# Are isotopic mixtures ideal?*

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*Abstract*: Isotopic mixtures have long been considered as textbook examples of ideal solutions. High-precision vapor pressure measurements have shown that even these very simple mixtures exhibit deviations from the ideal behavior. The small, but still significant nonideality of isotopic mixtures can be accounted for in terms of the difference in the molar volumes of isotopic molecules. Theoretical analysis demonstrates that the internal vibrations of the molecules significantly contribute to the excess Gibbs energy, and the proper consideration of the volume dependence of molecular vibrations of the component molecules is essential to the understanding of the properties of isotopic mixtures.

## INTRODUCTION

Isotopic mixtures, i.e., mixtures of isotopomers (isotopomers are species that differ solely in isotopic content, e.g., $C_6H_6$ and $C_6D_6$) have long been considered as textbook examples of ideal solutions: "molecules which differ only by isotopic substitution...form ideal solutions" [1]; "we expect binary solutions to have ideal properties when the two components are isotopes of each other" [2]; "except for isotope mixtures, ideal solutions will occur rather rarely" [3]; "statistical theory predicts that mixtures of very similar species, in particular isotopes, will be ideal" [4]; "the only truly ideal solutions would thus involve isotopic species" [5]. In a recent edition of the last textbook [6], it is demonstrated on the example of the mixture of $C_6H_6$ and $C_6D_6$ [7] that even the mixtures of isotopic species exhibit very slight departures from ideal behavior.

The ideal behavior of isotopic mixtures is expected if one assumes that the intermolecular forces between pairs of like molecules of each type (e.g., $C_6H_6$–$C_6H_6$ and $C_6D_6$–$C_6D_6$) and between unlike molecules (e.g., $C_6H_6$–$C_6D_6$) are all the same, and further assumes the isotopomers to be the same size. Both assumptions are reasonable in first order. It follows that the detection of nonideality in isotopic mixtures thus will yield information on the validity of the above assumptions and it will test the principles of the underlying mixture theories, as well as the intermolecular potential models.

A comprehensive treatment of the nonideal behavior of isotopic mixtures can be found in two recent reviews [8,9]. This paper first describes briefly the experimental determination of nonideality in isotopic mixtures, then the nonideal behavior of these mixtures will be interpreted in terms of the intermolecular interactions which take place in the solutions. Finally, some selected mixtures will be treated in more detail.

## EXPERIMENTAL DETERMINATION OF THE DEVIATION OF ISOTOPIC MIXTURES FROM IDEAL BEHAVIOR

A mixture is said to be ideal if the chemical potential of component $i$, $\mu_i$, is a linear function of the logarithm of its mole fraction ($x_i$)

$$\mu_i(p,T,x_i) = \mu^0(p,T) + RT \ln x_i \tag{1}$$

where $\mu^0(p,T)$ is the chemical potential of the pure liquid component at the same pressure and temperature as the mixture. If the vapor nonideality and the effect of pressure on the liquid phase molar volume are neglected, then an ideal mixture obeys Raoult's law:

$$p_{\text{mixture}} = \Sigma x_i p_i^0 \tag{2}$$

where $p_{\text{mixture}}$ and $p_i^0$ are the vapor pressures of the mixture and of the pure component $i$, respectively.

The thermodynamic properties of real mixtures can be expressed in terms of excess functions that are in excess of those of an ideal mixture at the same conditions of temperature, pressure, and composition. For an ideal mixture, all excess functions are zero. Thus, the magnitudes of the excess Gibbs energy, excess enthalpy, and excess volume for isotopic mixtures indicate the extent of their nonideality. Excess enthalpies can be determined by calorimetric measurements or from the temperature dependence of the excess Gibbs energy. The determination of the excess volume requires very precise density measurements. The excess Gibbs energy can be obtained from the determination of the vapor pressure of isotopic mixtures of known composition. This is the most convenient way of the detection of the deviation of isotopic mixtures from the ideal behavior.

The nonideality of a binary isotopic mixture can be conveniently expressed in terms of the "excess vapor pressure", $\Delta p^E$,

$$\Delta p^E = \Delta p_{\text{mixture}} - [\, x'p'C' + (1 - x')pC \,] + p' \tag{3}$$

where $\Delta p_{\text{mixture}}$ is the experimentally observed vapor pressure difference between the mixture and reference (usually the lighter isotopomer), $x$ is the mole fraction, and $C$ is the factor correcting for vapor nonideality and liquid-phase molar volume (the prime denotes the lighter molecule). Note that $\Delta p^E$ reduces to exactly the deviation from Raoult's law provided one neglects the correction factors $C$ and $C'$. In practice, one measures the vapor pressure difference between the mixture and one of the pure isotopomers and simultaneously the vapor pressure difference between the separated pure isotopomers. In such a way, the nonideality can be assessed with the best possible accuracy [10]. The excess Gibbs energy ($G^E$), which plays a central role in the theory of excess properties of isotopic mixtures [8,9], can be calculated from the excess pressure ($\Delta p^E$) by using the method of Calado [11].

The value of the $\Delta p^E/p$ ratio gives one some feeling about the magnitude of the deviation of isotopic mixtures from ideal behavior. For example, the experimental $\Delta p^E$ of 3.2 Pa at 25 °C for the equimolar mixture of $C_6H_6$ and $C_6D_6$ (for comparison, the vapor pressure difference between $C_6H_6$ and $C_6D_6$ is 360 Pa) [7] corresponds to a nonideality of about 0.02–0.03 %. The excess vapor pressure corresponds to a value of $G^E = 0.58$ J/mol, which is two to three orders of magnitude smaller than the excess Gibbs energies typically observed in binary mixtures of nonisotopic simple molecules (see Table 1).

**Table 1** Excess Gibbs energy ($G^E$) for some equimolar mixtures and contributions to $G^E$ calculated from the volume dependence of the internal vibrations of the molecules ($G^E_{int}$).

|  | T (K) | $G^E$ (J/mol) | $G^E_{int}$ (%) | Ref. |
|---|---|---|---|---|
| $^{36}Ar/^{40}Ar$ | 85 | 0.021 | 0 | [12,13] |
| $H_2/D_2$ | 20 | 7.2 | 5 | [14] |
| $CH_4/CD_4$ | 100 | 0.60 | 33 | [15] |
| $C_6H_6/C_6D_6$ | 298 | 0.58 | 88 | [14,16] |
| $NH_3/ND_3$ | 230 | −5.86 | 92 | [17] |
| $NH_3/^{15}NH_3$ | 230 | −0.10 | 94 | [17] |
| Ar/Kr | 116 | 83.9 | | [18] |
| $Ar/C_6H_6$ | 91 | 317 | | [18] |
| Pyridine/CHCl$_3$ | 308 | −700 | | [18] |

## INTERPRETATION OF THE NONIDEAL BEHAVIOR OF ISOTOPIC MIXTURES

In general, a mixture of molecules A and B is ideal if the intermolecular interactions for A-A, A-B, and B-B pairs are the same and the molecules A and B occupy equal volumes. Since in the case of isotopic mixtures the intermolecular interactions between the different isotopomers in the mixture are the same within the framework of Born–Oppenheimer approximation (electronic structures are, to an excellent approximation, independent of isotopic substitution) the deviation from the ideality can be rationalized in terms of the difference in the molar volumes of isotopomers. This is the central idea of the theory describing the excess Gibbs energy of isotopic mixtures developed by Prigogine, Bingen, and Bellemans (PBB) [19,20] 50 years ago in order to interpret the properties of hydrogen ($H_2$, $D_2$, $T_2$, HD, HT, DT) and helium ($^3He$, $^4He$) isotopomer solutions. They suggested that $G^E$ can be calculated in a two-step process: (I) compression or expansion of the molar volumes of the pure components ($V^{0\prime}$, $V^0$) to the molar volume of the mixture ($V_m$), (II) mixing the two components now at the same volume. The essential point is that in the second step, the mixing process can be considered ideal (the interactions between the components as well as their volumes are the same), therefore, $G^E$ is equal to the amount of work done in compressing the lighter isotope and in expanding the heavier one to the molar volume of the mixture in step I (it is assumed that $V^{0\prime} > V_{mixture} > V^0$).

In step I, it is necessary to apply positive pressure to compress the lighter isotopomer from $V^{0\prime}$ to $V_{mixture}$ and negative pressure (tension) to expand the heavier isotopomer from $V^0$ to $V_{mixture}$. The relationship between $p$ and $V$ is defined by the equation of state, and the application of negative pressures involves the extrapolation of the $V$ vs. $p$ curve. Note that both terms are positive, i.e., $G^E$ calculated from PBB theory is always positive. The statement is equivalent to the prediction of positive deviations (only) from Raoult's law.

In an infinitely dilute solution, the process described above can be more easily visualized: First, the molar volume of the minor component or "solute" isotopomer is compressed or expanded to that of the "solvent" isotopomer and then the components are mixed. In this specific case, the excess chemical potential ($\mu^{E\infty}$) can be calculated from the knowledge of the difference in the molar volumes of isotopomers and the isothermal compressibility.

Jancsó and Van Hook [14,16] have suggested that the excess Gibbs energy obtained by the PBB theory may significantly underestimate the values of $G^E$ for molecules with internal vibrations. The reason is that since the compressibility is principally determined by the overall (external) motions of the molecules ("external degrees of freedom") in the intermolecular potential, the contribution to $G^E$ arising from the volume-dependent internal vibrations ("internal degrees of freedom) is not taken into account. During the compression/expansion step (I), the frequencies of the internal vibrations change and the work involved represents the internal contribution to $G^E$. The volume dependence of vibrational fre-

quencies ($\nu$) can be deduced from their more readily available pressure dependence using $(\partial\nu/\partial V) = -(\partial\nu/\partial p)(V/\beta)$, where $\beta$ is the isothermal compressibility. Table 1 shows that the contributions to $G^E$ calculated from the volume dependence of the internal vibrations of the molecules change from 5–94 % for the isotopic mixtures investigated.

In the following, the experimental determination and interpretation of the deviation of isotopic mixtures from the ideal behavior will be illustrated on the examples of some selected mixtures.

## SOME SELECTED ISOTOPIC MIXTURES

### $H_2/D_2$ mixture

The excess properties ($G^E$, $H^E$, $V^E$) of $H_2/D_2$ mixtures have been thoroughly studied [19–21]. The PBB theory satisfactorily describes the significant positive deviations from Raoult's law observed in these solutions: for example, at 20 K $G^E$(expt) = 7.2 J/mol for the equimolar mixture while the calculation gives 8.9 J/mol. The contribution of the H–H stretching vibration to the nonideal behavior of the mixture can be estimated from its frequency change during the process when $H_2$ is compressed to the molar volume of $H_2/D_2$ mixture. The value obtained (0.3 J/mol) is small compared with 8.9 J/mol; therefore, one can conclude that in the $H_2/D_2$ mixture $G^E$ is dominated by the compressibility term that is determined by the intermolecular potential [14]. This explains the success of the PBB approximation in the case of $H_2/D_2$ mixture.

### $C_6H_6/C_6D_6$ mixture

From the experimental excess vapor pressure for the equimolar $C_6H_6/C_6D_6$ mixture at room temperature (3.2 Pa), the value for $\mu^{E\infty}$ (2.3 J/mol) has been calculated from the equation $\mu^{E\infty} = 4G^E_{equimolar}$ [7]. The PBB approach using the difference in molar volumes (the molar volume of benzene is larger by 0.27 % than that of deuterated benzene [22]) and the isothermal compressibility of liquid benzene gives a value of 0.33 J/mol for $\mu^{E\infty}$ [14,16]. It accounts only for the contributions from the "external degrees of freedom" and neglects the internal vibrational contribution. In the calculation of the latter, only the CH stretching vibrations, which are the most pressure/volume dependent, were considered. Using the experimentally observed pressure dependence of the vibrational frequency (1.5 cm$^{-1}$/kbar), the isothermal compressibility and the difference in the molar volumes of benzene and deuterated benzene a value of 1.53 J/mol was obtained for the contribution of the six CH stretching vibrations. The agreement between the experimental (2.3 J/mol) and calculated (0.33 + 1.53 = 1.86 J/mol) $\mu^{E\infty}$ values can be considered satisfactory. Thus, it can be concluded that in the case of $C_6H_6/C_6D_6$ mixture, the volume dependence of the CH stretching vibrations gives the main contribution to the deviation from the ideal behavior.

It is interesting to note that according to the calculations described above the transfer of a $C_6H_6$ molecule from the neat liquid to the infinitely dilute solution in $C_6D_6$ corresponds to a change of 0.04 cm$^{-1}$ in the CH stretching frequency (~3000 cm$^{-1}$). Although the value of ~0.15 cm$^{-1}$ observed by Raman difference spectroscopic technique for this shift [23] is 3–4 times larger than the value deduced from the $G^E$ calculations, the direction of the shift is the same in both cases: The frequency of the CH stretching vibrations increases when "$C_6H_6$ is put into $C_6D_6$" (when $C_6H_6$ is dissolved in $C_6D_6$ it is slightly compressed, consequently the repulsive forces between molecules become dominant and thus the CH stretching frequency increases).

### $CH_4/CD_4$ mixture

This isotopic mixture consisting of simple, nonpolar, quasi-spherical molecules represents one of the simplest mixtures of polyatomic molecules; therefore, the prediction of its excess properties by any liq-

uid-state theory can be used to test the performance of that theory. The vapor pressure differences between the $CH_4/CD_4$ mixtures and $CH_4$ have been determined as a function of concentration and temperature [15]. The $G^E$ value obtained from the measured excess vapor pressure is, for example, 0.6 J/mol for the equimolar mixture at 100 K. The theoretical analysis has shown that the models generally used for simple mixtures, the "vdW-1 fluid theory" [24] and "1cLJ perturbation theory" [25], are inadequate in explaining the experimental results, while the isotope effect theory agrees well with experiment (Table 2). In this isotopic mixture, both external and internal vibrational contributions to $G^E$ are important (at 100 K they amount to 67 and 33 % of the total $G^E$, respectively). This explains the failure of the above mixture theories that model solutions in terms of structureless particles and thus do not take into consideration the internal vibrations of the molecules.

**Table 2** Values of the excess Gibbs energy ($G^E$) and excess enthalpy ($H^E$) (in J/mol) for the equimolar mixture of $CH_4$ and $CD_4$ at 100 K [15].

|  | $G^E$ | $H^E$ |
|---|---|---|
| Calculated |  |  |
|    vdW-1 fluid theory | 0.11 | 0.16 |
|    1cLJ perturbation theory | 0.12 | 0.19 |
|    Theory of isotope effects | 0.58 | 1.9 |
| Experimental | 0.60 | 1.5 |

There is another interesting fact that strongly supports the theoretical interpretation of nonideality of isotopic mixtures based on the molar volume difference between isotopomers. The theory predicts that when the molar volumes of the two isotopomers are equal to each other then $G^E = 0$. The molar volume of $CH_4$ is higher than that of $CD_4$ below 170 K, at this temperature there is no difference in the molar volumes of the two isotopomers and above this so-called "cross-over temperature" the molar volume of $CH_4$ becomes smaller than that of $CD_4$ [26]. The extrapolation of the isotopic mixture data ($G^E$ vs. $1/T$) gives $G^E = 0$ at $171 \pm 4$ K which is in excellent agreement with the molar volume cross-over temperature.

## $^{36}$Ar/$^{40}$Ar mixture

The experimental results show that the vapor pressure of the equimolar $^{36}$Ar/$^{40}$Ar mixture is greater (positive deviation from Raoult's law) than what would be expected if the solution were strictly ideal by approximately 2.5 Pa in the 85–96 K temperature range [12,13]. The excess Gibbs energy for the equimolar mixture calculated from the excess vapor pressure is extremely small (0.021 J/mol at 85 K). The calculations based on the vdW-1 fluid theory [24] and 1cLJ perturbation theory [25] yielded $G^E$ values, which are in poor agreement with experiments. The theory of isotope effects using the estimated difference between the molar volumes of $^{36}$Ar and $^{40}$Ar (0.23 %) gives $G^E$ values, which are much more consistent with the experimental data. The evidence of nonideal behavior in such a fundamental and simple system is relevant for the interpretation of the properties of liquid mixtures of more general importance. The problem of taking into account the contribution of quantum effects to the overall excess properties of nonisotopic mixtures of rare gases has been discussed in [12].

In a recent paper [27], it has been estimated that $G^E$ for an equimolar mixture of $^{80}$Kr and $^{84}$Kr would be about 0.001 J/mol at 116 K, while for the mixtures of neon isotopes the deviation from ideality is expected to be about 20 times greater than that observed in argon isotopic mixtures (0.021 J/mol).

## Isotopic mixtures of ammonia

The high-precision vapor pressure measurements on $NH_3/ND_3$ mixtures [17] show a *negative* sign for $G^E$ (negative deviation from Raoult's law), a type of behavior which has never been observed before in isotopic mixtures. For the equimolar mixture, $G^E$ is one order of magnitude higher than those of $CH_4/CD_4$ and $C_6H_6/C_6D_6$ mixtures (Table 1). The interpretation of the results is complicated by the fact that the mixture must be regarded as a quaternary mixture of $NH_3$, $NH_2D$, $NHD_2$, and $ND_3$ since the hydrogen atoms of the ammonia molecule undergo isotope exchange. The extension of the method of calculating the excess properties of binary isotopic mixtures for multicomponent mixtures was reported by Calado et al. [28]. The deviation of the $NH_3/^{15}NH_3$ mixture from ideal behavior is almost two orders of magnitude smaller than that of the deuterated ammonia system (Table 1). The detailed theoretical analysis showed that the contribution from the external modes to the overall $G^E$ is small and the negative deviation from Raoult's law is due to the large negative contributions of the stretching vibrational modes of the ammonia molecule.

## CONCLUSIONS

Athough isotopic mixtures represent the textbook examples of ideal mixtures, they exhibit small, but still significant deviations from ideal behavior. It has been demonstrated that the nonideality of isotopic mixtures can be rationalized in terms of the difference between the molar volumes of isotopomers. The internal vibrations of the molecules make significant contributions to the excess Gibbs energy, therefore those mixture theories that consider molecules as structureless particles fail to describe quantitatively the excess properties of isotopic mixtures.

## ACKNOWLEDGMENT

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