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Isotopic krypton mixtures revisited: Vapor pressure isotope effects

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The theory of nonideal, multicomponent, isotopic mixtures is used to calculate the vapor pressures of pure $^{80}\text{Kr}(l)$ and $^{84}\text{Kr}(l)$ from data on isotopic mixtures. The correction to ideal solution behavior, Δ , is found to be much smaller than the statistical deviations in the experimental data on the isotopic mixtures. It amounts to about 0.0005 and 0.0007 mmHg for the absolute vapor pressures of the pure isotopes at 116 and 123 K, respectively. The vapor pressure difference between pure isotopes is calculated to be 0.55₇₂ mmHg at 116 K after correction for nonideality compared with 0.55₇₃ mmHg based on ideal solution behavior. The corresponding differences are 0.83₈₁ and 0.83₈₂ mmHg, respectively, at 123 K. The theoretically important quantity, $\ln(p^{80}\text{Kr}(l)/p^{84}\text{Kr}(l))$, shows a decrease (almost irrespective of temperature) of about 0.01% if nonideality is taken into account. The pressure–temperature data for normal krypton given by Lee, Eshelman, and Bigeleisen [J. Chem. Phys. **56**, 4585 (1972)], in the temperature range 123.93–129.89 K cannot be reconciled with their vapor pressure equation for the normal liquid. We conclude that the Δ -correction can be safely discarded in the case of the vapor pressure isotope effect (VPIE) studies involving isotopic mixtures of krypton. Moreover, one can infer from this study that, in the case of the rare gases family, the borderline between still measurable and totally negligible nonideal behavior lies between the VPIEs found in mixtures of argon and those in mixtures of krypton, respectively. We anticipate that the case of neon isotopes deserve investigation since the deviations from ideality are expected to be about 400 times greater than those here predicted for krypton. © 2002 American Institute of Physics. [DOI: 10.1063/1.1514230]

I. INTRODUCTION

The study of isotopically substituted species plays a significant role in the theoretical analysis of liquids and liquid mixtures. Many of the tools introduced by modern statistical theories of fluids, such as the need for a specific model for the intermolecular potential or the accurate knowledge of the pair radial distribution function of the liquid, can be discarded when dealing with molecules whose sole difference lies in their isotopic constitution. This notion, originally developed in the so-called statistical mechanical theory of isotope effects in condensed phase¹ to account for the vapor pressure differences between pure isotopic substituted substances, asserts the quantum origin of isotope effects and enables their study in the liquid state by separating potential energy and structural considerations from purely kinetic energy effects arising from mass differences.

Later, the theory was extended to binary mixtures by considering the density dependence of the vibration quantum states of the molecules.^{2,3} This development introduced and

quantified the notion of nonideality in isotopic mixtures. The problem of nonideal, multicomponent isotopic mixtures was also addressed in this context;⁴ many mixtures are composed of more than two isotopic species, either as a result of the isotopic purity of the available samples or as a consequence of chemical isotopic exchange reactions between species.

Almost 30 years ago, Lee, Eshelman, and Bigeleisen⁵ reported data on the vapor pressure isotope effect (VPIE) between two distinct, isotopically impure, samples of krypton. Assuming ideality in the condensed phase, the experimental values were used to calculate the reduced partition function ratio¹ between ^{80}Kr and ^{84}Kr along the orthobaric line as a function of temperature, and the results were interpreted using the statistical mechanical theory of condensed phase isotope effects.¹

Since then, both experimental and theoretical vapor pressure isotope effect studies were extended to include isotopic liquid mixtures^{2,3,6} and two recent investigations can now assist in the reinterpretation of the original krypton data. First, it was shown that liquid mixtures of ($^{36}\text{Ar} + ^{40}\text{Ar}$) show positive, albeit small, deviations from ideality;⁷ and secondly, that liquid mixtures of ammonia ($\text{NH}_3 + \text{ND}_3$) ought to be treated as multicomponent nonideal mixtures⁸ in order to correctly estimate the corresponding VPIE in the mixture.

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In this paper, the original krypton data is reanalyzed at the light of the nonideal behavior exhibited by isotopic rare gas liquid mixtures. Excess molar Gibbs energies (activity coefficients) of liquid mixtures containing several isotopic forms of krypton are calculated and then used to refine the estimates of vapor pressure ratios between pure isotopic forms in an iterative fashion.

II. THEORETICAL BACKGROUND

One of the samples used by Bigeleisen and co-workers was at natural abundance of the isotopes of krypton (mainly ^{84}Kr) while the other was enriched in ^{80}Kr (hitherto referred to as the N and E samples, respectively).

None of the samples contained more than 60 mol % of any of the krypton isotopes (cf. Table I of Ref. 5). The VPIE between two particular krypton isotopes (^{84}Kr and ^{80}Kr in this case) had to be estimated by taking into account two basic assumptions: (i) the vapor pressure of any given isotope, p_i^0 , of mass m_i , was regarded as a mass weighted average of the vapor pressures of ^{84}Kr and ^{80}Kr ,

$$p_i^0 = p_{84}^0 + (p_{80}^0 - p_{84}^0) \frac{m_{80}}{m_i} \cdot \frac{(m_{84} - m_i)}{(m_{84} - m_{80})}; \quad (1)$$

and (ii) that each sample was an ideal multi-component mixture, i.e.,

$$p^m = \sum_i x_i p_i^0, \quad \text{with } m = N \text{ or } E. \quad (2)$$

Equation (1) reflects the so-called vapor pressure geometrical mean rule⁹ in an approximate form—the geometrical mean has been replaced by the arithmetic one. The validity of this approximation increases with decreasing relative mass difference between isotopic species and should hold for krypton. Vapor pressure and composition data from the two samples, N and E , permit us to calculate the two unknowns, p_{84}^0 and p_{80}^0 .

The second assumption corresponds, apparently, to a more severe approximation. For instance, it has been experimentally proven⁷ that argon mixtures of ^{36}Ar and ^{40}Ar are not ideal. Inasmuch as the quantum effects are smaller in krypton than in argon, we anticipate the nonideal solution behavior to be smaller for the krypton system than in the case of argon. The subject is, nevertheless, of interest both from the validity in the extrapolation of the experimental data on isotopically impure mixtures and the general theory of nonideal behavior of isotopic mixtures. Let us elaborate. It is theoretically predictable¹⁰ that, at a certain reduced temperature, the logarithm of the activity coefficient at infinite dilution, $\ln \gamma^\infty$ [see Eqs. (11) or (14)], scales approximately with $(\Delta M/M^3)\sigma^{-4}(\epsilon/k)^{-2}$. The Greek letters refer to the well-known intermolecular parameters of a given isotopic potential, while M and ΔM stand for the mass of a given rare gas and the difference in masses between two isotopes of that rare gas, respectively. In turn, the excess molar Gibbs energy, G^E [see Eq. (11)], scales, at a given reduced temperature, with $(\Delta M/M^3)\sigma^{-4}(\epsilon/k)^{-1}$ [the transformation only involves the concept of reduced temperature, $T^* = T/(\epsilon/k)$].

This means that, the ratio of nonidealities between different families of rare gases (and for $\Delta M = 4$ in the cases of argon and krypton or $= 2$ in the case of neon), expressed as ratios of G^E and compared at the same reduced temperature, is such that one obtains, for instance, $G^E(\text{Ar})/G^E(\text{Kr}) \sim 17$ and $G^E(\text{Ne})/G^E(\text{Ar}) \sim 22$.

A. Nonideality in multicomponent systems

If the samples of krypton are no longer regarded as ideal mixtures, Eq. (2) should be rewritten as

$$p^m = \sum_i \gamma_i x_i p_i^0 / \phi_i, \quad (3)$$

where γ_i is the activity coefficient of the i th component in the condensed phase and ϕ_i is a factor related to the ratio between the fugacity coefficients of the component at the mixture's pressure and at its vapor pressure. The latter coefficient can be calculated considering the gas virial expansion up to the second term and the quasi-incompressibility of the condensed phase between the two referred pressures,

$$\phi_i = \exp\left(\frac{(p^m - p_i^0)(B_i - V_i^0)}{RT}\right), \quad (4)$$

where B_i is the second virial coefficient (volume expansion) and V_i^0 is the molar volume of component i in the liquid phase. Isotopic differences in B_i 's were neglected.¹¹ This correction is very small at low pressure ($\phi_i \cong 1$).

The activity coefficient γ_i reflects the nonideality of the condensed phase and is related to the excess molar Gibbs energy of the mixture, G^E , by the expression

$$\ln \gamma_i = \left(\frac{\partial(nG^E/RT)}{\partial n_i}\right)_{T,p,n_{j \neq i}}. \quad (5)$$

The excess molar Gibbs energy is a function of T , p and composition but for liquids at low to moderate pressures it is a very weak function of p ($\partial G^E/\partial p = V^E$). Moreover, in the particular case of isotopic mixtures, V^E is extremely small, and, thus, the pressure dependence of G^E can certainly be discarded. Thus, at constant T ,

$$\frac{G^E}{RT} = f\left(\sum_i x_i\right). \quad (6)$$

In the case of isotopic binary mixtures, a power series known as the Redlich–Kister¹² expansion truncated after the first term has been usually employed,

$$\frac{G^E}{RT} = A x_i x_j, \quad (7)$$

because all isotopic mixtures so far studied have invariably shown^{2,3,7,8} that, within experimental precision, G^E has a symmetrical parabolic shape as a function of composition.

In the case of multicomponent systems this equation can be modified considering the following assumptions:^{4,8} (i) the quadratic form represented by the one-term Redlich–Kister expansion is strictly the result of interactions between different species (no x_i^2 or x_j^2 terms contribute to G^E). In a multicomponent system all different pairs must be accounted for:

one pair ($i-j$) in a binary system [Eq. (7)], 3 different pairs ($i-j$, $i-k$, and $j-k$) in a ternary mixture, 6 in a quaternary system, ..., and 15 in the samples of krypton under discussion; (ii) the contributions from all pairs are additive and in the case of isotopic mixtures the weight of each contribution [the A factor in Eq. (7)] can be correlated to the mass difference between the two components of a given pair (for instance the contribution to G^E from the $^{80}\text{Kr}-^{84}\text{Kr}$ interaction is two times the contribution from the $^{82}\text{Kr}-^{84}\text{Kr}$ pair and four times that from the $^{83}\text{Kr}-^{84}\text{Kr}$ pair); (iii) interactions between three or more species are not taken into account.

The molar excess Gibbs energy of a n -component isotopic mixture can be written as a one-term Redlich-Kister equation of the form,

$$\begin{aligned} \frac{G^E}{RT} &= A \sum_{j=1}^{n-1} \sum_{k=j+1}^n |m_j - m_k| \cdot x_j x_k \\ &= \frac{A}{2} \sum_{j=1}^n \sum_{k=1}^n |m_j - m_k| \cdot x_j x_k. \end{aligned} \quad (8)$$

This type of equation was employed in the study of quaternary mixtures of H/D substituted ammonia.⁸ From the experimental $p-x-T$ data obtained it was possible to extract the contribution to nonideality from the $\text{NH}_3 + \text{ND}_3$ pair and compare the result with the one estimated using the statistical theory of VPIE in mixtures.

In the case of the krypton N and E samples, n is six and Eq. (8) can be written taking $\ln \gamma_{\text{Kr}}^\infty$ as the weight of the $^{80}\text{Kr}-^{84}\text{Kr}$ contribution to nonideality,

$$\frac{G^E}{RT} = \frac{\ln \gamma_{\text{Kr}}^\infty}{4} \frac{1}{2} \sum_{j=1}^6 \sum_{k=1}^6 |m_j - m_k| \cdot x_j x_k. \quad (9)$$

The activity coefficient of each species in the mixture can be derived from Eq. (9) through the relation given by Eq. (5),

$$\ln \gamma_i = \frac{\ln \gamma_{\text{Kr}}^\infty}{4} \sum_{j=1}^6 \left[|m_j - m_i| x_j - \frac{1}{2} \sum_{k=1}^6 (|m_k - m_j| x_k x_j) \right]. \quad (10)$$

Again, vapor pressure and composition data of samples N and E , now manipulated through Eqs. (1) and (3), solve the two unknowns p_{84}^0 and p_{80}^0 at a given temperature. The only additional value needed to take into account the nonideal behavior of the mixtures is the contribution to nonideality from the $^{80}\text{Kr}-^{84}\text{Kr}$ interaction, $\ln \gamma_{\text{Kr}}^\infty$.

B. Accessing nonideality in binary monatomic mixtures

The theoretical prediction of activity coefficients for noble gas isotopic mixtures is greatly simplified since rotational and internal vibrational modes are absent. In a previous work, Rebelo *et al.*⁷ have shown the existence of an intimate relation between activity coefficients on the one hand and reduced partition function ratio, mass differences, and molar volume isotope effects (MVIE) on the other. Their development assumed (excluding the critical region) that the mean Laplacian of the isotope independent intermolecular

potential is much greater in the liquid than in the gas phase, $\langle \nabla^2 U \rangle_l \gg \langle \nabla^2 U \rangle_g$. Also, $\langle \nabla^2 U \rangle_l$ was approximated to follow the relation $\langle \nabla^2 U \rangle_l V = \text{constant}$, where V is the molar volume of the liquid along the orthobaric line. Enhanced generality can be achieved if one assumes instead^{13,14} that $\langle \nabla^2 U \rangle_l / [\rho^* (1 + \rho^*)] = \text{constant}$, where ρ^* is the reduced liquid density along the orthobaric line. Under this latter circumstance one obtains,^{7,15}

$$G^E / (RT x_1 x_2) = \ln \gamma^\infty = \ln \left(\frac{f_l}{f_g} \right) \cdot \frac{m}{m - m'} \cdot \frac{\Delta V}{V} \cdot 2\Gamma_T, \quad (11)$$

where G^E is the excess molar Gibbs energy of the binary mixture, γ^∞ is the activity coefficient of any of the two species at infinite dilution, (f_l/f_g) —which is intimately related^{15,16} to the VPIE—is the reduced partition function ratio in the liquid phase to that in the ideal gas, and m stands for the mass with the prime labeling the lighter isotope. $\Delta V/V$ represents the MVIE and Γ_T is the bulk Gruneisen parameter^{17,18} evaluated along an isotherm,

$$\Gamma_T = -\frac{1}{2} \left[\frac{\partial (\ln \langle \nabla^2 U \rangle)}{\partial (\ln V)} \right]_T = \frac{1}{2} \left[\frac{\partial (\ln \langle \nabla^2 U \rangle)}{\partial (\ln \rho)} \right]_T. \quad (12)$$

$\langle \nabla^2 U \rangle$ is the mean Laplacian of the intermolecular potential, and V and ρ stand for volume and density, respectively.

In the absence of experimental values of MVIE for monatomics these have to be estimated. The quantum-mechanical relation of Menes *et al.*¹⁷ is based on Bigeleisen's theory¹ and relates the MVIE to the temperature dependence of (f_l/f_g) through the expression,

$$\frac{\Delta V}{V} = -\frac{\beta_T \Gamma_T R T^2}{V} \cdot (d \ln(f_l/f_g) / dT), \quad (13)$$

where β_T is the isothermal compressibility. Equations (11) and (13) can be combined into a single expression for the activity coefficient,

$$\begin{aligned} \ln \gamma^\infty &= -2 \frac{\beta_T \Gamma_T^2 R T^2}{V} \frac{m}{m - m'} \cdot \ln \left(\frac{f_l}{f_g} \right) \cdot (d \ln(f_l/f_g) / dT) \\ &= -\frac{\beta_T \Gamma_T^2 R T^2}{V} \frac{m}{m - m'} \cdot \frac{d}{dT} \left(\ln \frac{f_l}{f_g} \right)^2. \end{aligned} \quad (14)$$

This theoretical framework was successfully applied to the interpretation of the VPIE in binary mixtures of ($^{36}\text{Ar} + ^{40}\text{Ar}$).⁷ The deviations from ideality measured experimentally and quantified by the molar excess Gibbs energy of the mixtures, confirmed the theoretical results, i.e., there is a small but measurable deviation from ideality even in such an "ideal" system.

III. RESULTS AND DISCUSSION

Krypton VPIE results are compiled in Table I. All experimental data (differential vapor pressure measurements between the N and E krypton samples) were taken from the original krypton VPIE paper.⁵

Columns 1–3 correspond to the original VPIE data.⁵ Column 4 corresponds to $\ln(f_l/f_g)$ values recalculated using the data of columns one to three and the ideal mixture ap-

TABLE I. Vapor pressure of the krypton N sample, p_N , VPIE between the E and N samples, $p_E/p_N - 1$ (both taken from the original Ref. 5), and reduced partition function ratio between ^{80}Kr and ^{84}Kr , $\ln(f_i/f_g)$, recalculated in this work using the ideal behavior approximation. Differences between values calculated using the ideal behavior approximation and the nonideal case are expressed as $\Delta = (\text{ideal} - \text{nonideal})$.

T (K)	p_N (mmHg)	$10^3(p_E/p_N - 1)$	$10^3 \ln(f_i/f_g)$	Δp_{80} (mmHg)	Δp_{84} (mmHg)	$10^6 \Delta \ln(f_i/f_g)$
115.80	548.333	0.91	0.99 ₃	0.0005	0.0004	0.111
115.81	548.786	0.91	0.99 ₃	0.0005	0.0004	0.111
115.84	549.877	0.90	0.98 ₂	0.0005	0.0004	0.111
115.85	550.685	0.90	0.98 ₂	0.0005	0.0004	0.111
115.87	551.556	0.97	1.05 ₈	0.0005	0.0004	0.111
115.87	551.661	0.89	0.97 ₁	0.0005	0.0004	0.111
115.89	552.220	0.91	0.99 ₃	0.0005	0.0004	0.111
115.90	553.033	0.93	1.01 ₅	0.0005	0.0004	0.111
116.04	559.161	0.89	0.97 ₁	0.0005	0.0004	0.110
116.95	603.445	0.96	1.04 ₅	0.0005	0.0004	0.107
117.08	610.228	0.89	0.96 ₉	0.0005	0.0005	0.106
117.32	622.570	0.94	1.02 ₃	0.0005	0.0005	0.105
117.33	623.028	0.93	1.01 ₂	0.0005	0.0005	0.105
117.34	623.517	0.91	0.99 ₀	0.0005	0.0005	0.105
117.37	625.104	0.87	0.94 ₇	0.0005	0.0005	0.105
117.54	633.929	0.82	0.89 ₂	0.0005	0.0005	0.104
117.81	648.076	0.86	0.93 ₅	0.0005	0.0005	0.103
118.37	678.037	0.85	0.92 ₃	0.0006	0.0005	0.101
118.37	678.340	0.86	0.93 ₄	0.0006	0.0005	0.101
118.49	684.589	0.83	0.90 ₁	0.0006	0.0005	0.101
119.18	723.916	0.84	0.91 ₁	0.0006	0.0005	0.098
119.18	723.950	0.84	0.91 ₁	0.0006	0.0005	0.098
119.18	723.979	0.84	0.91 ₁	0.0006	0.0005	0.098
119.98	771.279	0.82	0.88 ₈	0.0006	0.0005	0.096
119.98	771.335	0.82	0.88 ₈	0.0006	0.0005	0.096
119.98	771.335	0.82	0.88 ₈	0.0006	0.0005	0.096
119.98	771.409	0.82	0.88 ₈	0.0006	0.0005	0.096
119.98	771.487	0.82	0.88 ₈	0.0006	0.0005	0.096
120.61	810.506	0.80	0.86 ₅	0.0006	0.0005	0.093
121.10	842.650	0.78	0.84 ₃	0.0006	0.0005	0.092
121.18	848.039	0.79	0.85 ₄	0.0006	0.0005	0.092
121.23	850.688	0.84	0.90 ₇	0.0006	0.0005	0.091
121.23	850.732	0.84	0.90 ₇	0.0006	0.0005	0.091
121.23	850.743	0.84	0.90 ₇	0.0006	0.0005	0.091
121.23	850.772	0.84	0.90 ₇	0.0006	0.0005	0.091
121.23	850.787	0.83	0.89 ₇	0.0006	0.0005	0.091
121.28	854.501	0.77	0.83 ₂	0.0006	0.0005	0.091
121.37	860.161	0.80	0.86 ₄	0.0006	0.0005	0.091
121.38	860.939	0.82	0.88 ₆	0.0006	0.0005	0.091
121.38	860.978	0.76	0.82 ₁	0.0006	0.0005	0.091
121.54	871.900	0.79	0.85 ₃	0.0006	0.0006	0.090
121.91	897.213	0.77	0.83 ₁	0.0006	0.0006	0.089
121.92	897.342	0.77	0.83 ₁	0.0006	0.0006	0.089
123.31	998.009	0.75	0.80 ₇	0.0007	0.0006	0.085

proximation [Eqs. (1) and (2)]. There are differences between the original $\ln(f_i/f_g)$ values and the new recalculated ones. In the 115–123 K temperature range, the differences (never larger than 0.01) are attributed to rounding-off during the calculation, the use of auxiliary data taken from different sources, and to the small number of significant digits presented in the original paper [specially in the values of $(p_E/p_N) - 1$]. The exact masses of the various krypton nuclides were taken from Ref. 19. The N sample pressure data above 123 K (given in Table IV of Ref. 5) do not agree with the liquid–vapor pressure equation given in the same paper [Eq. (12) of Ref. 5]. Caution must be taken when applying the equation above 123 K. For the purpose of the present analysis it suffices to consider the VPIE data in the tempera-

ture range 115–123 K. Not all of the original VPIE data are included in the present study.

In order to recalculate the $\ln(f_i/f_g)$ values from the pressure data, according to the approximations performed by Lee *et al.*,⁵ it is necessary to know at each temperature the second virial coefficient, B_N , and the liquid orthobaric molar volume, V_N^0 , of normal krypton. The B_N values were calculated from a Beattie–Bridgeman equation taken from Hirshfelder, Curtiss, and Bird.²⁰ The V_N^0 values were taken from Streett and Staveley.²¹

The data in columns 1, 4, and 7 and also the original $\ln(f_i/f_g)$ data were used to produce Fig. 1, a plot of $T \ln(f_i/f_g)$ vs $1/T$. Again, the small differences between the original and

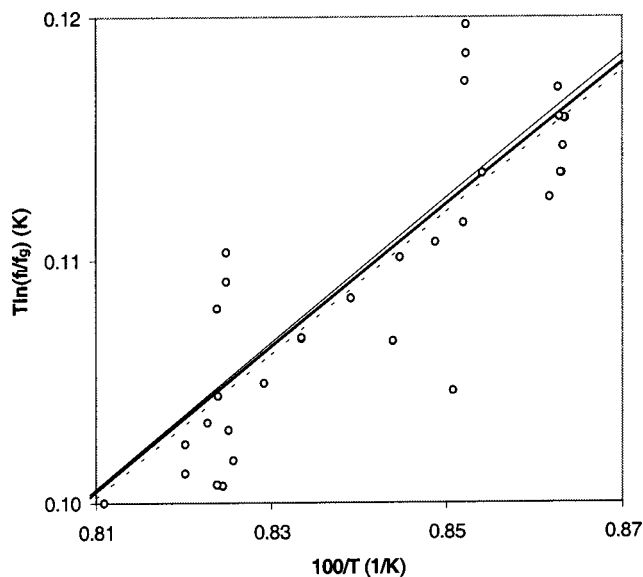


FIG. 1. Vapor pressure isotope effect between ^{80}Kr and ^{84}Kr , expressed as $T \ln(f_i/f_g)$ vs $1/T$. The circles represent the effect calculated from each experimental datum in Ref. 5. The three lines represent, respectively, the fit to the original data of Ref. 5 (thin solid line); the fit to the original data recalculated considering ideal behavior or with deviations from ideality in the krypton samples (the two situations yield two indistinguishable lines in the scale of the plot, thick solid line); and the fit (dashed line) to the original data recalculated considering deviations from ideality 17 times larger (arbitrary value which is close to the deviations found in argon mixtures) than those used in the previous set.

recalculated data (thin and thick solid lines) are within the rounding-off error.

As mentioned in the previous sections, if one seeks to introduce nonideal behavior in these multicomponent systems, then, the only quantity that has to be estimated is the activity coefficient at infinite dilution of one of the isotopes, $\ln \gamma_{\text{Kr}}^\infty$, in a reference binary mixture—in the present case the ($^{80}\text{Kr} + ^{84}\text{Kr}$) system. Equation (14) permits us to evaluate this quantity provided the values of the isothermal compressibility, β_T , and Grüneisen, Γ_T , coefficients in the liquid phase are known as a function of temperature. Isothermal compressibility data in liquid krypton were taken from Street and Staveley.²¹ The reported values were extrapolated to lower temperatures assuming a linear dependence with temperature near the triple point. For liquid krypton β_T varies from 1.66×10^{-4} to $2.23 \times 10^{-4} \text{ atm}^{-1}$ in the 116–130 K temperature range. The Grüneisen coefficients were estimated through Eq. (12) using the tabulated (see Ref. 13, Table II) temperature and density dependence of the mean Laplacian of the Maitland–Smith intermolecular potential, yielding values of 1.35–1.24 in the 116–130 K temperature range. These results correspond to a value of $\ln \gamma_{\text{Kr}}^\infty$ ranging from 4.83×10^{-6} to 3.09×10^{-6} . An equimolar binary mixture of ($^{80}\text{Kr} + ^{84}\text{Kr}$) would have an excess molar Gibbs energy of 1.2 mJ mol^{-1} at 116 K, decreasing to 0.9 mJ mol^{-1} at 130 K.

The VPIE between ^{80}Kr and ^{84}Kr can now be calculated using Eqs. (1) and (3) [the deviations from ideality contained in the γ_i and ϕ_i terms of Eq. (3) are calculated iteratively through Eqs. (4) and (10)]. The difference between the values of $\ln(f_i/f_g)$ ($^{84}\text{Kr}/^{80}\text{Kr}$) calculated under ideal and non-

ideal conditions are presented in the seventh column of Table I and also depicted in the $T \ln(f_i/f_g)$ vs $100/T$ plot of Fig. 1. A least-squares fit to the latter results in

$$\ln(f_i/f_g) = (21.21 \pm 1.71)/T^2 - (5.77 \pm 1.20) \times 10^{-4}. \quad (15)$$

The $T \ln(f_i/f_g)$ values are 0.01% smaller if nonideality is taken into account. Part of the difference between the vapor pressure of the two mixture samples is no longer solely attributed to the VPIE between pure nuclides but also a consequence of an “excess pressure” due to the interactions between different species.

The effect of nonideality can also be assessed through the estimation of new values for the vapor pressure of the pure nuclides, namely, ^{80}Kr and ^{84}Kr . These shifts are reported in Table I as vapor pressure differences calculated using “ideal mixture” and “nonideal behavior” assumptions (columns 5 and 6). The vapor pressure values are overestimated under the ideal mixture approximation by about 0.0005 mmHg at 116 K and 0.0007 mmHg at 123 K. This correction to ideal solution behavior tends to increase as temperature rises. For instance, by rescaling the T – p relation of the original paper of Lee *et al.*⁵ above 123.31 K using the vapor pressure equation of normal krypton, one finds a correction of 0.0008 mmHg at 130 K. These corrections are slightly smaller than the present limits of accuracy typically found for double differential techniques of vapor pressure measurements.^{7,15} For instance, excess molar Gibbs energies of mixing were detected in $^{36}\text{Ar} + ^{40}\text{Ar}$ mixtures using differential vapor pressure measurements with a temperature dependent accuracy^{7,15} in the range ± 0.0008 – 0.006 mmHg.

Figure 1 also shows the shift in $T \ln(f_i/f_g)$ resulting from an arbitrary overestimation of the deviation from ideality in comparison to that assumed in the current calculations. The arbitrary nonideality was fixed at a value corresponding to the nonideality found in ($^{36}\text{Ar} + ^{40}\text{Ar}$) mixtures, i.e., a 17-fold increase of G^E in relation to the predicted value for krypton mixtures. It is important to notice that the scatter of the original krypton data is such that masks the effect of the deviation from ideality even when the latter is overestimated up to the argon values. Nonetheless, deviations from ideality in argon mixtures were experimentally detected using a doubly differential technique.^{7,15}

Although we are quite confident that the actual deviations from ideality in krypton mixtures cannot deviate significantly from the estimated ones ($G_{1/2}^E \sim 1 \text{ mJ mol}^{-1}$), it is also true that there are no experimental data to compare with. On the one hand, the current calculations are supported by the good performance that similar ones produced in the case of the argons (where there are experimental data for $G_{1/2}^E$). On the other hand, and in the absence of experimental data, one has to rely on estimations of the density dependence of mean force constants and MVIEs.

The current work provides a detailed theoretical framework that enables one to accurately deal with the case of nonideal, multicomponent, isotopic mixtures. Although for the present case of krypton and for the corresponding available experimental data accuracy, the application of this development has proven that, in practice, the correction can be

discarded, this is per se an important conclusion. It substantiates the original assumption of Lee *et al.*⁵ of neglecting nonideal multicomponent behavior. Furthermore, the current development and its conclusions are significant in a theoretical sense. They provide the principles and fundamentals for treating such cases of multicomponent, monatomic, isotopic mixtures. Additionally, one can now immediately envisage those cases where the Δ -correction must also be significant from a numerical perspective. We refer, for instance, to the case of the isotopic forms of neon where deviations from ideality are expected¹⁰ to be about 400 times greater than those in krypton.

It is concluded that, in contrast to the case of ammonia⁸ (strongly interacting components), for krypton (weakly and heavier interacting components), deviations from ideal solution behavior do not introduce an important correction when compared with the available data accuracy.

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