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Vapor Pressure and Related Thermodynamic Properties of ^{36}Ar

J. C. G. Calado, F. A. Dias,[†] J. N. C. Lopes, and L. P. N. Rebelo^{*,†}

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

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The ^{36}Ar – ^{40}Ar vapor pressure isotope effect in the liquid and solid phases has been experimentally determined at about 100 temperatures between 83 and 97 K using a high-accuracy double-differential manometric technique. Differences between the vapor pressure of a highly enriched sample of ^{36}Ar and that of natural argon were measured simultaneously with the absolute vapor pressure of natural argon. Absolute and differential vapor pressure measurements show an estimated accuracy of 0.15% and 0.001%, respectively, with respect to the absolute vapor pressure of argon. Data were obtained in both the solid and liquid regions. The vapor pressure of ^{36}Ar is always higher than that of ^{40}Ar by about 0.5%. Triple-point temperatures and pressures were also measured for both isotopes. All data compare favorably with previous results reported in the literature and are nicely interpreted within the framework of Bigeleisen's theory of isotope effects. Using a large temperature extrapolation of our data, liquid–vapor isotope fractionation factors were successfully inferred from the vapor pressure measurements; the estimated values agree with the experimental ones up to close to the critical point. The isotopic difference in the molar enthalpies of vaporization and sublimation was also calculated from the vapor pressure data. Additionally, molar volume and second virial coefficient isotope effects are estimated using several different theoretical approaches.

1. Introduction

In the past few years we have studied a number of binary and pseudobinary systems involving liquefied gases of isotopically substituted species and their mixtures, namely, the methanes,^{1–3} ammonias,^{3,4} hydrogen chlorides,^{3,5} and hydrogen sulfides.³ These systems were chosen on account of their relative structural simplicity, and the study of their behavior has allowed us to test several of the most commonly used modern statistical theories of the liquid state.

Both the magnitude of the isotope effects (IE) on the physical properties of pure substances and mainly of the departures from ideality exhibited by their mixtures are inevitably very small. The experiments thus had to be of the highest possible precision and, this led us to conceive a truly doubly differential technique.¹ Although we successfully accomplished the main goals associated with the previously studied systems, both from an experimental point of view as well as on their theoretical interpretation at a molecular level, some problems remain. The analysis of IE on the physical properties of pure substances⁶ as well as that of the deviations from ideality in isotopic mixtures^{7,8} have clearly demonstrated that a proper consideration of the intra- and intermolecular vibrational motions of the component molecules and their density dependence is absolutely essential. To an excellent approximation, electronic structures are independent of the isotopic distribution of nuclear mass (Born–Oppenheimer approximation). Therefore, distinct isotopes of the same element are described by the same (isotope-independent) potential energy surface (PES). For polyatomic molecules, London dispersion forces depend on internal vibrational frequencies. These, in turn, can differ significantly between isotopomers of the same substance and thus the *effective* intermolecular PES should be

isotope-dependent. This effect results from the averaging of the forces over the isotope-dependent vibrations,⁹ but this concept in no way violates the B–O approximation. The most commonly used theories of liquid solutions,¹⁰ like the van der Waals-1 fluid theory and the one-center Lennard-Jones perturbation theory, disregard vibrational motions and vibrational interactions, choosing to model solutions in terms of structureless molecular entities, where excess properties emerge from the choice of different effective pair potential functions and/or in small deviations from the Lorentz and Berthelot combining rules. Intra- and intermolecular vibrational structures are therefore masked under the assignment of distinct effective potential parameters of the mixture constituents. Under these circumstances, mixtures of isotopic forms of rare gases (no internal structure) should be strictly ideal. The above-mentioned theories have been successfully applied to nonisotopic mixtures.

In contrast, condensed phase isotope effect theory^{6,7,11} uses identical PES's to describe the behavior of both isotopes (monatomics) and isotopomers (polyatomics). Here, the interpretation of IE's on the physical properties of pure substances and of the excess properties exhibited by isotopic mixtures is carried out through the quantum kinetic differences between the species moving on the same isotope- and concentration-independent PES. Recently available experimental results on mixtures of isotopomers have proven that vibrational motions of the component molecules are paramount to the understanding of their behavior⁷ and, in turn, that those theories which consider molecules as structureless entities are inadequate.² Since rare gases are structureless particles, theories here can be applied in their purest form. If the assumptions made within the theory of isotope effects are correct, a liquid mixture of two isotopic forms of a rare gas is *not* ideal, and the classical portion of the gas-phase second virial coefficient of the isotopes of the same element should be identical. Eventual isotopic differences in the latter property should arise from the translational quantum correction.

* To whom correspondence should be addressed. E-mail: luis.rebelo@dq.fct.unl.pt. Fax: (351)-21-294 8385.

[†] Present address: Departamento de Química, Centro de Química Fina e Biotecnologia, Faculdade de Ciências e Tecnologia da UNL, 2825–114 Caparica, Portugal.

With these ideas in mind, we embarked on a program to measure the small differences in the physical properties between ^{36}Ar and ^{40}Ar , and their solutions, namely, (i) the difference between their vapor pressures, (ii) the excess molar Gibbs energy of liquid mixtures containing these two isotopes and, finally, (iii) the differences between their second virial coefficients. The work reported herein is part of this general project. In order to test the accuracy and precision capabilities of our apparatus, the vapor pressure isotope effect of ^{36}Ar – ^{40}Ar was determined and compared with data already available in the literature. Differences in the molar enthalpies of vaporization as well as liquid–vapor isotope fractionation factors (LVIFF) are calculated from the vapor pressure measurements. Finally, molar volume isotope effects (MVIE) and second virial coefficient isotope effects (SVCIE) are predicted by using several different theoretical approaches.

The primary purpose of the experiments and theoretical predictions described here was to test the feasibility of performing measurements on the excess properties of liquid (^{36}Ar + ^{40}Ar) mixtures, to be reported in a forthcoming paper.

2. Experimental Section

The experimental setup used in the measurements reported in this work has already been described in detail,¹ but a small modification was introduced: in order to improve accuracy and sensitivity in the differential vapor pressure measurements, the previously employed 100 Torr (0.13 bar) full range capacitance manometers were substituted by manometers of 10 Torr (0.013 bar) full range with a resolution of 10^{-4} Torr (0.013 Pa) and a reproducibility of ± 0.002 Torr (0.26 Pa).

During the acquisition of each experimental datum, temperature was kept within better than 0.01 K for periods of half an hour (any temporary temperature changes that developed within the copper block that contains the liquid samples were found to be lower than $6 \mu\text{K s}^{-1}$), a value that equals its estimated accuracy. Furthermore, we estimate that temperature differences between the cells in the copper block never exceeded 10^{-4} K, judging from the observation of differential vapor pressures measured when the three cells were filled with the same liquid sample.

Natural argon (99.6% of ^{40}Ar , 0.06% of ^{38}Ar and 0.34% of ^{36}Ar) was supplied by Gasin, S.A., with a claimed chemical purity of 99.9995%. It was further purified by distillation two times in a low-temperature apparatus described elsewhere.¹² Samples of ^{36}Ar were purchased from Isotec, Inc. All experimental results reported herein were obtained with ultrapurified samples whose chemical and isotopic analysis are presented in Table 1. Because of the high enrichment of these samples, no corrections for either isotopic or chemical impurities were required. Throughout the text and for sake of simplicity, natural argon will be labeled as ^{40}Ar , while its isotopic counterpart will be referred to as ^{36}Ar . A double check of purity was made by examining the triple point pressure's constancy during melting. The results are summarized in Table 2 and compared with values obtained by other authors. For ^{40}Ar three distinct determinations were made: the first was performed in a triple-point cell connected to the low-temperature distillation apparatus, where the drift in the vapor pressure during melting can be detected but the temperature cannot be monitored. The second was made in the double differential vapor pressure apparatus, where both pressure and temperature were monitored. Finally, the intersection of the curves fitted to the ratio of vapor pressures between both isotopes (see next section) when one moves from $^{36}\text{Ar(l)}/^{40}\text{Ar(l)}$ to $^{36}\text{Ar(l)}/^{40}\text{Ar(s)}$ and $^{36}\text{Ar(l)}/^{40}\text{Ar(s)}$ to $^{36}\text{Ar(s)}/^{40}\text{Ar(s)}$

TABLE 1: Chemical and Isotopic Analysis of the Ultrapurified Sample of ^{36}Ar ^a

sample	^{36}Ar	^{40}Ar
chemical purity	99.996	> 99.9995
H ₂	0.0020	
N ₂	0.0005	
CO ₂	0.0003	
hydrocarbons	0.0005	
isotopic purity	99.9	99.6
^{36}Ar	99.9	0.34
^{38}Ar	0.1	0.06
^{40}Ar		99.6

^a Chemical analyses were done by gas chromatography and are expressed as mole percent. Isotopic analyses were done by mass spectroscopy and are expressed as atomic percentage. Isotopic and chemical purities (after two low-temperature distillations; see also Table 2) of natural argon (^{40}Ar) are also shown.

TABLE 2: Triple-Point Pressures and Triple Point Temperatures of ^{36}Ar and ^{40}Ar

reference	p/kPa	T/K
	Triple Point of ^{40}Ar	
13	68.905	83.80
14	68.749	83.78
15	68.896 ± 0.005	83.806
16	68.894	83.81
17	68.897 ± 0.01	83.80
this work ^a	68.898 ± 0.005	83.82 ± 0.01
this work ^b	68.904 ± 0.005	
this work ^c	68.976 ± 0.050	83.81 ± 0.01
	Triple Point of ^{36}Ar	
15	68.861 ± 0.003	83.747
16	68.862	83.75
this work ^c	68.864 ± 0.050	83.74 ± 0.01

^a Using the differential vapor pressure apparatus. ^b Using the triple-point cell. ^c By intersection of vapor pressure curves (see text).

yields, respectively, the triple point temperatures of ^{40}Ar and ^{36}Ar , from which the corresponding triple point pressures are assessed. In the case of ^{36}Ar , due to its high cost, only this last method was used. Our values agree well with those reported by other authors.

3. Results and Discussion

The absolute vapor pressure (p) of ^{40}Ar and the differential vapor pressure ($\Delta p = p' - p$) between ^{36}Ar and ^{40}Ar were measured at about 100 temperatures between 83 and 97 K. The results are recorded in Table 3 (as Supporting Information), where a subdivision between solid–solid (series I), solid–liquid (series II), and liquid–liquid (series III) regions has been made. By determining the apparent vapor pressure difference between two ^{36}Ar samples with a common sample of ^{40}Ar , an estimate of the uncertainty in a Δp measurement, E_p , is possible and is also given in Table 3.

Our thermometer's calibration was slightly shifted (≈ 0.1 K) in order to match the absolute vapor pressure equation of ^{40}Ar of Gosman et al.,¹³ which has thus served as a common reference for the results presented in this work:

$$\ln p = a_1/T + a_2 \ln T + a_3 T + a_4 + a_5 p \quad (1)$$

with $a_1 = -1.062\,454\,904 \times 10^3$, $a_2 = -4.271\,440\,691$, $a_3 = 1.524\,254\,979 \times 10^{-2}$, $a_4 = 2.992\,927\,939 \times 10^1$, and $a_5 = 2.465\,760\,638 \times 10^{-3}$. Pressure is in atm and temperature in kelvin.

Very recently, Gilgen et al.¹⁸ established a new equation for the vapor pressure of ^{40}Ar and critically reviewed the previously

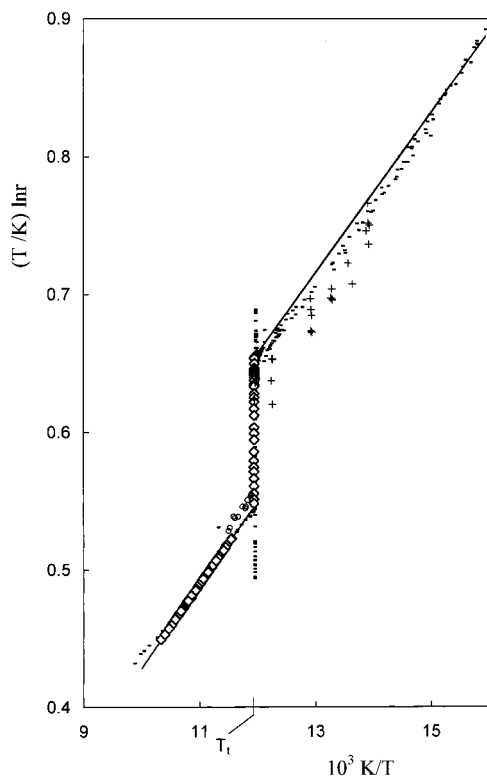


Figure 1. Plot of $(T \ln r)$ against T^{-1} : \blacklozenge , this work; \circ , ref 15; \times , ref 16; $+$, ref 19. The full lines (—) represent eq 2. T_t = triple-point temperature.

published data. This equation differs from that of Gosman less than 0.1% in p within our working temperature range. Since the vapor pressure of ^{36}Ar was differentially determined against that of ^{40}Ar , one can easily correct the established absolute vapor pressure of the former if a different reference equation is chosen for ^{40}Ar .

Vapor Pressure Ratio. The experimentally determined differential vapor pressures between the two argon isotopes are compared with available literature data^{15,16,19} in the range 63–101 K in Figure 1. The plotted points are marked as they appear in the published works and have not been corrected to 100% isotopic and chemical purity unless the authors had already done so. The full lines represent least-squares fitting of our experimental results to the equation

$$\ln r = A + B/T^2 \quad (2)$$

where $r = p'/p$. The prime signifies the lighter isotope. In the liquid region (83–97 K): $A = (-9.733\,633\,0 \pm 0.0299) \times 10^{-4}$, $B = (52.546\,125\,2 \pm 0.0444) \text{ K}^2$, with a standard deviation of the fit $\sigma = 3.0 \times 10^{-6}$. In the solid, $A = (-3.009\,825\,92 \pm 0.0229) \times 10^{-4}$, $B = (56.870\,869\,25 \pm 1.356) \text{ K}^2$, with $\sigma = 2.2 \times 10^{-6}$. The agreement between our results and those of Bigeleisen's group,¹⁵ which have been corrected by these authors for chemical and isotopic impurities, is excellent. The present fits are of just slightly higher internal consistency than those of ref 15. Figure 2, a and b, plots the residuals for $\ln r$ in the solid and liquid, respectively. For the liquid, the scatter in ref 15 is about 0.5% in $\ln r$, while ours is 0.1%.

A remarkable feature of the $\ln r$ plot is that the least-squares fit to our data in the solid (83.40–83.75 K) in the form of eq 2 represents quite well the low-temperature data of Bigeleisen, which spans a range of 20 K below our working temperatures (see Figure 1).

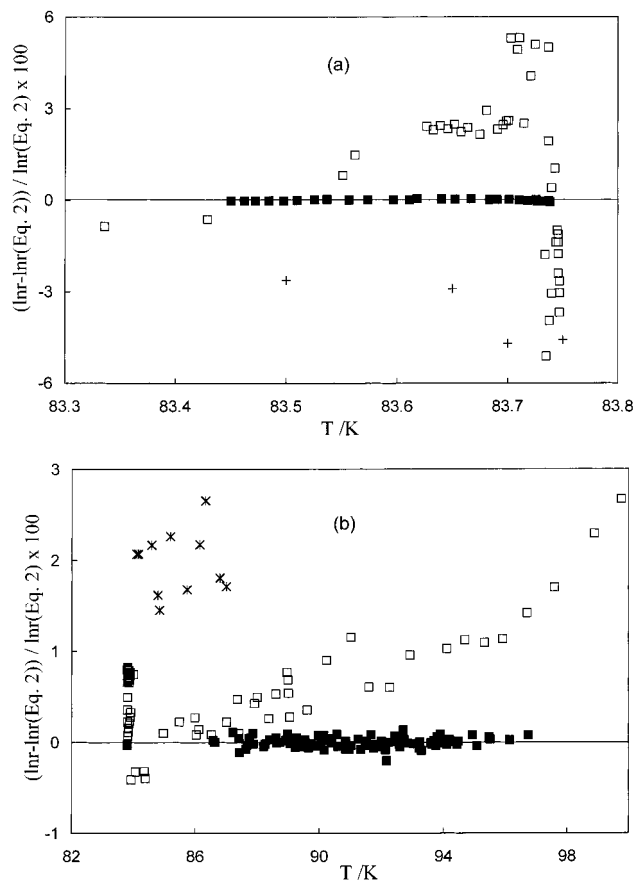


Figure 2. Residuals (in percentage) of the experimental values of $\ln r$ using eq 2 as a reference: \blacksquare , this work; \square , ref 15; \times , ref 16; $+$, ref 19. (a) Solid region; (b) liquid region.

Absolute Vapor Pressure of ^{36}Ar . We compare the present experimental p' values of pure ^{36}Ar with the literature. There are two possible ways of calculating the experimental absolute vapor pressure of ^{36}Ar . Either the observed Δp value is added to the experimentally determined vapor pressure of ^{40}Ar (see Table 3, Supporting Information) or these Δp are added to a smoothed vapor pressure equation for ^{40}Ar , which is being used as a reference pressure, in this last case within the liquid region the Gosman et al.¹³ Equation 1 was selected, while for the solid one we took the fit of Flubacher et al.²⁰ The comparisons are presented in Figure 3a,b (liquid) and c,d (solid). In Figure 3a,c, discrepancies between sets of results arise from errors in the ^{40}Ar vapor pressure as well as from inaccuracies associated with the Δp values, but in Figure 3b,d, deviations are solely due to the scatter and precision of the Δp data. For sake of simplicity only comparisons with our data are plotted. While absolute vapor pressure measurements show deviations of 0.15% (Figure 3a,c), differential determinations could be performed within $\pm 0.001\%$ (Figure 3b,d).

In the liquid region, our results compare very favorably with those of Bigeleisen's group¹⁵ as well as those of Clusius et al.¹⁶ Differences between sets never exceed 0.01% in the differential representation. As for the solid region, the measurements of Boato et al.¹⁹ are consistently 0.05% lower than ours or Bigeleisen's.

Determination of Other Properties. As in previous investigations, we were able to successfully check both the high internal consistency of our differential measurements and the theoretical soundness of eq 2. Using eq 2, one can accurately predict vapor pressures and closely related thermodynamic properties at temperatures well above the upper limit of the experi-

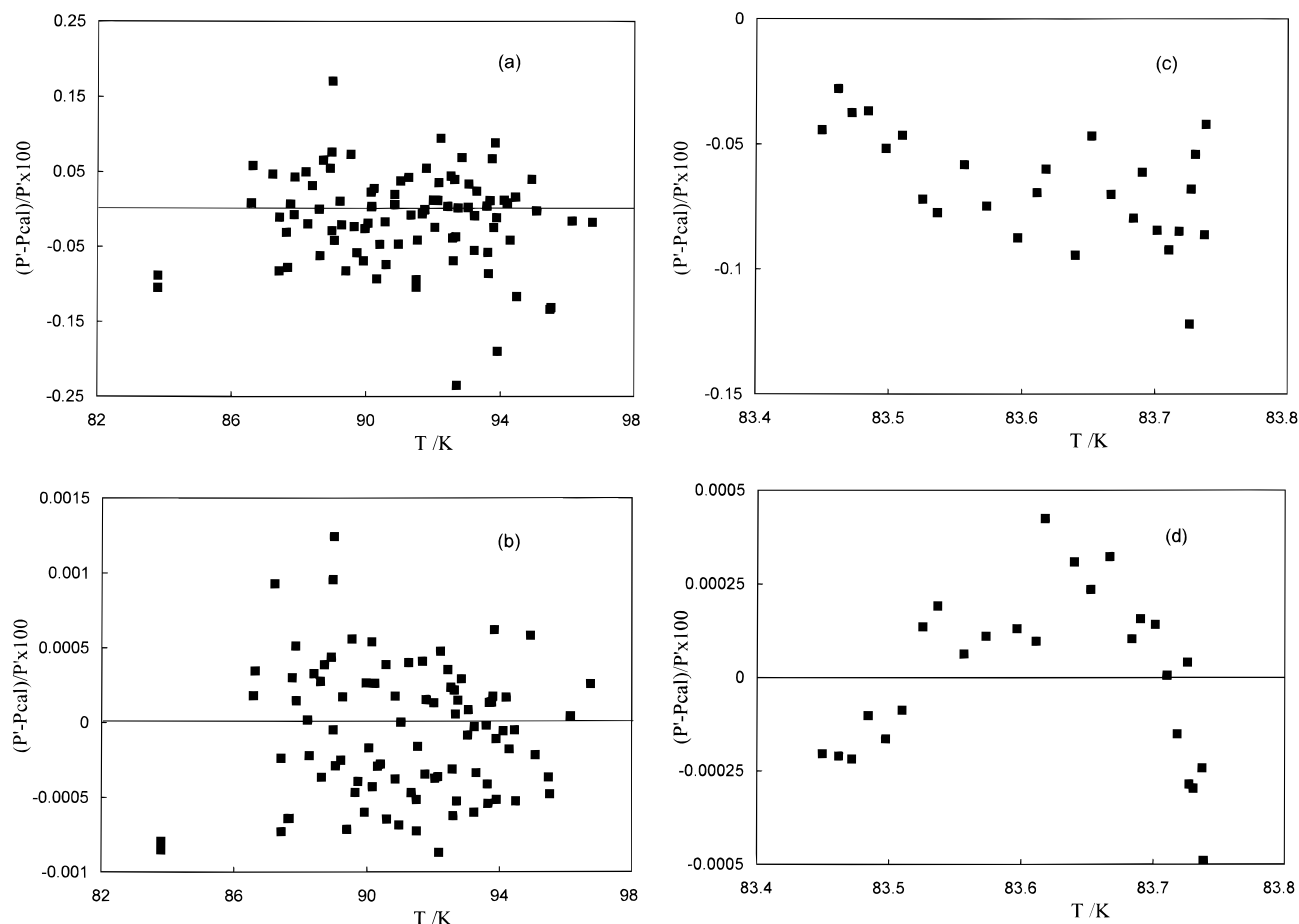


Figure 3. Comparison between the present experimental values of the vapor pressure of liquid ^{36}Ar (p') and those calculated (p_{cal}) from the combination of eq 1 and eq 2. (a) Experimental p' of ^{36}Ar obtained with the experimental p values of ^{40}Ar . (b) Experimental p' of ^{36}Ar obtained with the Gosman et al.¹³ Equation 1 for ^{40}Ar . In the case of solid ^{36}Ar : (c) experimental p' of ^{36}Ar obtained with the experimental p values of ^{40}Ar . (d) Experimental p' of ^{36}Ar obtained with the Flubacher et al.²⁰ vapor pressure data for ^{40}Ar (see text).

ments; i.e., large temperature extrapolations are valid. This is a general feature of the theory of isotope effects of Bigeleisen,¹¹ and, therefore, extrapolations (based on a more general equation containing an extra term to take internal vibrational structure into account) can also safely be performed in polyatomics. The methane molecule constitutes a good example. More than a decade ago, we demonstrated¹ the impressive agreement between a 60 K extrapolation of our data on methane to the region of experimental data of other authors. Because experimental vapor pressures of ^{36}Ar are not available above 3 bar, while liquid–vapor isotope fractionation factors (LVIFF) have been measured²¹ up to the critical point, we were restricted to comparisons with LVIFF. This quantity, labeled here as $\alpha = (xy'/x'y)$, where x and y are the liquid and vapor mole fractions in a binary mixture, respectively, is closely related to VPFE, (p'/p) . In previous works,^{22,23} where we studied the isotope effects of the partially deuterated methanes and their mixtures, we presented an almost exact equation that expresses that relationship. The following more approximate expression, which neglects excess energies of mixing, is adequate for the present purpose:

$$\ln \alpha^\infty \approx \ln \left(\frac{p'}{p} \right) \left[1 + \frac{p}{RT} (B - V + \frac{1}{2RT} (C - B^2)(p' + p)) \right] \quad (3)$$

where the symbol ∞ stands for infinite dilution, B and C are the second and third virial coefficients in the volume expansion of the gas-phase equation of state, and V is the molar volume of the liquid phase. In Figure 4 we compare predictions of \ln

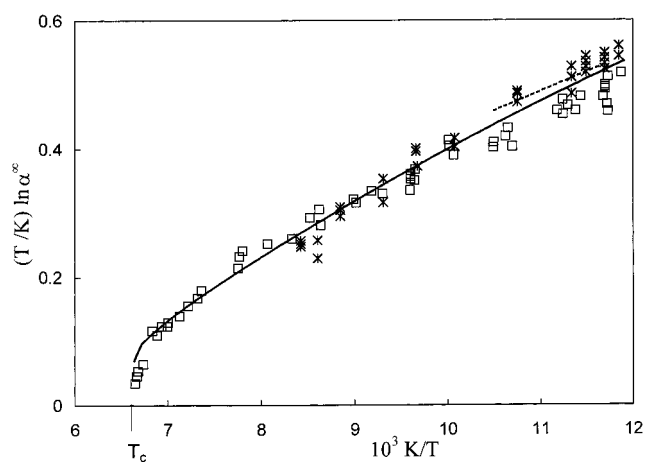


Figure 4. Comparison of experimental liquid–vapor isotope fractionation factors (α^∞ , \square , ref 21; $*$, ref 24) at infinite dilution, α^∞ , with those calculated (—) from eq 3. Dashed line (---) represents the plot of $T \ln r$ against T^{-1} , where $\ln r$ is taken from eq 2. T_c = critical temperature.

α^∞ obtained from a combination of eqs 2 and 3 with the available experimental data. The agreement is excellent, mainly if one takes into account that our values of $\ln r$ were extrapolated more than 45 K. In these calculations, values of B and C for argon were taken from the compilation of Dymond and Smith²⁵ and liquid densities from Wagner et al.¹⁸

TABLE 4: Calculated Values of $\Delta_{40}^{36}\Delta_c^g H_m = \Delta_c^g H_m(^{36}\text{Ar}) - \Delta_c^g H_m(^{40}\text{Ar})^a$

T/K	$\Delta_{40}^{36}\Delta_c^g H_m/\text{Jmol}^{-1}$	T/K	$\Delta_{40}^{36}\Delta_c^g H_m/\text{Jmol}^{-1}$
70	-14	110	-10
80	-13	130	-9.6
90	-11		

^a For $T < 83.74$ K, c = solid and for $T > 83.81$ K, c = liquid.

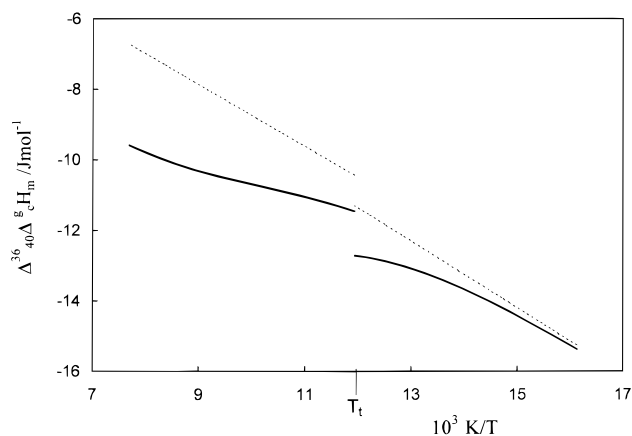


Figure 5. Values of the isotopic shifts in the molar enthalpies of vaporization and sublimation, $\Delta_{40}^{36}\Delta_c^g H_m$, against T^{-1} , obtained with eq 4 (full lines) and from a simple Clausius-Clapeyron relation (dashed lines) i.e., $\Delta_{40}^{36}\Delta_c^g H_m = -R \ln r/d(1/T)$. T_t = triple-point temperature.

Isotopic differences between the molar enthalpies of vaporization and sublimation can also be obtained from VPIE data by using the Clapeyron equation in the form

$$\Delta_{40}^{36}\Delta_c^g H_m = -Rd \ln r/d(1/T) - \left[\frac{(B-V)}{T} \right] d(p(r-1))/(d(1/T)) - \left[\frac{C-B^2}{RT^2} \left(\frac{d(pr)}{d(1/T)} \right) pr - \frac{dp}{d(1/T)} p \right] \quad (4)$$

where the indexes c and g refer to the condensed (liquid or solid) and gas phase, respectively. For the calculation of enthalpies of sublimation, values of B and C were obtained by a small extrapolation of the compilation of Dymond and Smith,²⁵ whereas solid densities were taken from Dobbs et al.²⁶ Equation 4 is an approximate expression. It has been derived from a previous one¹ where molar volume and second virial coefficient isotope effects were taken into account. Table 4 summarizes the results for rounded selected temperatures within a much larger temperature range than our working temperature. Credit to this spanning is given by the successful extrapolations of VPIE both in the high-temperature region (Figure 4) as well as in the low-temperature one (Figure 1). If one further neglects the contribution of the second term of eq 4—imperfection of the gas phase and molar volume of the condensed phase—the resulting difference in the molar enthalpies is in error by a factor that increases with increasing temperature and which amounts to ~30% at 130 K (see Figure 5). To the best of our knowledge, no calorimetric measurements are available for comparison.

Comparison with Theory. Within the limits of validity of the Born-Oppenheimer approximation, the motions of distinct isotopic forms of argon must be described by identical (isotopically independent) PES. Consequently, any difference in their physical properties is to be ascribed to distinct quantum kinetic

motions (mass dependent) on that PES. Bigeleisen's theory of isotope effects¹¹ gives a quantitative measure of that difference through the calculation of the so-called reduced partition function (f) ratio between the condensed (c) and vapor (g) phases for the two isotopes. Within the framework of the harmonic cell model,^{27,28} that reduced partition function ratio (RPFR) for the general case of polyatomic molecules (with internal structure) is directly related with vibrational frequencies (ν_i) associated with either the external (hindered rotation and hindered translation) modes or with the internal normal modes.

In the case of atomic systems the overall treatment is greatly simplified since neither rotation nor internal vibrations are present. Here, the RPFR can be simply written as

$$\ln \frac{f_c}{f_g} = \frac{h^2}{24k^2T^2} \frac{\langle \nabla^2 U \rangle_c}{4\pi^2} \left(\frac{1}{m'} - \frac{1}{m} \right) \cong \frac{h^2}{(24k^2T^2)} \sum_{i=1}^3 (\nu_i'^2 - \nu_i^2)_c = \frac{3}{40} \left(\frac{\theta_D'}{T} \right)^2 \left(1 - \frac{m'}{m} \right) \quad (5)$$

where m stands for the atomic masses and θ_D' is the Debye temperature.²⁹ The prime labels the lighter isotope. Since we assumed that the PES is isotopically independent, the mean square force constant, $\langle \nabla^2 U \rangle_c$, is also invariant with respect to isotopic substitution. The theory also shows that the RPFR is related to the VPIE through the following approximate equation

$$\ln(f_c/f_g) = \ln(p'/p) \times \left[1 + \frac{P}{RT} \left(B - V + \frac{1}{2RT} (C - B^2)(p + p') \right) \right] \approx \ln \alpha^\infty \quad (6)$$

Mean square forces can thus be obtained from VPIE data or LVIFF data. Bigeleisen's group performed a comprehensive study on the rare gases,^{15,21,30-32} mainly associated with the temperature and density dependence of $\langle \nabla^2 U \rangle_c$.

The theory of isotope effects also predicts quantitatively the large discontinuity of $\ln r$ near the triple point. Equation 5 shows us that this discontinuity is a direct consequence of the mean square force constant shift between the two condensed phases (solid-liquid) which, in turn, is due to the density shift on melting. The link between the densities ratio and the ratio of RPFR is obtained by application of the theory of isotope effects to Eyring's significant structure (SS) theory of liquids and can be approximately expressed as³³

$$\frac{\ln(f_s/f_g)}{\ln(f_l/f_g)} = \frac{V_l}{V_s} = \frac{\langle \nabla^2 U \rangle_s}{\langle \nabla^2 U \rangle_l} \approx \frac{\ln r_s}{\ln r_l} \quad (7)$$

Our experimental ratio of $\ln r$ near the triple point, 1.198 ± 0.001 , compares favorably with the published^{15,26,33} value of 1.15 for the ratio l/s of molar volumes of argon. It should be noted that SS theory cannot, by itself, predict isotope effects. Nonetheless, when one combines it with Bigeleisen's theory, the isotope effect shift on melting, which is basically a volume effect, is correctly determined.

Theoretical Estimations. As pointed out in the Introduction, some theoretical problems remain, including the isotope effects on the liquid molar volumes and the vapor phase second virial coefficients. The latter is more closely related to the intermolecular pair potential function. Both properties are difficult to measure. The expected isotope effects on these two physical properties are estimated to be about 1 order of magnitude smaller than that observed for the vapor pressure (which in the case of

TABLE 5: (ϵ/k , σ) Parameters and Corresponding Isotopic Shifts for a (6:12) LJ Pair Potential of the System $^{36}\text{Ar}/^{40}\text{Ar}$ ($\Delta = (^{36}\text{Ar}) - (^{40}\text{Ar})$)

series ^a	<i>T</i> /K	(ϵ_{40}/k)/K	$\Delta\epsilon/\epsilon \times 100$	$\sigma_{40}/\text{\AA}$	$\Delta\sigma/\sigma \times 100$
A	86	117.82	-7.5×10^{-2}	3.395	4.7×10^{-3}
	98	117.77	-6.5×10^{-2}	3.399	4.4×10^{-3}
B	86	117.82	-9.7×10^{-2}	3.395	6.5×10^{-2}
	98	117.77	-8.6×10^{-2}	3.399	5.4×10^{-2}

^a See text.

argon is about 0.5%), and differential experimental techniques are less applicable in MVIE and SVCIE than in VPIE.

In spite of the lack of experimental data on these quantities and to assist on the calculation of excess Gibbs energies of liquid mixtures of ($^{36}\text{Ar} + ^{40}\text{Ar}$), we have made theoretical estimates of MVIE and SVCIE using two different approaches: (a) the consideration of zero-point energy differences in isotopically independent PES's and (b) the assumption of effective isotopic shifts on classical potential parameters. In this latter case, we chose the LJ (6:12) pair potential to model the argon's PES. The determination of the effective ϵ and σ parameters for both isotopes can be done by adjusting the Lennard-Jones equation of state of Fischer et al.³⁴ to the vapor pressures and orthobaric molar densities, ρ , using interpolating reduced equations in an iterative process.³⁵ The results are presented in Table 5. For ^{40}Ar we used our experimental vapor pressure data and we took the orthobaric densities from Gilgen et al.¹⁸ The (ϵ/k , σ) parameters presented in Table 5 compare quite well with the values (117.70 K, 3.4039 Å) obtained by Fischer et al.³⁴ in the 84–122 K temperature range by adjusting the vapor pressure, and liquid and gaseous densities of Angus and Armstrong.³⁶ In the case of ^{36}Ar , we chose our experimental vapor pressures, but density data are absent. In view of this fact, we started by assuming, as a first approximation, that the molar densities of the isotopes are identical, i.e., $\rho'(36) = \rho(40)$. This way, we obtained a value for $\Delta\epsilon$ similar to that reported in Table 5 (series A), but $\Delta\sigma < 0$, which is not plausible. Considering that one should expect an effective $\Delta\sigma \geq 0$, we forced $\sigma(36)$ to be identical to $\sigma(40)$, determined the corresponding $\Delta\rho$ (now different from zero) and with this value recalculated $\Delta\sigma$. It is this last value that is reported in this table as series A. In series B of Table 5, ϵ and σ were obtained using values for the molar density of ^{36}Ar which were determined assuming that $\Delta V/V = 22.7 \times 10^{-4}$ at 86 K and $\Delta V/V = 19.3 \times 10^{-4}$ at 98 K (vide infra). The negative sign of $\Delta\epsilon$ was expected for a system that exhibits a normal isotope effect in the vapor pressure and its magnitude is smaller than that found in other isotopic pairs².

Molar Volume Isotope Effect. The MVIE ($\Delta V/V$) is strongly related with the magnitude of any excess Gibbs energy that may be observed in a binary isotopic mixture.^{7,8,37,38} It is thus paramount for the understanding of solution thermodynamics.

The first methodology used to estimate the size parameter of ^{36}Ar enabled us to make a crude estimation of the lower-limit value of the orthobaric MVIE in argon. This lower-limit value is obtained when one considers $\Delta\sigma = 0$ in the LJ equation of state and it produced the results presented as series I in Table 6. This can be easily double-checked by consideration of the validity of a simple principle of corresponding states, in which a representation of the experimental reduced molar volume for ^{40}Ar , $V/N\sigma^3 = f(kT/\epsilon)$, is assumed to equally be valid for ^{36}Ar . The results are presented as series II and show a similar magnitude for the MVIE when compared with series I. Steele^{39,40} also considers that a quantum translational (mass effect) will

TABLE 6: Molar Volume Isotope Effect, $\Delta V/V$, of the System $^{36}\text{Ar}/^{40}\text{Ar}$

reference	$(\Delta V/V) \times 10^4$	
	<i>T</i> = 86 K	<i>T</i> = 98 K
series I ^a	4.04	4.19
series II ^b	4.26	3.97
series III ^{39,40}	36.2	33.3
series IV ^{41,42}	23.0	18.0
series V ⁴³	5.37	4.70
series VI ⁴⁴	22.4	20.5

^a From Lennard-Jones equation of state with $\Delta\epsilon/\epsilon \approx -7 \times 10^{-4}$ and $\Delta\sigma/\sigma = 0$. ^b From a simple principle of corresponding states (see text). Note: $V_{40} = 28.465 \text{ cm}^3 \text{ mol}^{-1}$ at $T = 86 \text{ K}$ and $V_{40} = 30.101 \text{ cm}^3 \text{ mol}^{-1}$ at $T = 98 \text{ K}$ (from Gilgen et al.¹⁸). $\Delta = (^{36}\text{Ar}) - (^{40}\text{Ar})$.

emerge from isotopic dependent PES's. These two contributions are explicitly assigned in his expression

$$\frac{\Delta V}{V} = +3 \frac{\Delta\sigma}{\sigma} - \frac{\Delta\epsilon}{\epsilon} \frac{d \ln V}{d \ln T} + (\Lambda_{36}^{*2} - \Lambda_{40}^{*2}) \times 0.33 \quad (8)$$

The overall result presented as series III is thus the sum of a quantum kinetic contribution (where $\Lambda^* = h/\sigma(m\epsilon)^{1/2}$ is the reduced de Broglie's wavelength) plus the contribution from the isotopic shift in the potential parameters (see series B of Table 5). The first one accounts for about 70% of the overall result, while the second represents the remaining 30%.

In series IV, V, and VI we turn to theories which solely consider quantum statistical differences between isotopes moving on the same PES, namely, the quantum theory of corresponding states of de Boer,^{41,42} the theory due to Bartell and Roskos,⁴³ and the approach given by Menes et al.,⁴⁴ which is a natural extension of the theory of isotope effects of Bigeleisen to the interpretation of MVIE's.

In de Boer's method, the reduced volumes ($V/N\sigma^3$) of different monatomic liquids (Xe, Kr, Ar, and Ne) are plotted against the reduced de Broglie's wavelength at different reduced temperatures. Assuming identical ϵ and σ values for ^{36}Ar and ^{40}Ar , we obtained (graphically) the results reported in series IV of Table 6. Bartell and Roskos derived a "low-temperature" expression and a "high-temperature" one. We decided to use the latter approach in view of the fact that near 90 K, $\theta_D/T \approx 1$. The "high-temperature" approach relates $\Delta V/V$ with the average pair distance, $\langle r \rangle$, and with the a anharmonic parameter:

$$\frac{\Delta V}{V} = -\frac{3ah^2}{16\pi^2 kT \langle r \rangle} \left(\frac{1}{m'} - \frac{1}{m} \right) \quad (9)$$

The average distance can be approximately calculated from the knowledge of the Debye energies and the ϵ value for a LJ potential in liquid argon. At the referred temperatures selected in Table 6, we obtained 3.914 Å at 86 K and 3.919 Å at 98 K, to be compared with the distance at the minimum of the potential well, $R = 3.816 \text{ Å}$. Using these values of $\langle r \rangle$, the corresponding a values are 1.788 and 1.786 Å⁻¹, respectively. It is interesting to note that the calculated temperature shift in $\langle r \rangle$, $d\langle r \rangle = 0.005 \text{ Å}$, scales with the observed temperature shift in σ , $d\sigma = 0.004 \text{ Å}$ (see Table 5), which emphasizes the effective character of the pair potential parameters. Series V in Table 6 reports the results obtained using eq 9. In Bigeleisen's approach,⁴⁴ MVIE effects are related to VPIE through the temperature dependence of the RPF:R

$$\frac{\Delta V}{V} = -\frac{\beta \Gamma R T^2}{V} (d \ln(f_c/f_g)/dT) \quad (10)$$

TABLE 7: Second Virial Coefficient Isotope Effect of the System $^{36}\text{Ar}/^{40}\text{Ar}$

reference	$\Delta B/\text{cm}^3 \text{ mol}^{-1}$	
	$T = 86 \text{ K}$	$T = 98 \text{ K}$
series I ^a	0.25	0.17
series II ^b	0.19	0.13
series III ^c	0.28	0.22

^a Assuming an isotope-dependent (6:12) LJ potential in the classical part of B. ^bQuantum translational contribution; ^cFrom a simple principle of corresponding states (see text). Note: $B_{40} = -245.2 \text{ cm}^3 \text{ mol}^{-1}$ at $T = 86 \text{ K}$ and $B_{40} = -192.8 \text{ cm}^3 \text{ mol}^{-1}$ at $T = 98 \text{ K}$ (from Dymond and Smith²⁵). $\Delta = (^{36}\text{Ar}) - (^{40}\text{Ar})$.

We used our calculated RPFR (eq 6) in arriving at the numerical values presented as series VI in Table 6. Isothermal compressibilities were taken from Rowlinson,⁴⁵ while Grüneisen coefficients were calculated from the correlation suggested by Lopes et al.⁴⁶

The agreement between the results of Bigeleisen's and de Boer's approaches is excellent. The results obtained with the theory of Steele are too large (probably because in this methodology some contributions to the MVIE are being counted two times), while those acquired from the expression of Bartell and Roskos seem to be too small (they are very similar to the estimated lower-limit values for the MVIE). In contrast with the statistical-mechanics approach of Bigeleisen and Menes, Bartell and Roskos' theory is based on a model that emerges from pure mechanics (size effect by virtue of shifts in mean intermolecular distances). Taking the average between Bigeleisen's and de Boer's values, one obtains $\Delta V/V = 22.7 \times 10^{-4}$ at 86 K and $\Delta V/V = 19.3 \times 10^{-4}$ at 98 K. Using eq 10, it is also possible to estimate the MVIE in the solid and, consequently, to predict the magnitude of the discontinuity of this effect at the triple point. $\Delta V/V$ in the solid phase at the triple point (10×10^{-4}) is less than half of the estimated value in the liquid phase. This is mainly due to the large difference between the isothermal compressibilities in the two phases (in the solid,⁴⁷ $\beta_{\text{solid}} = 8.76 \times 10^{-5} \text{ bar}^{-1}$, while for the liquid,⁴⁵ $\beta_{\text{liquid}} = 24.5 \times 10^{-5} \text{ bar}^{-1}$). By using the calculated isotopic shift in the lattice spacing for solid argon as presented by Brown⁴⁸, one obtains $\Delta V/V \approx 20 \times 10^{-4}$ near 0 K.

Second Virial Coefficient Isotope Effect. With respect to the second virial coefficient we followed the treatment presented by Hirschfelder et al.,⁴⁹ where $B(T)$ is the sum of the classical contribution

$$B_{\text{cl}}(T) = -2\pi N \int_0^\infty [e^{-u(r)/kT} - 1] r^2 dr \quad (11)$$

plus the translational, rotational, and symmetry effect corrections. For argon only, the translational correction is applicable and we restricted the treatment to the first quantum correction. Therefore

$$B(T) = B_{\text{cl}}(T) + \frac{h^2}{m} B_{\text{tr}}^I(T) \quad (12)$$

where the first translational quantum correction is given by

$$B_{\text{tr}}^I(T) = +2\pi N \left(\frac{1}{48\pi^2 k^3 T^3} \right) \int_0^\infty e^{-u(r)/kT} \left(\frac{du(r)}{dT} \right)^2 r^2 dr \quad (13)$$

If one assumes that the isotopic differences can be modeled by the distinct assignments in the effective ϵ and σ parameters, then $\Delta B(T) = \Delta B_{\text{cl}}(T)$. The results are presented as series I in Table 7. Alternatively, if one assumes that the pair potential

that correctly describes the atomic motion is isotope-independent, the SVCIE should emerge from the quantum difference in the translational correction. That is to say that

$$\Delta B(T) = \left(\frac{h^2}{m'} - \frac{h^2}{m} \right) B_{\text{tr}}^I(T) \quad (14)$$

and the results are labeled as series II in Table 7. Finally, an argument of a simple principle of corresponding states similar to the one already used in evaluating ΔV produces the numerical values of series III. Very accurate experimental results for the MVIE and SVCIE are urgently needed in order to either discuss or compare these approaches or to demonstrate that others should be considered. As for the latter, a more thorough analysis than that herein presented is also awaiting the development of a theory of isotope effects (of second virial coefficients) based on a foundation identical to that laid by Bigeleisen.¹¹ That development is in due course.⁵⁰ Nevertheless, these first estimates will assist us on the calculation of the excess Gibbs energy in mixtures of ($^{36}\text{Ar} + ^{40}\text{Ar}$) as well as in the theoretical rationalization of experimentally detected deviations from the ideal behavior.

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Supporting Information Available: Experimental absolute vapor pressure (p) of liquid ^{40}Ar and differential vapor pressure $\Delta p = p' - p$ between ^{36}Ar (p') and ^{40}Ar (p) (Table 3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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