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The Triple-Point Temperatures of ^{20}Ne and ^{22}Ne

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Abstract

Interest in the triple points of neon isotopes has recently arisen as a result of the multi-institute project to understand how variations in the isotopic composition of natural neon influence the triple-point temperature of a particular sample. Given the challenges in determining with sufficiently low uncertainty both the relative isotopic concentrations, particularly of ^{22}Ne relative to ^{20}Ne , and the temperature differences among cells filled from different gas sources in order to determine the sensitivity coefficient with adequate confidence, modelling of the isotopic influence becomes an attractive alternative for correcting the triple points of ‘natural’ neon samples to a common composition. The modelling requires, among other things, knowledge of the triple-point temperatures of ^{20}Ne and ^{22}Ne .

The triple points of these pure neon isotopes have utility in their own right as secondary reference temperatures on the ITS-90, and one or both of these could replace ‘natural’ neon in a revised International Temperature Scale or approximation to the ITS.

The neon isotope triple-point temperatures (on the IPTS-68) reported by Furukawa, Kemp, and Sakurai in various publications from 1972 to 1986 predate the ITS-90, and so there is utility in contemporary measurements (on the ITS-90) with gas samples of recent production. At NRC, we find the triple point of ^{20}Ne to be at 24.54230 K (13.80 mK below the triple point of ‘natural’ neon) and that of ^{22}Ne to be at 24.68889 K (132.79 mK above the triple point of ‘natural’ neon), assuming our reference sample of ‘natural’ neon realizes the ideal ITS-90 temperature of 24.5561 K.

KEY WORDS: ^{20}Ne ; ^{22}Ne ; isotope; neon; triple point

1. Introduction

The triple point of neon is one of the defining fixed points of the International Temperature Scale of 1990 (ITS-90) [1]. The text of the ITS-90 prescribes that the substances used are of “natural isotopic composition”. The *Technical annex for the International Temperature Scale of 1990* [2] (adopted by the Consultative Committee for Thermometry in 2005) specifies reference isotopic compositions and off-composition correction functions for the triple points of water and hydrogen, but not for neon. Variations in the isotopic content of commercial neon are believed to be largely responsible for the observed variability in neon triple points of as much as 480 μK . The remaining fixed points of the ITS-90 are believed to have negligible sensitivity to variations in isotopic composition.

According to the International Union of Pure and Applied Chemistry Commission on Atomic Weights and Isotopic Abundances, neon in air consists of 90.48% ^{20}Ne , 0.27% ^{21}Ne , and 9.25% ^{22}Ne (concentrations expressed as atomic fractions) [3]. In recent years, efforts to correlate variations in the isotopic composition of natural neon with the triple-point temperatures of specific gas samples have failed to recommend a means to correct samples of different compositions to a common basis [4]. The goal of that work is to specify a reference composition (e.g. the IUPAC composition for neon in air) and a sensitivity coefficient (correction factor), i.e. the slope of the triple-point temperature versus the ^{22}Ne concentration or $^{22}\text{Ne}/^{20}\text{Ne}$ ratio.

Given the technical challenges in determining with sufficiently low uncertainty the relative isotopic concentrations (particularly of ^{22}Ne relative to ^{20}Ne) and the temperature differences among cells filled from different gas sources in order to derive the sensitivity coefficient with adequate confidence, modelling the isotopic influence represents an alternative means to obtain the sensitivity coefficient. The modelling requires, among other things, knowledge of the triple-point temperatures of ^{20}Ne and ^{22}Ne . The triple points of these pure neon isotopes have utility in their own right as secondary reference temperatures on the ITS-90, and one or both of these could replace ‘natural’ neon in a revised International Temperature Scale or approximation of the ITS. Aside from recent measurements at INRiM,

the neon-isotope triple-point temperatures (on the IPTS-68) reported by Furukawa, Kemp, and Sakurai in various publications [5-8] from 1972 to 1986 predate the ITS-90, and so there is utility in contemporary measurements (on the ITS-90) with gas samples of recent production.

In the sections that follow, we will describe the measurements of the triple points of ^{20}Ne and ^{22}Ne that were recently carried out at NRC. Thermodynamic calculations based on the ideal-solution model and the measured temperatures are used to compute the binary phase diagram as well as the isotopic sensitivity coefficient for the triple point of neon, of particular interest near the IUPAC composition for air. Finally, modelling of fixed-point measurements indicates that isotopic fractionation can explain the large melting range of neon fixed points of 'natural' isotopic composition.

2. Experiment

The triple-point measurements can be no better than the quality of the sample gases, so it is important that they be adequately characterized for chemical and isotopic purity. Table 1 lists the pertinent characteristics of the ^{20}Ne and ^{22}Ne samples measured at NRC. Samples of the gases were sealed inside copper fixed-point cells having the dimensions indicated in Fig. 1. The material is OFHC copper with the exception of the stainless-steel sleeve added to strengthen the cylindrical wall of the cell. Six capsule-type standard platinum resistance thermometers (CSPRTs) are used for the temperature determination of each melting plateau. The CSPRTs employed represent three manufacturers and include some that are quite old as well as two of recent production (Table 2). Five of these thermometers were used in the determination of the triple point of xenon [9]. The sealed cells are installed in a cryostat designed around a 2-stage closed-cycle cryocooler [10]. The CSPRT resistance ratios are determined using an Automatic Systems Laboratories F18 resistance bridge in conjunction with a $25\ \Omega$ Tinsley 5685A reference resistor thermostatted in a Guildline 9732VT oil bath at $25\ ^\circ\text{C} \pm 2\ \text{m}^\circ\text{C}$.

The reference 'natural' neon gas is from a cylinder supplied by Praxair. The reference sealed cell (Cu-M-1) was filled in 2004. The mean triple-point temperature measured during

2009 appears $34 \mu\text{K} \pm 25 \mu\text{K}$ hotter than the value from 2004, based on five CSPRTs common to both realizations. Given the ambiguity arising from isotopic variations of commercial neon samples, we have chosen to report the neon isotope triple point temperatures relative to Cu-M-1, the current NRC realization of the neon triple point, defined by the ITS-90 as 24.5561 K. In an effort to determine the extent to which our reference cell is of ‘natural’ isotopic composition, arrangements were made to have the Praxair gas analysed by the Noble Gas Laboratory at the University of Ottawa, a facility mainly devoted to geochemistry applications. The mean $^{22}\text{Ne}/^{20}\text{Ne}$ ratio was determined to be 0.1019 with a standard deviation of 0.0007 (based on 8 measurements). This compares favourably with the value 0.1022 ± 0.0003 derived from the IUPAC recommendations.

2.1 Neon-22

The measurements of the neon isotopes began with the ^{22}Ne sample supplied by Spectra Gases, which was used to fill cell Cu-M-10. Table 3 summarizes the values for the six CSPRTs from three melts carried out between 2009/08/19 and 2009/09/14. Pooling all 16 values of temperature leads to a mean value 132.63 mK hotter than the triple point of neon defined by our reference cell, Cu-M-1. The summary statistics at the bottom of each vertical column indicate the consistency of measurements for each thermometer. The statistics at the far right of each row indicate the consistency across the six CSPRTs on a run-by-run basis.

A sample melting curve appears at the top of Fig. 2 where a series of 0.2 J pulses was used to melt the sample over 30 hours. The bottom part of Fig. 2 shows the consistency of the plateau value following each heating pulse. From 4.8% to 99.8% liquid fraction, there is no discernible slope or trend, and the variations appear largely random within their standard uncertainty of $19 \mu\text{K}$. This is quite unlike the melting curves for the neon sample of natural composition studied by Wolber and Fellmuth [11], which exhibited a melting range of 0.3 to 0.4 mK, an effect they attribute to isotopic segregation during freezing. The very flat melting curve for cell Cu-M-10 supports the mass-spectrometry data from Table 1, which indicates that the sample is both chemically very pure and isotopically highly enriched. Nonetheless, a

correction to the measured triple point temperature is required to account for the 0.94% ^{20}Ne and 0.25% ^{21}Ne that is present. A correction of 157 μK has been added to the measured temperature, resulting in a value 132.79 mK hotter than the triple point of neon defined by our reference cell, Cu-M-1.

2.2 Neon-20

Investigation of the triple point of ^{20}Ne began with a sample supplied by Spectra Gases that was used to fill cell Cu-M-11. There was some reluctance in purchasing this sample due to the stated impurity content of 140 ppm of hydrogen and 150 ppm of helium. A recent summary of impurity effects in cryogenic gases [12] concludes that the effect of helium is probably negligible, nitrogen appears to depress the triple point by 8 $\mu\text{K ppmv}^{-1}$, and the influence of hydrogen is controversial – one author reports no effect and others show triple-point depressions ranging from 5 $\mu\text{K ppma}^{-1}$ to 10 $\mu\text{K ppma}^{-1}$ (other impurities are believed to freeze out and have no influence on the triple-point temperature). Table 4 summarizes the data obtained and Fig. 3 provides two representative melting curves. Based on three melts carried out between 2009/11/06 and 2009/12/01, the triple point is 13.55 mK below our reference cell containing ‘natural’ neon (Cu-M-1).

With some concern for the influence of impurities on the triple point temperature of cell Cu-M-11, a ^{20}Ne sample was obtained from Sigma-Aldrich (ISOTEC) and this was used to fill cell Cu-M-12. Unfortunately, it was not possible to obtain from the supplier an indication of the helium and, more importantly, the hydrogen content. Table 5 summarizes the data and Fig. 4 is a representative melting curve. Based on four melts carried out between 2009/12/14 and 2009/12/17, the triple point is 13.80 mK below our reference cell of ‘natural’ neon, Cu-M-1.

The difference of 250 μK between the two ^{20}Ne samples is clearly a less satisfactory situation than we had hoped for. The difference in triple-point temperatures may arise from either a difference in chemical purity or relative isotopic content. As hydrogen and nitrogen have the potential to depress the triple point, the Sigma-Aldrich sample may be of lower

chemical purity than the one from Spectra Gases. Assuming a sensitivity of $-15 \mu\text{K ppm}^{-1}$ based on the cryoscopic constant for neon [12], a difference in impurity content of 17 ppm^{-1} is sufficient to explain the difference. Based on the sensitivity coefficients reported for nitrogen and hydrogen, a value half that derived from the cryoscopic constant may be more realistic, and therefore a required impurity difference of 35 ppm^{-1} is more likely. The concentrations of nitrogen in Table 1 are insufficient to explain the temperature difference, so differences in the hydrogen concentration may be responsible – but the mass spectrometry is lacking.

Alternatively, the Spectra Gases sample may be enriched in ^{22}Ne relative to the Sigma-Aldrich sample. Though a consensus value for the isotopic sensitivity of the triple-point temperature is currently unavailable, our own data indicates that the triple points of ^{20}Ne and ^{22}Ne differ by 146.18 mK to 146.43 mK. An assumed linear variation in triple-point temperature between the pure-isotope values leads to a sensitivity coefficient of $146 \mu\text{K}$ per 0.1% fraction of ^{22}Ne in the predominantly ^{20}Ne sample. A temperature difference of $250 \mu\text{K}$ can be explained if the fractional content of ^{22}Ne in the Spectra Gases sample is greater by 0.17% compared to that of the Sigma-Aldrich sample.

2.3 Measurement uncertainty

The measurement uncertainty budget for the neon-isotope triple-point determinations is detailed in Table 7.

The uncertainty attributed to chemical impurities (only nitrogen and hydrogen are suspected to be influential) is sample-dependent. Based on the contents of Table 1, a nitrogen concentration of 2 ppmv^{-1} and a sensitivity of $8 \mu\text{K ppmv}^{-1}$ imply a potential temperature depression of $16 \mu\text{K}$, and we assume that this applies to the Spectra Gases ^{22}Ne sample as well. The Spectra Gases ^{20}Ne sample may contain four times this amount according to Table 1, so the corresponding uncertainty is $64 \mu\text{K}$. The case for hydrogen is considerably more challenging as mass-spectrometry data are lacking for the Sigma-Aldrich ^{20}Ne sample and the value of the sensitivity coefficient remains controversial (0 to $10 \mu\text{K ppm}^{-1}$). The ^{22}Ne

sample appears to contain less than 0.1 ppm H₂, so a temperature depression of 1 μ K (or less) is anticipated from this source (we assume a sensitivity coefficient of 10 μ K ppm⁻¹). The Spectra Gases ²⁰Ne may contain 140 ppm H₂, but this implies a temperature depression of 1.4 mK. However, the worst-case melting range for this cell is only 200 μ K (Fig. 3, top) and its triple point is 250 μ K *above* that of the Sigma-Aldrich ²⁰Ne sample which has a narrower melting range. Given the conflicting data, the influence of hydrogen has been neglected in the uncertainty budget.

The expected variability in isotopic composition is sample-dependent and directly related to the uncertainty of the mass spectrometry. For the Sigma-Aldrich ²⁰Ne sample, we assume an uncertainty of 0.01% (corresponding to a triple-point uncertainty of 15 μ K) based on the data in Table 1. A similar value has been attributed to the Spectra Gases samples, though this is merely an estimate.

The remaining components are largely sample-independent. The uncertainty in determining the fixed-point value is estimated from the plateau flatness for cell Cu-M-10 (estimated as the standard deviation from 5% to 99% liquid fraction, lower part of Fig. 2). The 1.5 μ K uncertainty due to the hydrostatic pressure is determined by the product of half the calculated liquid height within the cell and the temperature variation with depth of the neon triple-point temperature (1.9 mK·m⁻¹) [1]. The uncertainty due to stray heat flux is estimated from the sensitivity of the plateau temperature to changes in the control set-point of the cryostat shield near the fixed-point cell [13]. Fig. 5 shows that the plateau temperature changes by 1.3 mK for a change in shield temperature of 200 mK. Though this was obtained during a freeze, a similar magnitude can be expected for the melt as (for this type of cell) the stray heat flux is mainly determined by the cell geometry. Since the adiabatic setting for the shield temperature (obtained by balancing to achieve near-zero temperature drift in the all-solid state near the phase transition) is believed to be better than 2 mK, we estimate this component as 10 μ K. The uncertainty due to the CSPRT self-heating correction is estimated from the average standard deviation of the self-heating for the six CSPRTs (10 μ K) after pooling data from all of the triple-point determinations. The uncertainty component due to the accuracy of the resistance bridge assumes a ratio uncertainty of 5×10^{-8} of full scale, consistent

with the manufacturer's claims and in-house characterization experiments using an Automatic Systems Laboratories Ratio Test Unit (a transformer-based device) and an Aeon Resistance Bridge Calibrator. The uncertainty associated with the stability of the standard resistor is based on a temperature coefficient of $3 \text{ ppm} \cdot \text{K}^{-1}$ and a bath stability of $\pm 2 \text{ mK}$. The uncertainty propagated from the triple point of water (TPW) is the product of the TPW realization uncertainty for capsule-style thermometers ($100 \text{ } \mu\text{K}$) and the nominal resistance ratio (0.0085). The melt-to-melt repeatability of $48 \text{ } \mu\text{K}$ is the standard deviation of the average temperature from Tables 3-5. The uncertainty due to CSPRT stability is calculated as the average of the six individual CSPRT standard deviations from Tables 3-5 respectively. Assuming all of the components to be uncorrelated, the combined standard uncertainty ($k=1$) is $41 \text{ } \mu\text{K}$ for the Sigma-Aldrich ^{20}Ne and Spectra Gases ^{22}Ne samples and $73 \text{ } \mu\text{K}$ for the Spectra Gases ^{20}Ne sample.

3. Discussion of Experimental Results

The triple points of ^{20}Ne and ^{22}Ne (on the IPTS-68) reported by Furukawa, Kemp, and Sakurai [5-8] are summarized in Table 6. While some neon-isotope triple-point measurements existed prior to Furukawa's report, they are not of equivalent metrological quality. Additionally, the boiling point of oxygen marked the lower limit of ITS-48 and therefore low-temperature measurements prior to 1968 relied on laboratory scales, making comparisons challenging. In 1996, the Consultative Committee for Thermometry's Working Group 2 estimated the triple point of ^{20}Ne as $24.541 \text{ K} \pm 0.001 \text{ K}$ on the ITS-90 [14]; no value was reported for ^{22}Ne , probably due to a lack of corroborating data for Furukawa's value.

Based on our measurements of the Sigma-Aldrich ^{20}Ne sample and the Spectra Gases ^{22}Ne sample, we estimate $T_{\text{tp}}(^{20}\text{Ne}) = 24.54230 \text{ K}$ and $T_{\text{tp}}(^{22}\text{Ne}) = 24.68889 \text{ K}$ (assuming that our reference sample of 'natural' neon realizes the ideal ITS-90 temperature of 24.5561 K). The difference in triple-point temperatures of 146.59 mK compares well with Furukawa's value of 147 mK from 1972. Pavese et al. [15] recently reported temperatures of 24.5422 K and 24.6888 K for the triple points of ^{20}Ne and ^{22}Ne , respectively, with an expanded

uncertainty of 0.00032 K. The INRiM results are in good accord with the values reported here, and especially the difference of 146.60 mK in their triple point temperatures compared to 146.59 mK for the NRC measurements

4. Modelling of the Binary Phase Diagram

Assuming an ideal solution of the two isotopes ^{20}Ne and ^{22}Ne , the values of their melting temperatures and their latent energy of fusion can be used to calculate their liquidus and solidus lines in the binary phase diagram, as well as the distribution coefficients.

Let Y and Z be the names of the 2 isotopes. Then, by definition, the equilibrium distribution coefficient (k) of the isotope 'Z' is given by the ratio of its concentrations (x) in the solid ('S') and the liquid ('L') phase:

$$k_Z = \frac{x_{ZS}}{x_{ZL}} \quad (1)$$

In thermodynamic equilibrium, the change of the Gibbs free energy (or the chemical potential) for the melting of a given isotope is zero. The Gibbs free energy of the isotope can be expressed using the enthalpy and entropy of the pure isotope and an additional term to account for the isotope not being pure but in solution, which according to Raoult's law is $RT \ln x$ (R is the gas constant). Thus:

$$\begin{aligned} 0 &= \Delta G = G_L - G_S \\ &= H_L - TS_L + RT \ln x_{ZL} - H_S - TS_S + RT \ln x_{ZS} \\ &= \Delta H - T \cdot \Delta S + RT \ln x_{ZL} - RT \ln(k_Z \cdot x_{ZL}) \\ &= \Delta H - T \cdot \Delta S - RT \ln k_Z \end{aligned} \quad (2)$$

Assuming that enthalpy and entropy are constant with temperature, and the pure isotope melts at T_Z , we have:

$$\Delta S = \frac{\Delta H}{T_Z} \quad (3)$$

where ΔH and T_Z are the corresponding latent heat of fusion and triple-point temperature.

Thus equation (2) implies:

$$0 = \Delta H \left(1 - \frac{T}{T_Z} \right) - RT \ln k_Z \quad (4)$$

or equivalently

$$\ln k_Z = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_Z} \right) \quad (5)$$

This equation is equivalent to the Van't-Hoff equation for a melting process whose equilibrium constant K is the reciprocal distribution coefficient. Analogously, the distribution coefficient for the other isotope is given by:

$$\ln k_Y = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_Y} \right) \quad (6)$$

In an ideal mixture of two isotopes, knowing both distribution coefficients as functions of the temperature T is sufficient to calculate the concentrations of the two isotopes in the equilibrium state and thus the phase diagram of the binary system. Neglecting the presence of other isotopes and setting the sum of the concentrations of the two isotopes in each phase to 1, we find:

$$k_Y = \frac{x_{YS}}{x_{YL}} = \frac{1 - x_{ZS}}{1 - x_{ZL}} \quad (7)$$

Then, employing Eq. (1) and eliminating x_{ZS} gives x_{ZL} as an implicit function of the temperature T :

$$x_{\text{ZL}} = \frac{1 - k_{\text{Y}}}{k_{\text{Z}} - k_{\text{Y}}} \quad (8)$$

and thus, using Eq. (1) again:

$$x_{\text{ZS}} = k_{\text{Z}} \frac{1 - k_{\text{Y}}}{k_{\text{Z}} - k_{\text{Y}}} \quad (9)$$

Fig. 6 shows the computed neon phase diagram, as well as an enlarged portion near the ‘natural’ composition. We have used the values $T_{\text{tp}}(^{20}\text{Ne}) = 24.54230 \text{ K}$, $\Delta H_{\text{f}}(^{20}\text{Ne}) = 331.5 \text{ J}\cdot\text{mol}^{-1}$, $T_{\text{tp}}(^{22}\text{Ne}) = 24.68889 \text{ K}$, and $\Delta H_{\text{f}}(^{22}\text{Ne}) = 333.6 \text{ J}\cdot\text{mol}^{-1}$. The temperatures are our own estimates, and the heats of fusion are from Clusius *et al.* [16].

The first derivative of Eq. (8) with respect to the temperature gives (the inverse of) the sensitivity coefficient of the isotope in solution. In the vicinity of the ‘natural’ neon composition (i.e. 9.25% ^{22}Ne), the ideal-solution model predicts a liquidus slope of 0.1472 K for ^{22}Ne , which is only slightly different from the linear value of 0.1466 K derived from the triple-point temperatures of the (assumed) pure isotopes. If we assume the sensitivity coefficient of ^{21}Ne to be half that of ^{22}Ne (and thus model neon with 9.25%+0.27%/2 ^{22}Ne and 0% ^{21}Ne), the phase diagram predicts the melting temperature of ‘natural’ neon to be about 24.566123 K. Considering that the functions $x(T)$ take only the two experimental values for the triple-point temperatures of ^{20}Ne and ^{22}Ne into consideration, but are not fitted to the ITS-90 value, the very small difference of 23 μK with respect to the ITS-90 value shows consistency amongst the two measured triple-point temperatures and indicates the adequacy of the ideal-solution model.

The sensitivity coefficient of ^{22}Ne in pure ^{20}Ne has been estimated to be about 0.1474 K, the one for ^{20}Ne in pure ^{22}Ne to be -0.1458 K. Considering the uncertainties of 41 μK for each of the triple-point temperatures, the uncertainty of the sensitivity coefficients

is less than 10^{-4} K (equivalent to less than 0.1%). The distribution coefficient of ^{22}Ne is about 1.009 in 'natural' neon, and 1.010 in pure ^{20}Ne . These values are extremely close to 1, so isotopic fractionation is rather faint; but due to the relatively large concentration of the minor isotope ^{22}Ne of 'natural' neon (second to no other fixed point in the temperature range of the ITS-90 below 0 °C) isotopic fractionation can still have a considerable influence on the phase-transition temperature curves. The difference in temperature between the liquidus and solidus at a given concentration in the diagram suggests a melting range of the order of 100 μK .

5. Modelling of a Neon Fixed Point

Using the phase diagram of the two dominant neon isotopes, phase-transition temperature curves of natural neon can be modeled with sufficient accuracy, favoured by the low uncertainty of the values of the equilibrium distribution coefficient (at least 4 digits can be assumed to be reliable).

In order to calculate the effect of the presence of isotopes, both the isotopic composition at the phase boundary and its specific influence are to be considered. The latter, the specific influence of the isotope concentration on the temperature, is already given implicitly by $x_{\text{ZL}}(T)$ (Eq. (8)). A model of the former relies on assumptions about the distribution and redistribution of the isotopes in the fixed-point sample, resulting in a function that predicts the concentration for a given melted fraction, e.g. $x_{\text{ZL}}(F)$.

One distribution model to consider is that for thermodynamic equilibrium during the full phase transition. The distribution of the minor isotope is given by Eq. (1) and the principle of mass conservation:

$$x_{\text{ZL}}F + x_{\text{ZS}}(1 - F) = x_{\text{ZL}}F + kx_{\text{ZL}}(1 - F) = x_{\text{Z0}} \quad (10)$$

where x_{Z0} is the overall concentration of the isotope. Hence:

$$F(x_{\text{ZL}}) = \frac{\frac{x_{\text{Z0}}}{1 - k_{\text{Z}}} - k_{\text{Z}}}{1 - k_{\text{Z}}} \quad (11)$$

Using this and Eq. (8) gives the function $F(T)$ drawn as curve A in Fig. 7. An explicit solution in the form $T(F)$ is much less elegant and not necessary for our purposes. We have used the same values as mentioned previously and $x_{\text{Z0}} = 9.25\% + 0.27\% / 2$. (Again, we assume an ideal mixture of ^{22}Ne and ^{20}Ne , and account for the presence of ^{21}Ne in natural neon by adding half its amount to the concentration of ^{22}Ne .) The melting range in this case is about 120 μK .

Thermodynamic equilibrium is never achieved in a real fixed-point; instead, a quasi-static state is more realistic. Particularly in the solid phase, inhomogeneities are almost stable as diffusion is very slow. So, when melting an inhomogeneous sample sufficiently slowly, regions with less ^{22}Ne melt first, regions with more ^{22}Ne later. In this way, a quasi-static melting curve is similar to the quasi-static version (i.e. without thermal effects) of the preceding freeze. The relevant isotopic distribution can be modeled using the Gulliver-Scheil equation [17]. The model assumes a homogeneous liquid phase (due to convection and diffusion) and neglects diffusion in the solid phase. Then, the impurity/isotope distribution is given by:

$$x_{\text{ZL}} = x_{\text{Z0}} \cdot F^{k_{\text{Z}} - 1} \quad (12)$$

In order to derive a function $T(F)$, $x_{\text{ZL}}(T)$ needs to be transformed to a function of the form $T(x_{\text{ZL}})$. Circular dependencies (because the concentration x given by the distribution model depends not only on F but also on k which itself depends on T) make an exact solution of the form $T(F)$ overly complex. The implicit solution $F(T)$ can be derived using Eq. (12) in the form:

$$F = \left(\frac{x_{\text{ZL}}(T)}{x_{\text{Z0}}} \right)^{\frac{1}{k_{\text{Z}}(T) - 1}} \quad (15)$$

where $x_{\text{ZL}}(T)$ is given by Eq. (8). Using the same values as before, the temperature curve is shown as curve B in Fig. 7. Close to the liquidus point, the two models show similar behaviour, but they differ significantly for smaller F values, i.e. at the beginning of a melt and at the end of a freeze respectively. The melting range given by the Gulliver-Scheil model is almost 300 μK for an F interval from 10% to 90%.

For comparison purposes, Fig. 7 also shows measured temperature curves of real neon fixed points. Curve F is a melt obtained with a ‘natural’ neon cell at NRC. It seems that waiting times of 0.5 h to 2 h are insufficient to approach equilibrium in this case. Particularly at large F values, the temperatures differ from the modelled behaviour but instead are very close to the liquidus temperature. This is probably the result of minimal isotopic fractionation during the recalescence of the preceding freeze.

The curves C, D and E have been taken from [11]. Each of their data points represents the extrapolation of the temperature over an extensive waiting time of 10 h and more. Although the measurements were taken after differently prepared freezes, the curves lie very close to each other (for details, please refer to [11]). Comparison with the modelling results reveals that the long relaxation times permit a more ideal behaviour.

6. Conclusion

We find that the triple points of ^{20}Ne and ^{22}Ne differ by 146.59 mK. Assuming that our reference sample of ‘natural’ neon realizes the ideal ITS-90 temperature of 24.5561 K, the triple point of ^{20}Ne is 24.54230 K (13.80 mK below the triple point of ‘natural’ neon) and that of ^{22}Ne is 24.68889 K (132.79 mK above the triple point of ‘natural’ neon).

Based on these measurements and the very reasonable assumption that ^{20}Ne and ^{22}Ne form an ideal solution, we recommend an isotopic sensitivity coefficient of 0.1472 K for ^{22}Ne in ‘natural’ neon. The sensitivity coefficient of ^{22}Ne in pure ^{20}Ne is only slightly larger: 0.1474 K.

We conclude that adequate data exists to correct for the effect of isotopic variations in ‘natural’ neon with sufficient precision. There seems no need to derive the slope empirically by comparing samples of slightly differing compositions near the natural value, as the results presented here are believed to be more reliable. Little more remains than to agree on a reference composition in order to resolve the isotopic ambiguity of the ITS-90 definition. However, practical implementation will require adequate chemical metrology.

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Table 1. Characteristics of the neon isotopic samples investigated. The values for the Sigma-Aldrich ^{20}Ne sample are from the certificate of analysis supplied with the cylinder. The values for the Spectra Gases ^{20}Ne sample were contained within an e-mail received from the supplier, but a certificate of analysis was not supplied with the sample. The Spectra Gases ^{22}Ne sample has two sets of results: the one on the right was included in the same e-mail message as the ^{20}Ne data; the one on the left is from an independent third-party (Atlantic Analytical Laboratory) and was delivered with the gas sample.

Sample Information	^{20}Ne	^{20}Ne	^{22}Ne	
Supplier	Sigma-Aldrich	Spectra Gases	Spectra Gases	
NRC Sealed Cell #	Cu-M-12	Cu-M-11	Cu-M-10	
Mass Spectrometry (ppm v/v)				
Nitrogen	2	<(2 to 8)	nd (<2)	<2
Oxygen	<1	<(1 to 7)	nd (<2)	<1
Argon	<1	–	nd (<2)	–
Carbon Dioxide	2	<0.1	nd (<2)	<0.1
Hydrogen	–	<140	nd (<5)	<0.1
Krypton	–	–	nd (<5)	–
Carbon Monoxide	<1	<0.1	nd (<2)	<0.1
THC ($\text{CH}_4 + \text{C}_2\text{H}_6$)	2	–	–	–
Water	–	<1	–	<1
Helium	–	<150	nd (<5)	<7
Helium-3	–	–	nd (<5)	–
Neon-20	>99.99 atom%	>99.9%	0.094%	–
Neon-21	<0.01 atom%	–	0.025%	–
Neon-22	<0.01 atom%	–	>99.8%	>99.9%

Table 2. The CSPRTs used to determine the neon triple-point temperatures.

Manufacturer	Serial Number
Hart Scientific	HS113
Hart Scientific	HS114
Leeds and Northrup	1158066
Leeds and Northrup	1872182
Leeds and Northrup	1876687
Tinsley	213865

Table 3. Cell Cu-M-10 was filled with the ^{22}Ne supplied by Spectra Gases. The CSPRT temperature differences (in mK) are tabulated with respect to the Praxair research-grade neon contained within cell Cu-M-1. Bold values indicate our estimate of the temperature difference between this cell and cell Cu-M-1 and the standard deviation of this difference.

Cu-M-10	213865	1872182	HS114	1876687	HS113	1158066	Average	Std Dev
2009/08/19	132.71	132.58	132.57	132.66	132.67	132.62	132.64	0.057
2009/08/21	132.71	132.55	132.57	132.66	132.64	132.59	132.62	0.062
2009/09/14	132.74	132.60	–	132.64	–	132.61	132.65	0.067
Average	132.72	132.57	132.57	132.66	132.65	132.61	132.63	0.014
Std Dev	0.017	0.026	0.004	0.012	0.019	0.014		

Table 4. Cell Cu-M-11 was filled with the ^{20}Ne supplied by Spectra Gases. The CSPRT temperature differences (in mK) are tabulated with respect to the Praxair research-grade neon contained within cell Cu-M-1. Bold values indicate our estimate of the temperature difference between this cell and cell Cu-M-1 and the standard deviation of this difference.

Cu-M-11	213865	1872182	HS114	1876687	HS113	1158066	Average	Std Dev
2009/11/06	-13.45	-13.59	-13.55	-13.59	-13.55	-13.56	-13.55	0.051
2009/11/26	-13.45	-13.60	-13.55	-13.60	-13.54	-13.54	-13.55	0.056
2009/12/01	-13.47	-13.64	-13.57	-13.61	-13.51	-13.54	-13.56	0.063
Average	-13.46	-13.61	-13.55	-13.60	-13.53	-13.55	-13.55	0.006
Std Dev	0.011	0.026	0.011	0.012	0.021	0.010		

Table 5. Cell Cu-M-12 with the ^{20}Ne from Sigma-Aldrich (i.e. ISOTEC). The CSPRT temperature differences (in mK) are tabulated with respect to the Praxair research-grade neon contained within cell Cu-M-1. Bold values indicate our estimate of the temperature difference between this cell and cell Cu-M-1 and the standard deviation of this difference.

Cu-M-12	213865	1872182	HS114	1876687	HS113	1158066	Average	Std Dev
2009/12/14	-13.75	-13.86	-13.86	-13.81	-13.81	-13.81	-13.82	0.044
2009/12/15	-13.72	-13.82	-13.86	-13.77	-13.77	-13.81	-13.79	0.048
2009/12/16	-13.75	-13.84	-13.83	-13.79	-13.79	-13.78	-13.80	0.036
2009/12/17	-13.73	-13.85	-13.86	-13.77	-13.83	-13.84	-13.81	0.052
Average	-13.74	-13.84	-13.85	-13.79	-13.80	-13.81	-13.80	0.011
Std Dev	0.013	0.018	0.012	0.020	0.023	0.023		

Table 6. Estimates of the triple points of ^{20}Ne and ^{22}Ne from the literature. With the exception of the CCT Working Group 2 assessment, the temperatures are on IPTS-68.

Authors	Year	$T_{\text{tp}} (^{\text{nat}}\text{Ne})$ (K)	$T_{\text{tp}} (^{20}\text{Ne})$ (K)	$T_{\text{tp}} (^{22}\text{Ne})$ (K)
G.T. Furukawa	1972	24.553	24.540	24.687
R.C. Kemp, W.R.G. Kemp	1981	–	24.5457	–
R.C. Kemp, H. Sakurai	1986	24.5570	24.5394	–
H. Sakurai	1986	24.5612	24.5474	–
CCT WG2 (ITS-90)	1996	–	24.541	–

Table 7. The uncertainty budget for the neon-isotope triple-point temperatures.

	Spectra	Spectra	Sigma-
	Gases	Gases	Aldrich
Uncertainty components, Type B	²²Ne	²⁰Ne	²⁰Ne
	(μK)	(μK)	(μK)
Chemical impurities	16	64	16
Isotopic composition	15	15	15
Determination of fixed-point value	19	19	19
Hydrostatic pressure	1.5	1.5	1.5
Heat flux	10	10	10
CSPRT self-heating correction	10	10	10
Accuracy of resistance bridge ratio	13	13	13
Standard resistor	2	2	2
Uncertainty propagated from the TPW	0.8	0.8	0.8
Uncertainty components, Type A			
Repeatability (melt-to-melt)	14	6	11
CSPRT stability	16	15	18
Combined standard uncertainty	41	73	41

FIGURE CAPTIONS

Fig. 1. Drawing of the sealed cell. The cell is fabricated from copper with the exception of a stainless-steel sleeve for additional strength.

Fig. 2. A representative melting curve for the Spectra Gases ^{22}Ne sample using 0.2 J pulses.

Fig. 3. Representative melting curves for the Spectra Gases ^{20}Ne sample using 0.4 J pulses.

Fig. 4. A representative melting curve for the Sigma-Aldrich (ISOTEC) ^{20}Ne sample using 0.4 J pulses.

Fig. 5. The sensitivity of the measured triple-point temperature to changes in the shield setting.

Fig. 6. The phase diagram of the two neon isotopes ^{20}Ne and ^{22}Ne assuming an ideal solution with almost coincident liquidus and solidus lines. To the right, an enlarged section near the 'natural' composition of neon is shown. The difference in temperature between the liquidus and solidus for a given concentration suggests a melting range of order 100 μK and the likelihood of isotopic fractionation during freezing.

Fig. 7. Modelled temperature curves for the phase transition of neon of 'natural' isotopic composition together with actual measurements of neon fixed points. A - modelling of thermodynamic equilibrium, B - Scheil model, C - melt after slow freeze, taken from [11], D - melt after slow refreeze, taken from [11], E - melt after fast freeze, taken from [11], F - measurement at NRC with shorter waiting times than for curves C, D and E.

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