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I.O.S.

PREPARATION OF THE I.O.S. TEMPERATURE STANDARD TRIPLE POINT CELLS

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1. INTRODUCTION

Up to the present time, information on the preparation of triple point cells used at I.O.S. Wormley has come from two sources. The first comes from reports (1) and certificates issued by the National Physical Laboratory who manufacture and calibrate the cells. The second source, which the author wishes to acknowledge, is N.D. Smith, now retired from I.O.S., who was responsible for the formation and operation of the temperature calibration standards room at the laboratory.

The intention of this report is to bring under one cover a description of the methods developed at I.O.S. Wormley of the preparation of the triple point cells of water, phenoxybenzene and ethylene carbonate. It is not intended that this report be taken as a definitive statement on the preparation of triple point cells.

PREPARATION OF PHENOXYBENZENE TRIPLE POINT CELL

(26.8685° CELSIUS)

WARNING: THE CHEMICAL CONTENTS OF THE CELL CAN CAUSE SKIN DAMAGE. IT IS ADVISABLE TO WEAR RUBBER GLOVES FOR PROTECTION IN THE EVENT OF CELL BREAKAGE.

After the cell has been prepared, it is placed in a 1 litre Dewar flask. This flask is suspended in a second, larger, Dewar flask containing water. This water is temperature controlled and circulated by a temperature controller. To attain temperature stability the controller requires a 250 mm/min flow of cold tap water. Fig. 1 shows the arrangement. Switch on the temperature controller at least 5 hours before preparing the cell to allow the system to stabilise. The stabilised temperature is measured by the hg in glass thermometer and should be 26.85±0.5°C.

Check that the cell is half filled with water, top up if necessary and lightly stopper.

Completely immerse the cell in a suitable container (e.g. plastic bucket) which contains water at a temperature of 50°C±2°C. Leave until the solid is completely melted which should be no more than half an hour. Mix the liquid phenoxybenzene thoroughly by rotating and inverting the cell five or six times, being careful to invert the cell slowly to avoid damage due to 'hammering'.

Prepare a second container (plastic bucket) and fill with tap water and ice to reduce the contents to 1°C±0.5°C. Completely immerse the cell into the ice cold water. Remove the cell after four minutes and, with care, invert the cell to mix the liquid. This ensures that the cell does not freeze. Replace the cell in the cold water and leave for two minutes and repeat the mixing procedure. After approximately ten minutes remove the cell from the cold water and place the bottom of the cell in melting ice. Solidification of the phenoxybenzene should occur within ten seconds and should spread slowly upwards through the cell to the meniscus.

If solidification does not take place, return the cell to the cold water for approximately half a minute and then try again. If the process spreads only part way up the cell and stops, return the cell to the cold water and repeat the procedure after half a minute. If this fails then the cell is returned to the hot water and the process repeated. If solidification is satisfactory then place the cell into the temperature controlled flask.

Place a ¼ inch diameter brass rod into water which is approximately at 50°C and leave for one minute. Remove the rod from the water and carefully place into the cell, leave for one minute. Remove the rod from the cell and return to the hot water. Remove cell from flask and gently invert cell several (3) times, allowing time at each inversion for the liquid phenoxybenzene to drain through the solid. Return the cell to the flask and again place the rod into the cell and repeat the procedure until the volume of the liquid approximates the volume of gas space above the solid. This normally requires three immersions of the brass rod. Insulation, such as cotton wool, is then placed round the neck of the cell and the system allowed to stabilise for fifteen to twenty minutes.

The cell is now ready for use.

PREPARATION OF THE ETHYLENE CARBONATE TRIPLE POINT CELL (36.3241° CELSIUS)

WARNING: BOILING WATER IS USED IN THE PREPARATION OF THIS CELL. USE RUBBER GLOVES AND HAVE A SOURCE OF COLD WATER AVAILABLE IN CASE OF ACCIDENT.

The equipment to keep the ethylene carbonate cell in the triple point condition is similar to that of the phenoxybenzene cell as shown in Fig. 1. In this instance, however, there is no need for cold tap water within the circulating unit. Switch on the power to the temperature controller at least five hours before preparing the cell. The controller circulates water, at 36.3°C±1°C, in the outer Dewar flask, in which the smaller Dewar flask containing the prepared cell will be placed.

Remove the cell from storage container, check for damage and half fill the cell with water. Apply stopper, and place cell in a safe place.

Using hot tap water, fill and flush out a one litre conical flask and a plastic bucket. Place the flask in the bucket then carefully pour boiling water into the flask allowing it to overflow into the bucket. Sufficient water should be available to bring the level of the water in the bucket to the neck of the flask. Using a four litre kettle two fillings are found to be satisfactory.

Remove the stopper from the cell then quickly and totally immerse the cell into the near boiling water. It is important that the latter instruction is followed implicitly, as fracture of the glass can occur if large temperature gradients are allowed to build up over short time periods and across small areas of the glass. After ten minutes immersion, remove the cell from the flask and, with care to avoid 'hammering', rotate and invert the cell several times to mix the liquid ethylene carbonate. Do not forget to stopper the cell. Return the cell to the hot water and repeat the procedure until all the solids have gone.

The cell is then completely immersed in a container of water which has previously been prepared to a temperature of 25°C±1°C. This is left for fifteen minutes, by which time the liquid ethylene carbonate can be considered as supercooled. Gently remove the cell from the water and give it a small vertical shake, the cell should produce an audible 'crack' and the liquid ethylene carbonate begin to solidify. This process starts at the surface of the liquid and works steadily downwards. Dry the outside of the cell and place in the preheated Dewar flask. After a stabilisation period of one hour, the cell will then be ready for use. However, if the liquid does not solidify after five or six vertical shakes the cell should be returned to the water for a further two minutes before another attempt is made.

Triple point temperature: 36.3241° Celsius.

To store the cell after use, switch off the power to the temperature controller, and allow the cell to reach room temperature over a twenty-four hour period. Empty and dry the re-entrant tube and store away in its container.

PREPARATION OF THE WATER TRIPLE POINT CELL

(0.010° CELSIUS)

The water cell can be prepared by two methods. The first method is similar to that used in preparing the ethylene carbonate and the phenoxybenzene cells. Here, the cell is first raised above the triple point temperature, to liquify the contents, then placed in a lower temperature, about -8°C, to supercool it. It is then removed from this cold medium and given a small physical shock which will cause the supercooled medium to solidify. To complete the preparation the solid is then reduced to a 'mush' partly by applying heat so that the cell contains water as solid, liquid and gas in equilibrium, i.e. the triple point state.

Although this method is successful, it does require equipment to supercool the cell. The second method, used at I.O.S. Wormley and described below, uses a different technique.

Apart from the cell, the materials required to set up the water triple point are a 15 litre Dewar flask, crushed ice and dry ice (carbon dioxide).

Normally two cells are prepared so that a double check can be made when making a temperature measurement. The cells are checked for damage and the re-entrant tube cleaned and dried. They are then placed in the Dewar flask with the crushed ice, and left for at least two hours for liquid in the cell to cool down to the ice temperature. At approximately fifteen minute intervals during this period, the cells are removed from the flask, inverted five or six times to mix the water, and returned to the flask. Care should be taken when inverting the cell to avoid 'hammering' which could damage the cell. After the liquid has cooled, a small quantity of dry ice powder is placed in the bottom of the re-entrant tube so that an ice bowl is formed round the tube. The dry ice is constantly replaced so that eventually the ice is 10 to 15 millimetres thick at the bottom. Once this stage is reached, further dry ice is added to bring the level of ice formed within the cell half way up the tube. The cell is then left in the crushed ice for about five minutes allowing the temperature in the re-entrant tube to rise to near that of the crushed ice. Remove the cell from the Dewar flask and

half fill the tube with water at 20°C. This will then melt the ice directly in contact with the glass and allow the ice sheath to rotate when the cell is twisted. At this stage, the cell is then returned to the Dewar flask and crushed ice to allow the water in the tube to stabilise at the triple point temperature. After two hours the cell will be ready for use.

REFERENCE

(1) VAUGHAN, M.F. 'Diphenyl Ether Triple Point Cells'. NPL Report Chem 86, July 1978.

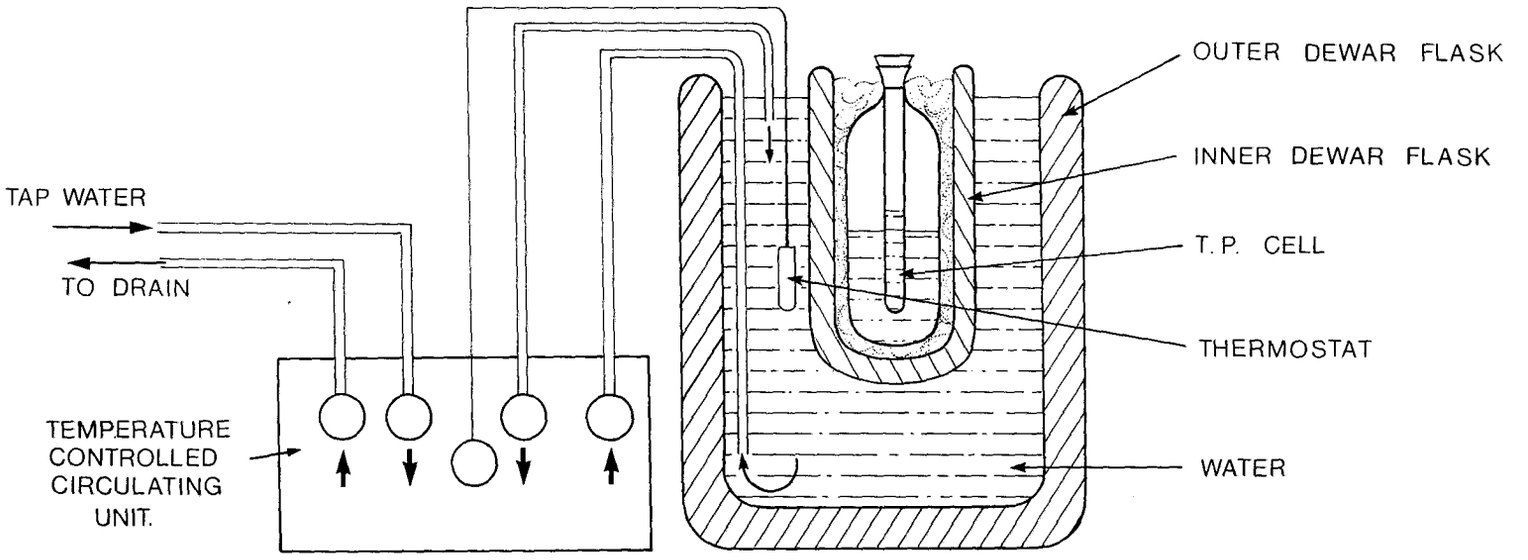

FIG. 1 ARRANGEMENT FOR KEEPING THE 26·8685 °C AND THE 36·3241 °C TRIPLE POINT CELLS FOR LONG PERIODS.