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Estimating the Triple-Point Isotope Effect and the Corresponding Uncertainties for Cryogenic Fixed Points

W. L. Tew

Abstract The sensitivities of melting temperatures to isotopic variations in monatomic and diatomic atmospheric gases using both theoretical and semi-empirical methods are estimated. The current state of knowledge of the vapor-pressure isotope effects (VPIE) and triple-point isotope effects (TPIE) is briefly summarized for the noble gases (except He), and for selected diatomic molecules including oxygen. An approximate expression is derived to estimate the relative shift in the melting temperature with isotopic substitution. In general, the magnitude of the effects diminishes with increasing molecular mass and increasing temperature. Knowledge of the VPIE, molar volumes, and heat of fusion are sufficient to estimate the temperature shift or isotopic sensitivity coefficient via the derived expression. The usefulness of this approach is demonstrated in the estimation of isotopic sensitivities and uncertainties for triple points of xenon and molecular oxygen for which few documented estimates were previously available. The calculated sensitivities from this study are considerably higher than previous estimates for Xe, and lower than other estimates in the case of oxygen. In both these cases, the predicted sensitivities are small and the resulting variations in triple point temperatures due to mass fractionation effects are less than 20 μK.

Keywords Atmospheric gases · Isotopes · Mass fractionation · Noble gases · Oxygen · Temperature · Triple point · Vapor-pressure isotope effect · Xenon

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1 Introduction

Most of the atmospheric gases are now commercially available in chemical purities approaching 99.9999% or slightly better in some cases. As these gases are separated and purified, they undergo phase changes with the potential to mass fractionate the final gas product. Many of these commercially prepared gases are now used as fixed-point temperature standards for the International Temperature Scale of 1990 (ITS-90) [1] below 0°C. There has been a steady improvement in the reproducibility of the phase-transition temperatures as the available chemical purities of these gases have increased [2]. In the course of these technological and metrological advances, the need has arisen to estimate the components of uncertainty that account for isotopic variations in the gas samples used in triple-point realizations.

While isotopic variations in many elemental and molecular materials are well-documented [3], the effect of these variations on the thermometric triple-point realizations is only partially documented and some gaps in our knowledge currently exist. The physics of the vapor-pressure isotope effect (VPIE) has been understood since the successful theory of Bigeleisen [4]. In the case of the noble gases, a rather complete set of VPIE data are available for Ne, Ar, and Kr, while practically no data are available for Xe [5]. Similarly, full data sets are available for H_2 and N_2, but there are no reliable VPIE data on O_2 below 63 K. In contrast, the triple-point isotope effect (TPIE) is not well understood, and very few quantitative predictions are available. The use of the established VPIE theory, however, can provide insight and allow estimation of the TPIE sensitivity coefficients in some cases. When the VPIE theory is applied together with some simplifying assumptions regarding the effects of isotopic solutions, calculations of uncertainty estimates for isotopic variations in the gas-based fixed points are possible.

2 Vapor-Pressure and Triple-Point Isotope Effects

The qualitative features of the VPIE and TPIE are illustrated in Fig. 1. For the class of substances considered in this article, all exhibit the so-called "normal" VPIE where the vapor pressure of the lighter isotope is always greater than that of the heavier isotope at all temperatures in which a condensed phase exists [5]. In this case, two isotopes with atomic masses M and $M'(M > M')$, vapor pressures p and $p'(p < p')$, and triple points T_{tp} and T'_{tp} exhibit similar but shifted $p-T$ diagrams. In particular, the triple-point shift $\Delta T_{\mathrm{tp}} \equiv T_{\mathrm{tp}} - T'_{\mathrm{tp}}$ coincides with a discontinuity in the relative volatility, normally expressed as $\ln(p'/p)$, between the solid ('s') and liquid ('l') phases. Results of the VPIE theory have been combined with the Eyring liquid structure theory by Jeevanandam [6] to explain the magnitude of the discontinuity $\Delta \ln(p'/p) \equiv \ln(p'/p)_{\mathrm{s}} - \ln(p'/p)_{\mathrm{l}}$ in terms of the change in molar volumes V_{s} and V_{l} between the two phases. A simplified form of Jeevanandam's result is

$$\ln\left(p'/p\right)_{\mathrm{l}} \cong (V_s/V_{\mathrm{l}}) \ln\left(p'/p\right)_{\mathrm{s}}, \tag{1}$$

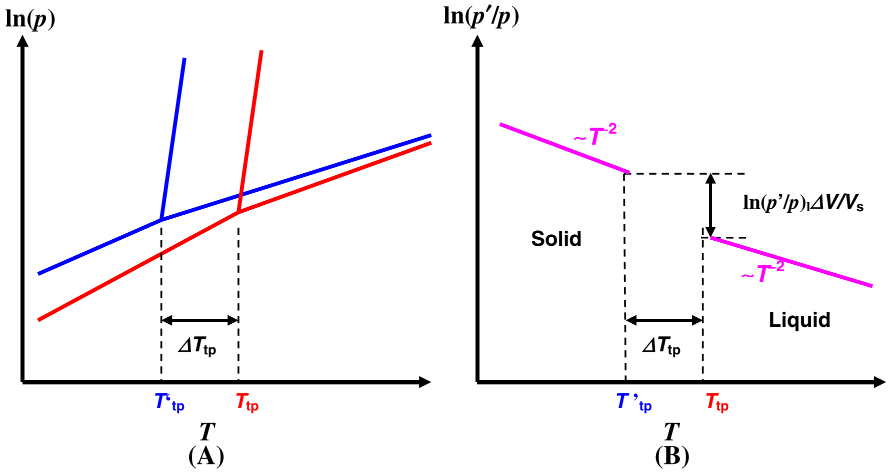

Fig. 1 Qualitative features of the normal VPIE and TPIE for two isotopes: (**A**) p–T diagrams for two isotopes show higher vapor pressures for the lighter isotope and a higher triple point for the heavier isotope and (**B**) relative volatility versus temperature shows how the triple-point shift coincides with a discontinuity in $\ln(p'/p)$. The features have been exaggerated for clarity, and neither figure is to scale

where we have neglected the non-ideal behavior in both the liquid and the vapor and any isotopic dependence in the molar volumes.[1] We further restrict the discussion to systems exhibiting small VPIEs, or $\ln(p'/p) \ll 1$ which necessarily excludes H_2 and He. Equation 1 has been experimentally verified for the noble gases and the isotopic forms of CO. Given these assumptions, we will show that the triple-point shift ΔT_{tp} is approximately proportional to Jeevanandam's discontinuity. This will lead to a simple expression that is useful for predicting the magnitude of the TPIE.

The theoretical treatment of the VPIE involves thermodynamic relations for the reduced partition function ratio f for the condensed phase 'c' (s or l) and the vapor phase 'v' which are closely related to the relative volatility according to

$$\ln\left(f_{\text{c}}/f_{\text{v}}\right) \cong \ln\left(p'/p\right)_{\text{c}}\left(1 + pB_p\left(T\right) - \frac{pV}{RT}\right) \tag{2}$$

where $B_p(T)$ is the 2nd pressure virial coefficient, V is the molar volume of the vapor, and R is the universal gas constant. We neglect the non-ideal gas correction, which is $\leq 10\%$ at the triple points of the substances considered here. The theoretical expressions for $\ln(f_{\text{c}}/f_{\text{v}})$ can be simplified in terms of the lowest-order quantum corrections associated with both external and internal degrees of freedom commonly expressed as

$$\ln\left(p'/p\right)_{\text{c}} \cong \ln\left(f_{\text{c}}/f_{\text{v}}\right) \cong \left(\frac{A_{\text{c}}}{T^2} - \frac{B_{\text{c}}}{T}\right) \tag{3}$$

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[1] Equation 1 is not applicable to certain molecules with strong liquid-phase association. This is the case most notably in water where use of Eq. 1 would predict the wrong sign for the VPIE.

where the coefficient A_c involves differences of summations $\Sigma(\nu_i'^2 - \nu_i^2)_c$ over external modes ν_i of the condensed phase and B_c involves differences of summations over the internal modes in both condensed and vapor phases [5]. Hence, the B term plays no role in the calculations of the noble-gas VPIEs, and in practice, it is often acceptable to neglect the B term for some diatomic molecules as well.

Given theses considerations, it is natural to approximate the total vapor pressure of a condensed phase in the following form,

$$\ln(p)_c \cong F_c(T) + \frac{a_c}{T^2} \tag{4}$$

where $F_c(T)$ contains the phase-dependent but isotope-independent functional form for the vapor-pressure and a_c contains the isotope dependence implied by Eq. 3 such that $A_c = a_c' - a_c$. At $T = T_{tp}$, we have $\ln(p)_s = \ln(p)_l$ which leads to the result,

$$T_{tp}^2 = \frac{a_s - a_l}{F_l(T_{tp}) - F_s(T_{tp})}. \tag{5}$$

Equation 5 is essentially the same as that used by Bigeleisen [4] for a related derivation in Sect. 5 of his original article, but in our case we will now recast the equation in a form that is more readily applied to thermometry. From this result, in combination with Eq. 3, it is straightforward to show that the isotope shift is proportional to Jeevanandam's discontinuity or,

$$\frac{\Delta T_{tp}}{T_{tp}} \cong \frac{1}{2}\frac{T_{tp}^2 - T_{tp}'^2}{T_{tp}^2} \cong \frac{\Delta \ln(p'/p)}{2\left(F_l(T_{tp}) - F_s(T_{tp})\right)}. \tag{6}$$

The numerator of Eq. 6 can now be combined with Eq. 1 to yield,

$$\frac{\Delta T_{tp}}{T_{tp}} \cong \frac{\ln(p'/p)_l}{2\left(F_l(T_{tp}) - F_s(T_{tp})\right)}\frac{\Delta V}{V_s}, \tag{7}$$

where $\Delta V = V_l - V_s$ is the change in the molar volume from the liquid-to-solid phase at the triple point. Equation 7 is shown in terms of the relative volatility in the liquid phase at the triple point and the solid molar volume, but according to Eq. 1 it should be equally valid for the complementary combination $\ln(p'/p)_s \Delta V/V_l$. The form given in Eq. 7, however, is better suited to identifying empirical trends since far more VPIE data are available for the liquid phase than for the solid phase.

The leading terms in $F_l(T)$ and $F_s(T)$ are $-h_{vap}/RT$ and $-h_{sub}/RT$, respectively, where h_{vap} and h_{sub} are the enthalpies of vaporization and sublimation. Since at the triple point the enthalpy of fusion is $h_{fus} = h_{sub} - h_{vap}$, the difference $F_l(T_{tp}) - F_s(T_{tp})$ is $\sim h_{fus}/RT_{tp}$, which is $\sim$1.7 for the rare gases. While order-of-magnitude estimates may be obtained using this approximation, there are other constant and temperature-dependent terms in both $F_l(T_{tp})$ and $F_s(T_{tp})$ which will contribute to the difference. Normally, these terms are treated as empirical fitting constants for developing experimental vapor-pressure equations. For our purposes here we treat the factor

$[F_l(T_{tp}) - F_s(T_{tp})]^{-1}$ of Eq. 7 as a single empirical parameter or 'triple-point constant' $k_E \sim 1$ which is fit to the VPIE data for a given element 'E' where the triple-point shift is known. In general, k_E will be different for each chemical species. Hence, our final result from Eq. 7 is given by

$$\frac{\Delta T_{tp}}{T_{tp}} \cong k_E \frac{\ln\left(p'/p\right)_l}{2} \frac{\Delta V}{V_s}. \tag{8}$$

It is readily seen from Eqs. 7 or 8 that in the limit of small VPIEs, the TPIE is a product of two small quantities and therefore essentially a second-order effect since $\Delta V/V_s$ does not exceed 15% in the noble gases and is $\leq$16% for the diatomic species considered below. In addition, since the VPIE theory predicts that $\ln(p'/p) \sim T^{-2}$ and $\ln(p'/p) \sim \Delta M/MM'$, the same scaling laws should hold true for the TPIE. Furthermore, in a crude way $T_{tp} \sim M$ between elements, so the relative isotope shift $\Delta T_{tp}/T_{tp}$ should scale $\sim \Delta M/M^3$. This explains why the TPIE is primarily a problem confined to the cryogenic range of light-element fixed points.

3 Noble Gases

For the noble gases Ne, Ar, and Kr, reasonably complete data for both the VPIE and TPIE exist [5]. A selected sub-set of this data is summarized in Table 1. In the case of Xe, there are no experimental VPIE data derived from differential pressure measurements. There are only the attempts by Clusisus [14] to measure the related fractionation factor $\ln(\alpha) \sim \ln(p'/p)_l$ in distillation experiments which failed, evidently because the effect was too small to measure. Other later distillation work [15] has purported to resolve a finite value for $\ln(\alpha) \sim 1 \times 10^{-4}$ at 165 K. In general, such distillation measurements are less accurate than differential pressure VPIE values, so we need another way to account for the true magnitude of the VPIE in Xe.

Fortunately, two recent theoretical calculations of $\ln(f_c/f_v)$ are available for Xe. Lopes et al. [12] applied the integral equation theory for Lennard-Jones fluids to calculate VPIE parameters for the noble-gas series in the liquid phase. Their treatment yields $\ln(f_l/f_v) = 2.7 \times 10^{-4}$ at a reduced temperature of $T^* = 0.75$ for the isotope pair ^{130}Xe–^{136}Xe. When scaled by T^{-2} to the triple point ($T^* = 0.715$), we have $\ln(f_l/f_v)_{TP} = 0.3 \times 10^{-5}$. It is worth noting that Lopes et al. identify a scaling relationship of $\ln(f_c/f_v) \sim \Delta M/M^3$ based on a corresponding-states argument, which is the same scaling we have argued above should exist for the relative TPIE.

In an independent and nearly simultaneous paper, Chialvo and Horita [13] report similar VPIE calculations for the noble gases based on numerical simulations of atomic Lennard-Jones fluids and solids. In their case, the results are in terms of the fractionation factor $\ln(\alpha(T))_c$ which is nearly equivalent to $\ln(f_c/f_v)$. Their calculations for the isotope pair ^{132}Xe–^{136}Xe yield $\ln(\alpha_{132-136}(T_{tp}))_l = 0.000215$ and $\ln(\alpha_{132-136}(T_{tp}))_s = 0.000265$ for the liquid and solid, respectively. These results must be scaled by the ratio of the mass differences (6/4) to compare with the ^{130}Xe–^{136}Xe $\ln(f_l/f_v)_{TP}$ value from Lopes et al. as described above. The scaling yields $\ln(\alpha_{130-136}(T_{tp}))_l = 0.000323$ which is within 8% of the Lopes et al. $\ln(f_l/f_v)_{TP}$

Table 1 VPIE and TPIE data and estimates for the noble-gas series

Isotope pair	$\ln(p'/p)_l^a$	$\Delta V/V_s^b$	$T_{tp}(K)^c$	$\Delta T_{tp}/T_{tp}$	k_E
^{20}Ne , ^{22}Ne[d]	0.046	0.150	24.69	6.0×10^{-3}	1.7
^{36}Ar , ^{40}Ar[e]	0.0066	0.146	83.806	7.0×10^{-4}	1.5
^{80}Kr , ^{84}Kr[f]	0.0010	0.144	115.78	8.6×10^{-5}	1.15
^{130}Xe , ^{136}Xe[g]	0.00031	0.148	161.4	2.8×10^{-5}	1.2 ± 0.2

[a] Values taken at $T = T_{tp} > T'_{tp}$

[b] Values derived from tabulated molar densities in Ref. [7]

[c] Approximate temperatures for heavier isotope on ITS-90

[d] $\ln(p'/p)_l$ and ΔT_{tp} data: Refs. [8] and [9]

[e] $\ln(p'/p)_l$ and ΔT_{tp} data: Ref. [10]

[f] $\ln(p'/p)_l$ and ΔT_{tp} data: Ref. [11]

[g] $\ln(p'/p)_l$ taken from Refs. [12] and [13]; and ΔT_{tp} extrapolated (see text)

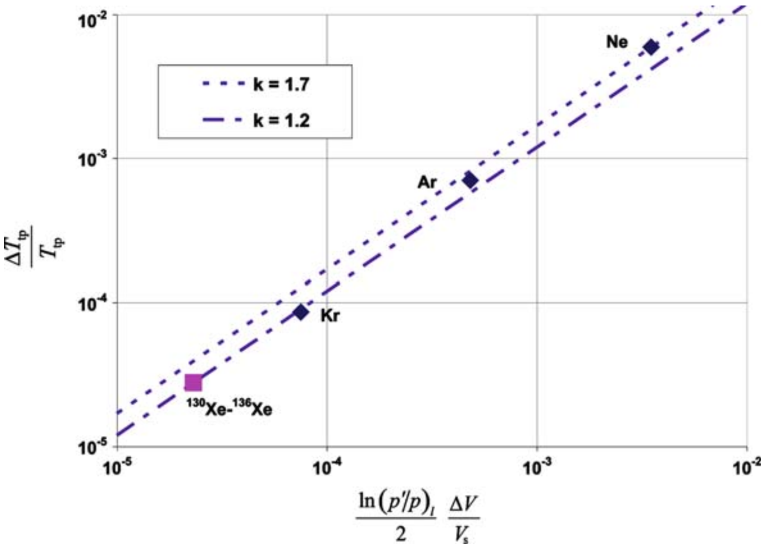

Fig. 2 TPIE and VPIE data for the noble-gas series Ne through Xe from the literature. The data are for $\{^{20}\text{Ne}, ^{22}\text{Ne}\}$, $\{^{36}\text{Ar}, ^{40}\text{Ar}\}$, $\{^{80}\text{Kr}, ^{84}\text{Kr}\}$, and $\{^{130}\text{Xe}, ^{136}\text{Xe}\}$. The value of $\ln(p'/p)$ for Xe is taken from VPIE calculations, and the $\Delta T/T$ value is based on the assumed value $k_{Xe} = 1.2$ being close to that of Kr

results. It is worth noting that the values used by the two groups for the Lennard-Jones energy parameter ε for Xe differ by ∼2.8%. For the values of $\ln(p'/p)_l$ given in Table 1, we have averaged these two calculated values for the Xe TP.

The VPIE and TPIE data for Ne, Ar, and Xe from Table 1 are plotted in Fig. 2 in the form derived in Eq. 8. These noble-gas triple-point constants k_{NG} range from 1.2 to 1.7. This close correspondence between the noble-gas elements is expected given that Eq. 8 is effectively in a reduced form. The correspondence is imperfect because of the approximations made in deriving Eq. 8. This is particularly true for Ne, where non-ideal behavior is expected to be the largest and the magnitude of the 4th order quantum (i.e., $\sim h^4$ in the Kirkwood-Wigner expansion for the calculation of A_l) terms are not negligible [13]. For these reasons, we identify the linear trend which matches that of Kr to be the best estimate for the corresponding TPIE of Xe. The resulting extrapolation from Kr yields $k_{\mathrm{Xe}} = 1.2$ and a value of $\Delta T_{\mathrm{tp}}/T_{\mathrm{tp}} = 28\,\mu\mathrm{K}\cdot\mathrm{K}^{-1}$ or $\Delta T_{\mathrm{tp}} = 4.5\,\mathrm{mK}$ for the ^{130}Xe–^{136}Xe substitution. The rough estimate provided by $k_{\mathrm{Xe}} \sim RT_{\mathrm{tp}}/h_{\mathrm{fus}}$ is a factor of two lower than the empirical value.

In order to turn the above estimate of ΔT_{tp} for a binary substitution into a single sensitivity coefficient for an isotopic mixture, such as the nine naturally occurring Xe isotopes, it is necessary to make some simplifying assumptions. The first is that of ‘perfect’ isotopic solutions, where the triple point T_{mix} of a mixture of two isotopes, ^{i}E and ^{j}E, of an element ‘E’ is linear in either mole fraction x_i or x_j. In this simple case, the mean molar mass of the binary mixture is $M_{\mathrm{mix}}(\mathrm{E}) = x_i M_i + x_j M_j$ and $\mathrm{d}T_{\mathrm{mix}}/\mathrm{d}M_{\mathrm{mix}} = (T_j - T_i)/(M_j - M_i) =$ constant, where T_j and T_i are the pure-component triple points. This is consistent with the small VPIE approximation of $\ln(f_{\mathrm{c}}/f_{\mathrm{v}}) \ll 1$ and $\Delta M/M \ll 1$ and the general scaling relationship already identified, $\Delta T \sim \ln(f_{\mathrm{c}}/f_{\mathrm{v}}) \sim \Delta M$. As more isotopes are considered, it is only necessary to assume a linear temperature–mass approximation for any combination in order to prove that two arbitrary binary mixtures 1 and 2 will have the same T_{mix} when $M_{\mathrm{mix}-1} = M_{\mathrm{mix}-2}$. The result can be generalized to arbitrary multicomponent mixtures to show that T_{mix} is linear in M_{mix} or $\mathrm{d}T_{\mathrm{mix}}/\mathrm{d}M_{\mathrm{mix}} =$ constant. For the lightest atoms, this approximation is less accurate due to the VPIE scaling for $\ln(p'/p) \sim \Delta M/MM'$. For example, in the case of Ne, $(T_{21} - T_{20})$ and $(T_{22} - T_{20})/2$ should differ by $(22/21) - 1 \cong 5\%$.

The estimated TPIE shift $\Delta T_{130\text{–}136} = 4.5\,\mathrm{mK}$ is then readily converted into a more useful parameterization as a mass sensitivity coefficient, $\mathrm{d}T_{\mathrm{Xe}}/\mathrm{d}M(\mathrm{Xe}) = 4.5\,\mathrm{mK}/6\,\mathrm{g}\cdot\mathrm{mol}^{-1}$, or $0.75\,\mathrm{mK}\cdot\mathrm{mol}\cdot\mathrm{g}^{-1}$. This result is a factor of 3–4 times larger than two such estimates given by Hill and Steele [16]. They obtained $0.18\,\mathrm{mK}\cdot\mathrm{mol}\cdot\mathrm{g}^{-1}$ from a linear extrapolation of $\log(\mathrm{d}T_{\mathrm{tp}}/\mathrm{d}M)$ versus M for the noble-gas series, and they cite another independent estimate of $0.23\,\mathrm{mK}\cdot\mathrm{mol}\cdot\mathrm{g}^{-1}$ attributed to Van Hook.[2] To test any of these predictions, samples of Xe would need to be enriched (or depleted) in the heavier isotopes by known amounts to more than 10% in M(Xe) from its normal composition while maintaining chemical impurities $\lesssim 0.1\,\mu\mathrm{mol}\cdot\mathrm{mol}^{-1}$. Such samples are not readily available and would be expensive to prepare.

4 Diatomic Molecules

The liquid-phase VPIE data are available for the isotopic mixtures of diatomic molecules: $\{^{14}\mathrm{N}_2, ^{15}\mathrm{N}_2\}$; $\{^{12}\mathrm{C}^{16}\mathrm{O}, ^{12}\mathrm{C}^{18}\mathrm{O}\}$; $\{^{12}\mathrm{C}^{16}\mathrm{O}, ^{13}\mathrm{C}^{16}\mathrm{O}\}$; all three main variations of $\{^{14}\mathrm{N}^{16}\mathrm{O}, ^{x}\mathrm{N}^{y}\mathrm{O}\}$; and $\{^{16}\mathrm{O}_2, ^{18}\mathrm{O}_2\}$. Data are also available for the linear tri-atomic

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[2] Van Hook’s estimate for $\mathrm{d}T_{\mathrm{Xe}}/\mathrm{d}M(\mathrm{Xe})$ is actually consistent with our analysis if the value given in Ref. [14] for $\ln(p'/p)$ is used instead of the new theoretical estimates from Refs. [12] and [13] that we have used.

Table 2 VPIE and TPIE data and estimates for selected diatomic and tri-atomic molecules

Isotope pair	$\ln(p'/p)_l^{\mathrm{a}}$	$\Delta V/V_{\mathrm{s}}$	$T'_{\mathrm{tp}}(\mathrm{K})^{\mathrm{b}}$	$\Delta T_{\mathrm{tp}}/T_{\mathrm{tp}}$	k_{E}
$^{12}C^{16}O$, $^{13}C^{16}O^{c}$	0.011	0.087	68.15	9.0×10^{-4}	1.95
$^{12}C^{16}O$, $^{12}C^{18}O^{c}$	0.0081			6.9×10^{-4}	1.86
$^{14}N^{16}O$, $^{15}N^{16}O^{d}$	0.0325	0.160	109.49	9.0×10^{-4}	0.35
$^{14}N^{16}O$, $^{14}N^{18}O^{d}$	0.0447			1.27×10^{-3}	0.355
$^{14}N^{16}O$, $^{15}N^{18}O^{d}$	0.0770			2.03×10^{-3}	0.33
$^{14}N_2$, $^{15}N_2^{e}$	0.0132	0.084	63.15	6.3×10^{-4}	1.14
$^{14}N^{14}N^{16}O$, $^{15}N^{14}N^{16}O^{f}$	0.00189	0.20	182.26	3.3×10^{-4}	1.75
$^{16}O_2$, $^{16}C^{18}O^{g}$	0.0184	0.034	54.358	3.7×10^{-4}	1.17 ± 0.83
$^{16}O_2$, $^{18}O_2^{h}$	0.0370			7.4×10^{-4}	1.17 ± 0.83

[a] Values taken at $T = T_{\mathrm{tp}} > T'_{\mathrm{tp}}$

[b] Approximate temperatures for lighter isotope on ITS-90

[c] $\ln(p'/p)_{\mathrm{l}}$ and ΔT_{tp} data: Ref. [17]

[d] $\ln(p'/p)_{\mathrm{l}}$ and ΔT_{tp} data: Ref. [18]

[e] $\ln(p'/p)_{\mathrm{l}}$ and ΔT_{tp} data: Ref. [19]

[f] $\ln(p'/p)_{\mathrm{l}}$ and ΔT_{tp} data: Ref. [20]

[g] $\ln(p'/p)_{\mathrm{l}}$ extrapolated from data in Ref. [17]; and ΔT_{tp} inferred (see text)

[h] $\ln(p'/p)_{\mathrm{l}}$ extrapolated from data in Ref. [21]; and ΔT_{tp} inferred (see text)

variation of $\{^{14}N_2^{16}O, ^{15}N^{14}N^{16}O\}$. In the case of O_2, there are no differential pressure data for $T < 63$ K, and only one set of distillation data below that point. In the solid phase, only the CO series VPIE has been measured. TPIE data are also available for all of these systems except for oxygen. An abridged summary of these VPIE and TPIE data is given in Table 2.

In order to estimate the TPIE for $\{^{16}O_2, ^{18}O_2\}$, we need to first establish a value for $\ln(p'/p)_{\mathrm{l}}$ near the triple-point temperature. In the absence of any detailed VPIE calculations, we use the established VPIE data which exists above 63 K and extrapolate down to the triple point at 54.358 K by scaling as T^{-2}. Figure 3 shows differential pressure data for the VPIE of these isotopic molecules. The data from Clusius et al. [21] for $\{^{16}O_2, ^{18}O_2\}$ are in good agreement with that from Johns [17] for $\{^{16}O_2, ^{18}O^{16}O\}$, as they differ by the expected factor of two to better than 1%. By extrapolating the functional forms for $\ln(p'/p)_{\mathrm{l}}$ as derived by those authors (i.e., fitted forms of Eq. 3) to 54.358 K, the factor of two in the VPIE ratios continues to hold true. Based on this extrapolation, we calculate $\ln(p'/p)_{\mathrm{l}} = 0.037$ for $\{^{16}O_2, ^{18}O_2\}$ at the triple point, as is indicated in Table 2.

The difficulty in the case of oxygen is that we have no empirical guide for k_{O_2} other than that provided by other similar diatomic molecules. A rough estimate is provided by $k_{O_2} \sim RT_{\mathrm{tp}}/h_{\mathrm{fus}} = 1.02$, but based on TPIE data from similar diatomic molecules, this estimate could be as much as a factor of ~3 too low. Figure 4 shows that each molecular series exhibits a different slope (i.e., values for k_{E}) for the TPIE to VPIE

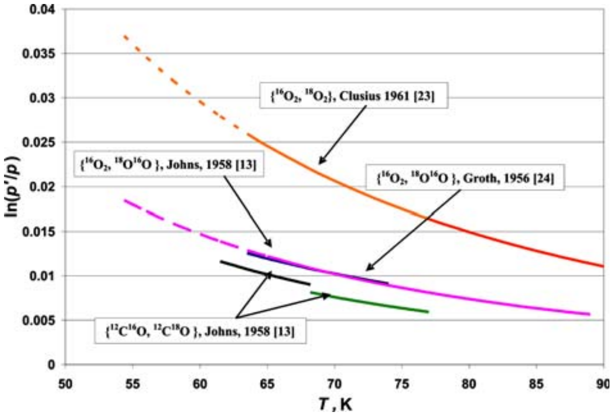

Fig. 3 The VPIE data for the isotopic pairs: $\{^{16}O_2, ^{16}O^{18}O\}$ from Johns [17] and Groth [22]; $\{^{16}O_2, ^{18}O_2\}$, from Clusius [21]; and $\{^{12}C^{16}O, ^{12}C^{18}O\}$ also from Johns [17]. The extrapolations of the Johns and Clusius data to the triple-point temperature for O_2 yield values for $\ln(p'/p)$ in the expected ratio of 2.0

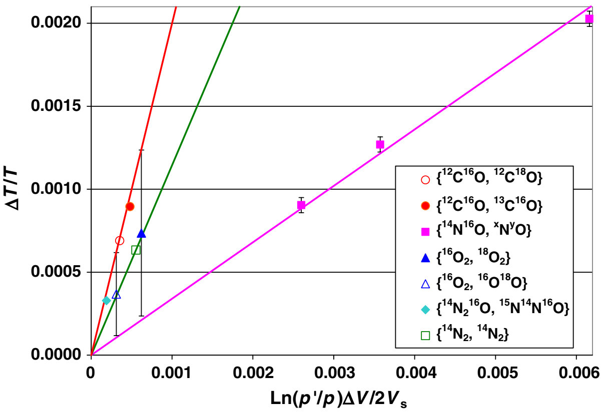

Fig. 4 TPIE and VPIE data for diatomic molecules and N_2O. The range of observed triple-point constants is $k_E = 0.34$ to 2.0. The $\Delta T/T$ values for $\{^{16}O_2, ^{18}O_2\}$ and $\{^{16}O_2, ^{16}O^{18}O\}$ are based on an assumed proportionality of $k_{O_2} = 1.17 \pm 0.83$, close to that of $\{^{14}N_2, ^{15}N_2\}$

data. The values of k_E range from 0.33 to 2.0, with $k_{N_2} = 1.14$ for N_2 being very close to that of Kr. The relatively low values of k_{NO} for the NO series are related to the fact that NO exhibits association in the liquid phase through the formation of dimmers [23], which results in the relatively high values of $\ln(p'/p)_l$ but apparently has less of an effect on the triple-point temperatures. Even in the case of CO and N_2, however, there is a significant difference in the triple-point constants and these two molecules normally exhibit a high degree of correspondence. The only possible improvement to this situation might come from a special application of corresponding states to a detailed theory for the value of k_E, which is beyond the scope of this paper.

In the absence of any other quantitative information for oxygen, we assume that $k_{O_2} = 1.17 \pm 0.83$ for oxygen and consider the value sufficiently uncertain to accommodate the entire range of known TPIE/VPIE proportionalities. This results in a range of TPIEs for $\{^{16}O_2, ^{18}O_2\}$of $\Delta T_{tp}/T_{tp} = (730 \pm 520)\,\mu K \cdot K^{-1}$ or $\Delta T_{tp} = (40 \pm 28)$ mK. The nominal value of $\Delta T_{tp}/T_{tp}$ is close to the value for the $\{^{36}Ar, ^{40}Ar\}$ system. Expressed as a sensitivity coefficient, we have $dT_{O_2}/dM(O_2) = (10 \pm 7)\,mK \cdot mol \cdot g^{-1}$. By comparison, even the upper limit of $17\,mK \cdot mol \cdot g^{-1}$ is 3.7 times smaller than a recent upper-bound estimate of $62.5\,mK \cdot mol \cdot g^{-1}$ given by Pavese [2] and ∼6 times smaller than an earlier estimate [24]. The large uncertainty of k_{O_2} is of little practical consequence in thermometry due to the small variations of ^{18}O among terrestrial sources of oxygen as will be seen in the following section.

5 Uncertainties in the Triple Points due to Isotopic Variations

In this section, we give examples of how the triple-point temperatures of actual gas samples may be expected to vary from known isotopic variations in commercial sources of gas as well as in other terrestrial sources in the case of oxygen. We treat three of the ITS-90 defined fixed points, Ne, Ar, and O_2, as well as Xe, which has been suggested as a suitable fixed point for the purposes of future scale definitions [16].

5.1 Xenon

The isotopic variations in commercial sources of Xe gas are given for six samples by Hill and Steele [16]. Since those isotopic assays are incomplete, listing concentrations for only seven of the nine isotopes, we analyze those and other reported Xe compositions from the literature in terms of the fractionation trends in the ratios $n(^{129}Xe)/n(^{132}Xe)$ and $n(^{131}Xe)/n(^{132}Xe)$. These three Xe isotopes are the most abundant, so those ratios would in general be expected to have the highest accuracy. The analysis assumes that all gases have been subjected to similar fractionation effects in the course of purification and that the degree of fractionation is correlated in any two isotope ratios, $R_{i,k}$ and $R_{j,k}$, according to

$$R_{i,k} = R^0_{i,k} \left(\frac{R_{j,k}}{R^0_{j,k}} \right)^{(M_i - M_k)/(M_j - M_k)}, \qquad (9)$$

where $R_{j,k} \equiv n(^{j}Xe)/n(^{k}Xe)$ and $R^0_{j,k}$ refers to an initial or nominal composition, in our case the recommended [3] value for Xe in the earth's atmosphere. Equation 9 can be used to calculate a mass fractionation line on the isotope ratio plot and also allows the mean molar mass M(Xe) to be calculated for samples with known isotope ratios based on the assumed correlation.

The data on the ratios $^{129}Xe/^{132}Xe$ and $^{131}Xe/^{132}Xe$ from commercial gas sources as reported in Ref. [13] and elsewhere in the literature are shown in Fig. 5. The mass fractionation line is referred to the composition of the Xe isotope standard IRMM-2000 [25]. Much of the data are uncertain to the point where it could be argued that all of the samples are practically equivalent. A maximum-to-minimum variation in the mean molar mass of these gases of $\Delta M_{com}(Xe)/M(Xe) \sim 215 \times 10^{-6}$, however,

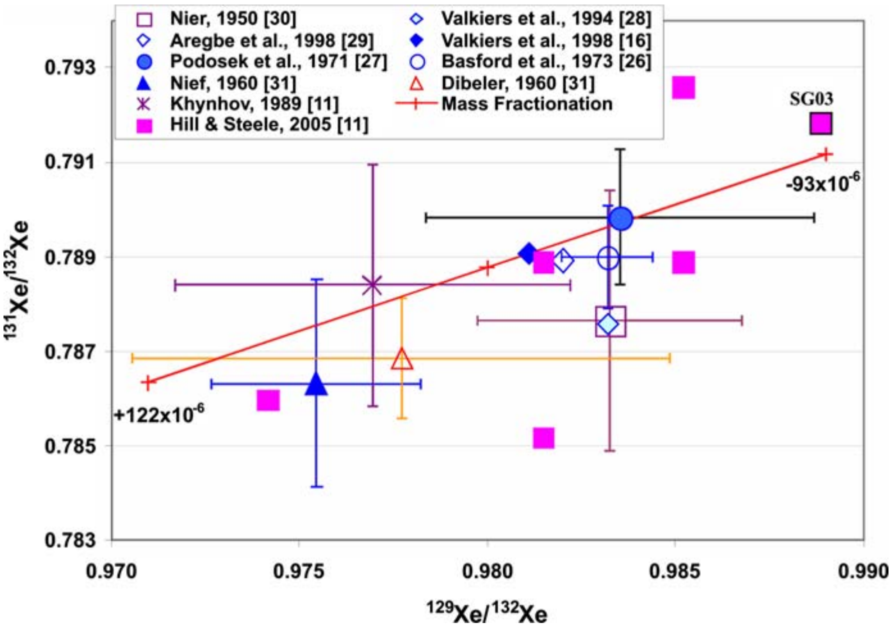

Fig. 5 Isotope ratio plot for reported values of various commercial Xe gas. The uncertainties for the NRC samples [16] are not shown for clarity but are estimated to be 0.5%. The mass fractionation line is calculated with respect to the Xe isotope reference gas IRMM-2000 [25] on which the currently recommended molar mass [3] is based. The other data are taken from the literature: Nier 1950 [26]; IRMM, 1994 [27]; IRMM L'Air Liquide 1998 [28]; Podosek et al. 1971 [29]; Basford et al. 1973 [30]; Nief NBS-104 and Dibeler NBS-104 [31]; Khynhov, 1989, as cited in [16], and Hill and Steele [16]

cannot be ruled out. Assuming that this apparent isotopic variability is real, and a sensitivity of 0.75 mK·mol·g^{-1} derived above, this corresponds to variability in the Xe TP of only 21 µK. Since this is a 'worst-case' estimate, the actual uncertainty in the TP realization in practice would be less than this and would have no measurable impact on the reproducibility of the fixed point.

It should be noted that one of the samples studied by Hill and Steele, NRC-SG03, is from a specially prepared batch of Xe which is probably the highest chemical purity Xe gas ever commercially produced, with a Kr impurity $<0.05\,\mu\text{mol}\cdot\text{mol}^{-1}$. The lighter noble-gas impurity can only be removed by multiple distillations, so it is probably not a coincidence that this sample appears to be the lightest commercial Xe of any reported. Even in this extreme case, however, the isotopic fractionation in Xe appears to be relatively unimportant to the triple-point temperature.

5.2 Argon

A similar analysis can be done for the Ar isotopes, but in this case a point on the three-isotope plot of $^{36}\text{Ar}/^{40}\text{Ar}$ versus $^{38}\text{Ar}/^{40}\text{Ar}$ uniquely specifies the composition. Unlike the other noble gases, Ar is nearly mono-isotopic with $x_{40\text{Ar}} = 99.6\%$. Therefore, any mass fractionation is expected to be small. This is evident for Fig. 6, which shows the known variations in high-purity commercial Ar as reported in the literature.

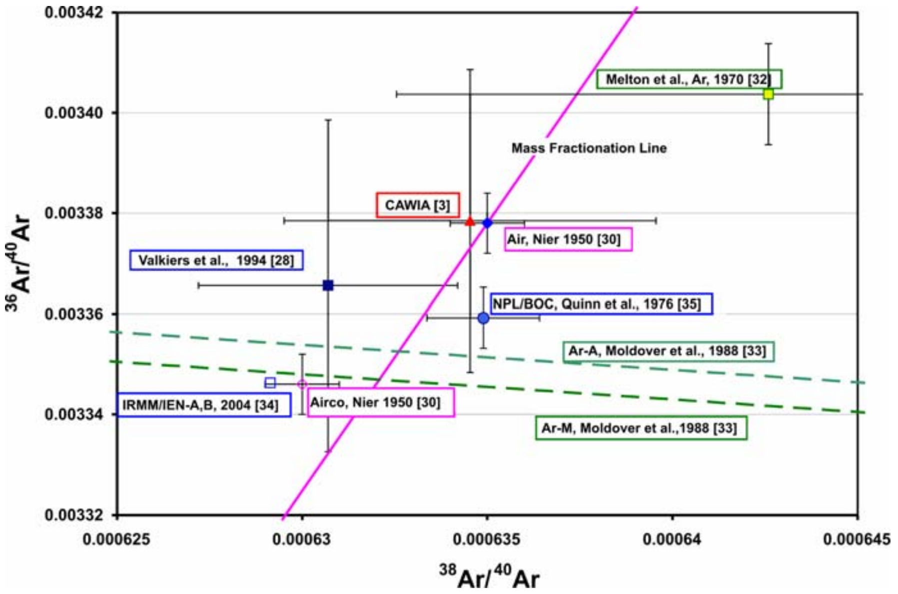

Fig. 6 Isotope ratio plot for reported values of various commercial and other separated Ar gas. The two NBS samples Ar-A and Ar-B are from Moldover et al. [32] where the mean molar masses are known, but not the individual ratios. The other data are taken from the literature: Nier [26]; IRMM, 1994 [27]; Melton et al. [33]; Quinn et al. [34]; IRMM/IEN [35]. 'CAWIA' is the recommended composition [3]

Based on these data, the maximum-to-minimum relative variation in the molar mass of commercial Ar gas is $\Delta M_{\mathrm{com}}(\mathrm{Ar})/M(\mathrm{Ar}) < 8 \times 10^{-6}$ and the corresponding variability of ~5 μK in the triple point is completely negligible.

5.3 Neon

A full treatment of the TPIE in neon is being presented in another paper in this symposium with new experimental data [36]. A three-isotope plot for Ne similar to Figs. 5 and 6 appears in that paper. We only remark here that the degree of fractionation exhibited in commercial neon gas is much larger than previously thought [3]. The data now suggest that relative variations in the neon molar mass from commercial gas sources to be $\Delta M_{\mathrm{com}}(\mathrm{Ne})/M(\mathrm{Ne}) \cong 324 \times 10^{-6}$. This variation is ~10 times larger than the currently recommended uncertainty [3] of 30×10^{-6} in the Ne atomic weight. For a nominal TPIE sensitivity of $73.5\,\mathrm{mK \cdot mol \cdot g^{-1}}$, this implies variations in the Ne TP of $\Delta T_{\mathrm{NeTP\text{-}com}} \cong 0.48\,\mathrm{mK}$, or $\Delta T_{\mathrm{NeTP\text{-}com}}/T_{\mathrm{NeTP}} \cong 20\,\mu\mathrm{K \cdot K^{-1}}$. In comparison, acoustic gas thermometers using ^{4}He can now achieve uncertainties in this temperature range of $<10\,\mu\mathrm{K \cdot K^{-1}}$ [37], indicating that the current "natural isotopic composition" definition [1] used for the Ne TP in the ITS-90 is inadequate.

5.4 Oxygen

The isotopic variations of oxygen in the terrestrial environment are well-documented [38]. However, very little information is available in the case of commercial O_2

Table 3 An abridged summary of the isotopic variations in natural and anthropogenic sources of oxygen

Source[a]	$\delta^{18}\mathrm{O}_{\mathrm{VSMOW}}$ ($^0/_{00}$)[b]	$^{18}\mathrm{O}/^{16}\mathrm{O}$ ($^0/_{00}$)	$^{17}\mathrm{O}/^{16}\mathrm{O}$ ($^0/_{00}$)	$\Delta M/M$ (10^{-6})	ΔT_{Max} (mK)
Mineral—low	−15.5	1.9741	0.3768	−4.1	−0.002
VPDB	30.91	2.0672	0.3860	8.1	0.004
Mineral—high	40	2.0854	0.3877	10.5	0.006
Atmospheric	23.8	2.0529	0.3846	6.2	0.003
VSMOW	0	2.0052	0.3799	0.0	0.000
Cont. water—low	−62.8	1.8792	0.3673	−16.5	−0.009
Cont. water—high	31.3	2.0679	0.3860	8.2	0.004
CO comm. gas	−229	1.5460	0.3319	−60.3	−0.033
N_2O	109	2.2237	0.4009	28.6	0.016
O_2 com. gas A[c]	49.9	2.1053	0.3897	13.1	0.007
O_2 com. gas B[c]	52.4	2.1103	0.3901	13.7	0.007
Pure $^{16}O_2$[d]	−1000	0.0000	0.0000	−274.4	−0.150
Pure $^{18}O_2$[d]					68

The triple-point shifts ΔT_{Max} are calculated using the maximum predicted mass sensitivity coefficient of $17\,\mathrm{mK \cdot mol \cdot g^{-1}}$ (see text)

[a] Values taken from Ref. [38] unless otherwise noted

[b] $^0/_{00} \equiv 1 \times 10^{-3}$

[c] Commercial gas compositions reported in Tiggleman [39] (performed by FOM-Instituut voor Atoom-en Molecuulfysica, Amsterdam) as normalized mole fractions and converted here to $\delta^{18}\mathrm{O}_{\mathrm{VSMOW}}$ values

[d] Calculated estimates

gas. Measurements on two commercial gas bottles from the 1970s are reported by Tiggleman [39] as ∼50$^0/_{00}$ and 52$^0/_{00}$ enriched in ^{18}O with respect to reference oxygen derived from Vienna-Standard Mean Ocean Water (VSMOW). This is to be compared with the composition in the earth's atmosphere which is 23.8$^0/_{00}$ enriched. It is also possible to produce O_2 gas in the laboratory by thermal decomposition of mineral oxide reagents [40] or by electrolysis of water, all of which exhibit some range of isotopic variation.

An abridged summary of both anthropogenic and natural sources of oxygen are shown in Table 3. The first column of $\delta^{18}\mathrm{O}_{x,\mathrm{VSMOW}}$ is defined in the usual way,

$$\delta^{18}\mathrm{O}_{x,\,\mathrm{VSMOW}} = (R_{18}(x) - R_{18}(\mathrm{VSMOW}))/R_{18}(\mathrm{VSMOW}) \tag{10}$$

for an isotope ratio $R_{18}(x) = n(^{18}\mathrm{O})/n(^{16}\mathrm{O})$ of the sample 'x' with respect to VSMOW. The ^{17}O content is calculated according to Eq. 9 where $R_{j,16} \equiv n(^{j}\mathrm{O})/n(^{16}\mathrm{O})$ for $j = 17, 18$ except that the exponent is 0.52 instead of 0.50 [41]. The contribution of the ^{17}O content to the predicted ΔT values is only ∼6% of the total effect, so the exact exponent used in Eq. 9 is unimportant. The final column in Table 3 is the maximum temperature shift with respect to a VSMOW-equivalent O_2 gas based on the maximum mass sensitivity coefficient of $17\,\mathrm{mK \cdot mol \cdot g^{-1}}$. From these values, it is clear that O_2 TP realizations using gas derived from different sources would not be expected to differ by more than ∼16 µK. The only possible exceptions would be if highly unusual sources, such as commercial CO gas, were used as a precursor for an O_2 gas synthesis. Furthermore, O_2 derived from mineral oxide decomposition and that derived by commercial distillation of air would be expected to have triple points differing by no more than ∼10 µK.

6 Conclusion

The TPIE of the noble gases as well as some linear molecules is predictable from knowledge of the VPIE for those substances. Even when no VPIE data are available, some reasonable estimates or calculations for $\ln(p'/p)$ are possible. The mass sensitivity coefficients can be calculated for both Xe and O_2 to within uncertainty bounds of ∼20% and ∼70%, respectively. The triple-point mass sensitivity coefficient predicted here for Xe is ∼4 times greater than other predictions given elsewhere. In contrast, our upper bound coefficient for O_2 is a factor ∼4–6 times smaller than other previous predictions. Using our estimated sensitivities, the predicted variations in triple-point temperatures of Ar, O_2, and Xe due to mass fractionation effects are less than 20 µK.

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