

Non-ideality in Isotopic Mixtures

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1 Introduction

Ideal mixtures deserve special attention because: (i) their behaviour is the simplest conceivable from either a mathematical or a physical point of view, (ii) it is found experimentally that almost-ideal mixtures do exist so the ideal model is a useful one. Although any real mixture cannot be completely ideal, the resemblances between many real mixtures and the ideal abstraction are more striking than the differences.¹ Isotopic mixtures, *i.e.* mixtures of isotopomers (isotopomers are species that differ solely in isotopic content *e.g.* CH₄ and CD₄) have long been considered as textbook examples of ideal solutions: for example Guggenheim states, 'statistical theory predicts that mixtures of very similar species, in particular isotopes, will be ideal',¹ Levine writes 'the only truly ideal solutions would thus involve isotopic species',² earlier Lewis and Randall had written 'molecules which differ only by isotopic substitution ... form ideal solutions',³ and more recently Münster claims 'except for isotope

mixtures, ideal solutions will occur rather rarely'.⁴ Other examples abound.

The ideal behaviour of isotopic mixtures is expected if one assumes that the intermolecular forces between pairs of like molecules of each type (*e.g.* CH₄-CH₄, CD₄-CD₄) and between unlike molecules (*e.g.* CH₄-CD₄) 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 non-ideality in isotopic mixtures 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.

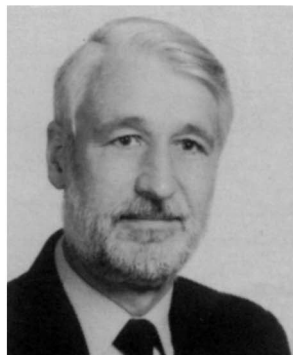
This review is concerned with the experimental determination of non-ideality in solutions of isotopomers, and with the interpretation of such non-ideality in terms of the intermolecular interactions which occur within the solutions. A more comprehensive treatment of the subject can be found in a recent review.⁵

Gábor Jancsó was born in 1941 in Budapest, Hungary. He graduated with a degree in chemistry from Eötvös Loránd University in 1964 and immediately joined the Central Research Institute for Physics of the Hungarian Academy of Sciences where he is currently a Senior Research Scientist. In 1969—1970 and 1976—1977 he spent one-year study leaves with W. A. Van Hook at the University of Tennessee. From 1982 to 1984 he was a visiting scientist at the Max Planck Institut für Chemie in Mainz where he worked with K. Heinzinger. His research interests include the investigation of the effects of isotopic substitution on the properties of liquids and mixtures, molecular dynamics simulation of liquid water and aqueous solutions, and studies of the effects of intermolecular interaction on the vibrational properties of molecules in the condensed phase. More recently he has become involved with studies of the structural and dynamic properties of aqueous solutions using neutron diffraction.

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Nunes da Ponte. He joined the New University of Lisbon in 1983 and has been an Assistant Professor since 1989. In 1989 he received the Student Government Association award for pedagogical and scientific abilities. Rebelo has served as Visiting Scientist and/or Postdoctoral Researcher at Cornell University (1985), the Central Research Institute for Physics, Budapest (1987), and the University of Tennessee (1990—1991). He has served as Member-Elect on the Board of Directors of the Portuguese Chemical Society (1987—1989). He is currently Principal Investigator of several research projects in the areas of cryogenic thermodynamics at moderate and high pressures, molecular thermodynamics of isotopically substituted species, and phase equilibria in polymer solutions.

W. Alexander Van Hook was born in 1936 and received his education at the College of the Holy Cross (B.S.-mcl, 1957) and Johns Hopkins University (M.A. 1960, Ph.D. 1961, mentor Paul Emmett). After a postdoctoral stay at Brookhaven National Laboratory spent with Jacob Bigeleisen and Max Wolfsberg, he joined the University of Tennessee where he is presently Professor of Chemistry. Van Hook spent 1967—1968 on a Fulbright fellowship at the Université Libre de Bruxelles studying with I. Prigogine and G. Thomaes, and a good deal of 1972 at the Boris Kidrič Institute of Nuclear Sciences, Belgrade, on a National Academy of Sciences Exchange Fellowship. Other shorter study visits have been spent at Lanzhou and Peking Universities, PRC, and in Budapest and Lisbon. Van Hook's research interests are in isotope effects on the properties of condensed phases, solution thermodynamics, and related areas.



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

$$\mu_i(p, T, x_i) = \mu_i^0(p, T) + RT \ln x_i \quad (1)$$

where $\mu_i^0(p, T)$ is the chemical potential of the pure liquid component at the same pressure and temperature as the mixture. This 'thermodynamic definition' of ideal mixing is equivalent to the one based on Raoult's law for a liquid mixture provided the vapours behave as perfect gases, and provided the effect of pressure on the chemical potential of the liquid phase can be neglected. In the case of an ideal solution there is no heat evolved in the mixing process and neither is there any volume of mixing.

The properties of real mixtures may be expressed in terms of excess molar properties. An excess property is defined in terms of the deviations of the real mixture from those of the ideal mixture of the same composition (in other words 'excess' means 'difference' between real and ideal). The magnitudes of the excess Gibbs energy (G^E), excess volume (V^E), and excess enthalpy (H^E) for mixtures of isotopomers indicate the extent to which these mixtures are non-ideal. For the excess Gibbs energy the measurement of the vapour pressures of isotopic mixtures of known composition is the most convenient way to determine non-ideal behaviour, and that is the focal point of this review. Excess enthalpies can be determined by calorimetric measurements or from the temperature dependence of G^E using the Gibbs-Helmholtz relation. The determination of excess volume in isotopic mixtures requires very precise density measurements.

We will proceed first by describing the experimental technique used to measure vapour pressure differences between separated isotopomers and their mixtures. Using the theory of condensed phase isotope effects⁶ we will then show how the vapour pressure differences between isotopomers can be related to the intermolecular forces acting in the liquid phase. Following this general description we will describe studies on some selected isotopic mixtures in detail. An important result will be the clear demonstration that the proper consideration of the vibrational properties of the component molecules is absolutely essential to the understanding of isotopomer mixtures.

2 Vapour Pressure Measurements

Small differences in vapour pressure like those between separated isotopomers, or those between an isotopomer mixture and one or the other pure compound, are usually expressed in terms of logarithm of the pressure ratio, $\ln p'/p$ (the prime denotes the lighter molecule). This so-called vapour pressure isotope effect (VPIE) is said to be normal if $\ln p'/p > 0$, *i.e.* if the lighter isotopomer has a higher vapour pressure than the heavier one, and inverse if $\ln p'/p < 0$. The temperature at which the vapour pressures of the isotopomers are the same ($\ln p'/p = 0$) is called the crossover temperature. For small differences $\ln p'/p \approx \Delta p/p = (p' - p)/p$. It follows that the best possible precision can be obtained by measuring Δp and p simultaneously using a differential technique as shown in Figure 1a. Here the sample cells (A, A') containing the pure isotopomers are thermostatted, the temperature is measured with a platinum resistance thermometer, and the absolute pressure of the reference sample, are determined with pressure transducers (P, ΔP). For experiments on isotopic mixtures an additional differential vapour pressure must be measured, *i.e.* that between the mixture and one of the pure isotopomers. If this is done simultaneously with the differential vapour pressure measurement between the separated pure isotopomers by using a third cell, one obtains a truly double-differential method and the non-ideality can be assessed with the best possible accuracy.⁷ The non-ideality of the binary isotopic mixture can be conveniently expressed in terms of the excess pressure, Δp^E

$$\Delta p^E = \Delta p_{\text{mixt}} - [x'p'C' + (1 - x')pC] + p' \quad (2)$$

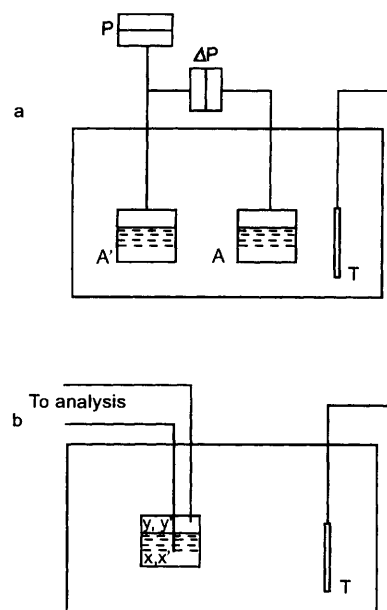


Figure 1 Schematic diagrams of common experimental techniques used for the determination of vapour pressure differences between isotopic isotopomers (a) and for the determination of the isotope separation factor (a) in a one-plate fractionation experiment (b). A and A' are sample containers for pure isotopomers, P and ΔP are pressure and differential pressure transducers; y , y' and x , x' are the concentrations of the two isotopomers in the vapour and liquid phases, respectively; T is a resistance thermometer.

where Δp_{mixt} is the experimentally observed vapour pressure difference between mixture and reference (usually the lighter isotopomer), x is the mole fraction and C is the factor correcting for vapour non-ideality and liquid phase molar volume.⁸ (Note that Δp^E reduces to exactly the deviation from Raoult's law provided one neglects the correction factors C and C' .) The difference between the $\Delta p^E/p$ ratio and zero gives one some feeling about the magnitude of the deviation of isotopic mixtures from ideal behaviour. For example, the experimental data for an equimolar mixture of C_6H_6 and C_6D_6 shown in Figure 2 exhibit a non-ideality of about 0.02–0.03%, which corresponds to a Δp^E value of 3.2 Pa (0.024 mm Hg). For comparison, the vapour pressure difference between C_6D_6 and C_6H_6 is 360 Pa at room temperature. The small scatter of the data around the correlation line demonstrates the high precision which can be achieved by present-day differential vapour-pressure measuring techniques.

Another and quite different approach to determine the VPIE involves a measurement of the isotope separation factor (α) defined by the equilibrium between the liquid phase and its saturated vapour in a one-plate fractionation experiment. We define $\alpha = (y'/y)/(x'/x)$, where y and x are the concentrations in

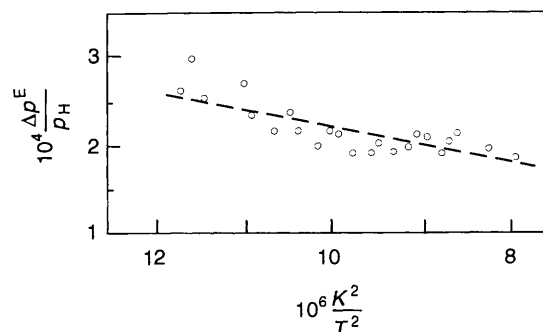


Figure 2 Excess pressures of equimolar mixtures of C_6H_6 and C_6D_6 . For definition of Δp^E see equation 2, p_H is the vapour pressure of pure C_6H_6 .

the vapour and liquid phase, respectively (Figure 1b) The concentration ratios are straightforwardly related to the corresponding pressure ratios and free energy differences using standard thermodynamic relations The accuracy of this method is limited by the accuracy of the isotopic analysis of the two coexisting phases, an improvement can be achieved by multiplication of the elementary separation process, *e.g.* by using distillation columns

The relationship between α and the vapour pressures of the pure isotopomers is given in the limit of infinite dilution ($x' \cong 1$) to a good approximation by the equation^{5,6}

$$\ln \alpha \approx \frac{(V^0 - V'^0)^2}{2\beta V^0 RT} = \left[\ln \frac{p'}{p} \right] \left[1 + \frac{p(B - V^0)}{RT} \right] \quad (3)$$

Here B is the second virial coefficient of the gas, β is the isothermal compressibility of the liquid, and V^0 is the molar volume of the liquid In fractionation experiments the measurement is always made on an isotopomer mixture, never on pure separated isotopes, and this must be kept in mind throughout the interpretation We will return to this important consideration later

3 Vapour Pressure Differences between Pure Isotopomers

Before we turn to a discussion of the excess properties of isotopic mixtures we first address the question of why there is any difference at all in the vapour pressures of isotopomers Our interpretation of the VPIEs⁶ is carried out within the framework of the Born–Oppenheimer approximation which states that the electronic structure of atoms and molecules is essentially independent of the isotopic distribution of nuclear mass It follows that the *potential energy is isotope independent* In other words isotope effects are nuclear mass effects resulting from the motion of nuclei of different mass on the same (or identical) potential energy surface(s) It may be noted in passing that this idea has been widely exploited by spectroscopists when they determine force constants from vibrational frequencies of isotopic molecules

The isotope separation factor can be expressed in terms of the equilibrium constant for the liquid–vapour phase equilibrium

$$X_{\text{liq}} + X_{\text{vap}} = X_{\text{liq}} + X'_{\text{vap}}$$

X and X' denote different isotopomers, also

$$K = \frac{[X_{\text{liq}}][X'_{\text{vap}}]}{[X'_{\text{liq}}][X_{\text{vap}}]} \quad (4)$$

Thus K is identical with the distillation separation factor Consequently α and VPIE may be expressed in terms of isotopic ratios of gas-phase and liquid-phase partition functions (Q)⁶

$$K = (Q'/Q)_{\text{vap}} / (Q'/Q)_{\text{liq}} \approx \alpha \approx p'/p \quad (5)$$

(The precise relationship should include the correction terms given in equation 3)

A theory of VPIEs based on the above concepts was worked out by Bigeleisen⁹ in 1961 In model calculations of Q'/Q it is often assumed that all the degrees of freedom except the rotational and translational ones of the gas can be treated as harmonic oscillators In the vapour phase each freely rotating and translating gas molecule has $3n - 6$ vibrational modes (n is the number of atoms in the molecule, $3n - 6$ is the number of internal degrees of freedom) In the condensed phase the $3nN$ (N is the number of molecules) degrees of freedom are very often treated within the framework of a simplified cell model of the condensed phase In this model¹⁰ an 'average' condensed phase molecule is assumed to have $3n$ degrees of freedom, of these, $3n - 6$ are similar to the vibrational modes of the gas-phase molecule The other six external degrees of freedom correspond

to the gas-phase translations and rotations which have become bound in the condensed phase The assignment of positive force constants (binding) to the external degrees of freedom will always work in the direction of normal VPIE ($p' > p$) This is a consequence of the fact that the heavier isotopomer lies deeper in the intermolecular potential well than does the lighter isotopomer (see the left side of Figure 3) It therefore requires a higher heat of vaporization (this reasoning is valid strictly only at low temperatures)

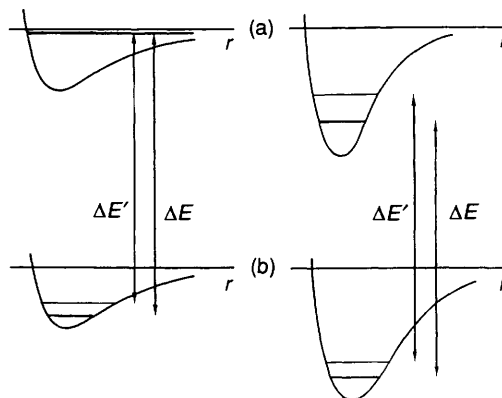


Figure 3 Potential energy curves for an external motion (left-side) and for an internal vibration (right-side) compared in the vapour (a) and liquid (b) phase For the external motion the zero-point energy change on condensation, $[(E'_v - E'_1) - (E_v - E_1)] = \Delta E' - \Delta E = E_1 - E'_1 < 0$, and this leads in the direction of a normal VPIE ($p' > p$) For the internal vibration in the ordinary case (which is shown) $\Delta E' - \Delta E = [(E'_v - E_v) - (E'_1 - E_1)] > 0$, and this leads in the direction of an inverse VPIE ($p > p'$) The diagrams are schematic, the shifts very much exaggerated in order to better illustrate the arguments in the text

For monatomic substances the only degrees of freedom are translational and a normal VPIE is always observed, but for polyatomic molecules the effect of condensed-phase intermolecular forces on the internal vibrations must be also considered In most cases we know from IR and Raman investigations that the frequencies of the internal vibrations shift toward lower frequencies (red shift) when the molecule passes from the vapour phase to the condensed phase (Such frequency shifts are rather small, *e.g.* the CH stretching frequency, which lies around 3000 cm^{-1} in the vapour phase, decreases by about 10 cm^{-1} on condensation) When substituted into the partition function ratios which express the VPIE (equation 5) such a red shift (equivalent to a lowering of the internal force constant on condensation) leads to an inverse VPIE ($p > p'$)

The discussion in the last paragraph is nicely illustrated in Figure 3 where we consider a typical vibration at lower temperature, [*i.e.* in the zero-point energy (ZPE) approximation where the population in excited vibrational levels is negligible] For an internal degree of freedom the reduced mass of that particular vibrational motion results in the more lightly substituted isotopomer lying higher in the vibrational potential well (right side of Figure 3) In the harmonic approximation the isotopic ZPE difference is proportional to the square root of the force constant describing that particular vibration If, on condensation, the frequency of interest decreases (*i.e.* shifts to the red), its force constant decreases, and the corresponding ZPE difference in the condensed phase will be smaller than that in the vapour phase, and it is this negative difference of zero-point energy differences (liquid–vapour) which accounts for a negative (inverse) contribution to the VPIE For an external motion (hindered translation or rotation, left side of Figure 3) the gas-phase force constant is zero since the corresponding gas-phase frequency is zero On condensation, then, the frequency and its associated force constant increase (*i.e.* shift to the blue) This accounts for a positive (normal) contribution to VPIE

The observed VPIE is the result of the interplay between the normal isotope effect from hindered translations and rotations and the inverse isotope effect arising from the internal degrees of freedom. The temperature dependence of the effects is different: the normal isotope effect usually falls off more steeply with temperature (proportionally to T^{-2}) then does the inverse isotope effect (T^{-1}). (The reason for the difference lies in the fact that the ZPE approximation is often inadequate for the low lying external frequencies and vibrational excitation must be considered. This leads to the T^{-2} dependence for these frequencies.) With internal and external effects of opposite sign, each proportional to different powers of temperature, it is not surprising that the VPIE can and often does cross from positive to negative (the crossover effect, at low enough temperature the T^{-2} term must dominate and the VPIE is necessarily positive). At higher temperature yet, the inverse VPIE (when it occurs) must display a maximum before it decays to zero at very high temperature. A good example which illustrates the crossover is the case of heavy water/light water. H_2O has a higher vapour pressure than D_2O up to 493 K (crossover temperature), but above this temperature D_2O is more volatile than H_2O . At higher temperature yet, the inverse effect would decay to zero, but before that decay is observed the critical point is reached, the distinction between condensed and vapour phase vanishes, and the point becomes moot.

The theoretical analysis described above couples thermodynamic observation with spectroscopically observed frequency shifts on condensation for isotope-sensitive vibrations. By combining the available spectroscopic data on vapour-liquid vibrational frequency shifts with experimental VPIE data it follows that one can obtain information about the details of the intermolecular interactions in the liquid phase.⁶⁻¹¹ For example, VPIE studies have furnished information on the vibrational coupling between internal vibrations and molecular translations and/or rotations which occurs in the condensed phase, on the density dependence of the force constants which govern the external molecular motions and internal vibrations in the liquid, on changes in vibrational anharmonicity which occur on condensation, and on the magnitude of the 'dielectric correction' to IR absorption peaks in condensed phases.

4 Theory of the Excess Functions of Isotopic Mixtures

The basic theory describing the excess functions of isotopic mixtures was developed by Prigogine, Bingen, and Bellemans¹² (PBB) forty 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. The central idea of the PBB model is the assumption that since the intermolecular forces between different isotopomers are the same (Born-Oppenheimer approximation *vide supra*) the deviations from ideality in isotopic mixtures can be rationalized in terms of the differences in the molar volume of isotopomers (molar volume isotope effect, MVIE, usually $V^{0'} \geq V^0$). The physical origin of the MVIE is well understood in terms of vibrational amplitude isotope effects which are a consequence of vibrational motion on an isotope-independent intramolecular potential surface.⁶

PBB suggested that the excess Gibbs energy of mixing (G^E) can be calculated in a two-step process: (i) compression or expansion of the molar volumes of the pure components 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 (W) done in compressing the lighter isotope and in expanding the heavier one to the molar volume of the mixture.^{12,13}

$$G^E = W = -x' \int_{V^0}^{V_m} p dV - x \int_{V^0}^{V_m} p dV \quad (6)$$

In step one it is necessary to apply positive pressure to compress

the lighter isotopomer from $V^{0'}$ to V_m and negative pressure (tension) to expand the heavier isotopomer from V^0 to V_m . 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 in equation 6 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 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 ($\mu^{E\infty}$), written here for the heavier isotopic species, can be given as⁵

$$\mu^{E\infty}(V^{0'}) = RT \ln \gamma^\infty = (V^{0'} - V^0)^2 / 2\beta V^0 \quad (7)$$

where β is the isothermal compressibility and γ^∞ is the activity coefficient associated with the free energy transfer of the heavier isotopomer from its pure liquid state to infinite dilution in the lighter isotopomer as a solvent. One expects that $\gamma^\infty = \gamma^{\infty'}$, i.e. symmetrical behaviour around $x = x' = 0.5$, in which case G^E can be represented with a one-term expansion of the Redlich-Kister type, $G^E \approx xx' \mu^{E\infty}$. By using this expression infinite dilution values of G^E can be obtained from experimental data at finite concentrations (or *vice versa*).

Jancso and Van Hook¹⁴ have suggested that the expression $(V^{0'} - V^0)^2 / 2\beta V^0$ may significantly underestimate the value of $\mu^{E\infty}$ for molecules with internal vibrations. The reason is that the compressibility is principally determined by the overall (external) motions of the molecules in the intermolecular potential. Therefore the expression containing β does not take proper account of the contributions of internal degrees of freedom to G^E (or $\mu^{E\infty}$). The internal vibrations are volume dependent. Consequently during the compression/expansion step (I), their frequencies change, and the work involved represents the internal contribution to G^E . By using a harmonic oscillator model, and writing the partition function, Q , of an 'average' molecule in the liquid phase in terms of $3n - 6$ internal and 6 external degrees of freedom, and recalling $A = -RT \ln Q(\nu_1, \nu_2, \dots)$ one obtains¹⁴

$$\mu^{E\gamma}(V^{0'}) = -RT \int_{V^0}^{V^{0'}} \sum_1^{3n} \left(\frac{\partial \ln Q}{\partial \nu} \right)_T \left(\frac{\partial \nu}{\partial V} \right)_T dV \quad (8)$$

where A is the Helmholtz energy and ν_i is the i -th vibrational frequency. The volume dependence of vibrational frequencies can be deduced from their more readily available pressure dependence using $(\partial \nu / \partial V) = -(\partial \nu / \partial p)(V/\beta)$. Another approach is to use the Gruneisen parameters, $\Gamma_i \equiv -\partial \ln \nu_i / \partial \ln V$, which can be determined from the change in vibrational frequency and molar volume on melting, or from the temperature dependence of the vibrational frequencies in the liquid phase.¹⁵ The use of Γ_i parameters is equivalent to the assumption of the quasiharmonic approximation widely employed by solid-state scientists. In this approximation the vibrations are assumed to remain harmonic about the new mean positions as the solid (liquid) phase expands.

In the following section examples of measurements on some selected isotopic mixtures will be considered and the experimental excess thermodynamic data will be compared with the results of model calculations.

5 Excess Properties of Some Selected Isotopic Mixtures

5.1 $^{36}\text{Ar}/^{40}\text{Ar}$ Mixtures

Theoretical analysis of the experimental data for mixtures of monatomic isotopes is considerably facilitated by the fact that in this case there are neither rotational nor internal degrees of freedom. The comparison of the isotope separation factors (α) obtained from one-stage liquid-vapour equilibrium measure-

ments with VPIE values obtained from differential vapour pressure measurements on separated isotopes yields values for $\ln \gamma^{x'}$ (see equations 3 and 7) Bigelsen *et al*¹⁶ have investigated the ³⁶Ar/⁴⁰Ar system and from their experimental data one obtains $\ln \gamma^{x'} = -3 \times 10^{-4}$ at 83 K. The negative sign is surprising and it cannot be rationalized in terms of the PBB theory (equation 7) or equation 8.

In an analysis of the PBB theory Singh and Van Hook¹⁷ argued that the assumption of zero excess free energy of mixing for step II (step II refers to the process where the two isotopomers at identical molar volumes are mixed) can be expected only under congruent conditions. By congruent they refer to a hypothetical situation where the radial distribution functions describing the liquid are identical for each of the separated isotopes. If one assumes that the separated isotopes are congruent in their pure liquid states, they can no longer be congruent after one of the isotopomers had been compressed (expanded) to the molar volume of the order. This is a consequence of the fact that compression (expansion) along a normal thermodynamic equilibrium path not only shifts the radial distribution function along the *r* axis (*i.e.* shifts the scale), but also changes its shape (*i.e.* changes the arrangement and/or number of neighbours around a central particle). The corrected calculation¹⁷ based on congruent expansion gives $\ln \gamma^{x'} = -2 \times 10^{-4}$, in reasonably good agreement with the observed value. Although the congruent/non-congruent correction for this mixture of monatomic isotopomers is important and even determines the sign of the effect, we do not expect it to make a significant contribution in the general case (*i.e.* for mixtures of polyatomic isotopomers). In isotopic mixtures of polyatomic molecules a considerable part (sometimes most) of G^E arises from the internal degrees of freedom, and in most cases the 'congruent correction' can be safely neglected.

5.2 H₂/D₂ Mixtures

The excess properties (G^E , H^E , V^E) of H₂/D₂ mixtures have been thoroughly studied.^{12,13} The PBB theory satisfactorily describes the significant deviations from Raoult's law observed in these solutions: for example, at 20 K $G^E(\text{expt}) = 7.2 \text{ J mol}^{-1}$ for the equimolar mixture, while equation 6 gives $G^E(\text{calc}) = 8.9 \text{ J mol}^{-1}$. At infinite dilution equation 7 gives $\mu^{E\infty}(\text{calc}) = 22 \text{ J mol}^{-1}$ which compares favourably with the experimental value $\mu^{E\infty}(\text{expt}) = 29 \text{ J mol}^{-1}$. The contribution of the H-H stretching vibration can be estimated from its frequency change during the process when H₂, initially at its equilibrium molar volume, is compressed to the equilibrium molar volume of D₂. From the known values for the pressure-dependence of the vibrational frequency ($\partial \nu / \partial p = 2.5 \text{ cm}^{-1} \text{ kbar}^{-1}$), the compressibility, and the MVIE one finds that the intramolecular vibrational frequency of H₂ blue-shifts 0.22 cm^{-1} during the compression from $V^0(\text{H}_2)$ to $V^0(\text{D}_2)$. That shift corresponds to a contribution of 1.3 J mol^{-1} to G^E . Thus in this case the internal contribution is only a small fraction of the effect calculated from equation 7. We conclude that in H₂/D₂ mixtures G^E is dominated by the compressibility (equation 7), which, in turn, is principally determined by the intermolecular part of the potential.

5.3 CH₄/CD₄ Mixtures

This system consists of simple, non-polar, quasi-spherical molecules and represents one of the simplest possible mixtures of polyatomic molecules. Therefore the prediction of its excess properties by any liquid-state theory should be as simple and direct as possible and can be used to test the performance of that theory. The vapour pressure differences between CH₄/CD₄ mixtures and CH₄ have been determined as a function of concentration and temperature.¹⁸ The excess free energies (G^E) and enthalpies (H^E) are shown at 100 K and 100–120 K, respectively in Figure 4. The experimental data are nicely represented by $G^E = x x' \mu^{E\infty}$.

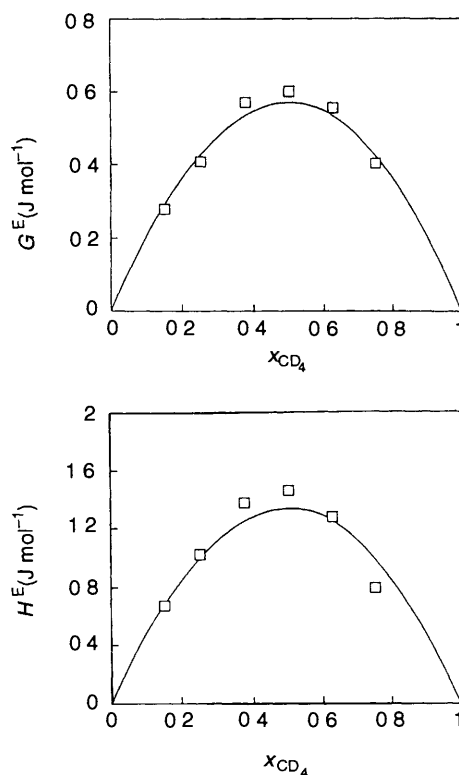


Figure 4 Excess free energy (G^E) and excess enthalpy (H^E) for the CH₄/CD₄ mixture as a function of the mole fraction of CD₄ at 100 K and 100–120 K, respectively

It is interesting to compare interpretations of G^E for isotopomer solutions using conventional and widely employed liquid-state structureless particle models, with the $3nN$ dimensional harmonic cell model described earlier in this review. Two popular and successful theoretical models for simple liquid mixtures were selected for comparison: the one-fluid van der Waals theory developed by Leland *et al*¹⁹ (VDW-1 model) and the WCA-based perturbation theory of Kohler *et al*²⁰ (lcLJ model). In the application of both theories effective isotope-dependent Lennard-Jones potential parameters (σ, ϵ) and an adjustable parameter (k_{HD}) describing the deviation from the Berthelot geometric mean rule [$\epsilon_{HD} = (1 - k_{HD})(\epsilon_{HH}\epsilon_{DD})^{1/2}$] were used. The results found for the equimolar mixture at 100 K are presented and compared with the experimental data in Table 1.

The calculations based on equation 8 used the Gruneisen parameters $\Gamma_{\text{rot}} = 0$ and $\Gamma_{\text{tr}} = 1.8$ and density dependent internal vibrational frequencies which are consistent with previous VPIE calculations. The results of the cell model calculation¹⁸ agree much better with experiment than do those of VDW-1 and lcLJ models (see Table 1). Detailed analysis of the cell model

Table 1 Values of the excess properties obtained for an equimolar mixture of CH₄ and CD₄ at 100 K (J mol^{-1})^a

	k_{HD}^b	G^E	H^E
VDW-1 model	0	-0.02	-0.01
	2.9×10^{-5c}	1.04	—
lcLJ model	0	-0.012	-0.0016
	2.6×10^{-5c}	1.02	—
Theory of isotope effects, equation 8		0.58	1.9
Experimental		0.60	1.5

Ref. 18. ^b Value describing the deviation from Berthelot rule (see text). Obtained by fitting to reproduce H^E .

results shows that 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 models that do not consider internal vibration explicitly. Also, in dealing with structureless particle models it is difficult to ensure consistency with the Born–Oppenheimer principle. An attractive feature of the cell model is that Born–Oppenheimer consistency is an integral part of the model.

There is another interesting point of experimental detail which confirms the cell model interpretation. The theory predicts $G^E = 0$ when $MVIE = 0$ (see equations 7 and 8). For the CH_4/CD_4 system $MVIE$ is normal ($V^{0'} > V^0$) for $T/\text{K} < 170$, but becomes inverse ($V^0 > V^{0'}$) at 170 ± 2 K.²¹ An extrapolation of the isotopomer mixture data (G^E vs. $1/T$) gives $G^E = 0$ at 171 ± 4 K. The agreement is excellent.

5.4 $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$ Mixtures

The vapour pressure of C_6H_6 , C_6D_6 , and their equimolar mixture has been determined between 279 and 353 K.⁸ The vapour pressure of C_6D_6 is 2.8% higher than that of C_6H_6 at the melting point, and the relative vapour pressure difference slowly decreases with increasing temperature. The inverse VPIE is mainly due to the vapour–liquid red-shift in the six CH stretching vibrational frequencies, the contribution from the hindered translational and rotational motions accounts for less than 10% of the total VPIE.¹⁴ A careful analysis of the temperature-dependence of the VPIE yielded values for the volume dependence of the liquid phase carbon–hydrogen stretching frequencies which are in reasonable agreement with those obtained from spectroscopic studies at elevated pressure and/or from analysis of the excess free energy of the isotopomer mixture (*vide infra*).

A value for $\mu^{E\infty} = 4G_{\text{equimolar}}^E$ has been calculated from the experimental excess pressures displayed in Figure 2 and is compared with theoretical values in Table 2. To calculate the contribution of carbon–hydrogen stretching vibrations to G^E we used the available experimental data for $\partial v_{\text{CH}}/\partial p$, $1.5 \text{ cm}^{-1} \text{ kbar}^{-1}$, isothermal compressibility, and $MVIE$ (the molar volume of benzene is 0.27% larger than that of deuterated benzene). The PBB approach predicted very nearly the same G^E as did the contribution from the external degrees of freedom in the cell model formalism (0.33 vs. 0.21 J mol^{-1}). Once again this demonstrates that the PBB model accounts only for the external contribution, which, roughly, is only about 10% of the total effect. It neglects the much more important contribution of internal vibrations. A second calculation which carried out the compression along a congruent path slightly improved the agreement with experiment. The agreement between the calculated and observed excess enthalpies is less satisfactory.

According to the calculations described above the free energy change accompanying the transfer of a C_6H_6 molecule from the neat liquid to infinitely dilute solution in C_6D_6 corresponds to a change of 0.04 cm^{-1} in the CH stretching frequency ($\sim 3000 \text{ cm}^{-1}$). The spectroscopic observation of such a small frequency

shift is not possible by ordinary IR or Raman techniques because of the peak broadening in the liquid phase. However, the Raman difference technique reported by Laane and co-workers²² enables the detection of shifts of even this order of magnitude. The frequency shifts Laane observed spectroscopically in $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$ mixtures were interpreted²² in terms of additive resonant intermolecular coupling and volume effects. It is the latter effect that is relevant to G^E since it takes into account the change in the molar volume when one isotopomer is dissolved in the other. When C_6H_6 is dissolved in C_6D_6 it is slightly compressed, consequently the repulsive forces between molecules become dominant and the CH stretching frequency increases. Although the magnitude of this volume effect ($\sim 0.15 \text{ cm}^{-1}$) was found to be three or four times larger than the value deduced from the G^E calculations, the direction of the shift is the same in both cases. If one considers the very small magnitude of the shifts together with the uncertainties in the calculations and experiments, both thermodynamic and spectroscopic, one can conclude that the results of Raman difference spectroscopy of isotopic mixtures lend strong support to the present model of excess thermodynamic functions of isotopic mixtures.

5.5 $\text{H}_2\text{O}/\text{D}_2\text{O}$ Mixtures

Experimental data on various excess properties of $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures have accumulated for more than sixty years. The interpretation of the thermodynamic properties of this mixture is complicated by the existence of the disproportionation equilibrium $\text{H}_2\text{O} + \text{D}_2\text{O} = 2 \text{HOD}$, *i.e.*, the $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture should be treated as a three-component system. The concentration of the different species in the liquid phase can be calculated from the equilibrium constant, taken as 3.8 at 298 K. However, there is another complication in the understanding of this system, namely that the bulk properties of HDO are not directly measurable, because this molecule cannot be isolated.

The enthalpy of the disproportionation reaction (ΔH) is large and the ratio $\Delta H^E/\Delta H$ is difficult to measure because ΔH^E is quite small. Calorimetric measurements (*e.g.* Koga²³) are apparently not sensitive enough to permit an unambiguous conclusion regarding ideality in $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O}$ mixtures. Vapour pressure measurements on $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures²⁴ show that the mixtures do not deviate from the ideal behaviour within the limits of the experimental data. (The vapour pressure of HDO can be calculated from the expression $\ln(p_{\text{HOH}}/p_{\text{DOD}})/\ln(p_{\text{HOH}}/p_{\text{HOD}}) = 1.92 \pm 0.02$; if the so-called 'law of the geometric mean' were valid for this system then instead of 1.92 one would use 2.00 for the ratio).

The most reliable measure of excess properties in water isotopomer mixtures come from analysis of distillation data at high dilution which give $\ln \gamma^\infty$ values of $8 \pm 2 \times 10^{-4}$ and $-4 \pm 2 \times 10^{-4}$ for isotopic substitution at hydrogen and oxygen, respectively.²⁵ Note the opposite signs of the excess free energies, which nicely correlate with the observed molar volume isotope effects (the molar volume of HDO is *larger* by 0.17%, and that of H_2^{18}O is *smaller* by 0.15% than is the molar volume of H_2^{16}O).⁶ The observation is important. The $\ln \gamma^\infty$ values calculated from equation 8 are in good agreement with experiment.¹⁷ The PBB approach or any of its subsequent modifications taking account of contributions from external degrees of freedom alone predict positive values for both isotopic mixtures and thus are necessarily in error.

5.6 Polymer/Polymer Isotopomer Solutions

In the sections above selected examples of excess free energies in isotopomer solutions have been given. In every case the effects are small, difficult to measure, not at all dramatic. It is only natural to look for ways to enhance the effects in order more convincingly to demonstrate their existence and more easily to measure their consequences. Since, in first approximation, the excess free energy parameter scales in proportion to the number of isotopic substitutions, and the fractionation, vapour pressure

Table 2 Calculated and observed partial molar excess free energies ($\mu^{E\infty}$) and enthalpies ($H^{E\infty}$) of benzene at infinite dilution in deuterobenzene at 298 K (J mol^{-1})^a

	$\mu^{E\infty}$		$H^{E\infty}$	
	(calc)	(obs)	(calc)	(obs)
Contributions to $\mu^{E\infty}$				
Internal	1.53			
External	0.21			
Total	1.74	2.3 ± 0.2	7.0	4.4 ± 2
Congruent path ^b	1.9			
PBB	0.33			

^a Ref. 5. ^b See text.

enhancement, or other parameter of experimental interest scales in proportion to G^E/T , we conclude that studies are best carried out with T as low as possible, or on molecules with many isotopically substituted bonds. We have already described low temperature experiments in the sections on hydrogen, argon, and methane solutions. For hydrogen, especially, the excess effects are large, not the least because the temperature is so very low ($\approx 20\text{K}$). For most liquids, however, it is impossible to lower the temperature very far—freezing intervenes. Fortunately the alternative path is open. By increasing the number of substituted bonds, *i.e.* making the molecule larger and larger, it is possible to increase G^E/T to the point where the solution becomes so non-ideal that phase separation occurs. Since the excess free energy per bond is so small, one is well into polymer/polymer solutions before this happens. The observation of precipitation in any isotopomer mixture is exciting. It offers incontrovertible proof that the rather subtle effects we have been describing in this review do in fact exist. It demonstrates that they have important physical consequences. In the next few paragraphs we will review some of that evidence.

Within the past few years Bates and co-workers²⁶ have reported phase separation in isotopomer mixtures of H/D polymers including polystyrenes, polybutadienes, and polyethylene/polypropylene. Light and neutron scattering techniques have been employed. The authors extracted a Flory–Huggins excess free energy parameter (χ) from the scattering data. As this interaction parameter, $\chi = (G^E/V)/\phi\phi'$ increases to its critical limit, $\chi = 2RT_c$, the solution demixes at an upper critical solution temperature T_c . The ϕ 's are volume fractions but for isotopomer solutions mole fractions would serve equally well.

The thermodynamics of demixing of isotopomer solutions of polymers was originally considered by Buckingham and Hentschel²⁷ but their theory was developed at the PBB level and has proved to be inadequate. Following Singh and Van Hook²⁸ we write the excess free energy of the solution of polymer isotopomers as

$$\Delta E/RT = \phi\phi'(N\Gamma r/2)(\Delta V/V)(u'-u) \quad (9)$$

Here N is the number of monomer units per molecule, r the number of H/D substituted bonds per monomer, Γ the Gruneisen parameter for the effective frequency (taken as the CH(CD) stretch), $\Delta V/V$ is the MVIE, and $u = hc\nu/kT$. The zero-point energy approximation is employed. For polymers the relative contribution of external lattice modes is negligible and their effect is not included in equation 9. The conditions for phase separation are obtained by differentiating the total free energy with respect to concentration and setting second and third derivatives to zero. This gives $\phi' = \phi = 0.5$ and

$$(N_c\Gamma r/2)(\Delta V/V)u'(1 - (\mu'/\mu)^{1/2}) = 2 \quad (10)$$

N_c is the critical polymerization number, μ' and μ are the reduced masses for the CH and CD oscillators, respectively. The excess free energy *per* H/D substituted bond is small, just as small, for example, as the tiny effects discussed in the sections on small molecules above. However the effects are cumulative, and as the total number of substituted bonds, Nr , increases, the excess free energy becomes large enough to cause phase separation. For polybutadiene the critical polymerization number N_c is found to be 1.3×10^3 monomer units. It is convenient to compare theory and experiment using $\mu^{E\infty}/RT = \ln\gamma^\infty$. γ^∞ is the activity coefficient per monomer unit, and for the one-term Flory–Huggins model describes the free energy of transfer of a given isotopomer from its Raoult's law reference state to an infinitely dilute solution, with the other isotopomer as solvent, in this case $\ln\gamma^\infty = 2/N_c$. For polybutadiene, experiment gives $10^4 \ln\gamma^\infty = 9 \pm 2$, the calculated value is 11 ± 4 . The PBB approximation yields 4 ± 1 and an alternative analysis by Bates and Wignall^{5, 26} gives $10^4 \ln\gamma^\infty = 14$. The authors²⁶ chose an interpretation somewhat different than the one we described above and in the earlier sections of this review. They related the

contribution of internal vibrational modes to polarizability isotope effects (PIE's), and employed typical values transferred from small molecule PIE's. This is a perfectly appropriate method, just like MVIE, the PIE is understood in terms of an isotope-independent potential energy surface describing the intramolecular vibrations. The two effects share a common origin.

The observation of demixing in polymer/polymer isotopomer solutions comprises a powerful verification of the general ideas presented in this review. The light scattering patterns which occur during the spinodal quench of isotopomer solutions offer incontrovertible evidence that a phase transition is occurring.

The demixing is dramatic confirmation of non-ideality in the isotopomer solutions. Its direct observation involves the recognition that χ itself scales proportionally to the number of substituted bonds in the isotopomers being compared. Although each CH/CD bond contributes only a very small amount to the excess free energy (as witness the minuscule effects in small molecule systems), they are additive and eventually result in precipitation.

6 Conclusions

High-precision measurements of the excess thermodynamic properties of mixtures of isotopomers have shown that even these very simple mixtures exhibit small, but still significant, deviations from ideal behaviour. The magnitude of the excess Gibbs energy in isotopomer solutions is two to three orders of magnitude smaller than excess free energies typically observed in binary mixtures of non-isotopic simple molecules. In the case of mixtures of H/D-substituted polymers the excess free energies are large enough to cause demixing.

Theoretical analysis demonstrates that the origin of non-ideality in isotopomer mixtures is closely connected with difference between the molar volumes of isotopomers (the MVIE). Excess thermodynamic properties can be evaluated by integrating the free energy, which is volume-dependent, across MVIE. This is most conveniently done by expressing the free energies in terms of vibrational properties of the component molecules. Thus the integration involves the volume-dependence of the vibrational properties of the component molecules. It is important to keep in mind that the MVIE is itself well understood in terms of isotope effects on vibrational amplitude, and amplitude isotope effects, in turn, can be quantitatively described using a set of isotope independent inter- and intramolecular force constants. Thus the development is self-consistent, and is also consistent with the Born–Oppenheimer principle.

Those mixture theories which consider molecules as structureless particles (*i.e.* do not include internal vibrations), fail to rationalize the excess properties of isotopomer mixtures properly. Although vibrational effects can be, and often are, neglected in theoretical treatments of mixtures of non-isotopomers (since the non-ideality there is mainly caused by differences in intermolecular forces), that cannot be so for isotopomer mixtures where the force fields are identical (or nearly so, Born–Oppenheimer approximation). Thus an important conclusion from the work reviewed above is that vibrational effects, although sometimes outweighed by other factors, do contribute importantly in determining the properties of mixtures and solutions. In isotopomer solutions it is essential to consider the density dependence of vibrations explicitly. In some cases the very small frequency shifts predicted from the analysis of isotopomer thermodynamics have been corroborated by Raman difference investigations.

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