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Melts through the triple points of argon, oxygen, neon and equilibrium hydrogen have been performed at the National Institute of Standards and Technology (NIST) for the purpose of realizing the International Temperature Scale of 1990 (ITS-90). The triple points have been realized in a single copper block using isothermal calorimetry with an apparatus constructed at NIST for realizing the ITS-90 between 0.65 K and 84K. We provide here a description of the apparatus and experimental procedure and present the results of these triple-point realizations. The expanded uncertainties ( $k=2$ ) of the realizations are approximately 0.07 mK, 0.05 mK, 0.21 mK, and 0.15 mK for argon, oxygen, neon and equilibrium hydrogen, respectively. We discuss the differences between the assigned triple-point temperatures of these realizations and those given by the previously-used ITS-90 reference thermometers of NIST, which have calibrations traceable to earlier realizations of the IPTS-68 at NIST and at the National Physical Laboratory (UK).

## **Realization of the ITS-90 Triple Points Between 13.80 K and 83.81 K at NIST**

### **1. INTRODUCTION**

By January 1, 1990, the National Institute of Standards and Technology (NIST) had realized all fixed points of the International Temperature Scale of 1990 (ITS-90) [1] down to the triple point of argon for the routine calibration of standard platinum resistance thermometers (SPRTs). Before 1996, however, the fixed points below 83.8058 K had not been realized. Consequently, between 1990 and 1996 customer SPRTs were calibrated against the NIST reference capsule SPRTs [2], which disseminated the interim NIST ITS-90 wire scale through use of a comparison block at the fixed-point temperatures. These reference capsule SPRTs, which had previously served as NIST's reference thermometers for the IPTS-68, had had their calibrations converted to the ITS-90 [2]. The thermometers had been calibrated against NIST realizations of the triple points of oxygen and argon from earlier years [3]. For the region 13.8 K to 24.6 K, the thermometers had calibrations traceable to the National Physical Laboratory (NPL) realization of the IPTS-68.

In this paper, we present results of realizations of the cryogenic triple points from the NIST low-temperature ITS-90 facility. The triple points realized are those of equilibrium hydrogen (13.8033 K), neon (24.5561 K), oxygen (54.3584 K) and argon (83.8058 K). For temperatures below 83.8 K, the triple-point temperatures assigned by the ITS-90 are compared with those indicated by capsule SPRTs calibrated on the interim NIST ITS-90 wire scale. The triple point of argon realization performed in this facility is compared with that performed in a different apparatus at NIST [4].

### **2. APPARATUS**

The measurements were performed in NIST's low-temperature ITS-90 realization facility, which was designed to realize the ITS-90 below 84 K using the guidelines published by BIPM [5]. The source of the Ar used for the results reported in this paper has a manufacturer's specified purity of 99.9999%. The supplier of the Ne has specified it to be 99.999% pure. Its isotopic composition is approximately that found in nature. The purity of the H<sub>2</sub> used in the

realization was specified by the manufacturer to be 99.9999%. The O<sub>2</sub>, which was prepared at NIST through thermal decomposition of KMnO<sub>4</sub> [3], has a purity that is estimated to be greater than 99.9999%.

The triple-point cells are located inside a cylindrical oxygen-free high conductivity copper block, which has been described in a previous publication [6]. Each gas has its own separate cell. The block has four horizontal wells located immediately underneath the cells; two of these were designed to contain SPRTs and the other two rhodium-iron resistance thermometers (RIRTs). The e-H<sub>2</sub> and Ne cells each have a volume of 3 cm<sup>3</sup> and the Ar and O<sub>2</sub> cells have a volume of 20 cm<sup>3</sup>. The e-H<sub>2</sub> cell contains about 0.5 cm<sup>3</sup> of FeO(OH) powder, which is used as a catalyst for the conversion of ortho-hydrogen and para-hydrogen to their equilibrium distribution [5,7].

For the results presented in this paper, the SPRTs with serial numbers 1842385 and 1004131 and the RIRT with serial number B168 were placed in the thermometer wells of the copper block. SPRT 1842385 had been calibrated in 1992 from 13.8033 K to 273.16 K using the appropriate fixed point realizations from 83.8058 K to 273.16 K and against NIST's reference SPRTs for the lower temperatures. RIRT B168 was calibrated in 1992 against NIST's previous reference RIRTs, the calibrations of which were traceable to NPL-75 [2]. The resistances of the thermometers were measured with a commercial AC bridge operating at 30 Hz using a thermostatically controlled 100 Ω, 10 Ω, or 1 Ω standard resistor (calibrated at NIST) as the bridge reference resistor, as appropriate.

The copper block is located inside a vacuum jacket immersed in a dewar of cryogenic liquid (N<sub>2</sub> or <sup>4</sup>He). A cylindrical copper shield surrounds the block. A second cylindrical copper shield surrounds the first. There is a minimal thermal connection between the inner shield and the block consisting only of the thermometer lead wires and heater wires. The thermometer lead wires are made of a low thermal conductivity material. The block and the inner shield are heated by the use of resistive wire. The inner shield is temperature-controlled at approximately the triple-point temperature  $T_{TP}$  with a PID controller. The sensor for the controller is an RIRT located on the top plate of the inner shield.

The fill-tubes of the triple-point cells pass through eight small circular copper platforms which are soldered to the tubes at eight evenly spaced distances along the tubes (one platform is used for all tubes at a given location). Calibrated diode thermometers are mounted on these platforms to measure their temperatures in order to insure that the fill-tubes are warmer than the copper block. The bottom-most of the eight platforms has a strong thermal connection to the inner shield, which thereby minimizes the heat leak down the fill-tubes from room temperature to the copper block.

### 3. MEASUREMENT AND DATA ANALYSIS PROCEDURE

The cryogenic liquids used for the triple-point realizations were N<sub>2</sub> (for Ar and O<sub>2</sub>) and He (for Ne and e-H<sub>2</sub>). For the O<sub>2</sub> triple-point realization, the dewar containing the liquid N<sub>2</sub> was pumped to lower the temperature of the N<sub>2</sub> to a temperature useful for cooling the O<sub>2</sub> cell below its triple point. When filling a triple-point cell, its associated external stainless-steel flask was filled with the appropriate amount of gas, which was then condensed into the cell. After filling, the cell was sealed with a valve at the top of the cryostat. For the e-H<sub>2</sub> cell, care was taken to ensure that the sample was in ortho-para equilibrium before performing the triple-point measurements. First, the condensed H<sub>2</sub> was left exposed to the catalyst near 14 K for about 24 h. Then, the H<sub>2</sub> vapor above the liquid, which was not exposed to the catalyst, was evacuated for 15 seconds. This vapor was replaced by e-H<sub>2</sub> boiling off from the liquid. This procedure was repeated several times.

Before each melt, the cell block was cooled below the triple-point temperature. It was then heated to 0.05 K below the triple point temperature. A heater on the lowest fill-tube platform was used to raise the platform temperature to about 20 mK above  $T_{TP}$  for 30 minutes in order to melt any solid sample that may have formed in the fill-tube, allowing it to fall into the cell. The cell temperature was raised through the triple-point temperature with successive constant increments of heat. After each increment of heat, the cell was allowed to come to thermal equilibrium. During this time, the temperature was monitored with one of the resistance thermometers. The size of the heat increments was typically 1/12 the heat-of-fusion. The cell temperature at the beginning of the melting run was such that after two increments of heat the cell temperature would be about 1 mK below  $T_{TP}$ . Beginning at this point, the cell temperature was monitored for about 1 hour to check for drifts due to spurious heat leak. Since it came mostly from the fill-tubes, it could be minimized by adjusting the temperature of the lowest fill-tube platform; this was done by changing the inner shield temperature. Once the heat leak was sufficiently small (temperature drifts less than 0.1 mK/h), the next increment of heat was applied to the cell to begin the melt.

The period of time allowed for reaching thermal equilibrium after each heat increment was determined by experimentation. The waiting period became longer as more of the solid was melted and the distance between the cell walls and the solid/liquid interface increased. At the end of the waiting period, the resistance  $R$  of the monitoring thermometer (SPRT 1842385 for Ar, O<sub>2</sub>, and Ne, and RIRT B168 for H<sub>2</sub>) was measured using a current of 1 mA, 1 mA, 2.828 mA and 0.283 mA for Ar, O<sub>2</sub>, and Ne, and H<sub>2</sub>, respectively. Data consisting of this final resistance as a function of applied heat was used to determine the beginning of the melt, the end of the melt, and the heat-of-fusion. Subsequently, plots of thermometer resistance as a function of  $1/F$ , where  $F$  is the fraction of material melted, were made. Using only those values measured within the region  $1.5 < 1/F < 5$ , the final resistance was extrapolated to  $1/F = 1$  to provide the liquidus point resistance  $R_l$  [5,7]. Between 8 and 15 melts were performed for each substance in order to optimize sample preparation and melting techniques and to study the reproducibility of the melts. The dependence of  $R_l$  on the fill level  $h$ , which is caused by hydrostatic head effects [5,7], was corrected for by extrapolating  $R_l$  to its zero fill-level value  $R_l(h=0)$ , yielding the assigned triple-point resistance  $R_{TP} \neq R_l(h=0)$ . The fill level  $h$  of the cell was calculated using the measured heat-of-fusion of the sample.

At an appropriate point on the plateau of one of the melts (where  $1.5 < 1/F < 5$ ), the resistances of both SPRTs in the copper block were measured with two currents: 2 mA and 2.828 mA for e-H<sub>2</sub> and Ne, and 1 mA and 1.414 mA for O<sub>2</sub> and Ar. The two current measurement provided the plateau resistance  $R_p(F,I)$ , where  $I$  is the current. For the thermometer used to obtain the  $1/F$  plot, the difference between  $R_{TP}$  and  $R_p(F,1 \text{ mA})$  was determined and used to correct the two-current resistance measurements, yielding  $R_{TP}(I)$  for all thermometers. After the realizations were complete, the SPRT resistances were measured at the triple point of water (TPW) to determine the resistance ratios  $R_{TP}/R_{TPW}$  for the cryogenic triple points. For  $T < 83.8$  K, the numerical value of the temperature corresponding to  $R_{TP}$  on the interim NIST ITS-90 wire scale,  $T_{90\text{wire}}$ , was compared with the ITS-90 value, yielding the difference  $\Delta T_{90}(T_{TP}) \neq T_{TP} - T_{90\text{wire}}$ . The value of  $R_{TP}(I)$  for Ar was compared to the resistance measured in the other Ar triple-point realization apparatus at NIST [3].

#### 4. MEASUREMENT UNCERTAINTIES

The discussion here is based on the ISO guidelines for the evaluation of uncertainties [8]. The expanded uncertainty  $U$  assigned to the ITS-90 realizations is calculated with the equation

$$U = k \sqrt{\sum s_i^2 + \sum u_i^2}$$

where  $k$  is the coverage factor,  $s_i$  and  $u_i$  are the Type A and Type B standard uncertainties, respectively, for each known component in the measurements. Type A standard uncertainties are based on the statistical analysis of the measurements and Type B standard uncertainties are estimated since they cannot be directly measured. The expanded uncertainty is computed with  $k=2$ . The results are provided in Table 1 with the individual uncertainty components given in SPRT resistance units, and the total uncertainty is given in both units of resistance and temperature. The two are interchangeable through the conversion factor  $dR/dT$ , which is 0.0062  $\Omega/K$ , 0.031  $\Omega/K$ , 0.10  $\Omega/K$ , and 0.11  $\Omega/K$  at the triple points of e-H<sub>2</sub>, Ne, O<sub>2</sub>, and Ar, respectively.

Type A uncertainties from determination of  $R_{TP}$  from the  $R$  versus  $1/F$  plots are given as  $s_{TP}$ . Type A uncertainties from the measurement of  $R_p(F,I)$  are designated  $s_p$ . Type B uncertainties due to impurities also may be estimated from the  $R$  versus  $1/F$  plots. The value of  $R$  at  $1/F=0$ ,  $R_1^{pure}$ , theoretically corresponds to the value of  $R_1$  when the substance is pure [5,7]. A reasonable estimate of the uncertainty due to impurities would then be  $u_{Imp} = R_1^{pure} - R_1$ . We estimate the Type B uncertainty of  $R_{TP}$  from heat leak,  $u_{Leak}$ , to correspond to 0.02 mK for e-H<sub>2</sub> and Ne and 0.01 mK for O<sub>2</sub> and Ar. The Type B uncertainty due to an absence of thermal equilibrium when resistance measurements were made,  $u_{TE}$ , is estimated to correspond to 0.02 mK. Finally, the Type B uncertainty in the e-H<sub>2</sub> realization due to an absence of ortho-para equilibrium,  $u_{OP}$ , is estimated to correspond to 0.02 mK. The Type B uncertainty involving the previous calibration of the thermometer,  $u_{PCal}$ , is relevant when comparing the realized values of  $R_{TP}$  against their corresponding values on the interim NIST

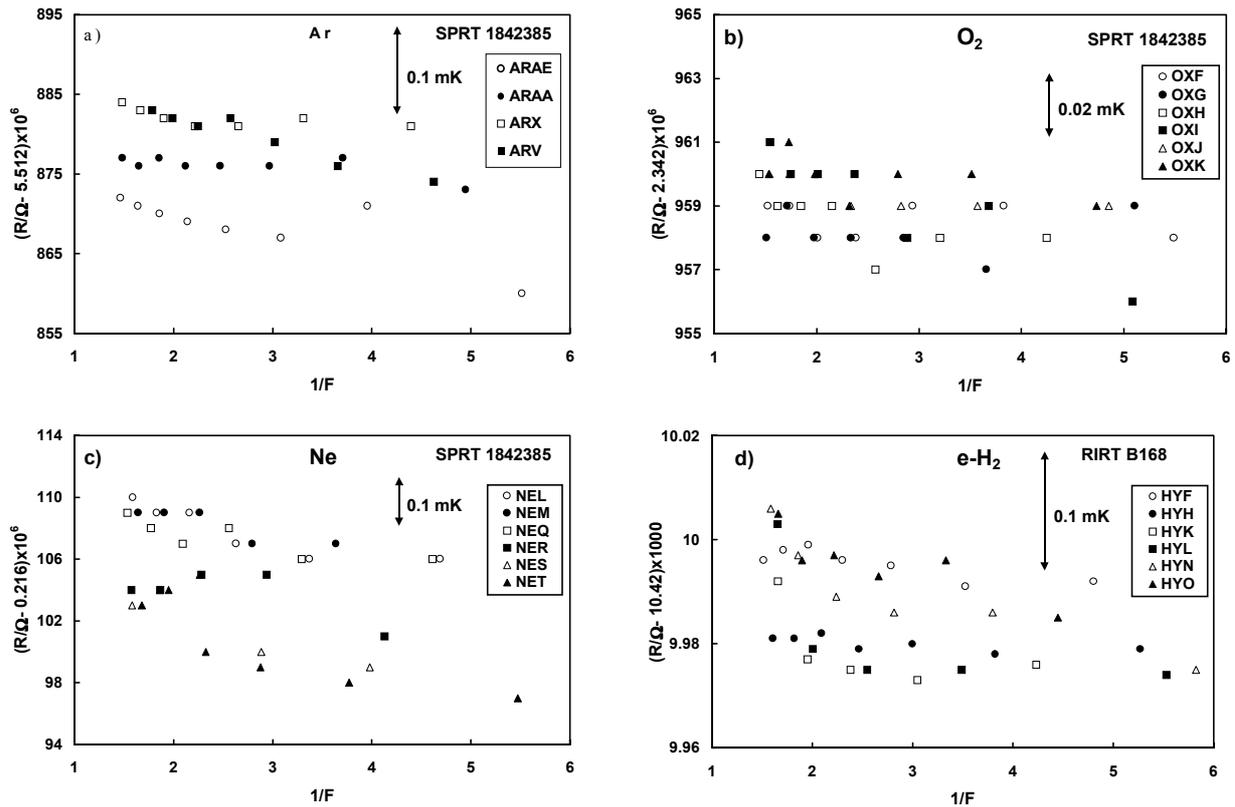
**Table 1.** The components of uncertainty for the triple-point realizations.

| Item   | e-H <sub>2</sub> | Ne   | O <sub>2</sub> | Ar   |
|--|------------------|------|----------------|------|
| Type A for $R_{TP}$ : $s_{TP}/mK$                          | 0.04             | 0.09 | 0.01           | 0.02 |
| Type A for $R_p$ : $s_p/mK$                                | 0.05             | 0.01 | 0.01           | 0.01 |
| Impurities: $u_{Imp}/mK$                                   | 0.02             | 0.04 | <0.01          | 0.02 |
| Heat Leaks: $u_{Leak}/mK$                                  | 0.02             | 0.02 | 0.01           | 0.01 |
| Thermal Equilibrium: $u_{TE}/mK$                           | 0.02             | 0.02 | 0.02           | 0.02 |
| Ortho-Para Equilibrium: $u_{OP}/mK$                        | 0.02             | --   | --             | --   |
| Prev. Resist. Therm.                                       | 0.39             | 0.10 | 0.10           | 0.06 |
| Total for $R_{TP}$ : $U_R/mK$                              | 0.15             | 0.21 | 0.06           | 0.07 |
| Total for $\Delta T_{90}(T_{TP})$ : $U_C/mK$               | 0.79             | 0.28 | 0.20           | 0.14 |
| Total for $R_{TP}$ : $U_R/(10^{-6} \Omega)$                | 0.9              | 6.4  | 5.6            | 7.8  |
| Total for $\Delta T_{90}(T_{TP})$ : $U_C/(10^{-6} \Omega)$ | 4.9              | 8.7  | 20.0           | 15.5 |

ITS-90 wire scale. The total uncertainty for  $R_{TP}$  is  $U_R$ , and that for  $\Delta T_{90}(T_{TP})$  is  $U_C$ .

## 5. RESULTS

Figure 1a shows the triple-point data for four fillings of 99.9999% pure argon. The plot displays the resistance of SPRT 1842385 as a function of  $1/F$ . The fill levels are  $h = 1.0$  cm, 2.6 cm, 4.2 cm and 5.6 cm for the melts designated ARAE, ARAA, ARX and ARV, respectively. The value of  $R_1$  increases monotonically with the fill level by an amount corresponding to 0.034 mK/cm, which is in excellent agreement with that expected from the hydrostatic head effect for argon ( $dT_{TP}/dh=0.033$  mK/cm [1]). The value of  $R_{TP}$  as determined using these four melts yields  $R_{TP}(1 \text{ mA}) = (5.512\,868\,8 \pm 0.000\,002\,0) \Omega$ . The Type A uncertainty and the impurity uncertainty each correspond to 0.02 mK. Additional melts performed with 99.99999% pure argon agree with these results to within the measurement uncertainties (0.04 mK). Comparison of  $R_{TP}$  with the triple-point resistance obtained from the



**Figure 1.** Data from melts through the triple points of Ar, O<sub>2</sub>, Ne and e-H<sub>2</sub>. Results are shown for several fillings for each material. Plots are of the thermometer resistance  $R$  as a function of  $1/F$ , where  $F$  is the fraction of material melted. The thermometer used with Ar, O<sub>2</sub> and Ne is standard platinum resistance thermometer 1842385 and that used with e-H<sub>2</sub> is rhodium-iron resistance thermometer B168.

other Ar triple-point realization apparatus at NIST [4] yields  $\Delta T_{90}(T_{TP}) = (60.06 \sim 0.14)$  mK. The triple-point data for two fillings of oxygen are shown in Fig. 1b. Three melts, designated OXF, OXG and OXH have fill levels of  $h=1.9$  cm. The last three melts, OXI, OXJ and OXK have fill levels of  $h=4.0$  cm. For SPRT 1842385, the average value of  $R_1$  for OXF, OXG and OXH is the equivalent of 0.02 mK below that for OXI, OXJ and OXK; this is close to the temperature difference expected from the hydrostatic head effect, 0.03 mK. The value of  $R_{TP}(1 \text{ mA})$  is  $(2.342\,956\,6 \sim 0.000\,000\,8)$   $\Omega$ . The Type A uncertainty corresponds to 0.01 mK. The impurity uncertainty is 0.004 mK. For this triple point, comparison with the interim NIST ITS-90 wire scale yields  $\Delta T_{90}(T_{TP}) = (-0.10 \sim 0.20)$  mK.

The triple-point data for three fillings of neon are shown in Fig. 1c. Again, the resistance is that of SPRT 1842385. The first three melts, designated NEL, NEM, and NEQ are for the same filling of neon, with  $h = 1.8$  cm. They yield similar results, with  $R_1$  differing by less than the equivalent of 0.04 mK. Two other two melts, NER and NES, were obtained with a different filling of neon, also with  $h = 1.8$  cm. The values of  $R_1$  also agree within the equivalent of 0.04 mK, but differ from the first three, being lower by the equivalent of about 0.16 mK. The last melt shown, NET, has  $h = 3.5$  cm. Its value of  $R_1$  is lower than those of NER and NES by the equivalent of 0.03 mK. The hydrostatic head effect, which is expected to cause a maximum difference of 0.034 mK, is unresolvable. The average value of  $R_1(2.828 \text{ mA})$  determined from these six melts is determined to be  $(0.216\,106\,9 \sim 0.000\,002\,9)$   $\Omega$  and we approximate  $R_{TP}$  as this value. The Type A uncertainty corresponds to 0.09 mK. The impurity uncertainty is 0.04 mK. Comparison with the interim NIST ITS-90

wire scale results in  $\Delta T_{90}(T_{TP}) = (60.48 \text{ } ^\circ 0.28) \text{ mK}$ .

Finally, the triple-point data for three fillings of equilibrium hydrogen are shown in Fig. 1d. The resistances in the figure are for RIRT B168. The melts HYF and HYH have  $h=4.0$  cm, the melts HYK and HYL have  $h=1.6$  cm, and the melts HYN and HYO have  $h=3.0$  cm. The predicted fill-level dependence from the hydrostatic head effect (0.008 mK for a height of 4.0 cm) is unobservably small, and indeed no dependence is evident in the plot. The average value of  $R_I(0.283 \text{ mA})$  for all six melts is  $(10.429\,995 \text{ } ^\circ 0.000\,010) \text{ } \Omega$ , and we approximate  $R_{TP}$  as this value. The Type A uncertainty corresponds to 0.04 mK. The impurity uncertainty is determined to be 0.02 mK. For this triple point, comparison with the interim NIST ITS-90 wire scale gives  $\Delta T_{90}(T_{TP}) = (60.85 \text{ } ^\circ 0.79) \text{ mK}$  for the SPRTs.

## 6. SUMMARY

We have successfully realized the triple points of Ar, O<sub>2</sub>, Ne, and e-H<sub>2</sub> in open cells in the NIST ITS-90 Low Temperature Realization Facility. The temperature values measured on the interim ITS-90 wire scale of NIST agree with the assigned values of all triple points to within 1 mK. In addition to the realization of these triple points, NIST also realizes the e-H<sub>2</sub> vapor pressure fixed points at 17.035 K and 20.27 K in this same facility. With the ability to realize the cryogenic fixed points of the ITS-90, NIST can now perform the direct calibration of SPRTs against all relevant ITS-90 fixed points down to 13.8 K [9].

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