Isotopic krypton mixtures revisited: Vapor pressure isotope effects

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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 $^{80}$Kr($l$) and $^{84}$Kr($l$) from data on isotopic mixtures. The correction to ideal solution behavior, $\Delta$, 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 0.8351 and 0.8362 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 $\Delta$-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 phase 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. 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; 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 Bigeleisen 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 ratio between $^{80}$Kr and $^{86}$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.

Since then, both experimental and theoretical vapor pressure isotope effect studies were extended to include isotopic liquid mixtures 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; secondly, that liquid mixtures of ammonia (NH$_3$ + ND$_3$) ought to be treated as multicomponent nonideal mixtures in order to correctly estimate the corresponding VPIE in the mixture.
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, $p^0_i$, of mass $m_i$, was regarded as a mass weighted average of the vapor pressures of $^{84}$Kr and $^{80}$Kr,

$$p^0_i = p^0_{84} + (p^0_{80} - p^0_{84}) \frac{m_{84}}{(m_{84} - m_{80})} \cdot \frac{(m_{84} - m_i)}{m_i};$$

(1)

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

$$p^m = \sum_i x_i p_i^0,$$

(2)

Equation (1) reflects the so-called vapor pressure geometrical mean rule 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, $p^0_{84}$ and $p^0_{80}$.

The second assumption corresponds, apparently, to a more severe approximation. For instance, it has been experimentally proven that argon mixtures of $^{36}$Ar and $^{40}$Ar are not ideal. As with many quantum effects in krypton than in argon, we anticipate the nonideal solution behavior to be smaller for the krypton system than in the particular case of isotopic mixtures. The excess molar Gibbs energy of the mixture, $G^E$, by the expression

$$G^E = \frac{\partial (nG^E/RT)}{\partial n_i} \tau_{p,n_i};$$

where $G^E$ 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.

The activity coefficient $\gamma$ reflects the nonideality of the condensed phase and is related to the excess molar Gibbs energy of the mixture, $G^E$.

$$\ln \gamma_i = \left( \frac{\partial (nG^E/RT)}{\partial n_i} \right)_T, p, n_i.$$  

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 $T$,

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

(6)

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

$$\frac{G^E}{RT} = Ax_i x_j,$$

(7)

because all isotopic mixtures so far studied have invariably shown 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: (i) the quadratic form represented by the one-term Redlich–Kister is strictly the result of interactions between different species (no $x^2_i$ or $x^2_j$ 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 \((i-j, i-k, \text{and } j-k)\) 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 \(^{80}\text{Kr}-^{84}\text{Kr}\) 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,

\[
\frac{G^E}{RT} = \frac{A}{2} \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} [m_j - m_k] x_j x_k.
\]

This type of equation was employed in the study of quaternary mixtures of \(\text{H/D}\) substituted ammonia. 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 \(\ln \gamma^E_{\text{Kr}}\) as the weight of the \(^{80}\text{Kr}-^{84}\text{Kr}\) contribution to nonideality,

\[
\frac{G^E}{RT} = \frac{\ln \gamma^E_{\text{Kr}}}{4} \sum_{j=1}^{6} \sum_{k=1}^{6} [m_j - m_k] x_j x_k.
\]

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

\[
\ln \gamma_i = \frac{\ln \gamma^E_{\text{Kr}}}{4} \sum_{j=1}^{6} [m_j - m_i] x_j - \frac{1}{2} \sum_{k=1}^{6} ([m_k - m_i] x_k x_i).
\]

Again, vapor pressure and composition data of samples \(N\) and \(E\), now manipulated through Eqs. (1) and (3), solve the two unknowns \(p^0_5\) and \(p^0_{40}\) 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, \(\ln \gamma^E_{\text{Kr}}\).

**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. 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, \(\langle \nabla^2 U \rangle \approx \langle \nabla^2 U \rangle^c\). Also, \(\langle \nabla^2 U \rangle^c\) was approximated to follow the relation \(\langle \nabla^2 U \rangle^c = \text{constant}\), where \(V\) is the molar volume of the liquid along the orthobaric line. Enhanced generality can be achieved if one assumes instead that \(\langle \nabla^2 U \rangle^c / (\rho^\ast (1 + \rho^\ast)) = \text{constant}\), where \(\rho^\ast\) is the reduced liquid density along the orthobaric line. Under this latter circumstance one obtains,\(^{7,15}\)

\[
G^E_i(\text{RT} x_1 x_2) = \ln \gamma^E = \ln \left(\frac{f_i}{f_g}\right) - \frac{m}{m-m_i} \cdot \frac{\Delta V}{V} \cdot 2 \Gamma_T,
\]

where \(G^E\) is the excess molar Gibbs energy of the binary mixture, \(\gamma^E\) is the activity coefficient of any of the two species at infinite dilution, \((f_i/f_g)\)—which is intimately related 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 \(\Gamma_T\) is the bulk Gruneisen parameter evaluated along an isotherm.

\[
\Gamma_T = -\frac{1}{8} \left[ \frac{\partial}{\partial (\ln \rho)} \left(\frac{\langle \nabla^2 U \rangle^c}{\rho^\ast (1 + \rho^\ast)}\right) \right]_T = \frac{1}{2} \left[ \frac{\partial}{\partial (\ln \rho)} \left(\frac{\langle \nabla^2 U \rangle}{\rho^\ast}\right) \right]_T.
\]

\(\langle \nabla^2 U \rangle^c\) is the mean Laplacian of the intermolecular potential, \(V\) and \(\rho\) 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. is based on Bigeleisen’s theory and relates the MVIE to the temperature dependence of \((f_i/f_g)\) through the expression,

\[
\frac{\Delta V}{V} = -\frac{\beta T \Gamma_T^2 RT^2}{V} \cdot (d (\ln (f_i/f_g))/dT),
\]

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

\[
\ln \gamma^E = \ln \left(\frac{f_i}{f_g}\right) - \frac{m}{m-m_i} \cdot \frac{d}{dT} \left[ \ln \left(\frac{f_i}{f_g}\right) \right]^2 - \frac{\beta T \Gamma_T^2 RT^2}{V} \cdot \frac{m}{m-m_i} \cdot \frac{d}{dT} \left[ \ln \left(\frac{f_i}{f_g}\right) \right]^2.
\]

This theoretical framework was successfully applied to the interpretation of the VPIE in binary mixtures of \(^{38}\text{Ar} + ^{40}\text{Ar}\).\(^3\) 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.\(^7\)

Columns 1–3 correspond to the original VPIE data.\(^5\) Column 4 corresponds to \(\ln (f_i/f_g)\) values recalculated using the data of columns one to three and the ideal mixture ap-
approximation [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 temperature 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., it is necessary to know at each temperature the second virial coefficient, \(B_N\), and the liquid orthobaric molar volume, \(V^0_N\), of normal krypton. The \(B_N\) values were calculated form a Beattie–Bridgeman equation taken from Hirshfelder, Curtiss, and Bird. The \(V^0_N\) values were taken from Street and Staveley.

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

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<td>0.85</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.090</td>
</tr>
<tr>
<td>121.91</td>
<td>897.213</td>
<td>0.77</td>
<td>0.83</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.089</td>
</tr>
<tr>
<td>121.92</td>
<td>897.342</td>
<td>0.77</td>
<td>0.83</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.089</td>
</tr>
<tr>
<td>123.31</td>
<td>998.009</td>
<td>0.75</td>
<td>0.80</td>
<td>0.0007</td>
<td>0.0006</td>
<td>0.085</td>
</tr>
</tbody>
</table>
ideal conditions are presented in the seventh column of Table I and also depicted in the $T \ln(f_i/f_g)$ vs $1/T$ plot of Fig. 1. A least-squares fit to the latter results in

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

(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. 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. For instance, excess molar Gibbs energies of mixing were detected in $^{36}$Ar+$^{40}$Ar mixtures using differential vapor pressure measurements with a temperature dependent accuracy in the range $\pm 0.0008$–$0.006$ 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 $(^{36}$Ar+$^{40}$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.

Although we are quite confident that the actual deviations from ideality in krypton mixtures cannot deviate significantly from the estimated ones ($G_{1/2}^E \sim 1$ 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 MVI$ar{E}$s.

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.\textsuperscript{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 $\Delta$-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 expected\textsuperscript{10} to be about 400 times greater than those in krypton.

It is concluded that, in contrast to the case of ammonia\textsuperscript{8} (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.

**ACKNOWLEDGMENT**

This work was financially supported by FCT under Contract POCTI No. 34955/EQU/2000.

\textsuperscript{9} J. N. C. Lopes, L. P. N. Rebelo, and J. Bigeleisen (in preparation).
\textsuperscript{18} Handbook of Chemistry and Physics, 80th ed., edited by D. R. Lide (CRC, Boca Raton, 1999).