

## Isotopic Effects in the Neon Fixed Point

Peter P.M. Steur<sup>1</sup>, Franco Pavese<sup>1</sup>, Bernd Fellmuth<sup>2</sup>, Yves Hermier<sup>3</sup>, Kenneth D. Hill<sup>4</sup>, Jin Seog Kim<sup>5</sup>, Leszek Lipinski<sup>6</sup>, Keisuke Nagao<sup>7</sup>, Tohru Nakano<sup>8</sup>, Andrea Peruzzi<sup>9</sup>, Fernando Sparasci<sup>3</sup>, Anna Szmyrka-Grzebyk<sup>6</sup>, Osamu Tamura<sup>8</sup>, Weston L. Tew<sup>10</sup>, Staf Valkiers<sup>11</sup> and Jan van Geel<sup>9</sup>

<sup>1</sup> *Istituto Nazionale di Ricerca Metrologica (INRIM), Torino, Italy*

<sup>2</sup> *Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany*

<sup>3</sup> *Laboratoire Commun de Métrologie LNE-CNAM (LCM), La Plaine Saint-Denis, France*

<sup>4</sup> *National Research Council (NRC), Ottawa, Canada*

<sup>5</sup> *Korean Research Institute of Standards (KRISS), Yusong, Daejeon, Korea*

<sup>6</sup> *Instytut Niskich Temperatur i Badan Strukturalnych (INTiBS), Wroclaw, Poland*

<sup>7</sup> *Geochemical Research Center, Graduate School of Science, University of Tokyo, Tokyo, Japan*

<sup>8</sup> *National Metrology Institute of Japan (NMIJ), AIST, Tsukuba, Japan*

<sup>9</sup> *Van Swinden Laboratorium (VSL), Leiden, The Netherlands*

<sup>10</sup> *National Institute of Standards and Technology (NIST), Gaithersburg, USA*

<sup>11</sup> *Institute of Reference Materials and Measurements (IRMM), EU-JRC, Geel, Belgium*

### Background

Similarly to the hydrogen fixed points [Fellmuth et al. (2005), Steur et al. (2005)], also the neon fixed point is affected by isotopic effects [Pavese et al. (2005)]. The isotopic composition of commercially available neon varies from an amount-of-substance ratio of about  $^{22}x = 0.0915$  moles  $^{22}\text{Ne}$  per mole Ne to about  $^{22}x = 0.0948$  moles  $^{22}\text{Ne}$  per mole Ne. It has been established [Pavese et al (2008a), Pavese et al (2008b)] that the discrepancies previously found at the triple point are mainly due to the variable  $^{22}\text{Ne}$  amount fraction in the neon used for its realization. Also the  $^{21}\text{Ne}$  amount fraction in the neon was found to vary, but its effect on the triple point temperature of neon can be estimated to be  $< 10(5) \mu\text{K}$ .

When the issue was raised in 2005, an international collaboration was set up in order to address this matter. Unexpected difficulties regarding isotopic analyses and the use of only ‘natural’ neon samples were shown to limit the obtainable uncertainties severely, even with state-of-the-art thermometry [Pavese et al (2010a)]. Recurrence was therefore made to samples of isotopically pure  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  with the intent to improve the old literature values for the difference ( $^{22}T_{\text{tp}} - ^{20}T_{\text{tp}}$ ) available at the time. Results on  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  were published shortly after [Pavese et al. (2010b) (2011), Hill and Fahr (2011)], with values for the temperature difference in good agreement. The latter publication presented also a theoretical model of the Neon phase diagram, showing the *liquidus* and *solidus* curves to have a quadratic dependence on  $^{22}x$  instead of the linear one assumed previously on the basis of  $^{20}T$  and  $^{22}T$  only [Tew 2011]. In an ultimate effort to confirm this behaviour, measurements have been performed on especially prepared gravimetrically-certified mixtures for three different values of  $^{22}x$  (0.062 088(20), 0.091 678(22) and 0.166 025(26)). The results of the latter demonstrate the validity of the theoretical model to within the experimental uncertainty [Steur et al. (2012)]. An overview of the work performed by the collaboration was presented recently [Pavese et al (2012)].

### Correction equation

An important result of the international collaboration was that, following demonstrated consistency with experiment, the theoretical calculations for the ideal isotopic ternary mixture was taken as the basis for all the correction equations. Based on this work, two equations were produced both taking as a reference the IUPAC (International Union of Pure and Applied Chemistry) isotopic composition [Wieser and Coplen (2011)] with  $T = T_{90}(\text{Ne})$ , but using different approaches for incorporating the (small) effect of  $^{21}\text{Ne}$ , while preserving the option of using pure  $^{20}\text{Ne}$ , for its superior thermometric quality. The differences between the equations amount to  $(4 \pm 2) \mu\text{K}$  for the range of measured ‘natural’ neon samples. The procedure for arriving at the equations is shortly summarized here, based on the paper presented at the 9<sup>th</sup> Symposium *Temperature, Its Measurement and Control in Science and Industry* [Pavese et al. (2012)]. For approach A, the non-linear equations for the binary mixture of  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  were solved (ideal-solution model). Then, an approximating quadratic polynomial was fitted to the data. For approach B, the quadratic polynomial was obtained by first defining the values of three points (the  $^{20}\text{Ne}$  temperature, the reference point and a point calculated theoretically in the binary ideal mixture of  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$ ) and then fitting these with a quadratic polynomial.

Both approaches refer to the *liquidus* curve for  $^{20}\text{Ne} - ^{22}\text{Ne}$  mixtures, based on the average of the ( $^{22}T - ^{20}T$ ) values published by INRIM [Pavese et al. (2011)] and NRC [Hill and Fahr (2011)].

Approach A assumes  $^{21}\text{Ne}$  to have a fixed effect in temperature, corresponding exactly to half the effect of  $^{22}\text{Ne}$ , based on the fact that its triple point temperature is halfway between  $^{20}T$  and  $^{22}T$  within the uncertainty of present knowledge (a few millikelvin), and thus using  $(^{22}x + ^{21}x/2)$  instead of  $^{22}x$  in the binary  $^{20}\text{Ne}$ - $^{22}\text{Ne}$  relationship passing through the IUPAC isotopic composition for  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$ .

Approach B considers instead the ternary mixture  $^{20}\text{Ne} - ^{21}\text{Ne} - ^{22}\text{Ne}$  making use of a *liquidus* curve on that surface exhibiting a constant ratio  $^{21}\text{Ne} / ^{22}\text{Ne}$  passing through the IUPAC isotopic composition. Any curve with constant ratio  $^{21}\text{Ne} / ^{22}\text{Ne}$  starts from the surface corner for pure  $^{20}\text{Ne}$  and, starting from the binary  $^{20}\text{Ne} - ^{22}\text{Ne}$  mixture for  $^{21}x = 0$ , rotates toward the  $^{21}\text{Ne}$ -rich side of the ternary surface for increasing  $^{21}\text{Ne} / ^{22}\text{Ne}$  ratios. The curve passing through the  $^{20}\text{Ne}$  corner and the IUPAC composition [ $^{21}x = 0.0027(1)$  and  $^{22}x = 0.0925(2)$ ] is used here, maintaining a constant ratio  $^{21}x / ^{22}x = (^{21}x / ^{22}x)_{\text{IUPAC}} = 0.029\,1892$ , closely approximating the ‘natural’ composition samples in the whole known composition range.

Both equations use

$$T_{\text{meas}} = {}^{\text{Ne}}T_{90} - \Delta T_{\text{ref}} + \Delta T(x),$$

where  ${}^{\text{Ne}}T_{90} = 24.5561$  K exactly and  $\Delta T(x)$ , expressed as the increase in temperature with respect to the measured value of  $^{20}T$ , differs for approach A or B.  $\Delta T_{\text{ref}} = T_{\text{IUPAC}} - ^{20}T = 0.013\,82(3)$  K, based on the measured values  $^{20}T_{90} = 24.542\,28$  K and  $^{22}T_{90} = 24.688\,85$  K. The dependence  $\Delta T(x)$ , see below, follows directly from the requirement that, with both approaches, the ITS-90 value is assigned to the IUPAC composition, i.e.  $T_{\text{IUPAC}} = {}^{\text{Ne}}T_{90} = 24.5561$  K. The uncertainty in  $\Delta T_{\text{ref}}$  derives directly from the uncertainty in  $^{20}T$  and  $^{22}T$ , see later on [see Pavese et al. (2010b)].

Equation A (approach A, pseudo-binary):

$$\Delta T(x) / \text{K} = \Delta T(^{21}x; ^{22}x) / \text{K} = 0.147\,349\,815 (^{22}x + ^{21}x/2) - 0.000\,778\,511 (^{22}x + ^{21}x/2)^2,$$

Equation B (approach B, ternary):

$$\Delta T(x) / \text{K} = \Delta T(^{21}x, ^{22}x) / \text{K} = 0.149\,4188 \cdot ^{22}x - 0.000\,1448 \cdot ^{22}x^2$$

(where the dependence on  $^{21}x$  is hidden because  $^{21}x / ^{22}x = (^{21}x / ^{22}x)_{\text{IUPAC}} = \text{const}$ ).

(Due to the rather different assumptions on which the two approaches are based, the additional assumption  $^{21}x / ^{22}x = (^{21}x / ^{22}x)_{\text{IUPAC}}$  does not yield the same coefficients in Equation A as in Equation B.) Both equations are valid in the range of ‘natural’ isotopic neon compositions. For pure  $^{20}\text{Ne}$ ,  $\Delta T(^{21}x, ^{22}x) = 0$ .

Since Equation A refers explicitly to both  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$ , and considering the excellent agreement between the two approaches, *in the following Equation A is the preferred suggestion for the correction equation.*

## Uncertainties<sup>1</sup>:

The correction method used for neon is different from that used for hydrogen for two reasons: (a) the ‘natural’ mixture is ternary instead of binary; (b) the measurement of ‘natural’ samples only does not allow obtaining a correction equation with sufficiently low uncertainty.

The method eventually chosen makes use of theoretical calculations (see [Hill and Fahr (2011), Tew 2010]), experimentally verified, and the equation is selected to obtain, as for hydrogen, a zero correction of a reference (ternary) composition, matching the measured values for samples of ‘natural’ composition.

This complicates the uncertainty evaluation of the correction. One aspect is the overall reliability in the equations expressed in temperature, with *components (i)-(iii)*, and the other is the *uncertainty in the slope (iv)* necessary to arrive at the uncertainty in the correction as applied by the user (not to be confused with the uncertainty in the realization of the fixed point):

- (i) the uncertainty associated with the theoretical calculations;
  - (ii) the degree of agreement between the above calculations and the experimental verification;
  - (iii) agreement of the selected correction equation with the correction, which may be expected considering the observed isotopic compositions of the 18 samples of ‘natural’ composition,
- and
- (iv) the resulting uncertainty contribution of the slope.

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<sup>1</sup> All uncertainties  $u$  are given for  $k = 1$ .

### (i) Evaluation of the uncertainty associated with the theoretical calculations

Basically two parameters enter the model, whose uncertainty propagates contributing to the *uncertainty* of the model. They are the enthalpy of fusion  $H_f$  for both isotopes and the difference  $^{22}T - ^{20}T$ . The value of  $H_f$  is taken from [Clusius 1960]. The absolute values reported by Clusius may be off by about 1% (which would result in a change in the (quadratic) liquidus curve by as much as 366  $\mu\text{K}$  at  $x = 0.5$ , and 131  $\mu\text{K}$  at  $x = 0.1$ ), but it is more likely that Clusius got the difference right (see below the accordance with the experimental verification). A 1% change in  $H_f$  for both isotopes (leaving the difference  $\Delta H_f$  unchanged) results in a difference of only 2  $\mu\text{K}$ . But also the statistical uncertainties in his data have to be taken into account, with a standard deviation of the mean of 0.062 cal/mol, in original units, (0.26 J/mol) on 79.204 cal/mol (331.39 J/mol) for  $^{20}\text{Ne}$  and 0.135 cal/mol (0.565 J/mol) on 79.74 cal/mol (333.6 J/mol) for  $^{22}\text{Ne}$ . These correspond to percentages of 0.08 and 0.17 for  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$ , respectively. Thus, the resulting uncertainty at  $x = 0.1$  becomes  $((0.08)^2 + (0.17)^2)^{0.5} \times 131 \mu\text{K} = 25 \mu\text{K}$ .

For the influence of the difference  $^{22}T - ^{20}T$ , the effect of a change in each of these temperatures turns out to be linear, as expected. A change of 30  $\mu\text{K}$  in  $^{22}T$  has an effect, at  $^{22}x = x_{\text{IUPAC}} = 0.0925$ , of only 3  $\mu\text{K}$ , and the same change in  $^{20}T$  (much closer) has an effect, at  $^{22}x = x_{\text{IUPAC}}$ , of 27  $\mu\text{K}$ . What actually enters in the model is the difference  $^{22}T - ^{20}T$ , and both temperatures are usually correlated, but the value of 27  $\mu\text{K}$  can be taken as the worst case. We compare its effect with the level of agreement with experiment, 11.1  $\mu\text{K}$  (see item (ii)). This agreement covers also how well the model approximates reality (such as effects of possible non-ideal behaviour of the neon mixture, the fitting residuals between the binary model and the approximating quadratic polynomial), and how well the pseudo-binary approach accounts for the influence of  $^{21}\text{Ne}$ . Thus, the overall estimate from all effects, due to the used model, becomes 38  $\mu\text{K}$  (see Table with uncertainty budget below).

### (ii) Evaluation of the degree of agreement between calculations and experiment

The model may be imperfect or incomplete if some of the assumptions for its derivation do not apply, or if other influencing parameters are ignored (e.g. non-ideality of the mixture). Therefore, an experimental verification was performed.

The uncertainty associated with each of the three points on the experimental *liquidus* line as  $\delta T = T_{\text{mixture}} - T_x$ , where  $T_x$  is the value for the same  $^{22}x$  on the line connecting  $^{20}T$  and  $^{22}T$ , is  $u = 40\text{--}43 \mu\text{K}$ , while correcting individually the measurements for the isotopic ( $^{21}x$ ) and chemical ( $\text{N}_2$ ,  $\text{H}_2$ ) impurities. Considering that this correction is not significantly different from mixture to mixture, one can use the average value, 41  $\mu\text{K}$ . The uncertainty in  $^{20}T$  and  $^{22}T$  is 30  $\mu\text{K}$ .

(ii1)

The experimental verification with three certified artificial isotopic *binary* mixtures of  $^{22}\text{Ne}$  in  $^{20}\text{Ne}$  allowed to fit a quadratic *liquidus* line through five points, including the two points for  $^{22}x = 0$  and 1, where  $\delta T$  was constrained to zero at both  $^{20}T$  and  $^{22}T$ . The uncertainty values being rather similar, we fitted the data points ignoring their individual differences and taking an average value. This *quadratic* fit of  $\delta T / \mu\text{K}$  yields a standard deviation of fit of 11.1  $\mu\text{K}$ , obviously a zero intercept and equal coefficients 827.5  $\mu\text{K}$  for the linear and quadratic terms (of opposite sign), with an uncertainty in each of 38  $\mu\text{K}$ . The value of 11.1  $\mu\text{K}$  is a measure of the consistency between the gravimetrically-prepared mixtures and the anticipated (quadratic) form of the equation. The fit and its associated uncertainty check only the binary  $^{20}\text{Ne}$ - $^{22}\text{Ne}$  model, without taking into account the effect of  $^{21}\text{Ne}$ . This latter effect was explicitly taken into account by approach A and approach B, leading to the two different equations. Given the small entity of the correction, an approximate value of the sensitivity coefficient (half the value for  $^{22}\text{Ne}$ ) was more than sufficient for this purpose. Correcting for the effect of  $^{21}\text{Ne}$  assuming  $^{21}x / ^{22}x = (^{21}x / ^{22}x)_{\text{IUPAC}} = \text{const}$ , Equation B deviates not more than 6  $\mu\text{K}$  from the quadratic fit function.

(ii2)

Another way of testing the consistency of the experiments with the ITS-90 value assigned to the IUPAC composition as the reference point, is fitting directly the assigned ITS-90 temperatures of the pure isotopes (24.542 28 K and 24.688 85 K) plus the reference (IUPAC) point (24.5561 K) to an exact quadratic polynomial, and comparing the agreement of the function so obtained with the values obtained for the three mixtures, where the reference point was corrected for the  $^{21}\text{Ne}$  content. Differences of 11.2 – 11.9 – 3.8  $\mu\text{K}$  were found for the mixtures with  $^{22}x = 0.062$ , 0.091 and 0.166, respectively, demonstrating the high level of overall consistency within the standard uncertainty  $u = 3.2 \mu\text{K}$ , considering the maximum difference and assuming a rectangular distribution. Without the correction of the reference point, Equation B deviates again not more than 6  $\mu\text{K}$  from the quadratic polynomial.

### (iii) Evaluation of the agreement of the selected correction equation with the correction, which may be expected considering the observed isotopic compositions of the samples of ‘natural’ composition

Both Equations A and B are approximations of the exact trend of the assumed model, and with respect to the

experimentally determined position of the samples of ‘natural’ neon. Thus, an uncertainty component has to be estimated, which may result from the fact that for the neon samples used, the concentration ratio  $^{21}\text{x} / ^{22}\text{x}$  is not constant and different from the IUPAC value.

On the *ternary-mixture liquidus* surface, the set of data for the observed variability of both  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  visually looks aligned on a segment of a  $^{21}\text{x} \approx \text{const}$  line bounded by the minimum and maximum observed values for  $^{22}\text{x}$ . This is due to the fact that the variability of  $^{21}\text{Ne}$  is very small in absolute values, being in fact bounded between 0.002 6464 and 0.002 6860 moles  $^{21}\text{Ne}$  per mole Ne, mean value 0.002 662(12) moles  $^{21}\text{Ne}$  per mole Ne; the average analytical uncertainty of the relevant isotopic assays is  $u = 0.27 \cdot 10^{-6}$  moles  $^{21}\text{Ne}$  per mole Ne, 4.4 times less the standard deviation of the dispersion in the values. This small variability of  $^{21}\text{Ne}$  in ‘natural’ neon can basically be considered irrelevant for the thermometric purposes, as the full range of the above observed variability corresponds to only 2.9  $\mu\text{K}$  ( $< 10(5)$   $\mu\text{K}$  for the full collection of historical data [Pavese et al. 2008a]).

Section (iii) of the uncertainty budget concerns the quality of the correction by Equation A within the concentration ranges of the measured samples of ‘natural’ composition. A direct verification of this quality is not possible due to the dependence on two concentrations. Therefore, this check has been performed through Equation B and the agreement between the two equations.

The line expressed by Equation B passes by definition through the reference IUPAC point at  $^{21}\text{x}_{\text{IUPAC}} = 0.0027$  moles  $^{21}\text{Ne}$  per mole Ne (with the IUPAC composition being basically at one bound of the observed variability segment – as in the case of water for the reference SLAP composition). The offset of the mean observed  $^{21}\text{x}$  ‘natural’ compositions, 0.002 662(12) moles  $^{21}\text{Ne}$  per mole Ne, with respect to the  $^{21}\text{x} = \text{const} = 0.0027$  moles  $^{21}\text{Ne}$  per mole Ne line corresponds to  $-3.9$   $\mu\text{K}$  maximum, and at the reference IUPAC point Equation B differs by the equivalent of  $-2.5$   $\mu\text{K}$ . For higher  $^{22}\text{x}$  values, it diverges having a higher slope on the ternary surface. However, the maximum deviation of Equation B with respect to the  $^{21}\text{x} = 0.0027$  moles  $^{21}\text{Ne}$  per mole Ne line at the opposite bound of the range of  $^{22}\text{Ne}$  in ‘natural’ neon variability is only 11  $\mu\text{K}$ , with  $u = 3$   $\mu\text{K}$  assuming a rectangular distribution. This difference, which represents the degree of approximation by Equation B, is caused by the requirement for Equation B to pass also through pure  $^{20}\text{Ne}$ , i.e. to be a  $^{21}\text{x}/^{22}\text{x} = \text{const}$  line.

In conclusion, for Equation B the uncertainty associated with corrections for the actual ‘natural’ compositions can be assumed to be equal to the uncertainty associated with the maximum difference with respect to Equation B at the bound of the composition range opposite to the IUPAC composition, estimated to be  $u_{\text{ii,B}} = 3$   $\mu\text{K}$ .

Finally, for Equation A, the same evaluation can now be performed indirectly, as the difference with respect to Equation B for the range of the isotopic compositions of the same 18 measured samples amounts to  $u_{\text{BA}} = 4$   $\mu\text{K}$ , which, summed in quadrature with the uncertainty above, of 3  $\mu\text{K}$ , yields a total of  $u_{\text{iii}} = 5$   $\mu\text{K}$ .

(Note: The standard deviation of the differences with respect to Equation B of the 18 measured ‘natural’ samples was 36  $\mu\text{K}$ , determined by the large uncertainty associated with the experimental thermal measurements on these samples, with  $u = (50\text{--}200)$   $\mu\text{K}$ . However, this component *does not enter in the uncertainty budget* for the correction equation, since the experimental values obtained from the ‘natural’ samples were *not* used in the derivation of either Equation. For this document, only the spread of the concentration values measured for these samples is of interest. The concentration values obtained do not fulfil the relation  $^{21}\text{x}/^{22}\text{x} = \text{const}$  completely.)

#### Summarizing table for items (i) – (iii):

Uncertainty source (items <i>in italics</i> are not relevant for the correction uncertainty)	$u$ ( $k=1$ ) / $\mu\text{K}$
<b>Item (i)</b>	
Enthalpy values	25
Pure isotope temperatures	27
Uncovered imperfections of the model (e.g. reciprocal solubility of the isotopes)	11.1
<b>Combined uncertainty of the theoretical model</b>	<b>38</b>
<b>Item (ii)</b>	
<i>Uncertainty associated with each of the three mixture points</i>	41
<i>Uncertainty in the pure isotope points</i>	30
Consistency of experimental points with three $T_{90}$ points (ii2)	3
Uncertainty of fit through the five experimental points $T$ values (ii1)	11.1
Effect of fit coefficients uncertainty near $x_{\text{IUPAC}}$ (ii1) slope	0.1
Consistency between the experimental points and the polynomial fitted to the ITS-90 value with the IUPAC composition, $^{20}T_{90}$ and $^{22}T_{90}$ (ii2)	3.2
<b>Combined uncertainty of the experimental verification of the theoretical model and the degree of consistency with ITS-90</b>	<b>11,5</b>

<b>Item (iii)</b>	
<i>Uncertainty of the experimental <math>T_{\text{Liquidus}}</math> values of the ‘natural’ neon samples</i>	50-200
<i>Agreement of the equations with measured temperature values of the ‘natural’ neon samples</i>	36
Agreement between Equation B and the observed isotopic composition of ‘natural’ neon samples	3
Agreement between equations A and B	4
<b>Combined uncertainty of the agreement of the selected correction equation with the correction, which may be expected considering the measured isotopic compositions of the samples of ‘natural’ neon</b>	<b>5</b>

<i>Uncertainty budget based on Equation A only (at <math>x_{\text{IUPAC}}</math>)</i>	<i><math>u</math> (<math>k=1</math>) / <math>\mu\text{K}</math></i>
Enthalpy values	25
Sensitivity to the pure isotope temperatures ( $u(T) = 30 \mu\text{K}$ )	27
Uncovered imperfections of the model (e.g. reciprocal solubility of the isotopes)	11.1
Influence of $^{21}\text{Ne}$ (agreement of Eq A with the curve at $^{21}x = \text{const}$ ) (from iii)	5
<b>Combined uncertainty</b>	<b>39</b>

When using ‘natural’ neon for realising the fixed point and the available assay uncertainty for  $^{22}\text{Ne}$  is  $10^{-4}$  mole  $^{22}\text{Ne}$  per mole Ne (0.1 % relative) or worse, the correction should not be applied. Instead, a fixed component should be added to the uncertainty budget,  $u_{\text{iso}} = 150 \mu\text{K}$ .

#### **(iv) Resulting uncertainty contribution of the slope**

The uncertainty to be associated with the correction of neon of ‘natural’ isotopic composition *is actually related only indirectly with the above components (i)-(iii)*, since the uncertainty in the correction is given (as in the hydrogen case) by two terms a) and b) to be summed in quadrature:

- a) (composition difference)  $\times$  (uncertainty in slope, in the range of ‘natural’ neon)
- b) (uncertainty in composition)  $\times$  (slope value, marginally  $^{22}x$  dependent)

In order to determine, from the model, the uncertainty in the slope, at  $x_{\text{IUPAC}}$ , due to the uncertainty in  $^{20}T$  and  $^{22}T$ , one calculates, from Equation A (with  $^{21}x = 0$ , a minor approximation), the values at  $^{22}x = 0$ ,  $^{22}x = x_{\text{IUPAC}}$  and  $^{22}x = 1$ , and the slope at  $x_{\text{IUPAC}}$  is computed. One then computes the slope at  $x_{\text{IUPAC}}$ , by recalculating the coefficients of the quadratic polynomial passing through the above three points, varying the value at  $^{22}x = 0$  with the uncertainty in  $^{20}T$ . This procedure is repeated also for  $^{22}x = 1$ . One then obtains a change in slope (at  $x_{\text{IUPAC}}$ ) of  $294.32 \mu\text{K}$  due to  $^{20}T$  and of  $3.06 \mu\text{K}$  due to  $^{22}T$ . These two contributions add up, in quadrature, to a total of  $294.34 \mu\text{K}$  for the uncertainty in the slope. A second contribution to the uncertainty of the slope comes from the values for the enthalpy of fusion. A variation in the heats of fusion of 0.08% and 0.17% (for  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$ , respectively) leads to a temperature difference of  $25 \mu\text{K}$ , whereas neon of IUPAC composition has an assigned triple point temperature of  $24.5561 \text{ K}$  and the estimated triple point temperature of  $^{20}\text{Ne}$  is  $24.54228 \text{ K}$ , so their difference amounts to  $13820 \mu\text{K}$ . Thus the relative change in the linear approximation of the slope is  $25/13820 = 0.18\%$ , which is equivalent to  $265 \mu\text{K}$ . Summation in quadrature of the two contributions then yields a total uncertainty in the slope of  $396 \mu\text{K}$ . Such a change of slope would amount to a temperature difference of  $1.4 \mu\text{K}$  only, over the whole range of ‘natural’ neon ( $^{22}x = 0.0915 - 0.0948$ ).

For the evaluation of item (b), a few (standard) uncertainty levels for analysis are given here: the recent ones given by KRISS (the older IRMM values were not far from these, and both are highly specialized laboratories) and the uncertainty level associated with a generic analysis laboratory. The maximum value given by KRISS, for the gravimetric mixtures is  $27 \mu\text{mol } ^{22}\text{Ne} / \text{mol Ne}$ . It is assumed that a generic laboratory may arrive at most at a value 10 times the previous values.

#### **Overall uncertainty evaluation of the effective correction**

Correction of ‘natural’ neon:

- for contribution (a), with a maximum value for the difference from the reference composition ( $\Delta^{22}x = 0.0023$ ),

- a value of  $0.0023 * 396 \mu\text{K} = 0.9 \mu\text{K}$  is obtained,
- for contribution (b), using the slope  $dT/dx$  at  $^{22}\text{x} = x_{\text{IUPAC}}$ , one arrives at a value for this item of  $0.147 20 * 0.000 027 = 4.0 \mu\text{K}$  in the case of KRISS and  $> 40 \mu\text{K}$  for a generic analysis.

Correction of pure  $^{20}\text{Ne}$ :

- The slope at  $^{21}\text{x} = 0$  and  $^{22}\text{x} = 0$  is given directly by the coefficient of the linear term of equation A, 0.147 35 K, while its uncertainty amounts to 207  $\mu\text{K}$ .
- For contribution (a), one thus obtains, using maximum  $^{21}\text{x}$  and  $^{22}\text{x}$  values found in the  $^{20}\text{Ne}$  samples, a value of  $207 * (0.001 530 + 0.000 550 / 2) \mu\text{K} = 0.4 \mu\text{K}$ .
- For contribution (b), with the given slope and the KRISS uncertainty for analysis, a value of  $0.147 35 * 0.000 027 \mu\text{K} = 4.0 \mu\text{K}$  is obtained (in this case the uncertainty of the analysis of the residual of  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  is expected to be similar also for a generic laboratory).

In table form:

	'Natural' Neon		$^{20}\text{Ne}$
	0.147 20 K		0.147 35 K
	@ $x_{\text{IUPAC}}$		
Slope uncertainty	396 $\mu\text{K}$		207 $\mu\text{K}$
Uncertainty components ( $k = 1$ )	Size / $\mu\text{K}$		Size / $\mu\text{K}$
Contribution (a)	0.9		0.4
Contribution (b)	4 - >40		4
<b>Total for the correction (rounded)</b>	4 - > 40		4 <sup>a)</sup>

<sup>a)</sup> This estimate is valid for the correction to pure  $^{20}\text{Ne}$ .

If the neon fixed point of the ITS-90 is realised via the triple point of  $^{20}\text{Ne}$ , the uncertainty of  $\Delta T_{\text{ref}}$  of 30  $\mu\text{K}$  has also to be considered.

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