



Cryogenic Triple Point Cells at NPL

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ABSTRACT

This paper discusses the practical realisation at NPL of the triple points of hydrogen, neon, oxygen and argon which are the primary reference (fixed) points of the International Temperature Scale of 1990 (ITS-90). Recent measurements of these points are compared with the results from previous work at NPL. Experiments on the triple points of nitrogen, carbon dioxide, xenon and deuterium, which are secondary reference points, are briefly discussed and values for their temperatures on the ITS-90 are given.

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1 INTRODUCTION

In the range from the triple point of hydrogen (13.8033 K) to the freezing point of silver (961.78°C) the International Temperature Scale of 1990 (ITS-90) [1] specifies a series of reference (fixed) points at which platinum resistance thermometers (PRTs) are to be calibrated, and it specifies the formulae which are to be used for interpolating values of temperature within this range. Since no single thermometer can be used over such a wide range, the scale is divided into sub-ranges which overlap and allow calibrations to be terminated at almost any desired fixed point.

The low temperature triple points specified in the ITS-90 are shown in Table 1.

TABLE 1

Triple Point	T_{90}/K
Hydrogen (H_2)	13.8033
Neon (Ne)	24.5561
Oxygen (O_2)	54.3584
Argon (Ar)	83.8054
Mercury (Hg)	234.3156
Water (H_2O)	273.16

In addition, two other fixed points, at 17 K and 20 K, using the boiling point of hydrogen at known pressures are required for a full calibration, but they are outside the remit of this report.

The thermometers suitable for use in this low temperature range are standard helium-filled (capsule type) thermometers, in which a coil of high-purity annealed platinum wire is mounted in a strain-free manner, with four connecting leads passing through a glass seal. For a calibration using the direct realisation of the ITS-90 a capsule PRT would be measured at each of the specified fixed points. PRTs that have been calibrated in this way can then be used as transfer standards for the calibration of secondary thermometers by comparison.

It is also usual to extend the calibration of capsule-type thermometers up to the melting point of gallium (29.7646°C), or sometimes the freezing point of indium (156.5985°C).

For completeness it should be mentioned that the ITS-90 extends to temperatures below 13.8 K using an interpolating constant volume gas thermometer and the vapour pressure equations for ^3He and ^4He which are specified for the range 0.65 K to 5.0 K.

This paper describes the facilities at NPL for the practical realisation of the cryogenic triple points which are the necessary first step to maintain and disseminate the ITS-90 in the range down to 13.8 K.

2 TRIPLE POINTS

2.1 FIXED POINTS

Many of the fixed points of earlier temperature scales were boiling points, with those of hydrogen, neon, oxygen and water having been used in the International Practical Temperature Scale of 1968 (IPTS-68). Their realisations generally entailed the use of a vapour pressure bulb connected by a tube to the filling system and a manometer, and possibly a gas analyzer. The only boiling points specified in the ITS-90 for the calibration of PRTs are those of hydrogen at one atmosphere and at a reduced pressure.

Triple points provide advantageous conditions for calibration since the three phases of the pure substance can only come into equilibrium at a fixed temperature and pressure. When the condition has been established, the system has no degrees of freedom and the temperature is self regulating. No pressure measurements are needed.

The accepted technique for realising this condition is to freeze the sample and control its environment, so that only a small amount of heat leaks to or from the sample. Then the sample is progressively melted in a series of steps, between which it is allowed to return to equilibrium, at each step a measurement of the thermometer resistance is made [2,3,4,5]. In this way a plot, or chart, of the melting plateau can be produced, and since the three phases are all present this represents a realisation of the triple point.

For commercially available research grade cryogenic gases, and using readily-available standard cryogenic equipment, triple point realisations can be reproducible to a few tenths of a millikelvin.

In recent years the experimental procedures have been further simplified by the development of cells of stainless steel and/or copper which are filled at room temperature with the required gas at high pressure, typically 50 atmospheres, and permanently sealed. When cooled in the cryostat the gas condenses and freezes, and the triple-point plateau can then be obtained as described above. These cells are very convenient to use, requiring no connections to a gas handling system. They can be kept as reference devices for many years, apparently without degradation, and they can be circulated for intercomparison between laboratories [6]. Such intercomparisons have shown that good agreement has been obtained with cells made in different laboratories with gases from different sources, and the technique is now firmly established as the basis for the realisation of the ITS-90.

The gases whose triple points are specified in the ITS-90 are argon, oxygen, neon and hydrogen (see Table 1), all of which can be realised with excellent reproducibility. The triple point of nitrogen (around 63.1 K) is similarly excellent, but being close to the oxygen point it was not required in the definition of the scale. Other gases whose triple points have been investigated include methane (90.7 K) krypton (115.7 K), xenon (161.4 K) and carbon dioxide (216.6 K). These are all suitable secondary points, with reproducibility ranging up to 2 mK for xenon, due to problems of contamination or isotopic variations. There is a continuing research interest in the triple point of deuterium (18.7 K), since its successful realisation would provide a triple point as a replacement for the two hydrogen vapour pressure points

at 17.0 K and 20.3 K. However hydrogen contamination of the deuterium is a major difficulty. If this could be overcome sealed cells alone could be used for the calibration of capsule platinum resistance thermometers down to 13.8 K.

NPL has prepared cells for most of these gases, and their use in implementing the ITS-90 is described below. Work on the mercury and gallium points, which are also required by the ITS-90 in the range covered by capsule PRTs has already been described by Chattle et al [7,8].

2.2 TRIPLE POINT CELLS

The NPL triple point cells are based on the design of Ancsin [9] and an example is shown in Figure 1.

The triple point cells are assembled from three parts. The tubular side walls of the NPL cell are made from stainless steel type AISI 316S (and not copper, as are Ancsin's). The top half often has an increased diameter to provide a larger gas space or "expansion volume". The top and base are normally both machined from OFHC copper and these are electron beam welded to the steel. After the manufacturing process, all the cells were vacuum leak tested. A further check is sometimes made after pressurisation, but before sealing the cell, by using the proprietary agent "SNOOP", a form of concentrated soap solution to detect high pressure leaks.

The tops can also be made from steel (although this choice can be constrained by the sealing method that is used). If steel is used it is advisable to machine the tops from plate steel, rather than bar, to avoid problems of porosity that can occur due to the bar rolling process used during manufacture. During the production of our first cells, when steel tops were used, leaks occurred on several cells which could be mapped from top to top. These had been machined from steel bar and it appeared that short-range imperfections caused the leaks. Thereafter the grade of steel used throughout our cells was altered to AISI 316S. A few special cells were designed with a steel top, but most tops are now made from OFHC copper.

The copper top contains an indium coated copper plug which is used to seal the cell after it has been filled with the sample gas (see below). It is held in place by a small steel locking bolt. Later designs allow for an alternative top whereby an extending copper tube can be pinch-sealed. This has only been used with deuterium cells, as it allows for a bake-out at a higher temperature than normal (see below).

The base projects up into the cell to form a copper block. The gap between the block and the lower side wall forms a narrow annulus, into which the condensed sample can drain and freeze. The copper block has a helical groove cut into its vertical sides to aid the drainage of the condensing liquid and to improve the thermal contact with the liquid/solid. (The NPL annular space is narrower than that of the Ancsin design). On the underside of this copper block are up to three blind holes (usually of diameter 5.2, 5.5 and 6 mm) for receiving thermometers. These are usually capsule platinum resistance thermometers (PRTs) or rhodium-iron resistance thermometers (RIRTs).

3 THE FILLING SYSTEM

A special system was designed and built in order to fill the triple point cells with high pressure gas. The NPL system was based on the design of Ancsin [10] and is shown in Figure 2. The cell is initially screwed on to the primary chamber of the filling system. A rubber O-ring provides a gas tight seal. The whole apparatus is evacuated via a turbo-molecular pump, which removes the initial trapped air. For some gases, eg argon, multiple high pressure purges by the gas are sufficient to reduce the impurity level in the cell before it is finally filled. For others, eg carbon dioxide, a vacuum bake (at 130°C) is always required

while deuterium cells require additional preparation (see below). In order to carry out the bake the system has a "Thermocoax" [11] heater wrapped around it and another heater is placed around the cell. During the evacuation phase the heaters can be used to warm the cell and system, up to a maximum of 130°C. This aids the removal of impurities, particularly absorbed water vapour. The maximum temperature is restricted by the melting point of indium and the use of rubber O-rings. Following a re-cool to room temperature the system and cell is purged, several times, with high pressure gas.

The apparatus and cells were designed to be pressurised up to 200 bar but are normally only filled to 50 bar. To seal a cell under pressure the copper plug with its tip coated with indium is compressed by a steel bolt against the narrow inlet port of the cell. The soft indium deforms, filling and sealing the port. It is kept in place by the steel bolt though it often forms a "cold weld" between the copper top and the copper plug. The steel bolt is turned by a rod terminating in a hexagonal head, which acts as a screw driver. As the pressurised gas would produce considerable force opposing this, a counterbalancing force is provided by a second pressurised chamber, so that both ends of the "screw driver" experience the same gas pressure during the sealing process. The additional pressure to deform the indium can be provided by turning the hand-wheel attached to the screw driver between the two sliding seals of the two chambers. Once the indium seal has been formed, the rod can be withdrawn. The two chambers are then de-pressurised and the pressurised cell can be disconnected from the filling system.

The system components, ie the chambers, the gas bottle(s) and the vacuum pump port are connected via 6 mm stainless steel tubing which can also be purged. The system contains an overpressure relief valve as a safety precaution.

In order to test for a high pressure leak after sealing the mass of the cell and its contents is determined on a precision balance immediately after filling and then at intervals usually of 1 day, 3 days, 1 week (and perhaps a month later if time permits).

The component parts of the cell, ie the body, indium coated plug and bolt, are normally weighed before filling, hence the mass of gas sealed in the cell can be determined. Once the cell has been proved leak tight a heater (usually 100 Ω of manganin resistance wire) is wound around the base.

For deuterium cells it is necessary to remove as much as possible of the absorbed water and hydrogen from the cell walls and the catalyst. In order to achieve this the cell and catalyst are vacuum baked at 400-500°C, for several days. In early experiments, when the cells had indium seals, it was necessary to bake the cell and catalyst in a vacuum chamber separated from the filling system. A new design of cell top, consisting of a projecting copper tube, now allows direct connection to a vacuum-bake/filling system. The cell can now be heated using Thermocoax heaters to around 450°C and the new filling tubes to >200°C, as all connections are now made with metal seals. Following the bake-out the cell can be filled directly (additional purging may precede the final fill if a sufficient quantity of high purity deuterium is available).

The cell is now sealed by pinching the soft copper tube until it breaks. No additional welding has, so far, been found necessary for filling pressures up to 50 bar. As for other cells the deuterium cell is repeatedly weighed, over a period of time, to check for leaks.

4 THE CRYOSTAT

The cryostat used in triple point realisations is an Oxford Instruments [12] standard 10 l modular liquid helium cryostat with a ^3He stage which permits operation between 0.5 K and room temperature, and is shown in Figure 3. The experimental chamber, referred to as the

inner vacuum chamber (IVC), hangs below the main cryogen bath and contains a temperature controlled copper block and shield manufactured to an NPL design. Access to the IVC is gained by removing the lower vacuum and radiation cans. The shield is wrapped in aluminized mylar to reduce radiation losses when it is at high temperatures. The holes in the shield, through which the thermometer and heater wires pass, are also covered with aluminized mylar when the cryostat is operated at high temperatures (>120 K). The temperature of the block/shield is controlled by an Automatic Systems Laboratories (ASL) F16 ac resistance bridge [13] which monitors a small rhodium-iron resistance thermometer placed in the control block. The offset signal, from the required setting, is amplified and fed to two $100\ \Omega$ heaters on the control block.

The cryostat was designed for more than one purpose. As well as the measurement of triple points it can be used for the measurement of ^4He and ^3He vapour pressures and for the intercomparison of up to twelve (4 lead) resistance thermometers. To do this below 4.2 K the cryostat has a "lambda plate" and ^4He and ^3He pots which can be used to cool the control block by pumped evaporation of helium liquid.

In order to connect up a possible twelve resistance thermometers (usually from H Tinsley [14]) 48 fine (0.075 mm) copper wires, about a metre in length, were fed down an evacuated tube into the IVC. In order to reduce the heat conduction down these wires they were bundled into four groups, with each group being formed into a helical coil, with a diameter equal to that of the vacuum tube inner wall diameter. The turns of the helix were spaced by tying them together with cotton thread and drawing them down the tube. They were then thermally anchored to the bottom of the main cryogen bath before being wrapped around the copper block support tubes and finally being connected to the anchor points on the copper control block itself.

The 48 wires are terminated on "Biccastrip" (strips of copper embedded in a thin layer of insulating plastic) strapped around the copper control block using adhesive backed aluminium 'pressure' tape manufactured by "3M". The original strip has so far held for over eight years. From this junction on the copper block, wires are connected to another thermal anchor on the measurement artefact itself, before being connected to the thermometers to be used in the experiment. The measurement artefact might be a copper comparison block, a suspended triple point cell or some other device.

A separate vacuum tube is used to carry the leads for the two control heaters (wound on copper bobbins and wired in parallel), the control RIRT, and several carbon resistors (mainly used for monitoring the cooldown). Several ultra-thin coax leads, from Lakeshore [15], also pass down this tube and have been used in capacitance experiments [16]. All these leads are thermally anchored at the base of the main cryogen bath and on the copper control block itself.

The cryostat is always initially cooled with liquid nitrogen in the main bath and the nitrogen jacket. The entrapped air of the IVC is used as the initial exchange gas. If cooling below 80 K is required a small amount of helium gas is introduced to the IVC as exchange gas after removal of the air.

For the oxygen, nitrogen, argon, xenon and carbon dioxide triple points nitrogen is used as the coolant in the main bath. When the oxygen and nitrogen triple points are used the nitrogen coolant is pumped well below its freezing point with a large rotary pump. (A good vacuum in the outer vacuum can (OVC) is also needed to achieve the lowest temperatures). The low temperature can be maintained for several days, particularly if a "double pump" technique is employed. To "double pump", the nitrogen is first frozen and the cell cooled (by exchange gas). Then the pumping is stopped after about half a day and the main bath vented with helium. It is then refilled with liquid nitrogen and the pumping restarted.

During the venting and re-pumping the exchange gas can be temporarily evacuated from the experimental chamber (or IVC), though this does not appear to be an important requirement.

For the hydrogen, neon and deuterium points liquid helium is used as the main coolant, with liquid nitrogen in the outer jacket. Further intermediate radiation shielding (at 50-60 K) of the helium bath is obtained via a gas-cooled shield, constructed of aluminium and thermally anchored to the neck of the main bath. This shield makes use of the enthalpy of the helium boil-off gas.

5 THE EXPERIMENTAL METHOD

5.1 THE ARRANGEMENT

The triple point cell under test is suspended from the copper control block within the IVC, inside the cell radiation shield. Triple point measurements require an adiabatic environment, so the cell is usually suspended using cotton thread. If "thin" triple point cells (ie not having an 'expansion volume' - see figure 1) are being measured then up to three can be suspended within the shield, and each might require three thermometers. Connections for cell heaters can also be made using some of the 48 fine copper wires.

The thermometer(s) are inserted into the cell(s) with a layer of vacuum grease for thermal contact and strips of copper shim for packing if required. The thermometer and heater leads are thermally anchored to the side of the cell using Biccastrip. A heater of about 100 Ω was wound around the base of the cell using a Manganin resistance wire. A layer of insulating mylar is wrapped around the cell to prevent shorting of any electrical connections. For higher temperature cells (carbon dioxide and xenon) aluminised mylar is also wrapped around the cell to reduce radiation transfer.

In the critical first cooldown the cell's temperature is reduced by the presence of the exchange gas in the IVC. Once the charge has been frozen the exchange gas is removed. Thereafter the cell's temperature is usually controlled by use of the radiation shield and the cell heater. However, for a quick re-freeze of the sample in a triple point cell or if the undercool is very large, a small amount of exchange gas can be re-introduced into the IVC and then pumped out after the freezing is complete.

5.2 THE PROCEDURE

In order to determine the triple point of a cryogenic substance adiabatic calorimetry of the melting process is used. It is not usual to use the freezing process for cryogenic fixed points due to the small heat capacity and low thermal conductivity of the samples. Either the large undercool, required to initiate the freeze, solidifies the whole sample or the thermal gradients during freezing lead to thermometric errors. Similarly it has been found that continuous heating leads to an over-estimate of the plateau temperature. The thermal conductivity of the sample is too low, particularly when fluid, to achieve fast equilibration of the temperature.

In adiabatic melting, the surroundings, viz the shield/block, are controlled so that no heat is transferred to, or from, the sample. Once the shield is set so that the drift in the cell temperature, at the plateau temperature, is negligible (see below) then a pulse of heat is applied to the cell, via its heater to melt a fraction of the sample charge.

Normally the pulse energy is adjusted to be about one tenth of the heat of fusion of the sample charge. Once the plateau is reached, the recorded cell temperature rises sharply during each pulse, but then drops back to the plateau temperature once the heating 'pulse' is completed. The response time depends on the cell contents, the cell design and the value of the triple point temperature. Once the sample temperature has stabilised a temperature

measurement can be made. This is repeated after each pulse, until the full melting plateau can be plotted out. The overheating during each pulse increases as the melted fraction increases.

As a test of the shield-cell interaction, the shield setting is increased or decreased by about 100 mK, at some point during the melt, and the increase or decrease in the cell temperature is monitored. As a general rule the cell temperature change is only about 0.1 mK; a factor 1000 less. However it may become more sensitive to the shield temperature setting near the end of the melt because the cell is less strongly coupled to the liquid/solid interface.

After the melt has been completed re-freezes are usually obtained slowly (often overnight) by a reduction in the shield's control temperature, causing radiative cooling. This slower freezing process may allow observation of the undercool and the shape of the freezing plateau.

The initial evaluation of the shield setting is usually made after the initial cooldown, whereupon the sample is solid. Once the exchange gas has been pumped out the shield temperature can be approximately set to about the plateau temperature. The cell is heated to just below the plateau temperature. (Usually one of the thermometers in the cell has some previous calibration which will approximately indicate when the cell is just below the plateau). The exact setting for the shield is deduced by observing its effect on the cell temperature just below the plateau. It can take some time for the cell to come to an equilibrium temperature so the shield is adjusted to stop the rise or fall in the cell temperature. (It is not possible to tune the shield setting exactly at the plateau temperature, when approaching from the frozen state as the melting process, rather than the shield, will control the temperature). As the effect of the shield setting is linear over small temperature differences, the balance point is found a few millikelvin below the melting plateau temperature. Then after the first pulse, knowing dR/dT of the controller thermometer, the shield controller is adjusted up to the adiabatic value for the plateau temperature.

Alternatively, following a plateau realisation - while the sample is fully molten - it is possible to find the adiabatic shield setting for the exact plateau temperature, as the sample will remain liquid. No freezing occurs because the necessary undercool/nucleation is not present.

5.3 THE MEASUREMENT SYSTEM

Most measurements were made with an Automatic Systems Laboratory (ASL) F18 resistance bridge which compares the thermometer resistance against either a 10 Ω or 100 Ω standard resistor of the Wilkins type. These are kept in a temperature controlled bath. All the final measurements were made in manual mode, the automatic mode of the resistance bridge being used to provide an approximate first balance point. Resistance thermometer heating effects can also be determined and it is possible to use the stable environment provided by the triple point to compare the two or three thermometers in the triple point cell.

During the initial measurements of the first argon cell produced at NPL it was possible to compare the ASL F18 ac (25 Hz) bridge ratio (in manual mode) against that of a manual dc Guildline 9970 current comparator bridge. No significant differences were found.

The actual plateaus are usually traced out, as offsets from a fixed bridge setting, by connecting the bridge output to a chart recorder. After a careful calibration of the chart recorder the plateau can be accurately monitored overnight.

Following Hermier of INM (personal communication), an automatic pulse system may be connected to the cell heater power supply which enabled the recording of heating pulses and the cell response overnight. The automatic system sends fixed heating pulses, to the cell

heater, at pre-set times and the output of the measuring bridge is recorded. Bridge ratio values could then be deduced from the calibrated chart recording the following day.

6 PRIMARY FIXED POINTS

6.1 INTRODUCTION

Hydrogen, neon, oxygen and argon provide the cryogenic triple points used in the realisation of the ITS-90. The temperatures of these fixed points are defined, on the ITS-90, as 13.8033 K, 24.5561 K, 54.3584 K and 83.8058 K respectively. As measurements have been made at these fixed points in the past at NPL, using the same small group of platinum resistance thermometers, it has been possible to compare the normalised resistance measurements made then and more recently. (The normalised resistance ratio is the resistance at the measurement point, divided by the resistance at the water triple point, normally referred to as the 'W ratio'). Differences would be due to either thermometer instabilities or the realisations themselves. From these comparisons the NPL master thermometer (PRT No. 1728839) has generally been found to be very stable; the differences from fixed point realisations of over a decade ago being 0.24, 0.1, 0.2, and <0.1 mK (in temperature equivalent) at the hydrogen, neon, oxygen and argon triple points respectively.

Details of the measurement at the four points are given below. Once the master PRT No. 1728839 was measured at all the triple points it was possible to produce a new ITS-90 calibration table for it. The table of resistance ratios and uncertainties in this calibration are reproduced in Tables 2 and 3 respectively. The uncertainty estimates at each point has been discussed elsewhere [17,18], the total 1σ uncertainty, for each point is respectively ± 0.14 , 0.17, 0.13 and 0.10 mK (see Table 3) The uncertainties are dominated by impurities and/or isotope effects.

There are two other primary cryogenic fixed points at ~ 17.0 K and ~ 20.3 K, which are not provided by triple points [6]. Results for these have been derived separately [17,22].

TABLE 2 W_{90} values for PRT No. 1728839 at the ITS-90 Fixed Points

T_{90}/K	$W_{90}(1728839)$
13.8033	0.00135062
17.0357	0.00246951
20.2711	0.00441940
24.5561	0.00864527
54.3584	0.0919604
83.8058	0.2160944

TABLE 3 Uncertainty Budget for Platinum Resistance Thermometer No. 1728839

1 σ Uncertainties (mK equivalent) in the
NPL realisation of cryogenic fixed points

SUBSTANCE PURITY	H ₂ 6N	Ne 5N	O ₂ 4N8	Ar 6N	Hg 6N	Ga 6N	H ₂ O -
TYPE B							
Chemical							
-impurities	0.02	0.02	0.10	0.05	0.04	0.03	0.03
-isotopic differences	-	0.15	-	-	-	-	0.02
-molecular	0.05	-	-	-	-	-	-
Thermal							
-determination of TP	0.03	0.03	0.03	0.03	0.03	0.03	0.03
-hydrostatic effect	<0.01	<0.02	<0.02	<0.03	0.02	0.01	0.01
-effect of heat fluxes	0.02	0.02	0.02	0.02	0.03	0.03	0.03
-self-heating correction	0.02	0.02	0.02	0.02	0.03	0.03	0.03
Electrical							
-accuracy of bridge	0.05	0.02	0.01	0.01	0.05	0.05	0.05
-std resistor accuracy	<0.01	<0.01	0.01	0.02	0.02	0.02	0.02
-std resistor	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01
Triple point of water	<0.01	<0.01	0.01	0.02	0.09	0.12	-
SUB-TOTAL	0.09	0.16	0.11	0.08	0.12	0.14	0.09
TYPE A							
Bridge reading	0.10	0.03	0.02	0.02	0.03	0.03	0.03
Plateau reproducibility	0.05	0.05	0.05	0.05	0.05	0.05	0.05
COMBINED TOTAL	0.14	0.17	0.13	0.10	0.14	0.16	0.11

The combined total uncertainty for the hydrogen vapour pressure points is estimated from previous work to be 0.2 mK.

Thermometer stability is not included

The rest of Section 6 gives details of the individual fixed point realisations.

6.2 HYDROGEN

Hydrogen is diatomic and each individual nucleus has a nett spin. These spins can be either parallel (ortho H_2) or anti-parallel (para H_2). At any temperature there is an equilibrium ratio of the amounts of ortho H_2 and para H_2 . However, the change from one equilibrium concentration to another, following a change in temperature is very slow. A catalyst, usually containing magnetic ions, is needed to speed up this change. Following work at NBS, now NIST, [19] hydrous ferric oxide ($Fe_2O_3 \cdot xH_2O$) became an accepted catalyst (though commercially, other catalysts may be used). To prepare our catalyst the recipe described by Ancsin [20] was followed, except that an additional grinding of the resultant granules was necessary. The granules were crushed to less than 1 mm diameter to allow them to be poured down the narrow entrance of the cell filling port. About 1 g of the catalyst was shaken to the bottom.

The hydrogen gas was 99.999% pure and obtained from Air Liquide. In order to fill a cell it was purged and vented six times at 50 bar and then finally sealed after the seventh filling, at 50 bar (1 bar = 101325 Pa) giving about 0.1 g of gas. To avoid loss of catalyst during purging, the filling system and cell was placed on its side and the gas was vented very slowly. Three similar hydrogen triple point cells have been made.

The first cell was measured using two RIRTs of serial nos. 221481 and 221484, manufactured by H Tinsley & Co. These thermometers hold the NPL-75 gas thermometry scale of Berry [21]. In order to realise the plateau 5-6 heat pulses of 8 mA for 3-4 minutes duration were passed into an 80 Ω heater, totalling about 7 J. At these low temperatures, the thermal equilibration time after each pulse, is usually less than twenty minutes. Two melts were performed and the thermometers intercompared at a measurement point about midway through the plateau. The plateau width was ≤ 0.1 mK. No change in temperature was seen between the two realisations of the plateau indicating that the catalyst worked very efficiently. Measurements made on the NPL-75 using RIRT 221484 gave 13.8035 K while RIRT 221481 gave 13.8039 K. The ITS-90 value for the hydrogen triple point is defined as 13.8033 K. Subsequent work [22] indicated that the temperature given by RIRT 221484 would read low with respect to other RIRTs calibrated against NPL-75.

Later a second hydrogen cell was produced and its triple point temperature measured using standard PRTs Nos. 1728839 and 1832689, (manufactured by Leeds and Northrup) and RIRT 221481. The measurements confirmed the difference of 0.6 mK between NPL-75, using this thermometer, and the ITS-90 at the hydrogen point. The 'W' resistance ratio of the standard PRT No. 1728839 was found to have changed by 0.24 mK when compared to much older measurements at NPL [23]. This new measurement provided a new calibration point for the two PRTs. During this second experiment the plateau was realised six times using around ten pulses of 20-16 mA for 30-45 s into a 100 Ω heater, about 11 J. The plateau range was 0.1 mK (25-95% melted); see figure 4.

In the third cell measurements were made with the same thermometers as used in the second cell. This acted as a test of thermometer stability and cell verification. The measurements again produced a difference between the ITS-90 values and the NPL-75 value of about 0.6 mK. They also showed a small difference between the platinum thermometers with the master PRT No. 1728839 now reading 13.8031 K, ~ 0.2 mK low with respect to the former calibration. This is within the uncertainty of the calibration, but it is a warning of a possible drift (which was confirmed in a later measurement in a neon triple point cell). As one is using the same apparatus there is a lower uncertainty to the ability to detect changes in calibrations.

6.3 NEON

Gas of purity 99.999% was obtained from Air Products and was checked by mass spectrometry to confirm that it had a normal isotopic composition. Over a period of several years three cells have been filled to between 30-50 bar pressure. One cell, filled to 30 bar, giving 1.4 g of gas with a melting enthalpy of ~ 19 J, gave a flat plateau and the thermometer's resistance was in agreement with older measurements made at this point. The cell's temperature on NPL-75 was measured using RIRT 221481 and the resistance of PRT 1728839 was determined.

To conduct the experiment the cell was gradually warmed to the plateau using currents varying between 20 mA and 3 mA into the $105\ \Omega$ heater. To melt the charge, approximately ten pulses of 20 mA were applied, each for 45 s. To freeze the cell, the shield set point was reduced by 0.6 K overnight. Three plateaus were recorded in this way; their values differing by ≤ 0.2 mK, while each individual plateau had a width of 0.1 mK. On NPL-75 the plateau temperature was 24.5563 K. The ITS-90 defines the neon triple point as having a value of 24.5561 K. Comparison with previous measurements [5] of the resistance of PRT 1728839 at the neon triple point showed good agreement (within 0.1 mK temperature equivalent) again showing the stability of this thermometer over more than a decade.

Another neon cell was produced some years later. This was measured using PRTs 1728839 and 1832689 and RIRT 221481. There were five realisations of the plateau, each with an enthalpy of about 8 J. (The new cell did not have an expansion volume, consequently the total cell capacity was reduced compared to the previous cell). The NPL-75 value determined from the rhodium iron measurements was again 24.5563 K, while PRT 1832689 (previously calibrated against 1728839) returned the ITS-90 value of 24.5561 K. However 1728839 now consistently gave a value higher by 0.4 mK, suggesting that it may have suffered some strain, prior to its use in the newer neon cell, and had increased its residual resistance.

Production of good triple point cells requires some care. It is appropriate here to describe an example of a gas filling problem with one early neon cell. When measured it gave a result equivalent to 2 mK below the expected value using PRT 1728839 and RIRT 221481. This seemed to be unreasonably different from older results; slightly higher resistance values had been obtained by Ward [24], whilst using the same thermometers during measurements in an open neon cell, but only by 0.2-0.5 mK. However the plateau was flat, with a width of < 0.2 mK, apparently implying no contamination. Impurities in the gas charge are normally evidenced by a pronounced slope on the melting plateau as well as a shift in its temperature. In a cell from another source, where the neon gas was suspected to be of lower purity, a plateau temperature below that expected had been measured, but the plateau also had a large slope.

However Ancsin [25] has reported low neon plateaus (by 2.25 mK), but flat, when his neon gas had been deliberately contaminated with > 150 vppm nitrogen. Ancsin also reported that oxygen did not have an effect on the neon plateau. It would therefore appear that the errant cell was not properly purged and probably still contained some air.

This incident shows the importance of being able to check an isolated fixed point measurement against either a known thermometer or another fixed point from an alternative source, such as is done during international comparisons (see section 8).

6.4 OXYGEN

Gas of purity 99.998% was obtained from Air Liquide and the cell was filled to a pressure of 50 bar. The cell contained about 2.5 g of oxygen with a heat capacity of 35 J. Frozen nitrogen was used as the cryogen. After finding the best shield setting, several three minute

pulses of 10-15 mA were applied to the cell heater (100 Ω), with intervening measurements, until the sample was molten.

Two separate plateaus were obtained, with results differing by about 0.1 mK. A repeat experiment on the same oxygen cell, with three realisations of the plateau, was performed some months later. The capsule PRT 1728839 was used in both experiments. The new plateaus gave results 0.1 mK higher, relative to the previous experiment over 15-95%, and were flat within 0.1 mK. These results were 0.2 mK lower (temperature equivalent) than the results of Compton and Ward [26] several years previously. This suggests that there were no problems with argon impurities which elevate the oxygen triple point temperature. Previously others [27] have found noticeable levels of argon in otherwise pure oxygen.

A multi-compartment cell from INM in Paris, containing oxygen produced by Air Liquide, has also been measured at NPL using standard PRT 1728839. This produced a triple point temperature 0.1 mK higher than the later value of the NPL cell.

More recently a second NPL oxygen cell has been produced and measured using PRTs 1728839 and 1832689. This confirmed the calibration of 1832689 within a few hundredths of a millikelvin. PRT 1728829 appeared to have changed from the second set of realisations in the first cell by about 0.15 mK.

6.5 ARGON

Gas of purity 99.999% was obtained from Air Liquide. The cell was filled to a pressure of 50 bar, giving a 3 g charge of 90 J heat capacity, and has been measured in three separate experiments over a period of one year, using different capsule PRTs. So far all measurements on the argon cell have been made in the "Ward-Compton" cryostat [13], using liquid nitrogen coolant, but the measurement procedures remain the same as previously described in section 5. The first experiment measured the plateau once using capsule PRTs Nos. 1728839, 1676928 and 1832691. Pulses of 8-10 mA for periods of 3-7 minutes were applied. The results obtained closely agreed with results previously obtained by Ward at NPL in 1978 [24].

The second experiment was used to calibrate some "secondary" standard PRTs for NPL, while the third experiment using PRT 1676928 was used to confirm the medium term stability of the cell and the PRT one year after the first measurement. Only two plateaus were measured on this occasion and the results agreed within 0.2 mK.

A measurement of the argon triple point produced in an INM multi-compartment cell gave a value which was 0.08 mK lower than the NPL cell (a difference which is within the measurement uncertainty).

7 SECONDARY FIXED POINTS

Apart from the fixed points specified in the scale, some other triple points have been measured accurately enough to enable temperature values to be given as determined on the NPL realisation of the ITS-90. (These values are not affected by the more recent shift in PRT No. 1728839 reported above).

7.1 NITROGEN

A cell was filled at 50 bar with gas of purity 99.999% from Air Liquide. Three plateaus were measured, using Leeds and Northrup standard capsule PRT No. 1832691, giving a width of 0.2 mK. This PRT has been calibrated by comparison with 1728839. From the measurements on this cell an ITS-90 value of 63.1511 K $\pm$ 0.5 mK (2σ) was determined for the nitrogen triple point.

7.2 CARBON DIOXIDE AND XENON

In the preparation of the ITS-90 there was some discussion about the need for a fixed point between the triple point of argon at ~ 83.8 K and the water triple point at 273.16 K. The mercury point, defined as 234.3156 K was finally chosen, but the triple points of carbon dioxide (at ~ 216 K) and xenon (at ~ 161 K) had been suggested as candidates.

Co-operative measurements were performed by NPL on cells of CO_2 and Xe. CO_2 cells were compared with the Institut National de Métrologie (INM) in France, on several occasions, while xenon cells from NPL, INM and the National Research Council of Canada (NRC), were measured at NPL.

As the details of the work have already been published [28] only a summary of the NPL results is given here. The CO_2 gas of 99.999% purity from BOC was introduced into the cell after it, and the filling system, had been vacuum baked to 130°C to remove as much water as possible (but without melting the indium plug awaiting insertion). The NPL xenon cell was filled with 99.999% pure gas from Air Products.

When cryogenic triple points occur at such "high" temperatures (161 K and 216 K), where the heat capacities of the construction materials are substantial and thermal time constants are long, more care is required in the freezing and melting techniques. Improper procedures can result in poor or non-existent plateaus, and apparently variable heats of fusion [29]. It is possible for the gas to condense at the top of the cell, instead of in the annulus around the thermometer well, at the bottom. To overcome these problems slow freezes are required and when warming up to the triple point after a freeze, excessive heating rates must be avoided. Also a long thermal equilibration time, of several hours, is required after applying a heat pulse, before a temperature measurement can be made.

The best value for the carbon dioxide triple point was determined to be $216.5913 \text{ K} \pm 0.3 \text{ mK}$ (1σ) on the NPL realisation of the ITS-90. When the three xenon cells were measured a 3 mK spread of results was obtained for the liquidus point of the plateau. (The liquidus point is the point where the amount of solid becomes vanishingly small). The average xenon triple point temperature, on the NPL realisation of the ITS-90, was $161.4059 \text{ K} \pm 1.0 \text{ mK}$ (at 1σ).

With careful measurement carbon dioxide makes a good secondary reference point, but differences between realisations of the xenon point are too great at present for it to be reliable to better than 1 or 2 mK. Moreover these differences are likely to be due to isotopic variations and may be difficult to overcome.

7.3 DEUTERIUM

A triple point which is of considerable interest is that of deuterium (or heavy hydrogen) near 18.7 K. It is a possible candidate to replace the two primary fixed points which are still required in the ITS-90 at ~ 17.0 K and ~ 20.3 K. Use of deuterium would produce a cryogenic scale down to 13.8 K based only on triple points and remove the need to accurately measure pressure within a cryostat, either for gas thermometry or for hydrogen vapour pressure determinations. Work on this point has been carried out at several laboratories [30,31,32,33,34].

As with hydrogen a spin conversion catalyst is required. The usual catalysts contain hydrogen (usually as water of hydration), but any hydrogen contamination of the deuterium gas will depress the triple point value, consequently the first aspect of the work at NPL has been to find an alternative non-contaminating catalyst. Gadolinium oxide (Gd_2O_3) appears to satisfy the requirements and the details have already been published [34]. A few other candidates have been investigated, but so far nothing better than Gd_2O_3 has been found. This

catalyst was then used with some very pure deuterium gas, made available under a EUROMET (European Metrology) agreement with the Istituto di Metrologia "G. Colonnetti" (IMGC), in Turin. The favourable results have been reported [35] with the latest value for the equilibrium deuterium triple point, on the NPL realisation of the ITS-90 using master PRT 1728839, being 18.6891 K. The measurement uncertainty for this particular determination was ± 0.4 mK at 1σ .

More recent measurements (unpublished) after 2½ years from the initial measurement have shown that the cell triple point temperature has decreased by only 0.2 mK, the majority of the change occurring within the first year. This cell would appear to be one of the best productions of the deuterium triple point so far.

Additional co-operative work has been performed with VNIIFTRI Laboratory (Russia). One of their deuterium cells was measured at both NPL and IMGC. At NPL it registered a triple point temperature of 18.688₈ K, ~ 0.3 mK lower than the EUROMET cell. The details have been published elsewhere [36].

At present there is still a need for an improvement in the cell design and the constructional materials in order to obtain the best conditions to maintain the long term purity of the deuterium sample. More sources of high purity deuterium, used to fill the cell, are also required. A faster acting catalyst would be an improvement, provided that it does not compromise the purity of the deuterium.

8 SUMMARY OF INTERNATIONAL COMPARISONS

In order to check that the realisation of an international temperature scale in one standards laboratory is satisfactory, and to test the reproducibility of the scale, it is necessary to make intercomparisons between the laboratories of calibrated standard PRTs and triple point cells.

A large intercomparison of platinum resistance thermometers was carried out by Ward and Compton [37]. In one aspect of that work they measured the differences in the calibrations of the thermometers at the fixed point temperatures. The results showed larger differences than had been expected and was a stimulus to the development of improved fixed points and techniques, and ultimately of the ITS-90.

Due to the relative long term stability of cryogenic thermometers, much of this data remains valid. Consequently more recent measurements made on fixed points in different laboratories, using these thermometers, can be related to each other. As time passes the usefulness of this data decreases, but it still remains as a useful first check.

NPL has also carried out a comparison of thermometers with VNIIFTRI [38]. The results contributed to the definition of the ITS-90 fixed point values.

In order to compare thermometers as above, it is necessary to transport them, with the consequent risk that the thermometer's calibration might shift during transport. An alternative method is to compare the realisations of two or more laboratories is to measure a triple point cell (or cells) in another laboratory, where the thermometer used will have been calibrated in the local cell(s). This can reduce the uncertainties, but the comparison is necessarily limited to measurements at the fixed points.

NPL took part in the international comparison of sealed triple point cells that was organised by the Bureau International des Poids et Mesures [6]. The results of this exercise confirmed that sealed triple point cells were a good means of realising fixed points.

More recently NPL has measured cells containing oxygen and argon from INM (France). The

results agreed with those from equivalent NPL cells within 0.1 mK. A NPL hydrogen cell has gone to INM. Measurements on secondary point cells of xenon from NRC (Canada) and INM have been made, whilst carbon dioxide cells have been exchanged between INM and NPL. Deuterium cells which have been measured in both Russia and Italy have also been measured at NPL and the results of these have already been mentioned [28,35,36].

9 CONCLUSION

Following the completion of the programme to produce the four cryogenic triple point cells, and using the previous work on the hydrogen boiling points [23] with a small correction for thermometer drift (described elsewhere [22]), NPL has the necessary cryogenic fixed points of the ITS-90, for the calibration of standard platinum resistance thermometers, and for the maintenance of the scale.

With the fixed points of water, mercury and gallium also available [7,8], NPL can provide calibrations for standard capsule PRTs from ~303 K (30°C) down to 13.8 K. If the indium point is used instead of the gallium point the upper level of the calibration can be increased to 156°C, but perhaps with some increase in the uncertainty. Using these principal standard thermometers, NPL is able to calibrate commercially available SPRTs by comparison, over the cryogenic range, with an uncertainty of ± 2 mK.

Under suitable conditions NPL can also provide cryogenic triple point cells to third parties, certified to agree with NPL's own reference cells.

From the work on carbon dioxide and xenon, NPL concluded that they were not ready for use in the ITS-90 [28]. In the event the mercury triple point at ~234 K [7,39,1] was used instead.

As the deuterium point is not fully developed, the ITS-90 continues to stipulate either two hydrogen vapour pressure points or two gas thermometry points at ~17.0 K and ~20.3 K. However, further work on the deuterium point may enable it to become a secondary reference point and perhaps an alternative fixed point of the International Temperature Scale.

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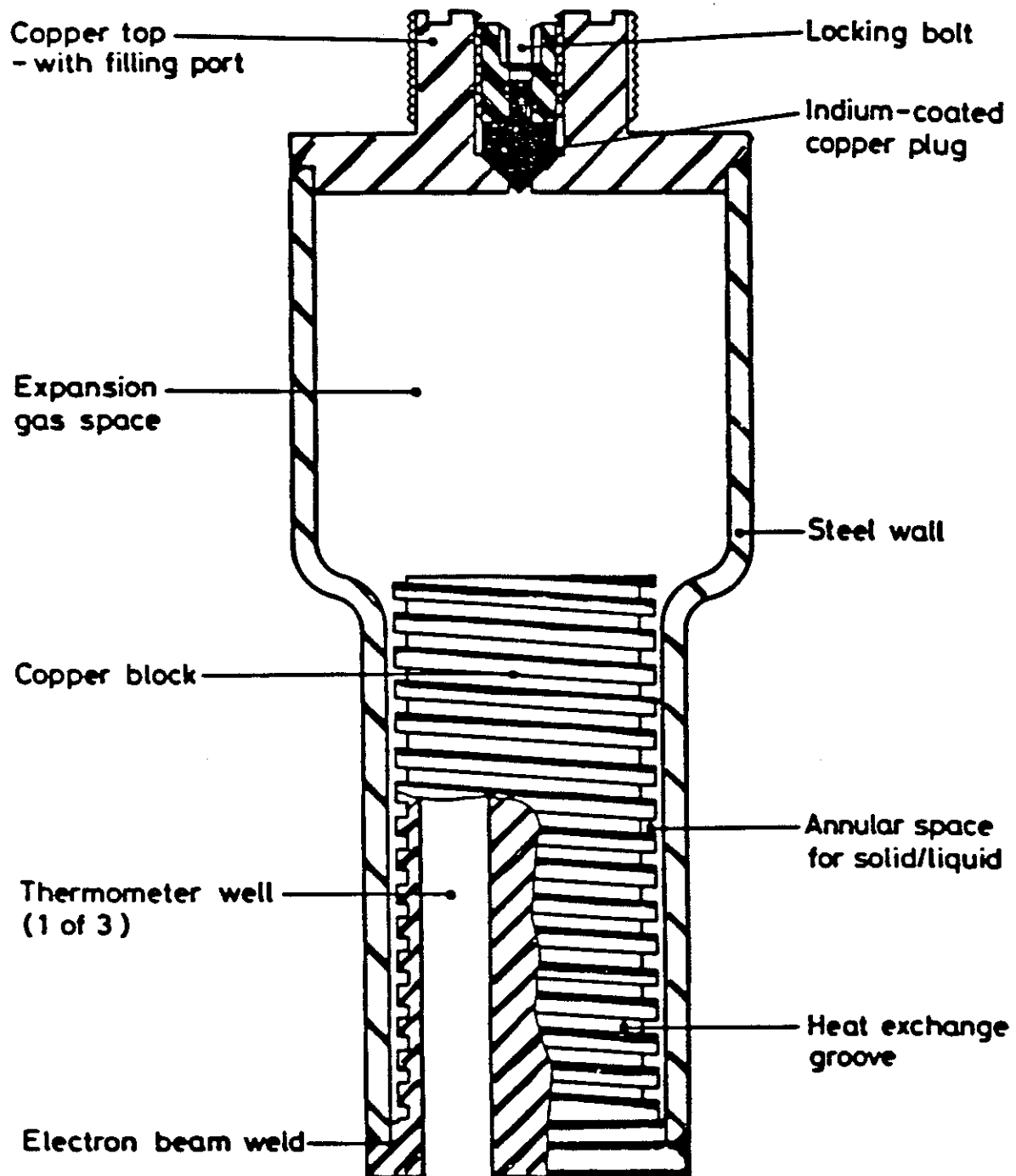


Figure 1 NPL Triple Point Cell

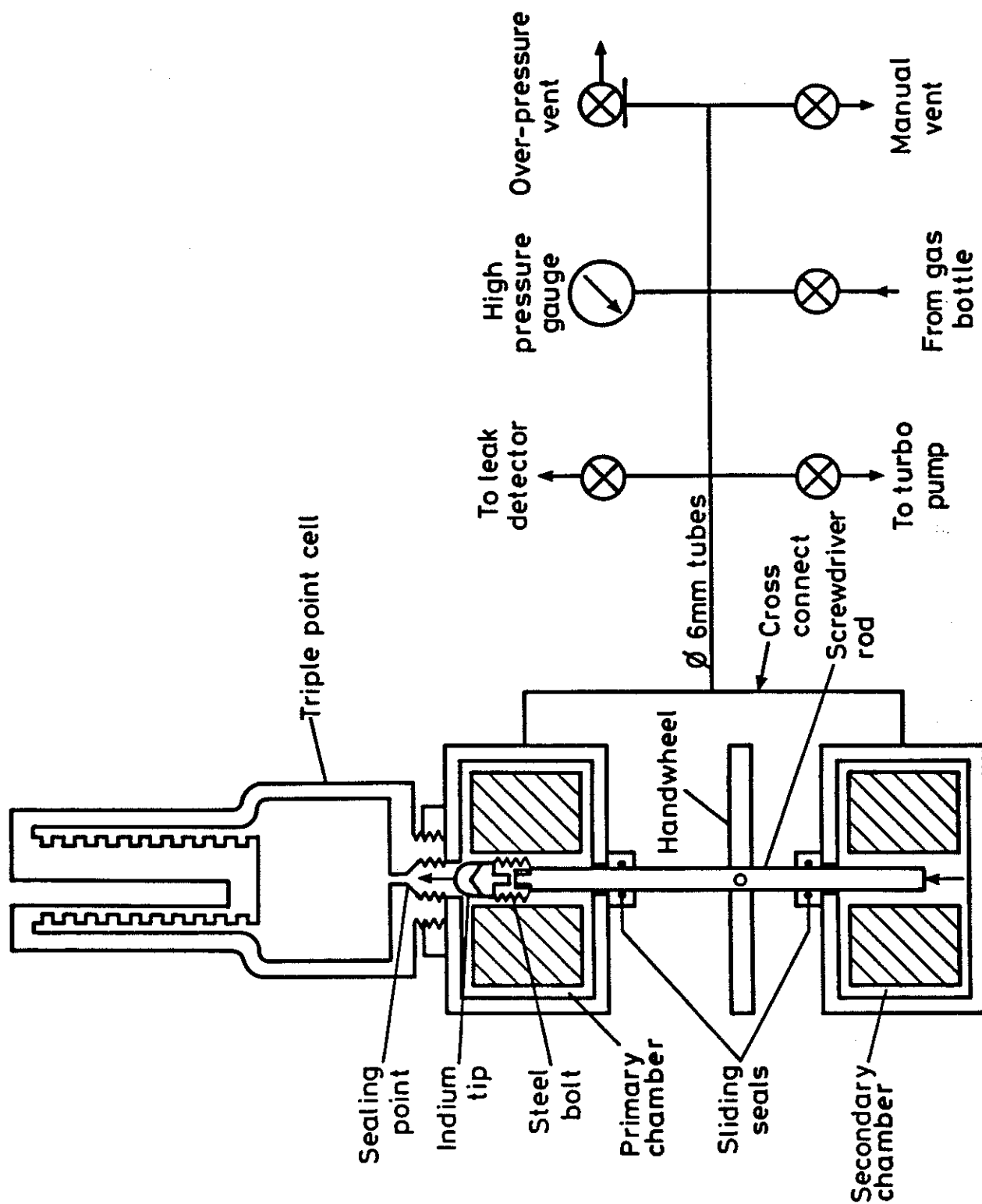


Fig.2 The NPL Filling System

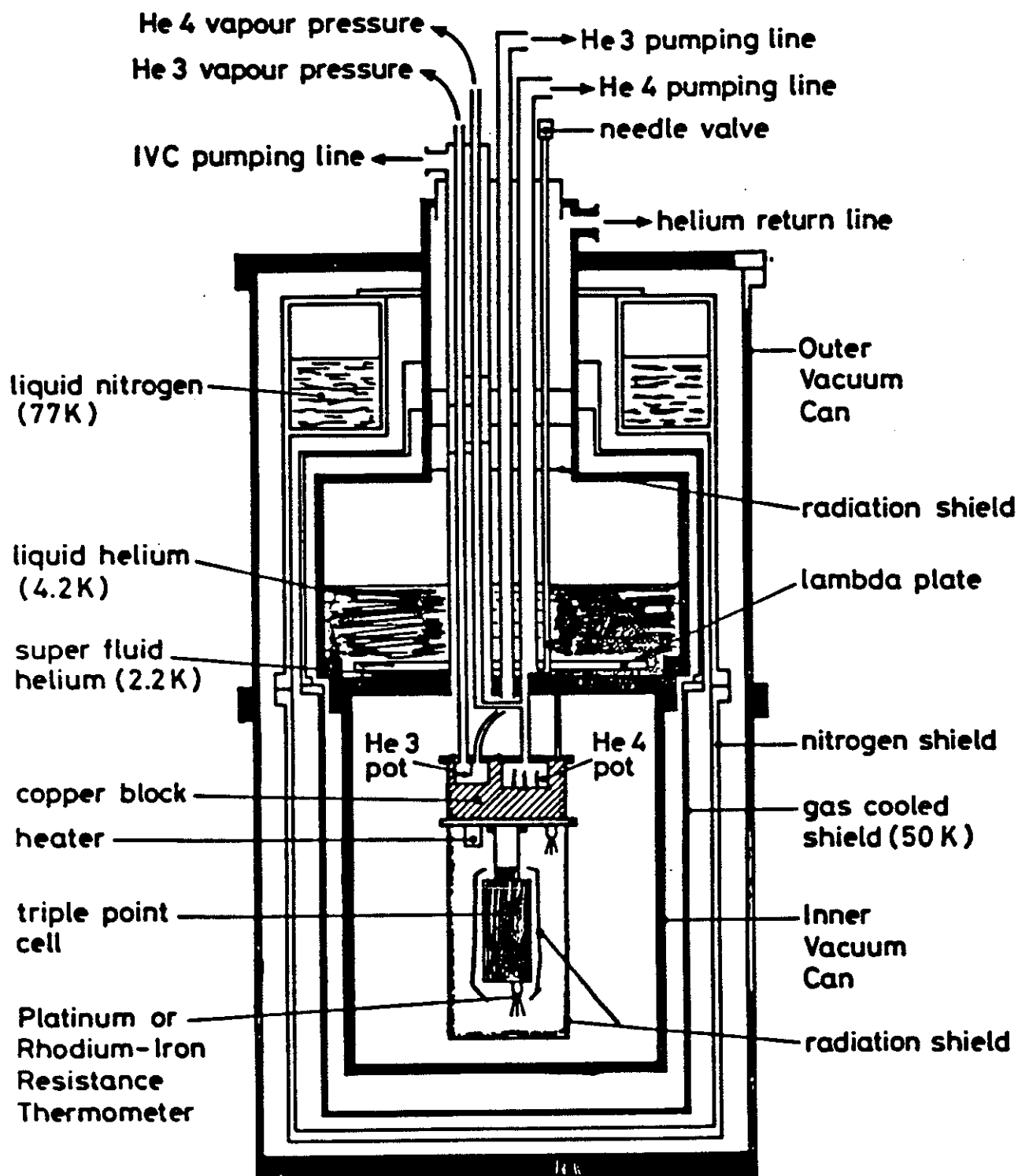


Figure 3 NPL Fixed Point/Comparator Cryostat

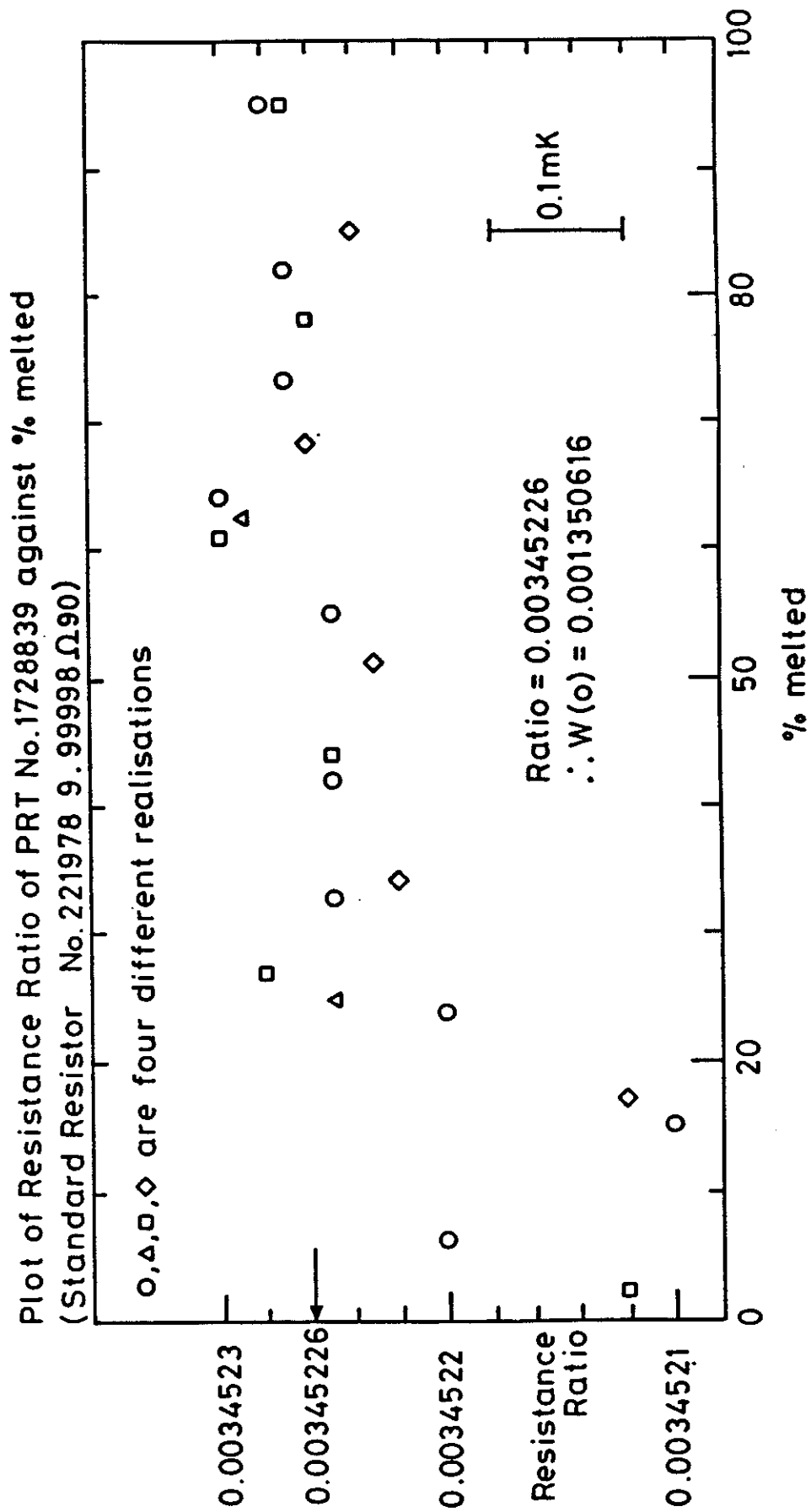


Fig.4 Hydrogen Triple Point Melting Plateau

