tube. The head is forced outwards by means of a wire spring 1 held in a hole through the brass cap. A wooden support D_2 fitted with a long groove and Springs 2,3, holds the base of the tap and the tubing on each side firmly against the tap head.

The apparatus has been tested and found to maintain temperatures constant to 0.1° for any length of time. The longest time for which the bath was required was six hours at a temperature of —140°, during which time no readjustment of the apparatus was necessary and a maximum variation of 0.1° was observed. Somewhat less than two liters of liquid air was used. This amount can be greatly reduced since no precautions were taken to heat-insulate the tube between the liquid-air container and the bath. If desired, the thermal regulator can be made more sensitive and the temperature variation reduced to 0.02°.

The above thermostat should prove useful in work where a constant low temperature is desired, such as in the pre-cooling of substances for calorimetric determinations of specific and latent heats and in the standardization of thermometers for low-temperature work.

Acknowledgment is made to the National Research Council of Canada for a Fellowship granted to one of us.

Summary

An automatic, low-temperature thermostat has been described which is cheap and easy to construct. It can be used for any temperature between that of the room and that of liquid air. It remains constant to 0.1° for any desired length of time. It has also been pointed out that the sensitivity can be increased if so desired.

Montreal, Canada

[Contribution from the Department of Chemistry, Columbia University, No. 530]

ACTIVITY COEFFICIENTS OF ELECTROLYTES. I. THE LIMITING LAW FOR A TRI-TRIVALENT SALT[1]

By Victor K. LaMer, Cecil V. King and Charles F. Mason

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Introduction

One of the most important generalizations which has been obtained from the theory of the complete dissociation of strong electrolytes involves the principle that as the dilution is increased the laws expressing the thermodynamic behavior of such solutions as a function of concentration become progressively simpler in character, until finally an ideal region of concentration is approached in which this behavior is determined solely by the numbers and valences of the ions involved and not by the specific individual properties of the ions.

As was shown previously,[2] this proposition can be expressed most con-

[1] An abstract of this paper was presented at the Philadelphia Meeting of the American Chemical Society, September, 1926. Part of the data are given in Dr. Mason's dissertation.

[2] Brönsted and LaMer, This Journal, **46,** 555 (1924). The constant α' in our paper is equal to 3/2.3 of the α of Brönsted and LaMer, otherwise the notation is the same.