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Isotope Effects in Solution Thermodynamics: Excess Properties in Solutions of Isotopomers

Gabor Jancso,[†] Luis P. N. Rebelo,[‡] and W. Alexander Van Hook*,[§]

Central Research Institute for Physics, Atomic Energy Research Institute, POB 49, 1525 Budapest 114, Hungary, Department of Chemistry, New University of Lisbon, 2825 Monte da Caparica, Lisbon, Portugal, and Chemistry Department, University of Tennessee, Knoxville, Tennessee 37996

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1. Introduction

In this review we consider recent studies of isotope effects (IE's) on the physical properties of solutions, such as vapor pressure, molar volume, compressibility, *etc.* Such IE's are of interest for two reasons: first, because they can sometimes be capitalized to separation processes, and samples of separated isotopes may be scientifically and commercially valuable and second, and more importantly to use, because the sign and magnitude of condensed phase isotope effects (CPIE's) are closely related to the nature of the intermolecular forces in liquids and solutions. Thus, appropriate IE data can probe the nature of molecular interaction and structure.

That CPIE's are especially useful probes for intermolecular forces results from the choice to describe molecules and their interactions in terms of their electronic properties (*i.e.*, wave functions). To an excellent approximation electronic structures are independent of the isotopic distribution of nuclear mass (Born–Oppenheimer approximation). It follows, for a given electronic state, that the function which describes the dependence of molecular (or intermolecular) energy on nuclear position is isotope independent. That function maps a surface in a multidimensional nuclear-displacement/energy space and is labeled the "potential energy surface (PES)". A thorough understanding of the PES, most often complicated and difficult to achieve, is prerequisite to a proper quantitative description of the system in modern statistical thermodynamic terms. In contrast to the PES, the total energy of the system (which includes both potential and kinetic parts) and the associated free energy are isotope dependent. That is because the kinetic energy terms accounting for motion on the PES are mass dependent. Moreover, kinetic energy is related to the structure of the molecules of interest, to their masses and mass distributions, and to the temperature, in a relatively simple way.

In the following sections we will compare properties of separated isotopes, A and A′ (the prime denotes isotopic substitution and will henceforth refer to the lighter molecule), and then discuss IE's on the properties of solutions. We will treat solutions of dissimilar molecules, comparing A dissolved in B with A′ in B, B′ in A, or B′ in A′, attempting a common description with a minimum set of parameters. Finally, we will turn our attention to mixtures of isotopomers, *i.e.*, A in A′, B in B′, *etc.* In such solutions both solute and solvent, and by extension the solution, share identical potential energy surfaces. It follows that the theoretical con-

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* To whom correspondence should be addressed.

[†] Atomic Energy Research Institute.

[‡] New University of Lisbon. On leave at University of Tennessee 1990–91.

[§] University of Tennessee.

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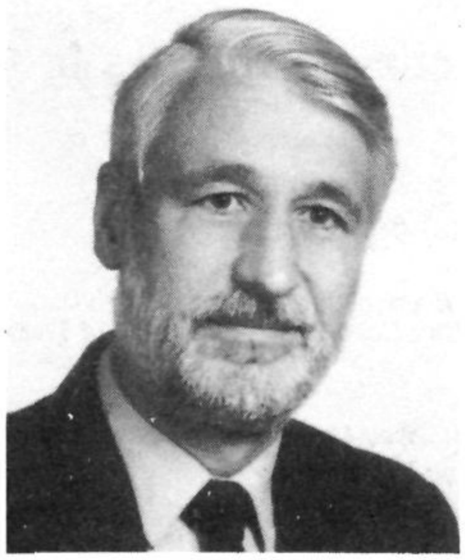


Gabor Jancso was born in 1941 in Budapest, Hungary. He graduated with a degree in chemistry from Eotvos Lorand University in 1964 and immediately joined the Central Research Institute for Physics of the Hungarian Academy of Sciences where he is currently a Senior Research Scientist. In 1969–1970 and 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 fur 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.

W. Alexander Van Hook was born 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 Universite Libre de Bruxelles studying with I. Prigogine and G. Thomaes, and a good deal of 1972 at the Boris Kidric 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.

Luis Paulo Rebelo was born in Lisbon, Portugal, in 1960. He graduated in 1982 in Chemical Engineering with honors from the Technical University of Lisbon. In 1989 he received his Ph.D. in Physical Chemistry from the New University of Lisbon under the supervision of Professor Jorge Calado and Professor Manuel 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.

struction used to rationalize isotope effects can be tested in a particularly straightforward way with such solutions. It is for that reason that the bulk of this review will focus on theory and experiment for such systems.

The analysis of isotopomer solutions will demonstrate that a proper consideration of the vibrational properties of the component molecules is absolutely essential to the understanding of these mixtures. At first glance that conclusion is a little surprising, since after all, we are dealing with systems which should be among the simplest of solutions, *i.e.*, the most nearly ideal. It is an important conclusion, however, because many modern theories of solution ignore the whole problem of vibration and vibrational interaction, choosing to model solutions in terms of structureless spherical or aspherical particles interacting *via* an appropriate intermolecular potential, where quantum mechanical effects are not explicitly addressed. Consequently, in the treatment of isotopic mixtures these effects are hidden under the assignment of choosing different effective potential parameters of the mixture constituents and/or in small deviations from the well-known Lorentz or Berthelot combining rules. Under those circumstances it is difficult to avoid *ad hoc* arguments. In contrast, condensed isotope effect theory uses identical PES's to describe the properties of both isotopomers. Therefore, deviations from ideality emerge directly from the quantum differences between components moving on the same isotope- and concentration-independent PES. From the analysis of the results obtained on mixtures of isotopomers emerges a warning: inadequacies in treating nearly ideal solutions (by ignoring vibration) likely carry over in the treatment of solutions of more general interest. Here vibrational effects may also be important, just not as obvious.

1.1. Vapor Pressure Measurements on Separated Isotopes

Any proper thermodynamic description must be clearly and unequivocally referenced to a well-understood standard state. The ideal gas reference state, with zero intermolecular interaction, is particularly appropriate for theoretical considerations. For solutions, however, a condensed phase reference state is

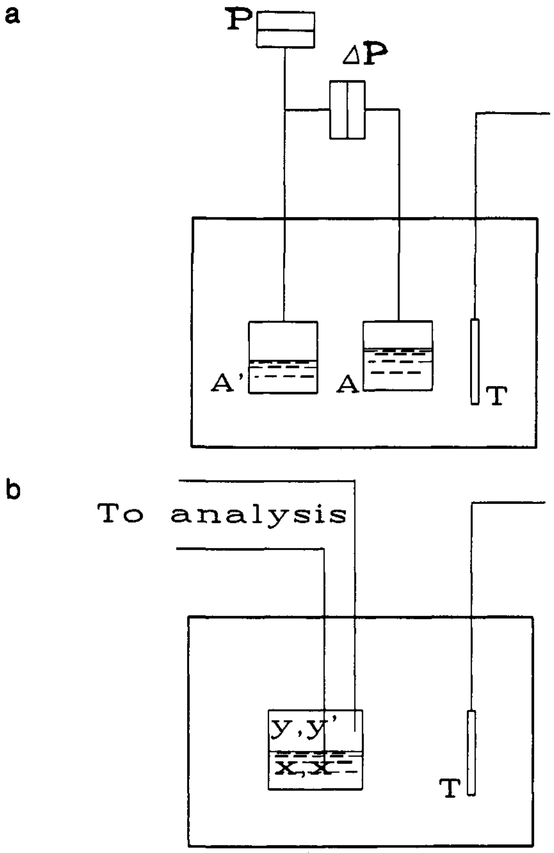


Figure 1. (a) Schematic diagram of an experiment designed to measure the vapor pressure isotope effect (VPIE) between samples of separated isotopomers, A′ and A. For example, A′ might be 100% C_6H_6 and A 100% C_6D_6. The sample cells, A′ and A, are thermostated, temperature is read from resistance thermometer T, the pressure difference between samples, and the absolute pressure of one sample, are measured with transducers P and ΔP. The transducers are thermostated at a slightly higher temperature than A′ and A to prevent condensation. (b) One-plate fractionation experiment (schematic). The experiment is designed to measure the concentration ratio of two isotopomers in each of two coexisting phases, for example, liquid (x'/x) and gas (y'/y). The liquid–vapor separation factor is $\alpha = (y'/y)/(x'/x)$. Temperature is measured with thermometer T, and liquid and vapor samples are removed through capillary sampling lines for later mass spectroscopic (or other) analysis.

normally employed. One can proceed from the ideal gas reference state to one or another of several possible and more convenient condensed phase references by considering free energy changes along the chain: ideal gas reference ↔ real gas ↔ pure liquid reference ↔ other condensed reference. To do so, begin by focusing on a measurement such as the one diagrammed in Figure 1a, where the vapor pressures of separated samples of purified isotopomers are compared in a differential measurement. The analysis below demonstrates that the vapor pressure isotope effect, VPIE = ln (P'/P), is related to the isotopic difference of Raoult's law standard-state free energies referring to the phase change.[1,2] For that reason it offers a convenient starting point for thermodynamic analysis.

Consider a two-component condensed phase in equilibrium with its vapor. The partial molar free energy (chemical potential) of each component in the binary mixture, μ_i(phase), can be written[3,4]

$$\mu_1(\mathrm{c}) = \mu_1(\mathrm{v}) = \mu_1^\circ + RT\ln P_1 + (B_{11} + 2y_2^{\,2}\eta_{12})P + \ldots \quad (1a)$$

$$\mu_2(\mathrm{c}) = \mu_2(\mathrm{v}) = \mu_2^\circ + RT\ln P_2 + (B_{22} + 2y_1^{\,2}\eta_{12})P + \ldots \quad (1b)$$

P is the total pressure and P_i the partial pressure, μ_i° is the chemical potential in the ideal gas reference state, and y_i is the gas phase and x_i the condensed-phase mole fraction of component i. Generalization to additional components is straightforward. In deriving eq 1 the virial expansion describing vapor nonideality has been written as a pressure series, $(PV/RT - 1)/P = B/(RT) + CP/(RT) + \ldots$, B is the second and C the third mixture virial coefficient. The mixture virial is written as a sum over pair interactions, $B(\mathrm{mix}) = y_1^2B_{11} + 2y_1y_2B_{12} + y_2^2B_{22}$, and η_{12} is an asymmetry coefficient, $\eta_{12} = B_{12} - (B_{11} + B_{22})/2$. Higher order terms in eq 1 may contain third, fourth, and higher virial coefficients.

1.2. The VPIE and Fractionation Factors

In the liquid the free energy of the pure condensed phase at the experimental temperature is often chosen as the standard state (Raoult's law reference), except if attention is focused on the more dilute component at high dilution when the Henry's law (infinite dilution) reference is favored. For the Raoult's law reference

$$\mu_i(\mathrm{c}) = \mu_i^\circ(\mathrm{c}) + RT\ln(\gamma_i x_i) + \int_{P_i^\circ}^{P} V_i(\mathrm{c})\mathrm{d}P \quad (2)$$

Note that $\gamma_i = 1$ and $\ln(\gamma_i) = 0$ when $x_i = 1$. Here γ_i is the activity coefficient, P_i° the vapor pressure of the pure component, P the vapor pressure of the solution, and V_i(c) the partial molar volume of component "i" in the condensed phase. The Henry's law reference is only appropriate for the dilute component, in this limit $\ln \gamma_i^* = 0$ when $x_i = 0$.

$$\mu_i(\mathrm{c}) = \mu_i^*(\mathrm{c}) + RT\ln(\gamma_i^* x_i) + \int_{P_i^\circ}^{P} V_i^\infty(\mathrm{c})\mathrm{d}P \quad (3)$$

The activity coefficient in the Raoult's law formalism is shown without a superscript, in the Henry case we write γ_i^*. In the Henry case V_i^∞(c) in eq 3 is the partial molar volume of the solute at infinite dilution. The integrals in eqs 2 and 3 can be neglected except when $P \gg P_i^\circ$.

To obtain an expression for the VPIE, equate expressions for μ_i(v) and μ_i(c), and μ_i'(v) and μ_i'(c) as given in eqs 1 and 2 and then by substraction find an expression for the ith component vapor pressure (i = 1 or 2) in a two-component solution

$$RT\ln(P_i'/P_i) = (\mu_i'^\circ(\mathrm{c}) - \mu_i'^\circ(\mathrm{v})) - (\mu_i^\circ(\mathrm{c}) - \mu_i^\circ(\mathrm{v})) + RT\ln(x_i'\gamma_i'/x_i\gamma_i) + \int_{P_i^{\circ\prime}}^{P} V_i'\mathrm{d}P - \int_{P_i^\circ}^{P} V_i\mathrm{d}P - (B_{ii}' + 2(1 - y_i')^2\eta_{ij}')P' + (B_{ii} + 2(1 - y_i)^2\eta_{ij})P \quad (4)$$

For the one-component case, $x_i = x_i' = \gamma_i = \gamma_i' = 1$ and $\eta_{ij} = 0$. From this point forward we will use Δ to represent isotopic differences (light − heavy) and δ for the phase differences (in the present case δ = vapor − condensed). The equation simplifies after neglecting differences in some small terms

$$\ln(P'/P) = -\delta\Delta(\mu^\circ)/RT + (BP - B'P')/RT \quad (5)$$

Introducing the Helmholtz free energy differences,

$\delta\Delta A° = \delta\Delta\mu° + \delta\Delta(PV)°$, so

$$\mathrm{VPIE} = \ln (P'/P) = -\delta\Delta A°/RT - (B'P'/RT)(1 - BP/B'P') + (P'V'/RT)(1 - PV/P'V') \quad (6)$$

Equation 6 is the familiar Bigeleisen equation for the VPIE.[1] It shows the VPIE to be proportional to the isotopic difference of free energy differences on the phase change (save for small corrections associated with IE's on vapor nonideality and condensed-phase molar volume). The result is an important one; it offers us an experimental probe capable of measuring subtle free energy differences.

The development above is concerned with measurements on samples of separated isotopes. The primed and unprimed species are individually referenced to separate Raoult's law standard states. An alternative approach is needed to treat distillation and other kinds of fractionation experiments. In distillation (Figure 1b) two phases, each containing both isotopomers, are equilibrated across the phase boundary. The fractionation factor, $\alpha' = (\alpha)^{-1}$ is defined

$$\alpha' = (y'/y)/(x'/x); \quad \mathrm{LVIFF} = \ln \alpha' \quad (7)$$

and it is a straightforward matter, using the equations above, to obtain in good approximation

$$RT \ln \alpha = -\delta\Delta A° + (B - B')P - RT \ln \gamma^{\infty} + P°'V°'(P° V_2^{e}/P°'V°' - \Delta V°/V°') \quad (8)$$

LVIFF is the liquid–vapor isotope fractionation factor. The higher order molar volume-dependent term in eq 8 can almost always be neglected; it is often argued that in dilute mixtures of isotopomers $V_2^e \approx \Delta V$. V_2^e is the excess partial molar volume of the solute, and $\Delta V/V$ is the molar volume isotope effect for the separated isotopomers. If in addition the pressure is low, and the virial coefficient isotope effect can be neglected, a simple result obtains

$$RT \ln \alpha = -\delta\Delta A° - RT \ln \gamma^{\infty} \quad (9)$$

The second term on the right is written in terms of γ^{∞}, the activity coefficient at high dilution referenced all the way back to the pure liquid. Expressed alternatively, $RT \ln \gamma^{\infty}$ is the free energy of transfer of the unprimed isotopomer from its Raoult's law standard state to the Henry's law standard state (*i.e.*, now at infinite dilution in the primed solvent). We will see that this term is often nonzero and cannot be neglected.

1.3. The Relation to Molecular Structure and Vibrational Dynamics

Molecular considerations are most conveniently introduced to eqs 6–9 by means of the canonical partition functions Q_c and Q_v. Since $A° = -kT \ln Q$ we have for the VPIE following Bigeleisen[1,2]

$$\ln (P'/P) = \ln (Q_v'Q_c/Q_vQ_c') + [(P'V' - PV) - (B'P' - BP)]/RT \quad (10)$$

An analogous equation for ln α is readily derived. Because partition functions are calculable (in principle) from molecular properties using fundamental theory, eq 10 and its analogue for ln α are important. They connect properties which can be measured with high experimental precision to basic theoretical ideas. The many dimensional canonical partition functions in eq 10 are complicated and difficult to evaluate. Except for unusually simple systems further approximations will be required. To simplify the discussion we now focus on the VPIE and defer treatment of excess chemical potentials in isotopic solutions (*i.e.*, of the ln γ term in the equations above).

In dealing with polyatomic molecules it is convenient to define an average molecular partition function $\ln (\langle Q \rangle) = \ln Q/N$. In the vapor this presents no problem; it is easy to show $\ln Q = N (\ln (q/N) + N$, so $\ln (Q/Q') = \ln (q/q')$, q is the microcanonical partition function. In the condensed phase caution is in order. Condensed phase Q's are sensitive functions of volume, $Q = Q(T,V,n)$, and must properly account for the effects of intermolecular interaction. In a vapor pressure measurement the isotopomers with partition functions Q and Q' are normally compared at identical temperatures, $T = T'$, but at different pressures, $P \neq P'$, and different volumes, $V \neq V'$. In a fractionation experiment the temperature, pressure, and volume are all common. (In the vapor pressure experiment P and P' define the VPIE and $V°$ and $V°'$ define the molar volume isotope effect (MVIE) under orthobaric conditions.) Consider the VPIE experiment. If the reduced radial distribution functions for the separate phases are identical for the two isotopomers (see section 2.5), the Q ratios of eq 10 can be expressed as the ratio of reduced partition functions in the two phases, $((s/s')f)$, and can also be expressed as the ratio of quantum mechanical to classical partition functions (s and s' are symmetry numbers)[1]

$$[(s/s')f]_j = [(\langle Q \rangle/\langle Q' \rangle)_{\mathrm{qm}}/(\langle Q \rangle/\langle Q' \rangle)_{\mathrm{cl}}]_i \quad (11)$$

Thus

$$\ln (P'/P) = \ln (f_c/f_g) + (RT)^{-1}[(P'V' - PV) - (B'P' - BP)] \quad (12)$$

In that case the liquids are said to be in congruent state.[5] Most often it is assumed that this equality is satisfied under orthobaric conditions. Under noncongruent conditions, for example, when the two isotopomers are to be compared at identical partial molar volumes, $V' = V$, or some other set of conditions, an additional term involving the pressure–volume integral from the congruent (V'^{*}) to noncongruent (V') state is required. This point has been explored in some detail by Singh and Van Hook.[5] (Immediately above we pointed out that most authors have assumed the separated orthobaric liquids to be in congruent state, but this is not self evident.)

$$\ln (P'/P) = \ln (f_c/f_g) + (RT)^{-1}[(P'V' - PV) - (B'P' - BP)] - (RT)^{-1}\int_{V'^{*}}^{V'} P' dV \quad (13)$$

Equation 13 straightforwardly relates vapor pressure ratios to the reduced partition function ratio, RPFR = f_c/f_g. For most applications $B \approx B'$, $V' \approx V$, and $\int P' \mathrm{d}V \approx 0$ and the equation simplifies:

$$\ln (f_c/f_g) = [\ln (P'/P)][1 + P(B - V)/RT] \quad (14)$$

Equation 14 has long been used in the analysis of VPIE data. The difference between VPIE and LVIFF was previously discussed by Bigeleisen and Roth[6] in connection with work on the neon isotopes. RPFR is available from theory following a variety of approximations. One of the most commonly employed was suggested in 1963 by Stern, Van Hook, and Wolfsberg (SVHW).[7] They used a harmonic oscillator, rigid rotor model in the vapor phase coupled with a $3n$ dimensional harmonic oscillator cell model in the condensed phase obtaining

$$\frac{f_c}{f_g} = \prod^{\mathrm{int}} \frac{[(u_i/u_i')_c \exp(u_i' - u_i)_c/2](1 - \exp(-u_i')_c)/(1 - \exp(-u_i)_c}{[(u_i/u_i')_g \exp(u_i' - u_i)_g/2](1 - \exp(-u_i')_g)/(1 - \exp(-u_i)_g} \times \prod^{\mathrm{ext}} \frac{u}{u'}[\exp((u' - u)/2)]\frac{(1 - \exp(-u')}{(1 - \exp(-u)} \quad (15)$$

In eq 15 $u_i = h\nu_i/kT$, with ν_i the frequency of the ith normal mode, and n is the number of atoms in the molecule. The $3n - 6$ frequencies ($3n - 5$ for linear molecules) describing the internal vibrations of the molecules are treated in the harmonic approximation in both phases, while the 6(5) external modes (corresponding to zero frequencies in the gas) are assumed to change to hindered translations and rotations (librations) in the condensed phase and are also handled in the harmonic approximation.

Equation 13–15 offer a formalism which correlates thermodynamically measured isotope effects with spectroscopic analysis, including (most importantly) the frequency shifts which occur on condensation. Thus, the calculation of f_c/f_g in the framework of the SVHW model requires a set of $3n - 6$ gas phase (or $3n - 5$ for the linear case) and $3n$ condensed-phase frequencies for each isotopomer. To minimize error one should select a best fit set of harmonic force constants (F matrix) for each phase. The isotope-independent F matrices are used to calculate consistent sets of frequencies for the different isotopomers in the two phases. The calculated frequencies are substituted in eq 15, and the result is subsequently compared with thermodynamic measurements using eq 13 or 14. Detailed calculations have been carried out for a large number of molecules[2,7-10] and consistency between spectroscopically measured phase frequency shifts and the thermodynamic effects demonstrated many times over. The agreement between theory and experiment extends to rather subtle points, such as the ordering of vapor pressures in sets of equivalent isomers (such as *cis*-, *trans*, and *gem*-$C_2H_2D_2$,[7,8] or *ortho*, *meta*-, and *p*-$C_6H_4D_2$,[9] or the equivalent isotopomers of ethane[10]). Jancso and Van Hook[11] have pointed out that in correlating the spectroscopic frequency shifts which occur on phase change (and the force constant changes related to them), with IE's, it is first necessary to correct empirically observed spectroscopic data for the dielectric contribution. Warner and Wolfsberg[12] have discussed this matter from a theoretical point of view.

Recapitulating: (1) The isotopic ratio of thermodynamic activities used to describe phase equilibria (in the simplest case, for liquid–vapor equilibria, the VPIE) is straightforwardly related to the reduced partition function ratio. This basic idea can be extended following a set of reasonable approximations to express thermodynamic isotope effects in terms of differences in the potential energies associated with translation, rotation, and vibration in the different phases, together with differences in the kinetic energy coupling translation, rotation, and vibration. (2) Extensive and elaborate calculations of the VPIE have been carried out on a wide variety of molecules. They quantitatively confirm, and in detail, the relations set forth in eqs 13–15.

2. Excess Free Energies in Mixtures of Isotopomers

2.1. Introduction

It is clear that the properties of a mixture of isotopic isomers will be only slightly different from the properties of one or the other separated sample. Thus, it is natural to anticipate that some kind of perturbation theory may be an appropriate route to their description. Perturbation theories can be divided into two major different approaches. The first, used by the Bochum group,[13] is an extension of the well-known WCA (Weeks, Chandler, Anderson)[14] method to mixtures. In the one-center Lennard-Jones version the Helmholtz free energy is written

$$A = A_i^\circ + 2\pi N\rho \sum x_i x_j \int (\mathrm{d}u_{\mathrm{att}}(r_{ij})/\mathrm{d}r_{ij}) g_{ij}^\circ(r) r^2 \mathrm{d}r \quad (16)$$

where the subscript "att" denotes the attractive part of the potential energy and the superscript ° on the radial distribution function, $g_{ij}^\circ(r)$, and on the Helmholtz free energy, A_i°, refers to a slightly perturbed hard-sphere model potential which, in turn, can be transformed to the effective HS model potential by convenient modulation of the reference potential energy surface (the so-called "blip" condition). Alternatively, following Gray and Gubbins[15] the potential energy function may be divided into anisotropic and isotropic parts. The use of a Pade approximant leads to

$$A = A^\circ(r) + a_2[1/(1 - A_3/A_2)] \quad (17)$$

which is readily generalized to mixtures. In eq 17 A_2 and A_3 are second- and third-order perturbation terms which involve complicated averaging over molecular orientation. The first-order term, A_1, is null as a consequence of the manner chosen to split the potential energy function. The higher order terms contain contributions due to dipole, quadrupole, octapole moments, *etc.*

Both the Bochum and Gubbins–Gray approaches emphasize anisotropy, in the first case a shape anisotropic, in the second an electrostatic anisotropy, but neither can simultaneously take care of both effects. Each of these commonly employed mixture perturbation theories is classical, and quantum mechanical effects are not explicitly addressed. Thus, for treatment of isotope effects, which we recall are purely quantum mechanical in origin, they are seriously handicapped. In a sense these approaches are equivalent to hiding the mixture isotope effects under the assignment of different and isotope-dependent potential parameters (ϵ and σ) and/or small deviations from the Lorentz and Berthelot combining rules. For that reason they lead to the very real danger of interpreting such parametrization in terms of a set of *isotope dependent* PES's, which is logically inconsistent. Therefore, we prefer to employ the usual formalism of IE's, which, as explained above, employs the theoretically defensible concept of identical PES's independent of mass. In this formalism deviations, if any, from ideality in solutions of isotopomers should emerge directly from quantum differences between the components moving on the same *isotope and concentration independent* PES's.

2.2. Isotope Effects in Mixtures

A number of authors (Prigogine,[16] Chester,[17] Bigeleisen,[18] Jancso and Van Hook,[19] Singh and Van Hook,[5,20] and Rebelo, Calado, and co-workers[21,22]) have considered excess free energy in mixtures of isotopes. We begin by expanding the Helmholtz free energy around the equilibrium volumes, V° and $V^{\circ\prime}$, of the separated samples at pressures P and P'

$$A(V) = A(V^\circ) + (\mathrm{d}A/\mathrm{d}V)(V - V^\circ) + (1/2)(\mathrm{d}^2A/\mathrm{d}V^2)(V - V^\circ)^2 + \ldots \quad (18)$$

$$A'(V') = A'(V^{\circ\prime}) + (\mathrm{d}A'/\mathrm{d}V)(V - V^{\circ\prime}) + (1/2)(\mathrm{d}^2A'/\mathrm{d}V^2)(V - V^{\circ\prime})^2 + \ldots \quad (19)$$

The contribution to the excess free energy is

$$A^{\mathrm{ex}}(V) = x'A'(V') + xA(V) - x'A'(V^{\circ\prime}) - xA(V^\circ) \quad (20)$$

The volume of the solution is the sum of the standard state and the excess partial molar volumes, but for solutions of isotope isomers, excess volumes are small. Neglecting terms of that order and higher, and differentiating $A^{\mathrm{ex}}(V)$ with respect to concentration, one obtains expressions for the excess partial molar free energies as a function of volume. Remember $\mu^{\mathrm{ex}}(V) = A^{\mathrm{ex}}(V) - x'(\partial A^{\mathrm{ex}}(V)/\partial x')$ and $\mu'^{\mathrm{ex}} = A^{\mathrm{ex}}(V) + x(\partial A^{\mathrm{ex}}(V)/\partial x')$. For the unprimed isotopomer

$$\mu^{\mathrm{ex}}(V) = x'^2[(V^{\circ\prime} - V^\circ)((\mathrm{d}A/\mathrm{d}V) - (\mathrm{d}A'/\mathrm{d}V)) + (1/2)(V^{\circ\prime} - V^\circ)^2((2x' - 1)((\mathrm{d}^2A/\mathrm{d}V^2) - (\mathrm{d}^2A'/\mathrm{d}V^2)) + \mathrm{d}^2A'/\mathrm{d}V^2)] \quad (21)$$

The excess chemical potential of the more dilute isomer at infinite dilution, written here for the unprimed isomer, is

$$\mu^{\mathrm{ex}}(V^{\circ\prime})^\infty = RT\ln(\gamma^\infty) = (V^{\circ\prime} - V^\circ)(\mathrm{d}A/\mathrm{d}V - \mathrm{d}A'/\mathrm{d}V) + (1/2)((V^{\circ\prime} - V^\circ)^2(\mathrm{d}^2A/\mathrm{d}V^2) \quad (22)$$

Here γ^∞ is the activity coefficient associated with the free energy of transfer of the "heavy" isotope from its neat or pure liquid Raoult's law standard state to infinite dilution in the "lighter" isotope as solvent (the Henry's law standard state).

2.3. The Dilute Case

To this point, the development has been thermodynamically sound, but difficulties arise as simplifications are introduced. Early on both Prigogine[16] and Bigeleisen[18] chose to discard the first term on the right-hand-side of eq 22 because $V^\circ \approx V^{\circ\prime}$ and $P = -\partial A/\partial V \approx P' = -\partial A'/\partial V$. Also, $\mathrm{d}^2A/\mathrm{d}V^2 = 1/(\beta V)$ where β is the isothermal compressibility, $-\mathrm{d}\ln V/\mathrm{d}P$. At that level of approximation

$$\mu^{\mathrm{ex}}(V^{\circ\prime})^\infty = RT\ln\gamma^\infty = (V^{\circ\prime} - V^\circ)^2/(2\beta V) \quad (23)$$

Since β and V must be positive, the excess free energy is always positive according to this analysis (but this is not universally observed); nevertheless, good harmony between experimental data and theory was obtained for mixtures of liquid hydrogen and deuterium.[16] A complementary approach was taken by Chester[17] at about the same time. He expanded the excess free energy of the isotopomer mixture in a Taylor series in powers of relative mass difference assuming the particles obey classical Boltzmann statistics. If the particles were assumed to follow classical mechanics the mixture would always be ideal, while for quantum particles at low enough temperature the excess free energy is always positive. Thus, the Prigogine and Chester methods lead to quite analogous results.

More recently, Jancso and Van Hook[19] have claimed that the identification of $\ln\gamma^\infty$ with $V(\Delta V/V)^2/(2\beta RT)$, $\Delta V/V$ the molar volume isotope effect, seriously underestimates the contribution of the internal degrees of freedom (especially that of the high-frequency motions, for example X–H *vs* X–D stretching motions). The reason, basically, is because high frequency modes make negligible contribution to β but do make an important contribution to the free energy and thus to free energy isotope effects. These authors, therefore, presented an alternative formalism. The basic mixing process still follows the original idea of Prigogine and collaborators[16] and is divided in two steps: (I) expand or compress the pure components from their equilibrium (standard state) molar volumes to the molar volume of the mixture, (II) ideal mixing at constant volume. In common with earlier authors,[16,18] the excess Helmholtz free energy associated with (II) is taken as zero, so A^{ex} for the mixing process is simply the work of compression (dilation) carried out in step I. Thus, for transfer to the infinitely dilute solution (compare with eq 22)

$$\mu^{\mathrm{ex}}(V^{\circ\prime})^\infty = RT\ln(\gamma^\infty) = -\int_{V^\circ}^{V^{\circ\prime}} P(V)\mathrm{d}V = \int_{V^\circ}^{V^{\circ\prime}} (\mathrm{d}A/\mathrm{d}V)_{\mathrm{T}}\mathrm{d}V \quad (24)$$

which for the commonly employed oscillator model can be rewritten

$$\mu^{\mathrm{ex}}(V^{\circ\prime})^\infty = RT\ln\gamma^\infty = -RT\int_{V^\circ}^{V^{\circ\prime}} \sum (\partial \ln q^i/\partial u_i)_{\mathrm{T}}(\partial u_i/\partial V)_{\mathrm{T}}\mathrm{d}V \quad (25)$$

where, as always, $u_i = hc\nu_i/kT$. Given detailed knowledge of the volume dependence of all $3n$ vibrational frequencies, eq 25 may be straightforwardly evaluated. In working out the integrals in eq 25 it is sometimes useful to employ the relation $(\partial\nu/\partial V)\mathrm{d}V = (\partial\nu/\partial P)(\partial P/\partial V)\mathrm{d}V = -(\partial\nu/\partial P)(V/\beta)\mathrm{d}V$. In favorable cases the frequency distributions can be factored into a high-lying set (generally the internal vibrations) to be treated in the zero-point (low-temperature) approximation and a group of low frequencies (often the lattice hindered translational and librational modes) to be treated in the high temperature approximation, then[19-21]

$$RT\ln\gamma^\infty = RT\sum_{\mathrm{int}}(u_i/2)(\Gamma_i)_{\mathrm{int}}(\Delta V/V) + RT\sum_{\mathrm{ext}}(u_i^2/12)(\Gamma_i)_{\mathrm{ext}}(\Delta V/V) \quad (26)$$

where Γ_i is the Gruneisen parameter for the *i*th normal mode.

The use of the Gruneisen parameter is concomitant with the assumption of the quasiharmonic approximation. In this theory, widely employed by solid-state scientists, the 3nN condensed-phase vibrations are each assumed to remain harmonic about their new mean positions as the solid expands. Thus, the individual force constants are each assumed to vary proportionally with the fractional volume change. The Gruneisen coefficients are the proportionality constants, $\Gamma_i = -\mathrm{d}(\ln \nu_i)/\mathrm{d}\ln(V)) = -(\mathrm{d}\ln \kappa_i/\mathrm{d}\ln V)/2$, where κ_i is the force constant corresponding to frequency ν_i. The approach, including its drawbacks, has recently been discussed.[21,23]

If preferred, the excess free energy can be rewritten in terms of the actual frequency shifts which occur on the transfer of the unprimed isotopomer between the two standard states

$$\mu^{\mathrm{ex}}(V^{\circ\prime})^{\infty} = RT\ln\gamma^{\infty} = RT((1/2)\sum(\delta u_i)_{\mathrm{int}} + (1/24)\sum(\delta u_i)^2{}_{\mathrm{ext}}) \quad (27)$$

using $u_i\delta u_i \approx \delta(u_i)^2/2$.

2.4. Mixtures of Isotopomers at Finite Concentrations

Excess free energies of isotopomer solutions in the midrange of concentration can be readily calculated from the thermodynamic identity

$$G^{\mathrm{ex}} = x\mu^{\mathrm{ex}} + x'\mu^{\mathrm{ex}'} = x\mu^{\mathrm{ex}} + (1-x)\mu^{\mathrm{ex}'} \quad (28)$$

employing expressions for μ^{ex} and $\mu^{\mathrm{ex}'}$ as given in eq 22. However, in the spirit of the approximations employed above, which neglect terms of order V^{ex} and higher, Rebelo *et al.*[21] have shown $\mu^{\mathrm{ex}} \approx x'^2(\mu^{\mathrm{ex}})^{\infty}$, $\mu^{\mathrm{ex}'} \approx x^2(\mu^{\mathrm{ex}})^{\infty}$ so

$$G^{\mathrm{ex}} = xx'^2(\mu^{\mathrm{ex}})^{\infty} + x'x^2(\mu^{\mathrm{ex}'})^{\infty} = x(1-x)^2(\mu^{\mathrm{ex}})^{\infty} + (1-x)x^2(\mu^{\mathrm{ex}'})^{\infty} \quad (29)$$

In the ordinary case we expect $\gamma^{\infty} = \gamma^{\infty\prime}$, *i.e.*, symmetrical behavior (around $x = x' = 0.5$), which means that deviations from ideality in mixtures of isotopomers can be represented with a one-term expansion of the Redlich–Kister type, $G^{\mathrm{ex}} \approx xx'(\mu^{\mathrm{ex}})^{\infty}$.

The model described above has been successfully employed to reconcile experimental data and theoretical estimates for isotopomer mixtures of H/D isotopes of benzene,[5,9,19] water,[24] methanes,[21,22,25] polystyrene and polybutadiene,[20] and ammonia.[22,26] These applications are discussed in more detail later in this review.

2.5. Mixtures of Monatomic Isotopomers: A Comment

Singh and Van Hook[5] (SVH) have argued that ideal mixing can only occur under conditions where the reduced radial distribution functions, $g(r^*)$ and $g'(r'^*)$, are identical (*i.e.*, under congruent conditions; here, the potential is expressed using energy and distance parameters, ϵ and σ, and $\epsilon^* = kT/\epsilon$ and $r^* = r/\sigma$). If the SVH argument is valid, corrections to the procedure outlined above become necessary. To develop such corrections first consider the application to the monatomic case where the focus is exclusively on the intermolecular part of the potential energy (the external modes). With the separated isotopomers in the congruent state, plots of $g(r^*)$ and $g'(r^*)$ will superpose; they are identical within the precision of the Born–Oppenheimer approximation (Figure 2). A compression or dilation of one or the other sample along an equilibrium path, (*i.e.*, $\Delta w = -\int P\mathrm{d}V$, with the relationship between P and V defined by the equation of state), has the effect of distorting the corresponding $g(r^*)$ function. This is well established by experiment, theory, and model calculation[27] (see Figure 2a). In fact, both the locations of the maxima for the $g(r^*)$ function as well as the shape of the function depend sensitively on particle density and, hence, on applied pressure. To rephrase matters, the condensed-phase structure is pressure sensitive, and by implication volume sensitive, this is not at all surprising. As SVH point out, a consequence is that if one begins with a pair of separated isotopomers in congruent state (the separated isotopomers under orthobaric conditions are often assumed to be congruent) and compresses one or both to a new state, but one which is still congruent with the first, the compression(s) cannot be along the normal equilibrium path(s). Under congruent compression (or dilation) the relative orientation of all molecules in the liquid remains unaffected by the compression (dilation) which does nothing more than displace $g'(r^*)$ to $g'(r^* + s)$ (see Figure 2b). On the path of most interest to us, the one leading to an infinitely dilute solution of one isotopomer dissolved in the other, $s \approx (1/3)(\Delta V/V)$ (*vide supra*), and the infinite dilution activity coefficient becomes

$$\ln(\gamma')^{\infty} \approx \ln(f_c/f_g)(\mathrm{d}\ln\langle\nabla^2 U\rangle/\mathrm{d}s)(\Delta V/(3V))(1/m')/(1/m' - 1/m) \quad (30)$$

In interpreting eq 30 remember the relation between $g(r)$, the pair potential function, $\phi(r)$, and the mean square potential (Laplacian), $\langle\nabla^2 U\rangle = 4\pi n\int g(r)(\partial/\partial r)(r^2\partial\phi/\partial r)\mathrm{d}r$.

Experimentally, for liquid argon $\ln\gamma^{\infty}$,[36] $= -3 \times 10^{-4}$ with a precision of about 25% as deduced from the measurements of Bigeleisen and co-workers.[28] Calculations based on eq 30 give -2×10^{-4}. The agreement between theory and experiment is more than satisfactory. Calculations along the equilibrium path predict positive values for $\ln\gamma^{\infty}$,[36]; that is, they do not even lead to the same sign as experiment. The result establishes the importance of making a clear distinction between the congruent and equilibrium paths.

2.6. MVIE Considerations: Monatomic and Polyatomic Fluids

In turning attention to polyatomic molecules it is necessary to consider the contributions of both internal and external degrees of freedom. In the monatomic case the fact that $\Delta V/V \neq 0$ is purely a consequence of isotope effects on overall particle motion (hindered translation) in the attractive well defined by the intermolecular potential. That same effect exists for polyatomic molecules, but superposed is the IE on the intrinsic size of the interacting molecules (*i.e.*, one might say on the core parameters). This latter effect is principally determined by vibrational amplitude effects in the intramolecular degrees of freedom.[29] Because these can be large, the core effect predominates in polyatomics and is primary responsible for the observed MVIE. Compressions (dilations) for the purpose of calculating G^{ex} in isotopomer mixtures should still be

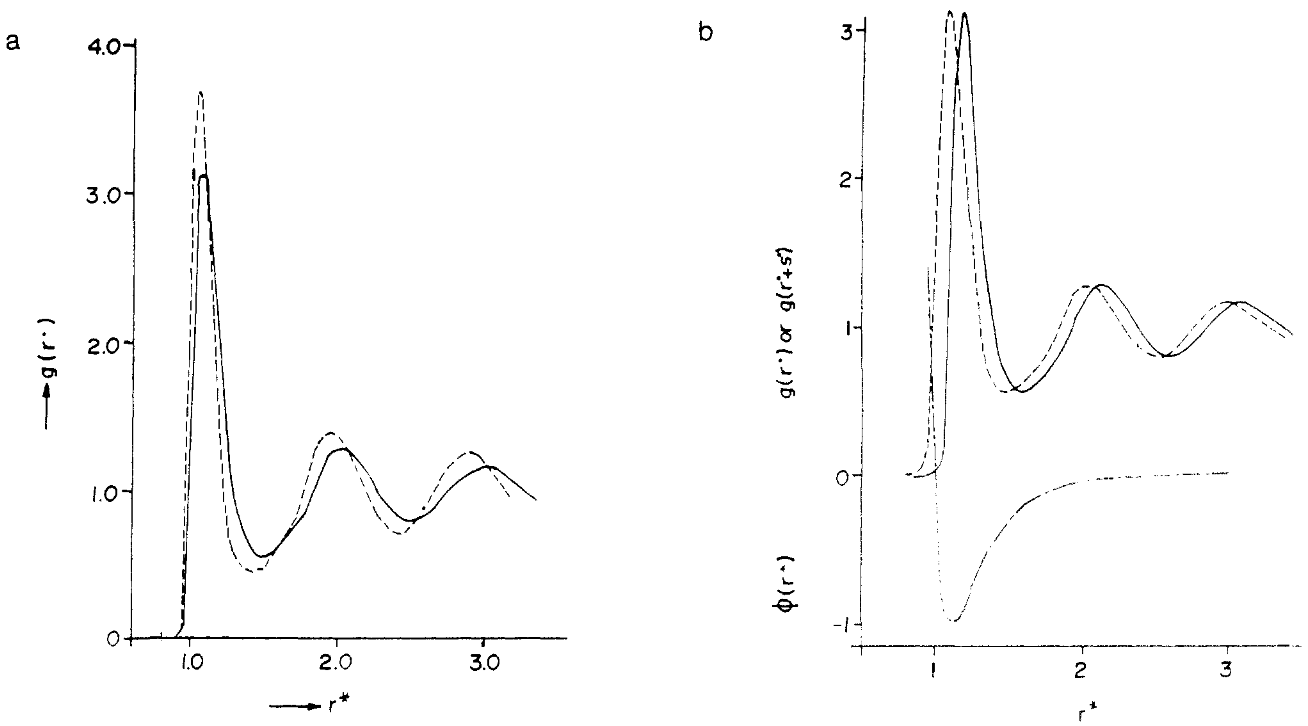


Figure 2. (a) Reduced radial distribution functions, $g(r^*)$, for a Lennard–Jones fluid near its triple point. T^* is the reduced temperature, ρ^* the reduced particle density, and r^* the reduced distance. Both position and shape of $g(r^*)$ depend sensitively on reduced density and hence pressure: – – –, $T^* = 0.658$, $\rho^* = 1.00$; —, $T^* = 0.658$, $\rho^* = 0.850$. From ref 5 (courtesy of American Institute of Physics). (b) Reduced radial distribution functions and reduced potential energy function for a Lennard–Jones liquid. The dotted upper curve shows $g(r^*)$ near the triple point, $T^* = 0.658$, $\rho^* = 0.850$, while the solid upper curve shows that same $g(r^*)$ after congruent compression equivalent to a 5% radial displacement. The change is exaggerated in comparison with realistic isotope effects. The dot-and-dash lower curve shows the reduced Lennard–Jones potential function describing this system. From ref 5 (courtesy of American Institute of Physics).

carried out congruently, but since the major part of the effect is contributed by the internal degrees of freedom the distinction is no longer so marked. Even so, SVH suggest that the nonequilibrium congruent compression will be better approximated using Gruneisen coefficients for internal modes taken from solid state rather than liquid data. They suggest considerably more entropic reorganization is found in liquid than in solid compressions and observed liquid-state values for Γ_i are less likely to approximate congruent conditions. The new calculations give mildly improved agreement with experiment[5] (*vide infra*).

2.7. A Cell Calculation for $A^{ex}(V)$

In an approach totally independent from the ones outlined above, Deiters[30] extended van der Waals-type equations of state to the treatment of quantum fluids. He considered each molecule to be confined to a cell with size proportional to the free volume, V_f; thus, $l^3 = 8V_f/n$. The energy eigenvalues of a particle in a cubic box of dimension l are calculated assuming an homogeneous background potential and hard sphere collisions with neighbors. The quantum correction is applied to a semiempirical equation of state derived by him. The extension to mixtures is carried out using eq 31.

$$A = n_1A_1^+(V_m^+,T) + n_2A_2^+(V_m^+,T) + RT(n_1 \ln x_1 + n_2 \ln x_2) - \int_{V^+}^{V} P(V,T,n;a,b,c,m)\,\mathrm{d}V \quad (31)$$

The A_i^+ denote the molar Helmholtz free energies of the pure substances in the perfect gas state at temperature T and very large volume V_m^+. The integrand is the equation of state of the mixture, which depends on a set of variables (volume, temperature, mole no.) and a set of parameters (a, b, c, and m). A one-fluid theory is used to determine concentration-dependent effective parameters which are thus taken as isotope dependent. It is not made clear if this procedure is consistent with Born–Oppenheimer considerations. Thus, Deiters' method is quite different from the usual approach which develops the IE's in terms of the contributions of internal vibrations to the excess free energy using an isotope-independent PES.

3. Applications and Experimental Observations

3.1. Introduction: Mixtures of Light Isotopomers, Aqueous Mixtures

It is only in the past 20 years that serious efforts have been made to determine excess properties in mixtures of simple isotopomers at temperatures where Boltzmann statistics apply. Most earlier measurements were reported for isotopic mixtures of very light molecules, $^3He/^4He$ and H_2/D_2, or for the aqueous system, $H_2O/HDO/D_2O$. Even so, the focus in this paper remains on non-hydrogen-bonded isotopomers of larger molecules. Straightforward application of the ideas developed above to hydrogen or helium mixtures is not possible because their low masses, and the fact that the very low temperatures defining the equilibrium liquids, require the use of quantum statistics for proper analysis. For that reason we will content ourselves with a brief review of the essential features of the experimental observations. For mixtures of isotopomers of water the complications have a completely different origin. Although a considerable amount of data exists for solutions of isotopic waters, the interpretation is obscured by the presence of the disproportionation equilibrium, $H_2O + D_2O \rightleftarrows 2\ HDO$, and other effects of hydrogen bonding. Again we will content ourselves with only a brief discussion (see immediately below and section 3.12).

Deviation from Raoult's law ideality is considerable in H_2/D_2 and $^3He/^4He$ mixtures. Thus, Hoge and Arnold[31] found an increase of 3%, as compared with the ideal solution, for the vapor pressure of an equimolar mixture of $H_2 + D_2$; Kerr[32] verified an expansion (positive excess molar volume) of some tenths of $cm^3 \cdot mol^{-1}$ for the pair $T_2 + D_2$; and Sommers *et al.*[33] reported $G^{ex} = 3\ J \cdot mol^{-1}$ for the equimolar mixture $^3He/^4He$. A negative V^{ex} was found by Simon and Bellemans[34] for the same system. Knaap *et al.*[35] measured V^{ex} for the mixtures H_2/D_2 and n-H_2/p-H_2 and H^{ex} for H_2/D_2, H_2/HD, and HD/D_2. Bigeleisen[18] has given an analysis of the vapor pressure and molar volume data. Measurements in the helium system have been reviewed by Oubuter and Yang.[36] The first comprehensive attempt to interpret excess effects in hydrogen and helium isotopomer solutions was made by Prigogine *et al.*[16]

Experimental data on excess properties of mixtures of water isotopomers have been accumulating for more than 50 years. Thus, very early Longsworth[37] and Swift[38] measured the densities of $(H_2O + D_2O)$ mixtures, and Puddington[39] and La Mer and Baker[40] studied vapor pressures and freezing points for the same system. A substantial amount of results have since been accumulated (see section 3.12).

3.2. Mixtures of Rare Gas Isotopes (Ar, Kr) and Separation Factors in Mixtures of Ar and Kr

High-precision fractionation data for monatomic fluids is of great interest for the testing of the modern theory of condensed-phase isotope effects. The analysis can focus exclusively on the intermolecular potential; complications from librational or internal vibrational degrees of freedom do not exist, and theory can be applied in its most rigorous form. For these reasons Bigeleisen *et al.*[28] measured fractionation factors for $(^{36}Ar/^{40}Ar)$ and $(^{80}Kr/^{84}Kr)$ mixtures using cryodistillation. Liquid and vapor phases in one-stage equilibrium with each other were withdrawn through fine steel capillaries into a high-precision isotope ratio mass spectrometer. The α values thus determined were compared with values obtained from VPIE measurements on the separated isotopes, again at high precision. The difference between the two measurements yields values for $\ln (\gamma')^{\infty}$ (see eqs 6 and 9). Singh and Van Hook[5] employed the argon data in developing the correlation between the excess free energies of mixtures of isotopomers and congruent compression (dilation), *vide supra*. For krypton, however, $\ln (f_c/f_g)$ and $\ln \alpha$ are much smaller, and highly enriched samples of the separated isotopes were not available. Therefore, it is not possible to obtain a precise enough value of $\ln(\gamma')^{\infty}{}_{Kr}$ to be useful. The relevant experimental and calculated results are compared in Table I. It is important to recognize that the observation of a negative sign for $\ln (\gamma')^{\infty}$ for argon was surprising and is most likely theoretically significant. At any level of approximation, a compression (dilation) calculated for the equilibrium path volume change (one continuously defined in terms of the equation of state) necessarily leads to the prediction of a positive excess free energy for the isotopomer solution. However, the observed effect is negative. It is of considerable interest, therefore, that integration long the theoretically calculated congruent path yields negative excess free energies, in good agreement with experiment. On the other hand, SVH interject a note of caution when they comment "a truly small amount of splash in the fractionation experiment would carry ^{40}Ar into the vapor lowering the fractionation factor in the observed direction". In other words, the experiments are difficult, the observed effects are very small, and independent confirmation from additional experiments is desired, perhaps by other techniques. A further discussion of possible entrainment effects has been given by Popowicz, Lu, and Bigeleisen.[25]

Table I. Experimental (Obsd) and Theoretical (Calcd) Activity Coefficients for Liquid ($^{36}Ar + {}^{40}Ar$) and Liquid ($^{80}Kr + {}^{84}Kr$) and Their Mixtures

system	T/K	$10^4 \ln (f_c/f_g)$ obsd	$10^4 \ln (\alpha)$ obsd	$10^4 \ln (\gamma')^{\infty}$ obsd	$10^4 \ln (\gamma')^{\infty}$ calcd
$^{36}Ar/^{40}Ar$	84	64[a]	61[b]	-3 ± 1[a,b]	-2[c]
	100	43	41	-2 ± 1	
	117.5	(26)	25	(−1)	
$^{80}Kr/^{84}Kr$	117.5		10[d]		
$^{36}Ar/^{40}Ar$ at infinite diln in Kr	117.5		29[e]	-4[d,e]	-4[e]
$^{80}Kr/^{84}Kr$ at infinite diln in Ar	117.5		6[e]	+4[d,e]	+4[e]

[a] Reference 28a. [b] Reference 28b. [c] Reference 5. [d] Reference 28c. [e] Reference 28d.

The Bigeleisen group[28] has also determined $l - v$ isotope fractionation factors for Ar–Kr binary mixtures at natural abundance $[(^{36}Ar/^{40}Ar + Kr)$ and $(^{80}Kr/^{84}Kr + Ar)]$. Some results are shown in the bottom section of Table I. The $^{36}Ar/^{40}Ar$ fractionation factor increases linearly from $\ln \alpha = 24.9 \times 10^{-4}$ in pure liquid argon to 29.1×10^{-4} at infinite dilution in Kr (117.5 K). Similarly, the $^{80}Kr/^{84}Kr$ separation factor at 117.5 K decreases from 9.8×10^{-4} in pure krypton to 6.4×10^{-4} at infinite dilution in argon. The shifts are the same size, although of opposite sign, within the precision of the measurements. The data afford a unique opportunity to further test the ideas above concerning excess free energy in isotopic mixtures because liquid argon and krypton can be treated with high accuracy using modified corresponding states theory. At 117.5 K, the experimental temperature, the reduced densities of Ar and Kr differ by more than 20%, as do the reduced temperatures. Even so, the Ar force constant, $\langle (\nabla^2 U)_{Ar} \rangle$, at $x_{Ar} = 0$, *i.e.*, at infinite dilution in Kr, is equal to $\langle (\nabla^2 U)_{Kr} \rangle$, at $x_{Kr} = 0$, and indicates the assumption of additive pair potentials is adequate for the treatment of the mean force constants of the two components in the mixture. A consequence is that α_{Ar} falls on dilution with Kr, in exact compensation to the rise in α_{Kr} which occurs in dilution with Ar (see Table I). The transfers $(x_{Ar} = 1) \Rightarrow (x_{Ar} = 0)$ and $(x_{Kr} = 1) \Rightarrow (x_{Kr} = 0)$ are not congruent, nor should they be so approximated, since in each case the reduced density and reduced temperature of the host lattice change markedly, in the first case from (ρ^*_{Ar},T^*_{Ar}) to (ρ^*_{Kr},T^*_{Kr}), in the second from (ρ^*_{Kr},T^*_{Kr}) to (ρ^*_{Ar},T^*_{Ar}). Bigeleisen and co-workers[28] have rationalized these results with theoretical calculations based on modified corresponding states theory and demonstrated quantitative agreement with experiment.

3.3. Comment on Isotopic Mixtures of Polyatomic Molecules

In the material below we turn our attention to mixtures of isotopomers of various polyatomic molecules. In such mixtures it is necessary to carefully distinguish the contributions of the external modes (the hindered translation or *intermolecular* and the librational) from those of the internal (vibrational or *intramolecular*) modes. Very often, in fact usually, the intramolecular contribution predominates. This is because the number of vibrational degrees of freedom (and correspondingly G^{ex}(intramolecular)) increases roughly in proportion to the number of atoms per molecule (more precisely with the number of vibrations and their derivatives with respect to V), so the relative contribution of external modes decreases with molecular complexity and molecular weight. Usually, the actual decline is even more marked since G^{ex} scales approximately in proportion to ν_{eff}^2, where ν_{eff} is an effective intermolecular frequency (lattice mode). In first approximation (using harmonic oscillator theory) $\nu_{eff}^2 \propto \mu^{-1}$, where μ is the oscillator reduced mass, so even the absolute (as opposed to the relative) contribution from the intermolecular modes becomes less and less significant as molecular complexity and/or molecular weight increases. Thus, for all but the simplest polyatomic molecules our attention will be focused mainly on isotope-sensitive intramolecular vibrations.

3.4. Mixtures of Deuteriomethanes (CH_4, CD_4, CH_3D, CH_2D_2, CHD_3)

Rebelo *et al.*[21] have reported measurements of the vapor pressure differences between isotopomer mixtures (CH_4 + CD_4) and CH_4 and between pure CD_4 and CH_4, all measured simultaneously (together with the total vapor pressure of the parent compound, CH_4). The authors collected data at 29 temperatures between 97 and 122 K and for six different compositions: $x(CD_4)$ = 0.15, 0.25, 0.375, 0.5, 0.625, and 0.75. Lopes[26] extended the study to include all possible binary combinations among intermediate deuteriomethanes. Earlier studies on VPIE or LVIFF studies for isotopic methanes have been reported by Grigor and Steele,[41] Armstrong, Brickwedde and Scott,[42a] Clusius and co-workers,[42b] and Bigeleisen and co-workers.[25,43] A schematic diagram of the experimental set-up used in the Lisbon apparatus is shown in Figure 3. In these investigations a double differential technique enabled accurate and direct reading of excess pressures as small as ≈2 Pa. To achieve such precision it is necessary to control temperature to better than the nearest mK and temperature differences from one sample to the other to better than 0.1 mK. For that purpose the samples are placed in a well-thermostated large copper block. Pressures are measured by quartz spiral and pressure differences by differential capacitance manometry.

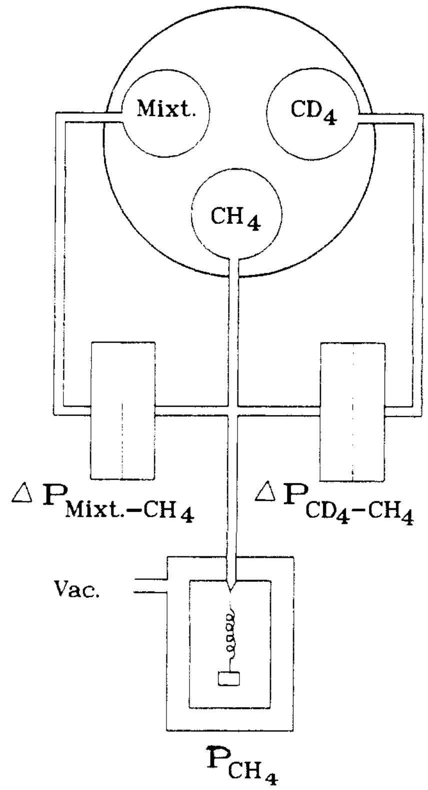


Figure 3. Schematic illustration of the double differential technique as used by Rebelo *et al.*[21] to determine excess pressures of isotopomer mixtures, the VPIE's of the separated isotopomers, and the vapor pressure of the parent compound. The three sample cells are contained in a common well thermostated copper block. Temperature differences between them are less than 0.1 mK. The example shows the configuration for measuring CH_4/CD_4 isotope effects. Pressure differences are determined between CH_4 and CD_4 with the right-hand transducer, between CH_4 and mixture with the left-hand one (these are differential capacitance monometers), and the total pressure is measured with the central transducer (a quartz spiral monometer). Gas handling lines and other necessaries are not diagrammed.

It is straightforward exercise to obtain excess free energies from the observed excess pressures. Two typical excess Gibbs free energy–concentration isotherms are shown in Figure 4. The curves exhibit very small positive deviations from Raoult's law and are approximately symmetric. The G^{ex} values are mainly a consequence of nonideality in the liquid-phase solutions which represents 93% of the whole effect. The balance is contributed from the gas imperfection term. Within experimental error, the data for all isotopomer pairs show simple curves which are symmetry centered at the equimolar composition and can be nicely represented with one-term Redlich–Kister fits, $G^{ex} = xx'\mu^{ex,\infty}$. Results are given in Table II which reports G^{ex} at $x = x' = 0.5$ (*i.e.*, $\mu^{ex,\infty} = 4G^{ex}(0.5)$) and excess enthalpies calculated from G^{ex} using the Van't Hoff relation. Popowicz, Lu, and Bigeleisen[25] compared LVIFF and VPIE data for CHD_3/CH_4 and CD_3F/CH_3F mixtures. For CHD_3/CH_4 they found $T^2 \ln \alpha$ calculated from LVIFF about 3% larger than that from VPIE measurements. That value is much higher than the one found in Table II.

The data in Table II show small but significant deviations from simple additivity (*e.g.*, G^{ex} (CH_4/CD_4) = $4{\cdot}G^{ex}(CH_4/CH_3D)$, *etc.*). This is as expected. Since deviations from the law of the geometric mean for the

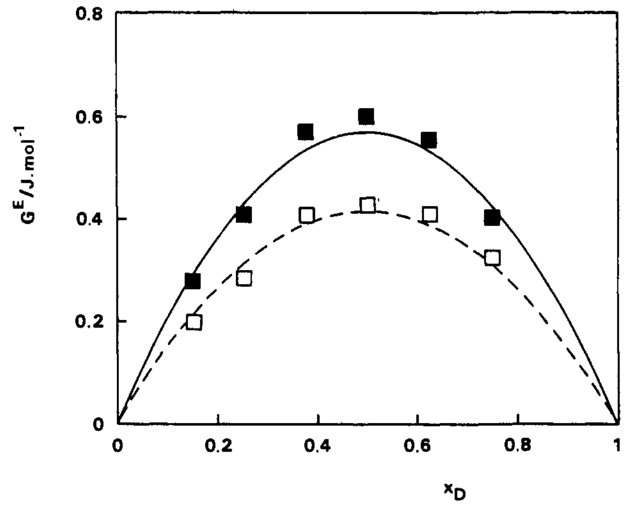


Figure 4. Plots of G^{ex} obtained from measured excess pressures of CH_4/CD_4 mixturs. The abscissa is the liquid phase mole fraction of CD_4, x_D: ■ = 100 K; □ = 120 K. The curves are least-squares fits to a one-term Redlich–Kister relation, $G^{ex} = x_D x_H \mu^{ex,\infty}$.

Table II. Excess Gibbs Free Energies and Excess Enthalpies for Mixtures of Methane Isotopomer Pairs at Equimolar Concentration in the Liquid State. A Conservative Estimate of the Experimental Precision Yields ±0.02 J·mol^{-1} and ±0.2 J·mol^{-1} for G^{ex} and H^{ex}, Respectively. Parenthesized Entries Represent Theoretically Calculated Values (Eq 26) Based on Vibrational Analysis Using the Method of Bigeleisen et al.[a]

isotopomer pair	G^{ex} (100 K)/ J·mol^{-1}	G^{ex} (120 K)/ J·mol^{-1}	(H^{ex}) (100–120 K)/ J·mol^{-1}
$CH_4 + CD_4$	0.57 (0.58)	0.42 (0.32) (0.44)[b]	1.3 (1.9)
$CH_4 + CHD_3$	0.32 (0.45)	0.23 (0.25)	0.82 (1.43)
$CH_4 + CH_2D_2$	0.22 (0.31)	0.14 (0.16)	0.62 (0.95)
$CH_4 + CH_3D$	0.13 (0.16)	0.09 (0.08)	0.36 (0.48)
$CH_3D + CD_4$	0.40 (0.44)	0.29 (0.24)	0.95 (1.43)
$CH_2D_2 + CD_4$	0.30 (0.29)	0.18 (0.16)	0.89 (0.95)
$CHD_3 + CD_4$	0.18 (0.14)	0.10 (0.08)	0.53 (0.48)

[a] Reference 43. [b] Following Deiters.[30]

vapor pressures (*e.g.*, 4 ln (P_{CH_3D}) = ln (P_{CD_4}) + 3 ln (P_{CH_4}), *etc.*), although significant, are small, it is not surprising that in Table II one finds only small (but still significant) deviations from simple relationships such as $G^{ex}(CH_4/CD_4) = 4G^{ex}(CH_4/CH_3D)$, *etc.* Bigeleisen *et al.*[43] have given a thorough treatment of the VPIE for the separated isotopes for both the solid and liquid phases. Their analysis included elaborate calculations which reconciled the available spectroscopic and thermodynamic data and demonstrated hindered rotation in both solid and liquid phases, as well as significant coupling between internal and external degrees of freedom and significant lattice mode anharmonicity.

Rebelo *et al.*[21] examined three different theoretical models when interpreting the experimental results reported in Table II. The best description was obtained using the statistical theory of condensed phase isotope effects, *vide supra*, where $\mu^{ex,\infty}(CH_4/CD_4) = RT \ln \gamma^\infty$, and is calculated with eq 26. The authors took $\Delta V/V$ for CH_4/CD_4 from experiment[41,42] and approximated it for the lower isotopomers using the law of the geometric mean. Consistency between VPIE calculations and the present isotope effects in isotopomer mixtures was assured by using the harmonic force field obtained by Bigeleisen *et al.*,[43] and they employed an internal Gruneisen coefficient to use with the CH stretching modes, $-(\Delta\nu/\nu)/(\Delta V/V) = -3.1 \times 10^{-3}$, which was obtained from the observed frequency shift and volume change on fusion. The external hindered translation Gruneisen constant was calculated from the thermodynamic identity $\Gamma_{tr} = \alpha V/(C_v\beta)$, where α is the coefficient of thermal expansion, and β is the compressibility. Plausible arguments were used to justify setting Γ_{rot} and Γ_{bend} equal to zero.[44] The calculated results are compared with experiment in Table II. They demonstrate good agreement between the statistical theory of condensed phase isotope effects, the experimental data, and the spectroscopic literature.

The statistical theory of isotopomer mixtures clearly predicts that $G^{ex} = 0$ at the molar volume crossover point, $\Delta V/V = 0$ (see eq 26, for example). Kooner and Van Hook[45] have reviewed molar volume isotope effect (MVIE) data. For nonpolar molecules H/D MVIE's are universally normal ($V_H > V_D$) at low temperature, but MVIE decreases markedly with temperature and generally crosses between $T/T_c = 0.8$ and 0.9, becoming inverse ($V_D > V_H$), and large, as the critical point is approached. For such liquids, *i.e.*, those nearing the high temperature–low density region just below the critical temperature, Kooner and Van Hook[45] predicted negative Gruneisen coefficients in harmony with the estimated values of Rebelo *et al.*[21] For the CH_4/CD_4 system $\Delta V/V = 0$ at $T/T_c = 0.895$, $T_{cross} = 170 \pm 2$ K,[41] while linear extrapolation of G^{ex}/T *vs* $1/T$ from Table II gives $T_{cross} = 171 \pm 4$ K, in excellent agreement. The other two models considered by Rebelo *et al.*[21] gave much less satisfactory results. They included a one-fluid van der Waals theory (VDW-1) developed by Leland, Rowlinson, and Sather[46] and a WCA-based perturbation theory reported by Kohler *et al.*[13] Both approaches calculate quantum corrections to the intermolecular part of the potential function (the external degrees of freedom) and do not explicitly include contributions from internal modes. Thus, agreement between calculation and experiment for G^{ex} and H^{ex} in methane isotopomer mixtures is not good because, for methane, internal modes make important contributions to the partition function. Nonetheless, these theories do have the advantage of allowing an estimate of the lattice mode contribution to the excess molar volume of isotopomer mixtures. The authors calculated excess volumes for the equimolar mixture, $V^{ex}_{CH_4/CD_4} = (15 \pm 2) \times 10^{-4}$ at 100 K and $(25 \pm 4) \times 10^{-4}$ cm^3·mol^{-1} at 120 K. However, as yet, there are no experiments to test this prediction.

3.5. HCl/DCl Mixtures

For hydrogen chloride isotopomer solutions two sets of independent data are available. Lewis, Staveley, and Lobo[47] reported the excess Gibbs free energy of an approximately equimolar mixture between 195–226 K, and Lopes[26] presents results for seven different compositions at two lower temperatures (Table III). It is useful to take this opportunity to re-emphasize the extremely small size of the effects we are discussing in all of these isotopomer solutions. Thus in the words of Lewis, Staveley, and Lobo,[47] "... the observed values of ΔP at 223 and 200 K both correspond to a value... of

Table III. Equimolar Excess Gibbs Free Energies and Excess Enthalpies for Liquid (HCl + DCl). The Values in Parentheses Represent Theoretical Estimates Using Eq 26

ref	T/K	G^{ex}/J·mol^{-1}	$H^{ex}(T)$/J·mol^{-1}
47	195–226	0.25 ± 0.05	
26	170	0.66 ± 0.02 (0.64)	2.1 ± 0.3 (1.3)
26	200	0.41 ± 0.02 (0.53)	

0.25 J·mol^{-1}. This is about three orders of magnitude less than the G^{ex} values found for liquefied gas mixtures of nonisotopic components. Thus for the argon–krypton system, which by ordinary standards is only slightly imperfect, G^{ex} for the equimolar mixture at 115.8 K is 85 J·mol^{-1}". The work of Lopes[26] (Table III) is the more extensive. $G^{ex}(x)$ is symmetrical about $x = 0.5$. The molar volume isotope effect has been measured by the Staveley group,[48] but within experimental error ($\approx$0.3%) it is impossible to distinguish the results for the two isotopomers. Excess free energies calculated from eq 26 are in agreement with experiment. The observation of a positive azeotrope around $T = 223$ K constitutes one interesting feature of the HCl/DCl mixture. At 223.35 K the vapor pressure of HCl is identical to that of DCl[47,48] (this is an example of a vapor pressure crossover, actually quite a common effect[2]). At the crossover temperature a positive deviation from Raoult's law will lead to a maximum in the pressure–composition diagram, *as observed. Vice versa*, a negative deviation will lead to a minimum in the diagram. As far as we know, this is the first "simple" isotopic mixture where azeotropic behavior has been observed.

3.6. H_2S/D_2S Mixtures

Lopes[26] measured excess pressures for five different compositions of ($H_2S + D_2S$) mixtures at two temperatures. Again, the data were symmetrical about $x = 0.5$ where $G^{ex} = -0.92 \pm 0.03$ J/mol at 190 K and -0.69 ± 0.06 J/mol at 230 K. MVIE data have been reported by Staveley *et al.*[49] The G^{ex} curves are symmetrical, and the system displays a negative azeotrope. The vapor pressure crossover occurs[2,49] at about 224 K. Notice that G^{ex} is negative even though the MVIE is normal (Lopes[26] claims the MVIE crossover temperature is not at $T = 271$ K as earlier reported,[49] but is found at 335 ± 10 K). Equation 26 correctly predicts the signs of both G^{ex} and H^{ex} and indicates $G^{ex} \approx 0$ at 346 ± 10 K.

3.7. Solutions of Ammonia Isotopomers

The Lisbon group has also obtained results for eight mixtures of protio and deuterio ammonias.[22,26] Due to fast chemical exchange, intermediate isotopomers (NH_2D and NHD_2) are produced. For atom fraction n_D, $n_D = n(D)/(n(D) + n(H)) = 0.5$, $G^{ex} = -5.9 \pm 0.3$ J/mol at 230 K and -5.0 ± 0.2 J/mol at 242 K. $\Delta V/V$ is available from the Staveley group,[50] and Gruneisen coefficients were estimated as described for methane. The calculated value (eq 26) is -6.5 J/mol which compares favorably with experiment. It is remarkable that solutions of ammonia isotopomers show a marked negative deviation from ideality. This property is shared with other highly complexed liquids (hydrogen sulfides and waters) and has been discussed by Dutta–Choudhury and Van Hook.[51]

3.8. Solutions of Protio-/Deuteriobenzenes and Cyclohexanes

Jakli, Tzias, and Van Hook[9] made high-precision measurements of VPIE's for the separated liquids C_6H_6 and C_6D_6 and C_6H_{12} and C_6D_{12} and also determined excess pressures for solution pairs C_6H_6/C_6H_{12} *vs* C_6D_6/C_6H_{12} and C_6H_6/C_6H_{12} *vs* C_6H_6/C_6D_{12} and isotopomer pairs C_6H_6/C_6D_6 and C_6H_{12}/C_6D_{12}. Jancso and Van Hook[9,19] and Singh and Van Hook[5] contributed to the interpretation of these results. Additionally, Lal and Swinton[52] have reported calorimetric measurements of excess enthalpies for the isotopomer mixtures, and Dutta–Choudhury, Dessauges, and Van Hook[53] measured excess volumes for the mixtures C_6H_6/C_6H_{12} and C_6D_6/C_6H_{12}, for the isotopomer pair C_6H_6/C_6D_6, and determined the effect of trace water on V^{ex} for C_6H_6/C_6D_6 isotopomer solutions. A sampling of the excess free energy results derived from the vapor pressure measurements is given in Table IV.

Section A of Table IV shows that the measurements for the parent mixture are in excellent agreement with the best previous data.[54,55] In calculating the IE on the excess free energies of the "nonisotopomer" solution pairs, C_6H_6/C_6H_{12} *vs* C_6D_6/C_6H_{12} and C_6H_6/C_6H_{12} *vs* C_6H_6/C_6D_{12}, the authors were careful to define ΔP^{ex} as "that pressure over and above the one to be expected where there is no isotope effect on the activity coefficients ($\gamma_H = \gamma_D \neq 1$), but where due account is taken of the isotope effects on the correction terms due to molar volume and gas imperfection." Figure 5a shows relative excess pressures, $\Delta P^{ex}/P_{C_6H_6}$ for C_6H_6/C_6H_{12} *vs* C_6D_6/C_6H_{12} solutions. The effects are small; they vary between 1×10^{-3} and 9×10^{-3} units. It is a sampling of the excess free energy differences derived from such ΔP^{ex} data which is used to calculate G^{ex} as found in Table IVb. Comparing entries in Table IVa and b, we see the isotope effect, $\Delta G^{ex}/G^{ex} = RT(\ln \gamma_H - \ln \gamma_D)/RT(\ln \gamma_H)$ is about -9×10^{-3} for cyclohexane (protio *vs* deuterio dissolved in benzene, at $T = 313$ K) and about double that for benzene (-2.1×10^{-2} for C_6H_6 *vs* C_6D_6 dissolved in cyclohexane), both at $x_{benzene} = 0.5$. Figure 5b shows excess pressures for the isotopomer solutions $C_6H_6/C_6H_{12}/C_6D_{12}$. Here the $\Delta P^{ex}/P$ values are nearly 1 order of magnitude smaller than for the mixed benzene(h/d)/cyclohexane(h/d) solutions (Table IVd).

Jancso and Van Hook[9] (JVH) have interpreted the data according to the ideas developed in the earlier part of this review. Their analysis considers contributions from the internal and external modes and is reviewed in Table V. The concentration dependence of the excess properties was assumed to be regular, so $G^{ex} = x_H x_D \mu^{ex,\infty}$ or $\mu^{ex,\infty} = 4G^{ex}_{(equimolar)}$. Using literature values for the MVIE of benzene and cyclohexane,[29,57,58] taking the Gruneisen parameter for external modes, $\Gamma_{ext} = 1$, and the pressure dependence of the CH stretching vibrations as 1.5 cm^{-1}/kbar, the entries in Table V were calculated using eqs 25 and 26. JVH found that almost all G^{ex} is contributed by the internal degrees of freedom and obtained satisfactory agreement between theory and experiment. Later Singh and Van Hook[5] improved slightly on the JVH analysis by electing to evaluate G^{ex} from the compressive work along a

Table IV. Excess Free Energies in Solutions of Benzene and Cyclohexane and Their Isotopomers, and in Solutions of Benzene and Cyclohexane Isotopomers

A. Excess Free Energies for C_6H_6/C_6H_{12} Solutions Derived from Vapor Pressure Measurements (J·mol^{-1})

	$X(C_6H_{12})$					
T/K	0.15	0.30	0.50	0.70	0.85	ref
313.15	161.5	257.8	298.1	246.8	149.6	9
	160.4	256.8	297.2	245.6	148.4	54
343.15	141	224	255	209	125	9
	136	219	254	210	126	55

B. Isotope Effects on Excess Free Energies for Benzene/Cyclohexane Solutions, ΔG^{ex} (J·mol^{-1})[a]

		$X(C_6H_{12})$					
T/K	case	0.15	0.30	0.50	0.70	0.85	ref
298.15	I	−1.0	−2.1	−2.6	−1.9	−0.8	9
	II	−0.7	−4.2	−7.5	−6.0	−2.6	9
313.15	I	−1.1	−2.2	−2.7	−1.9	−0.8	9
	II	−0.3	−3.4	−6.4	−5.2	−2.2	9

C. Isotope Effects on Excess Enthalpies for Benzene/Cyclohexane Solutions, ΔH^{ex} (J·mol^{-1})[b]

		$X(C_6H_{12})$					
T/K	case	0.15	0.30	0.50	0.70	0.85	ref
298.15	I			0			9
	II	−9	−23	−32	−24	−11	9
	III		−17 ± 4				56

D. Isotope Effects on Excess Functions for Equimolar C_6H_6/C_6D_6 and C_6H_{12}/C_6D_{12} Isotopomer Solutions

T/K	source	283.15	298.15	323.15	353.15	ref
$G^{ex}(C_6H_6/C_6D_6)$	excess p	0.61	0.58	0.54	0.48	9
$G^{ex}(C_6H_{12}/C_6D_{12})$	excess p	1.18	1.08	0.91	0.71	9
$H^{ex}(C_6H_6/C_6D_6)$	excess p			1.1 ± 0.2		9
	calorimeter			0.7 ± 0.2		52
$H^{ex}(C_6H_{12}/C_6D_{12})$	excess p			3.1 ± 0.2		9
	calorimeter			2.2 ± 0.3		52

[a] Case I compares C_6H_{12}/C_6H_6 and C_6D_{12}/C_6H_6 solutions; case II compares C_6H_{12}/C_6H_6 and C_6H_{12}/C_6D_6 solutions. In either instance $\Delta G^{ex} = G^{ex}_H - G^{ex}_D$. [b] The entries are derived from the vapor pressure measurements above, except for those labeled Case III which are calorimetric data from the literature

congruent path (modeled by the crystal properties) instead of the equilibrium one chosen by JVH. A marginal improvement was obtained.

It is interesting to compare the calculated and observed results in Table V with ones calculated by the Prigogine–Bingen–Bellemans[16] (PBB) approach. The PBB calculation gives nearly the same value as that calculated above from the external frequencies alone and by itself is obviously inadequate. This is because the compressibility is principally determined by the overall motions of the molecule in the intermolecular potential. The PBB approach accounts only for this external contribution; it fails to consider the much more important internal frequency contribution. The previous success of PBB for liquid hydrogen solutions is understandable, since, for these molecules, the single internal mode makes a relatively small contribution to the isotope effect.[19] Methane mixtures, treated elsewhere in this review, exemplify the intermediate case where the contributions of the internal and external modes are more nearly comensurate. Extension of the analysis to cyclohexane isotopomer solutions is straightforward. The cyclohexane/benzene ratio of MVIE's is 1.2,[57,58] the ratio of compressibilities is 1.2, and the ratio of the numbers of contributing frequencies is 2. Therefore, assuming that the pressure dependences,

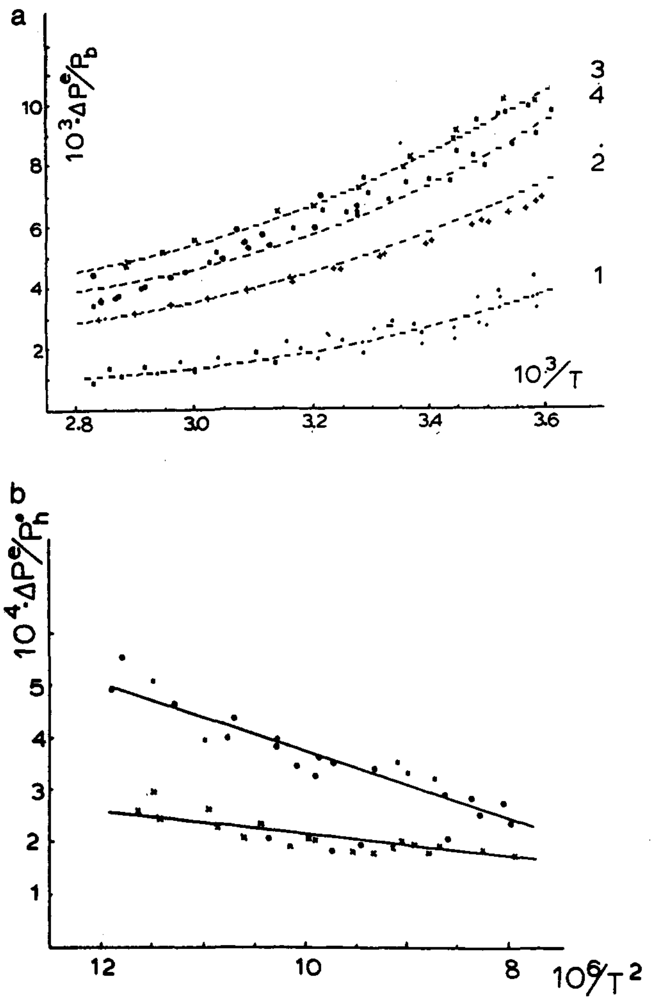


Figure 5. (a) Isotope effects on excess pressures of $C_6H_6/C_6H_{12}//C_6D_6/C_6H_{12}$ solutions, 1, 2, 3, and 4 refer to $x_{cyclohexane}$ = 0.25, 0.50, 0.75, and 0.90, respectively. The points are experimental, and the lines are fits to the thermodynamic analysis. From ref 9a (courtesy of American Institute of Physics). (b) Excess pressures of the equimolar solutions C_6H_6/C_6D_6 (lower line) and C_6H_{12}/C_6D_{12}, (upper line). The points are experimental, and the lines are least-squares fits. From ref 9a (courtesy of American Institute of Physics).

Table V. Calculated and Observed Partial Molar Excess Free Energies and Enthalpies of Solutions at Infinite Dilution for Solutions of Benzene Isotopomers C_6H_6/C_6D_6 (J·mol^{-1})[a]

T/K	$\Delta V/V$	contribns to $\mu^{ex,\infty}$	$\mu^{ex,\infty}$ (calcd)	$\mu^{ex,\infty}$ (obsd)	$H^{ex,\infty}$ (calcd)	$H^{ex,\infty}$ (obsd)
298	0.0027	internal	1.53			
		external	0.21			
		total	1.74	2.3 ± 0.2	7.0	4.4 ± 2
		SVH[b]	1.9			
		PBB[c]	0.33			
353	0.0021	internal	0.78			
		external	0.12			
		total	0.90	1.9 ± 0.2		
		PBB	0.14			

[a] Jakli, Tzias, and Van Hook, ref 9; Jancso and Van Hook, ref 9. [b] Singh and Van Hook, ref 5. [c] Prigogine, Bingen, and Bellemans, ref 16.

$d\nu/dP$, are about the same, one predicts a ratio of excess free energies for isotopomer solutions a little bit less than 2. The observed ratio is 1.8 and once again demonstrates consistency between theory and experiment.

Jancso and Van Hook[9] also discussed IE's in benzene/cyclohexane mixtures. For C_6H_6/C_6H_{12} *vs* C_6D_6/C_6H_{12} the excess partial molar volume at infinite dilution of C_6H_6 in C_6H_{12}, $V^{ex,\infty}(C_6H_6 \text{ in } C_6H_{12})$[59] is 11.5 times larger than the molar volume isotope effect, $(V^{\circ}(C_6H_6) - V^{\circ}(C_6D_6))$. If the volume dependence of the internal frequencies is the same in benzene–cyclohexane solutions as it is in benzene–benzene solutions (and there should be no very large differences as there are no specific interactions) then the ratio of excess free energies should also equal 11.5. The experimental value is 12 ± 3. The agreement is not so good for deuteration on cyclohexane.

The Tennessee group has also investigated excess volumes for benzene(H/D)/cyclohexane(H/D) and benzene(H/D) isotopomer solutions.[53] They report the excess volume of equimolar C_6D_6/C_6H_{12} solutions to be 1% more positive than C_6H_6/C_6H_{12} solutions at 298 K and 2% higher at 318 K. The excess volume in equimolar C_6H_6/C_6H_{12} solutions is 0.6538 $cm^3{\cdot}mol^{-1}$ at 298 K, slightly higher at 318 K, so $V^{ex}/V \approx 6.38 \times 10^{-3}$. The corresponding value at 298 K for transfer to the infinitely dilute solution in C_6H_{12} is $V^{ex,\infty}(C_6H_6)/V = 2.34 \times 10^{-2}$. This is about 1 order of magnitude larger than the MVIE for the separated isotopomers, $\Delta V/V = 2.7 \times 10^{-3}$. The equimolar excess volume isotope effect, $\Delta V^{ex} = (V^{ex}{}_H - V^{ex}{}_D)$, is $(-7.2 \pm 1.3) \times 10^{-3}$ $cm^3{\cdot}mol^{-1}$. The curve describing the concentration dependence of the effect is symmetric and within the precision of the measurement can be described by a one term Redlich–Kister fit of the form $\Delta V^{ex} = x(1 - x)\Delta V^{ex,\infty}$, $\Delta V^{ex,\infty}{}_{298} = (-0.029 \pm 0.005)$ and $\Delta V^{ex,\infty}{}_{318} = (-0.048 \pm 8)$ $cm^3{\cdot}mol^{-1}$, Thus, $\Delta V^{ex,\infty}(C_6H_6,C_6D_6)/V = -2.5 \times 10^{-4}$ at 298 K and -4.1×10^{-4} at 318 K, about 1 order of magnitude smaller and opposite in sign to the separated isotopomer MVIE and 2 orders of magnitude smaller than the limiting partial molar excess volume itself.

The concentration dependence of V^{ex} for C_6H_6/C_6D_6 isotopomer solutions as shown in Figure 6 is surprisingly complicated. The effects are very small, at most $V^{ex}/V = -7 \times 10^{-5}$, about 2 orders of magnitude smaller than MVIE for the separated isotopomers. The V^{ex} concentration curve displays both a maximum and a minimum (the second small maximum sketched in Figure 6 near $x(C_6H_6) = 0.05$ is an artifact of the fitting process and is not statistically significant).[53] At nearly equimolar concentrations there is reasonable agreement for V^{ex} from two laboratories.[52,53]

The complicated concentration dependence shown in Figure 6 was not expected for such simple, and very nearly ideal, solutions. In their interpretation the authors[53] remind us that the MVIE for separated isotopomers is well understood in terms of the isotope-independent PES describing the motions of these molecules. The dominant contribution to MVIE is made by the CH (CD) stretching vibrations, which are described with a set of isotope-independent force constants yielding a marked isotope dependence on the mean square amplitudes of vibration.[29] The external modes only make a small contribution to the partition function (and hence to MVIE). The analysis is considerably simplified by the fact that the center of mass and the center of interaction for C_6H_6 and C_6D_6 coincide.

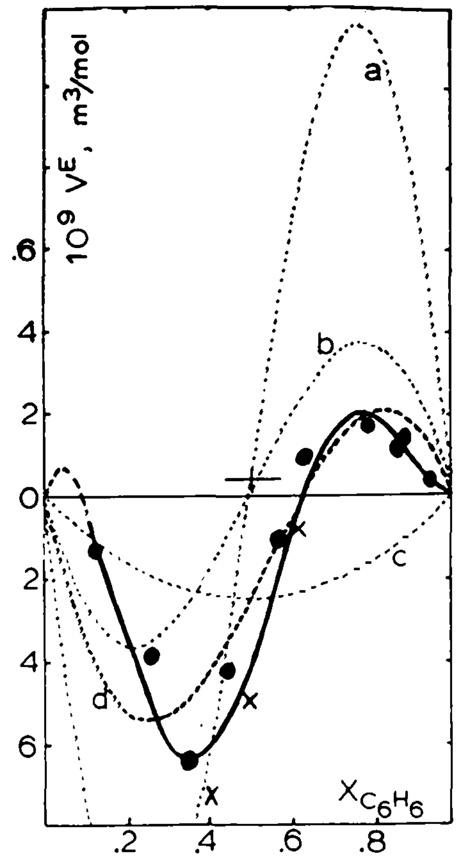


Figure 6. Excess volumes of C_6H_6/C_6D_6 solutions: (•,x,+) experimental points; solid curve = least-squares fit; (a) contribution of steric effect, random approximation; (b) steric effect, quasichemical approximation; (c) contribution of effect II, see text; (d) calculated total effect. From ref 53 (courtesy of American Chemical Society).

For these isotopomer solutions the simple idea that any partial molar solute property (at infinite dilution), including the partial molar volume, may be defined in terms of that property for the host lattice rationalizes the most prominent features of the Figure 6. Thus, consider the case of an infinitely dilute solution of C_6D_6 in C_6H_6. If the partial molar volume of the guest approaches that of the host (C_6H_6 in this example), then the volume of the corresponding solution exceeds that of the ideal solution. $V^{ex}(C_6H_6 \rightarrow 1)$ is positive. Just as clearly at the other extreme, C_6H_6 at high dilution in C_6D_6, the deviation from ideality must be negative. Obviously, solution properties do not change discontinuously, so a plot of V^{ex} *vs* concentration must show a maximum and a minimum, respectively, before joining at some intermediate concentration. More quantitatively the authors[53] find that this, the steric effect, is overestimated in the random phase approximation (curve a, Figure 6), more reasonably estimated using the quasichemical approximation (curve b, Figure 6). Superposed on the steric contribution to V^{ex} is a secondary effect from the intermolecular part of the potential. This was estimated two ways, either following Hildebrand and Scott[60] ($V^{ex,II}(0,5) = -2 \times 10^{-3}$ $cm^3{\cdot}mol^{-1}$) or, in good agreement, from the compressibility IE reported by Matsuo and Van Hook[61] ($V^{ex,II}/x_Hx_D \approx (V^{\circ}{}_H$

$- V°_D)(1 - \kappa_H V°_H/\kappa_D V°_D) = -1 \times 10^{-3}$ $cm^3 \cdot mol^{-1}$. By summing V^{ex}(steric) and $V^{ex,II}$ curve d in Figure 6 was obtained in remarkably good agreement with the experiment. In a related set of measurements Matsuo and Van Hook[61] attempted to determine excess compressibilities in C_6H_6/C_6D_6 mixtures but without success. Apparently the effects are too small.

It is clear that the measurements reported in this section corroborate the more important assumptions made during the development of the theory. That early approach expressed excess free energies for isotopomer mixtures in terms of the (congruent) compressive work across the separated isotopomer MVIE, $\Delta V = V_H° - V_D°$ and neglected any contribution from excess volume effects. In this section we found $\Delta V/V^{ex}$ for C_6H_6/C_6D_6 solutions to be on the order of 10^{-4}, which is certainly in line with the earlier assumption. We conclude that V^{ex} contributions to the excess free energies in isotopomer mixtures are of higher order and can be safely neglected. For the now thoroughly studied benzene/cyclohexane solutions, *theory and observation are in* reasonably good agreement. Further improvement can be expected as calculated or observed values for Gruneisen coefficients characterizing bending and skeletal modes become available, but these are expected to make markedly smaller contributions to G^{ex} for isotopomer solutions than do the stretching modes.[44]

3.9. Excess Free Energies and Demixing in H/D Polymer/Polymer Isotopomer Solutions

Over the past 5 years or so, Bates and Wignall[62] and Bates and Wilthuis,[63] and their co-workers have reported observations of phase separation in isotopomer mixtures of h/d polymers including polystyrenes, polybutadienes, and polyethylene/polypropylene mixtures. Light- or neutron-scattering techniques were employed. The isotopomer solutions show phase separation of the UCST (upper consolute solution temperature) type; see Figure 7. The authors extracted a Flory–Huggins interaction parameter from the scattering plots and reexpressed it in terms of the excess free energy for the isotopomer mixture.

For the simplest polymer solutions the free energy of mixing can be expressed using a one-term Flory–Huggins equation of state[64]

$$\Delta G^M/V = RT(\phi_1 \ln \phi_1/V_1 + \phi_2 \ln \phi_2/V_2) + \phi_1\phi_2\chi \quad (32)$$

where

$$G^{ex}/V = \phi_1\phi_2\chi \quad (33)$$

As the Flory–Huggins interaction parameter, χ, increases to its critical limit, $\chi = 2RT_c$, the solution demixes at an upper critical solution temperature, T_c (Figure 7a). The ϕ's in eqs 32 and 33 are volume fractions, but for solutions of isotopomers of equal polymerization, mole fractions, x_i, would serve equally well. In actual fact real demixing curves such as the ones sketched in Figure 7 cannot be accurately represented with ideas deduced from mean-field classical approaches such as Flory–Huggins theory or other analogues to regular solution theory. Modern nonclassical ideas (also known as scaling approaches) predict certain logarithmic singularities at the critical point which can be described using a set of universal

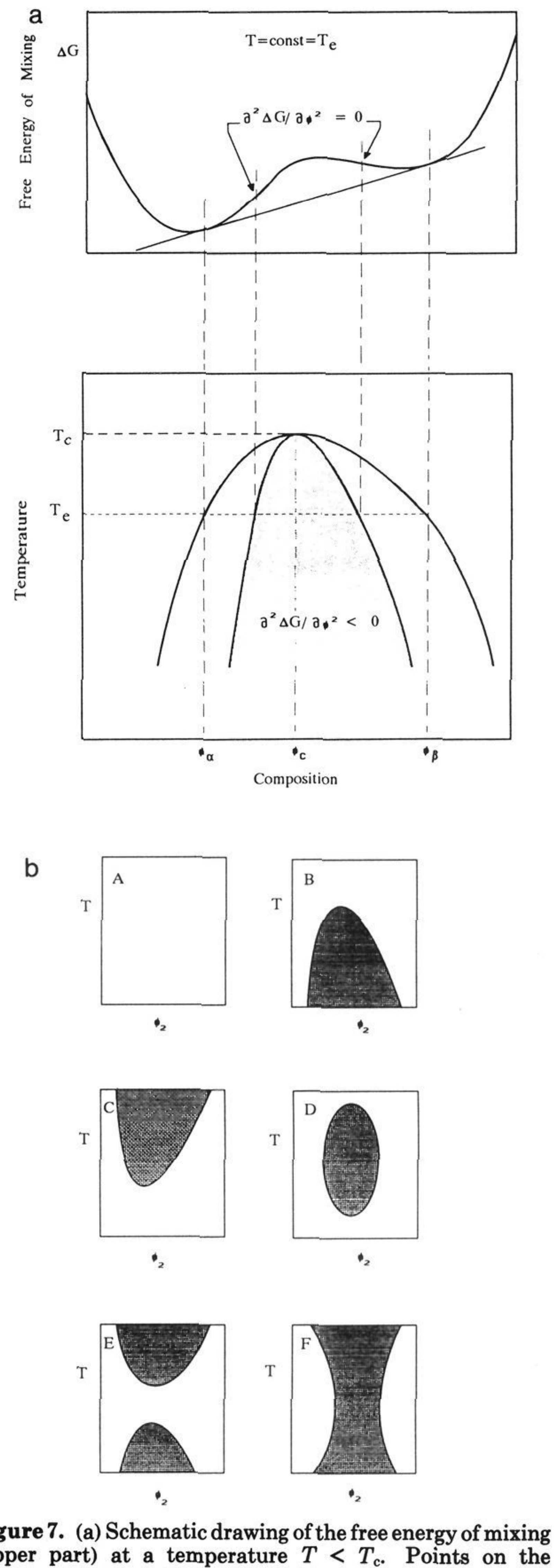


Figure 7. (a) Schematic drawing of the free energy of mixing (upper part) at a temperature $T < T_c$. Points on the coexistence (binodal) and spinodal curves are obtained from the free energy curve as shown. To examine a phase transition one can proceed from the homogeneous region ($T > T_c$, for example) and drop the temperature (or pressure, see below) through the metastable region between binodal and spinodal and thence into the absolutely unstable region (below the spinodal in this diagram). (b) Schematic drawing showing various types of temperature/liquid–liquid composition diagrams.

exponents.[65] Thus, for example, the near-critical coexistence curve is properly expressed

$$(\phi' - \phi'') = A(1 - T/T_c)^{\beta} + \text{higher order terms} = At^{\beta} + \text{HOT} \quad (34)$$

In eq 34, ϕ' and ϕ'', or x' and x'', are the concentrations of the coexisting phases, T_c the critical temperature, and $t = (1 - T/T_c)$. A is a nonuniversal width parameter, and β is the universal scaling exponent known theoretically and experimentally to be 0.325 ± 0.003. In the limit of arbitrary closeness to (T_c, ϕ_c or x_c), mean-field (classical) representations lead to an incorrect value for β, $\beta_{\text{mean-field}} = 1/2$. That erroneous value results because those theories—including Flory–Huggins theory—do not properly treat the long-range concentration fluctuations found near the critical point. It follows that blind application of mean-field theory near T_c is inappropriate. (Many authors have used the term "nonclassical" to describe scaling theories applied to solutions at or near critical conditions, i.e., where mean-field treatments can be misleading. In this context the meanings of the terms "classical" and "nonclassical" are quite different from those used earlier in the development of the theory of isotope effects which have to do with the use of classically *vs* quantum mechanically calculated partition functions.) At some distance from the critical point, however, the system returns to the mean-field domain, and it is again useful to employ analytic (classical or mean-field) representations of the free energy. These considerations are important. Only well into the mean-field region is it completely valid to use arguments based on the shape of the phase diagram in order to arrive at conclusions concerning the temperature, concentration, pressure, and isotope dependence of the free energy. Singh and Van Hook,[66] in agreement with other workers,[67] argue that the nonclassical range extends only to $t \approx 10^{-3}$, some argue not even that far, but others argue much further. At $T_c \approx 300$ K, $t \approx 10^{-3}$ amounts to $(T_c - T) \approx 0.3$ K, or less. The nonclassical theory makes no statement expressing T_c, ϕ_c, x_c, *etc.* in terms of the parameters describing PES, but limits itself strictly to expressing relative effects using expansions about the origin (T_c,ϕ_c or T_c,x_c), using reduced parameters like $t = (T_c - T)/T_c$. In contrast, mean-field theories permit the development of specific relations which express T_c, x_c, *etc.* in terms of the parameters used to describe the free energy function; these parameters, in turn, can be related to the ones defining the potential energy surface. It is tempting, therefore, to assume that since mean-field theories are useful over almost the entire phase diagram (except for that area quite close to the critical point), judicious extrapolation into the region of critical demixing will not involve very great error and should prove informative. It is in this context that we, along with numerous others,[68] have elected to employ classical theory to describe polymer demixing thermodynamics, albeit approximately.

Although not predicted by the simple theory, immiscibility curves can take many shapes. Figure 7 diagrams systems with UCST's, LCST's (lower critical solution temperatures), and both UCST's and LCST's. In real solutions it is sometimes possible to shift the system from one class to another by a judicious choice of conditions (pressure, temperature, molecular weight, isotope label, trace impurity, *etc.*). For example, in the acetone–polystyrene system,[69] *vide infra*, by changing molecular weight at constant pressure, by changing pressure at constant molecular weight, or by changing isotopic label either in the solvent or in the polymer, one can progressively move the coexistence loci from an UCST/LCST solution displaying a wide miscibility gap (dashed lines in Figure 8), through diagrams showing narrower and narrower miscibility gaps (the solid and dotted lines in the figure), to the point where the two branches eventually merge at an hypercritical point. At this point the diagram separates from an UCST/LCST configuration to an hourglass configuration (the left and right outermost lines in the figure). This is loose terminology. For systems of more than two components thermodynamics instructs us that a truly multidimensional hypercritical point is prohibited. Nonetheless, some kind of an UCST/LCST → "hourglass" transition does exist; the upper and lower branches merge, and the shape of that transition is reminiscent of a binary hypercritical or bicritical point.

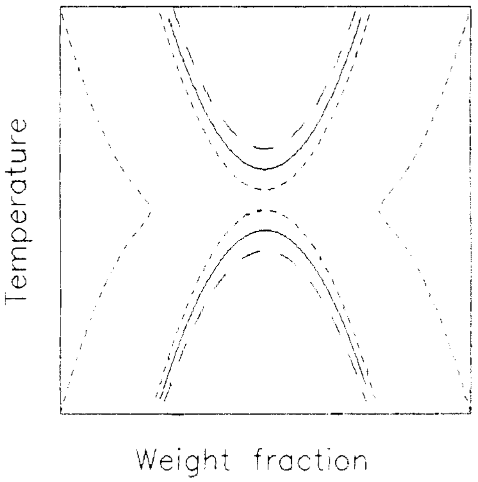


Figure 8. Schematic drawing showing the effect of isotope substitution, molecular weight, and pressure on phase diagrams of type E, Figure 7b. By lowering the pressure from dashed through solid to dotted line, raising the molecular weight (same order) or increasing the D/H ratio one moves in the direction of decreasing the region of miscibility. At low enough pressure, high enough molecular weight or D concentration, the two regions touch and the system collapses into the "hour-glass" configuration at its hypercritical or pseudohypercritical point. Actual polymer–polymer and polymer–solvent diagrams are often distorted from the idealized shapes shown in Figures 7 and 8.

We now return to the isotopomer demixing data of Bates and co-workers.[62,63] The thermodynamics of the demixing of isotopomer solutions of polymers was originally considered by Buckingham and Hentschel,[70] but their theory was developed at the PBB[16] level and has proved to be inadequate, eventhough they are to be credited with the first prediction of demixing in such solutions. Following Singh and Van Hook[20] the excess free energy of the solution of polymer isotopomers 1 and 2 can be written

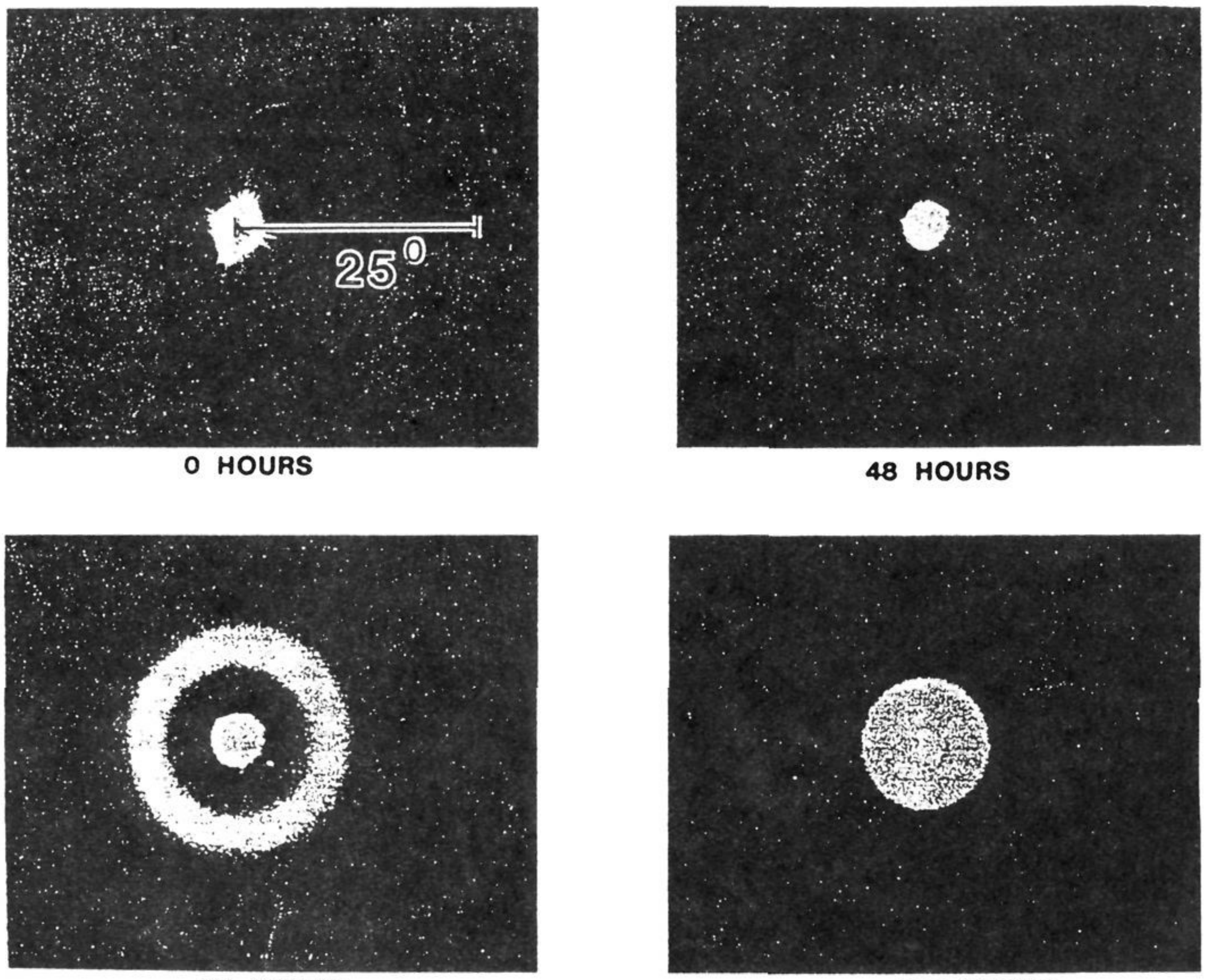
$$A^{\text{ex}} = \phi_1\phi_2(N\Gamma_i r_i/2)(\Delta V/V)(u_H - u_D) \quad (35)$$

Here N is the number of monomer units per molecule, r_i the number of H/D substituted bonds per monomer, Γ_i the Gruneisen coefficient for the effective frequency (as above taken as the CH(CD) stretch), $\Delta V/V$ the

Table VI. Excess Free Energies in Three Protio/Deuterio Polymer Mixtures

			$10^4 \ln \gamma^\infty$			
material	T/K	$10^3\Delta V/V$	expt$^{\text{ref}}$	calcd (SVH)^{20}	calcd (BW)^{63}	calcd (PBB)^{16}
polybutadiene	296	4 ± 1	9 ± 2^{62}	11 ± 4	14	4 ± 1
polystyrene	300	2 ± 0.5	4 ± 2^{62}	6 ± 2	10	
poly(ethylene–propylene)	370		$9 \pm 2(?)^{63,a}$			

[a] From $\chi/(RT) = \ln(\gamma^\infty) = 2/N_c$.



0 HOURS

48 HOURS

80 HOURS

240 HOURS

Figure 9. Light-scattering patterns photographed at various times following a temperature quench from 75 to 25 °C in an isotopomer solution of protio- and deuterio-1,4-polybutadiene. (From ref 63a. Courtesy of F. S. Bates and American Institute of Physics.)

MVIE, and $u_i = hc\nu_i/kT$. For polymers the relative contribution of external lattice modes is negligible, and their effect is not included in eq 35. The conditions for phase separation are obtained by differentiating the total free energy with respect to concentration and setting the second and third derivatives to zero. This gives $\phi_1 = \phi_2 = 0.5$ and

$$(N\Gamma_i r_i/2)(\Delta V/V)u_H(1 - \mu_H/\mu_D) = 2 \tag{36}$$

The μ_i's are reduced masses for the CH(CD) oscillators. The excess free energy *per* H/D substituted bond is small, just as small, for example, as the tiny effects discussed in the section on benzene and cyclohexane isotopomer solutions above. However, the effects are cumulative, and as the total number of substituted bonds, Nr_i, increases, the excess free energy becomes large enough to cause phase separation. For polybutadiene $r_i = 6$ and $\Delta V/V = 4 \times 10^{-3}$. Taking $\Gamma_i = 0.035$ (characteristic of CH stretching modes in solids[5]), and $u_H = hc(3000)/kT = 14.4$, the critical polymerization number N_c is found to be 1.2×10^3 monomer units. An improved estimate correcting for nonclassical curvature in the vicinity of T_c moves this to 1.6×10^3 units.[20] It is convenient to compare theory and experiment using $G^{\text{ex},\infty}/RT = \ln \gamma^\infty$. 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 reference state to an infinitely dilute solution with the other isotopopmer as solvent; thus $\ln \gamma^\infty = 2/N_c$. Numerical comparisons are shown in Table VI. The present method gives results in good agreement with experiment. As expected from the discussion of small molecule systems, the excess free energy calculated from the work integral involving only the external modes using eq 23, *i.e.*, the PBB method,[16] is grossly inadequate. In interpreting the data in Table VI Bates and Wignall[62] chose a method somewhat different than the one we have outlined above. 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

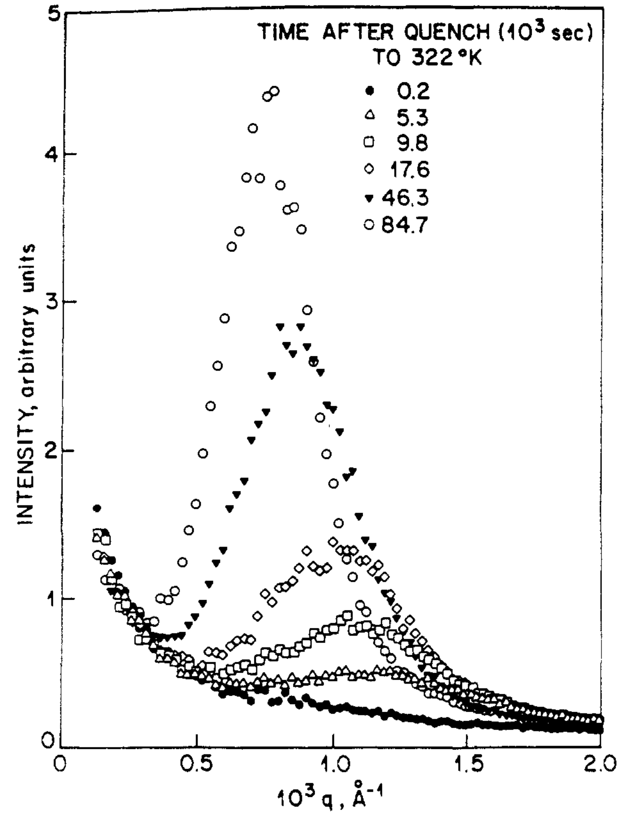


Figure 10. Representative one-dimensional light-scattering traces for a quench of an isotopomer solution of protio and deuterio-1,4-polybutadiene to 322 K. The upturn in intensity at low q is caused by stray light. (From ref 63a. Courtesy of F. S. Bates and American Institute of Physics.)

of the general ideas presented in this review. Figure 9 shows light-scattering patterns gathered by Bates and Wilthuis[63] for a spinodal quench of a polybutadiene-(H/D) isotopomer solution and offers incontrovertible evidence that a phase transition is occurring. In this experiment the system is disturbed from the homogeneous miscible region by lowering the temperature abruptly through the critical point and into the unstable region where spinodal decomposition occurs. (Recall that binodal loci, shown as the solid lines in diagrams like those in Figure 7a, represent concentrations with equal partial molar free energy in the two coexisting phases, α and β ($\mu_1{}^\alpha = \mu_1{}^\beta$, $\mu_2{}^\alpha = \mu_2{}^\beta$, *etc.*). The spinodal loci, shown as inner line at the bottom of Figure 7a, delineate the boundary between the metastable and the absolutely unstable part of the phase diagram. It is defined in terms of the points of inflection on the free energy–concentration surface.) The rapid quench technique allows the kinetics of the phase separation process to be studied. This can be seen by examining the developing scattering diffraction pattern of Figure 9 where phase separation is clearly apparent, or in alternative representation in Figure 10. A great advantage of studying the kinetics of phase transitions using isotopomer solutions of polymers is that the changes develop over comfortably long times as compared to phase separation in mixtures of small molecules. This permitted the authors to make careful, detailed, and important tests of the generalized theory of nucleation and phase separation.[71]

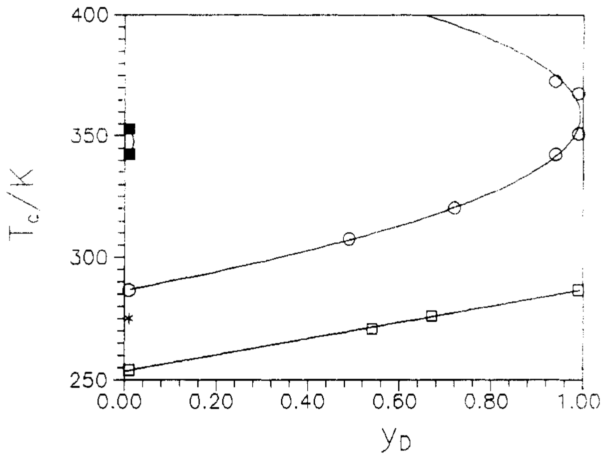


Figure 11. Critical loci for some [x_c(polystyrene) + $(1-x_c)((1-y_D)(CH_3)_2CO + y_D(CD_3)_2CO))$] solutions at p = 0.5 MPa: ■ = MW polystyrene, 22 000; ○ = MW polystyrene 13 500; * = MW polystyrene 11 600; □ = MW polystyrene 7500. See ref 69.

3.10. Demixing in Polymer–Solvent Systems

Van Hook and co-workers[69] have reported extensive cloud and spinodal data for the acetone–polystyrene, methylcyclopentane–polystyrene and propionitrile–polystyrene systems. The phase diagrams exhibit both upper and lower consolute branches (see E in Figure 7b). The hypercritical points for acetone–polystyrene solutions are at easily accessible pressures and molecular weights. The effects of pressure, molecular weight, and molecular weight distribution and solvent H/D fraction on the phase diagrams were explored. H/D isotope effects on the coexistence curves and their pressure dependences are both large. For example, the solvent isotope effect on the consolute temperature for acetone–polystyrene solutions is as large as 20 K. An increase in pressure, or a change in substitution from D to H on the solvent, increases the region of miscibility. Alternatively, changing from D to H on the polymer narrows the miscibility gap but not to the same extent. Also, there are striking isotope effects on the shape of the phase diagram, especially in that P–T–MW regime close to the hypercritical point. While many of these observations are not particularly germane to the point of principal interest in this review, the dependence of the upper (and lower) critical temperatures on D/H ratios in the solvent are pertinent because in certain cases they have been demonstrated to be connected with nonideality in D/H solvent isotopomer mixture.

Figure 11 shows isobaric plots of upper and lower critical solution temperatures for acetone(D/H)/polystyrene mixtures as a function of the deuterium fraction in the solvent, $y_D = n_{\text{acetone-}d}/(n_{\text{acetone-}h} + n_{\text{acetone-}d})$, for four molecular weights of solute polymer. In this diagram the volume fraction of solvent (D + H) is maintained at the concentration which specifies the critical loci, $\phi_{\text{acetone}}(\text{cr}) = ((V_{\text{acetone-}h} + V_{\text{acetone-}d})/(V_{\text{acetone}} + V_{\text{polymer}}))_{\text{cr}}$. In the regions inside the envelopes (*i.e.*, above the UCS locus, below the LCS locus, and to the left of the hypercritical point) the solutions are homogeneous. To the right of the hypercritical points the system has collapsed to the hourglass configuration and is in a two-phase heterogeneous region. At the left of the figure the two data points near T_c = 350 K (filled squares) refer to acetone/polystyrene solutions of MW

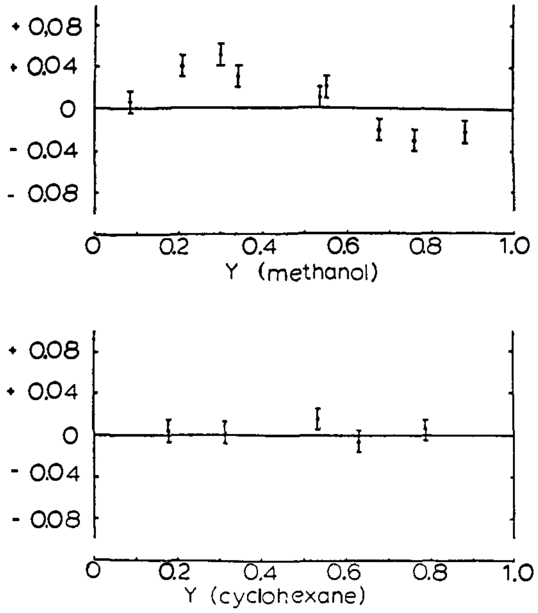


Figure 12. Effect of isotopic dilution on T_c in methanol/cyclohexane systems. $(T_c - T_{Raoult})/K$ is plotted against y. Top: $[x_c(C_6H_{12}) + (1 - x_c)((1 - y_D)CH_3OH + y_DCH_3OD)]$. Bottom $[x_c((1-y_D)C_6H_{12}+y_{D}C_6D_{12}) + (1-x_c)CH_3OH]$. (From ref 72. Courtesy of American Institute of Physics.)

= 22 000, and the hypercritical point for this system at P = 0.5 MPa is found at y_D = 0.05. An increase in pressure shifts all the curves to enhanced solubility. Thus, the hypercritical molecular weight for polystyrene-*h* at y_D = 0.05 is 22 000, but at a higher pressure than shown in Figure 11, is greater than 22 000. Alternatively, at a lower pressure than that of Figure 11, but at the same polymer molecular weight, y_D for the hypercritical point will be shifted to the left. Finally, as we show in the diagram, at the same pressure, but at a decreased molecular weight the hypercritical point is shifted to higher y_D. The data show an extremely large IE on the hypercritical molecular weight. At pure acetone-*d*, y_D = 1, the hypercritical MW is 13 500, and at y_D = 0, MW_{hyp} = 22 000. The IE amounts to a shift of 8500 molecular weight units (out of only 22 000). As T_{hep} is approached, the curvature in T_c − D/H plots increases dramatically and becomes unbounded at T_{hep}. Should molecular weight be decreased (see the lowermost curve), the hypercritical point is displaced to the right, but in this case will hypothetically fall off the diagram to the right-hand side. T_{hep} is inaccessible for this particular molecular weight. For the case shown, MW = 7500 Da, and the T_c − D/H plot is linear within experimental precision.

Singh and Van Hook[72] have given a mean-field analysis of the H/D dependence of T_c in binary mixtures with fractional deuteration. In that approximation they showed that the IE on T_c should vary smoothly with fractional deuteration and pointed out that isotope-dependent T_c's do not by themselves imply nonideality in isotopic mixtures. Their analysis of the nonlinear contribution to demixing data[72] in $[x_c(C_6H_{12}) + (1 - x_c)((1-y_D)CH_3OH + y_DCH_3OD)]$ and $[x_c((1-y_D)C_6H_{12} + y_DC_6D_{12}) + (1 - x_c)CH_3OH]$ solutions used symmetrical mixture theory. The data are shown in Figure 12. The "S" shape observed for deuteration at the hydroxyl group of methanol is interesting. The excess temperature found on cyclohexane deuteration is much smaller and indicates that whereas CH_3OH/CH_3OD mixtures show significant nonideality, the C_6H_{12}/C_6D_{12} mixtures are ideal within the experimental error of these measurements. The results were found to be consistent with Raman difference spectroscopic measurements (*vide infra*). Turning attention back to the H/D dependence of phase separation in acetone/polystyrene solutions near the hypercritical limit (Figure 11), we note the deviations are several orders of magnitude larger than in methanol/cyclohexane. These IE's have not yet been quantitatively interpreted, but for such large effects it is difficult to accept the SVH claim that nonlinearities in T_c/y plots are a direct measure of excess free energy in the solvent isotopomer solution. Rather, we suspect the observed hypercritical enhancements are an indication of nonclassical behavior, *i.e.*, of a departure from mean field theory. The approach to the hypercritical point follows the nonclassical prediction and displays a scaling exponent, $\beta \approx 1/3$.[69] In this regard it is interesting that little or no curvature is observed for polymer solutions well removed from the hypercritical region (line C, Figure 11), which, possibly, can be interpreted using the mean field analysis.[72]

3.11. Isotopomer Mixtures of Methanols, CH_3OH and CH_3OD

Measurements of the molar volumes of CH_3OH, CH_3OD, and CD_3OD, and apparent molar volumes for ($CH_3OH + H_2O$) and ($CH_3OD + D_2O$) solutions, were made by Bender and Van Hook.[73] They also measured V^{ex} in isotopomer mixtures ($CH_3OH + CH_3OD$) which was found to be zero within the experimental uncertainty. The solutions exhibit a small but non-zero excess molar Gibbs free energy[72] as discussed immediately above. The experimental observation of an S-shaped behavior for these T_c curves, and the intimation that it is a consequence of a similar S-shaped dependence of excess free energies for the methanol mixtures, suggests the need for independent measurements of the excess free energy (presumably by high precision measurements of the vapor pressure of CH_3OH/CH_3OD mixtures).

3.12. Mixtures of Water Isotopopmers

Although a voluminous literature exists describing and interpreting the effect of isotopic substitution on the properties of water and mixtures of isotopic waters, space does not permit us to review this topic in any great detail. However, we will describe a few studies on the excess thermodynamic properties of aqueous mixtures since they illustrate some of the concepts developed in this review in a particularly clear fashion. Jakli and Van Hook[24] presented a thermodynamic analysis of D/H and $^{18}O/^{16}O$ fractionation factors in water mixtures, comparing the data with VPIE measurements on the separated isotopomers.[74] Sufficient information on molar volume[53,75] and virial coefficient[76] isotope effects is available to accurately convert observed ($\ln \alpha - \ln (P'/P)$) values to the theoretically more useful ($\ln \alpha - \ln (f_c/f_g)$). Comparisons are given in Table VII which demonstrates agreement between theory and experiment within experimental error, ±0.0002 unit, for H/D and $^{18}O/^{16}O$ substitution. In the analysis of aqueous H/D mixtures it is necessary to take account

Table VII. Contributions to Excess Free Energy in Mixtures of Isotopic Waters at High Dilution (305 K). All Entries in the Table Have Been Multiplied by 1 × 10^4

	$B'P'(1 - BP/B'P')$	$-(P'V'/RT)(1 - P/P')$	$\ln(\alpha) - \ln(f_c/f_g)$ (calcd)	$\ln(\alpha) - \ln(P'/P)$ (calcd)	$\ln(\alpha) - \ln(P'/P)$ (exptl)
D/H	−1	<0.1	−7 ± 2	−8 ± 2	−8 ± 2
$^{18}O/^{18}O$	<0.1	<0.1	6 ± 2	6 ± 2	4 ± 1

of the ($H_2O + D_2O \rightleftarrows 2\ HOD$) disproportionation reaction.[77] In agreement with the conclusions of Jakli and Jancso,[78] Van Hook,[79] and Phutela and Fenby,[80] the present data can be interpreted as an ideal three-component mixture where the limiting HOD/DOD isotope effects show significant deviation from the low of the geometric mean. One finds ($\ln(P_{HOH}/P_{DOD})/\ln(P_{HOH}/P_{HOD}) = 1.92 \pm 0.02$ instead of 2. The analogous values for partial molar enthalpies and partial molar volumes are in the range 1.90–1.95. It is particularly interesting that the excess free energies calculated from Table VII are of opposite sign for isotopic substitution at hydrogen and oxygen. This straightforward prediction results from the fact that $\Delta V/V$ is of opposite sign for H/D ($\Delta V/V = -1.7 \times 10^{-3}$) and $^{18}O/^{16}O$ substitution ($\Delta V/V = 1.5 \times 10^{-3}$).[24] The magnitude of these effects, and their opposite signs, have been rationalized by Dutta-Choudhury and Van Hook[51] in terms of the vibrational dynamics of the condensed phase. Spectroscopic data required for the calculations in Table VII were available from Walrafen and Abebe.[81] Notice that if the excess free energies were calculable from the PBB approach, or one of its modifications, *i.e.*, from the contribution of the external degrees of freedom alone, $G^{ex} = -(V - V')^2/2\beta'V'RT$, it would be impossible to rationalize the opposite signs experimentally observed for the quantity [$\ln \alpha - \ln(P'/P)$].

In related work Fenby and co-workers,[82] Duer and Bertrand,[83] Koga,[84] and most recently Simonson[85] have made careful measurements of enthalpies of mixing for protio/deuterio water systems. Fenby and Bertrand[86] have developed a systematic thermodynamics for interpretation of this and other deuterium-exchange reactions. Bottomley and Scott[87] and Dutta-Choudhury and Van Hook[51] have determined excess volumes in in $H_2O/HOD/D_2O$ mixtures and given an interpretation of the results, and Kiyohara, Halpin, and Benson[88] have measured excess ultrasonic velocities (and hence excess isentropic compressibilities) in such mixtures.

3.13. Correlations with Spectroscopic Observations

The development emphasized in this review interprets the thermodynamic properties of transfer of an isotopomer between its Raoult and Henry standard states in terms of the volume dependence (and hence the MVIE) of the related partition function. The MVIE is well understood in terms of an isotope-independent potential energy surface describing both inter- and intramolecular degrees of freedom. The partition function may be straightforwardly expressed using a set of 3n harmonic or anharmonic oscillators, again using isotope-independent force constants. In the interpretation used throughout the present paper the problem is reduced to calculating, or estimating, the frequency shift corresponding to the transfer. A more direct and therefore more appealing route would be to directly determine the relevant frequency shifts which occur on the transfer between solvent states, thus removing our assumption that the transfer is equivalent to the congruent compression (or dilation). This is ordinarily not possible because liquid state spectral broadening is much larger than the relevant frequency shifts. Frequency shifts for transfer between isotopomer solvents amount to a few hundreths cm^{-1}, at most about 0.1 cm^{-1}. Liquid-state broadening, on the other hand, normally 2–10 or more cm^{-1} for nonassociated liquids, can increase to as many as several hundred cm^{-1} for hydrogen-bonded and other associated liquids. For that reason ordinary IR and Raman spectroscopic techniques will not suffice to yield the desired information; the required frequency shifts are too easily lost in condensed-phase broadening. Even so, Laane and coworkers[89] have reported a Raman difference technique which enables very small shifts in Raman bands to be detected with useful precision. They have used this technique to study solutions relevant to our interests. The results are reviewed in the following paragraph.

Meinander, Strube, Johnson, and Laane[89] interpreted difference Raman shifts in vibrational bands for isotopic dilution in liquid benzene(H/D) and pyridine(H/D) solutions in terms of additive resonant intermolecular coupling and volume effects. The former gives rise to a linear dependence of the frequency shift on mole fraction of the active species. The latter takes into account the change in molar volume upon solution which may increase (*e.g.*, C_6H_6 as solute in C_6D_6) or decrease (*e.g* C_6D_6 in C_6H_6) the repulsive branch of the intermolecular potential, and thence increase or decrease the vibrational frequency. The magnitude of the volume effect was found to be ≈0.15 cm^{-1}, about three to four times larger than the value deduced by Jancso and Van Hook[19] for benzene mixtures, but of the same sign. However, if one considers the more recent observations of Kamogawa and Kitagawa,[90] who observed a sudden increase in the C–D frequency shift of C_6D_6 solutes in C_6H_6 at mole fractions less than 0.1, followed by a leveling off, better agreement is found between the spectroscopically observed frequency shift and the shift calculated from the MVIE and employed earlier in the excess free energy calculation of C_6H_6/C_6D_6 mixtures.[19] Kamagawa and Kitagawa[90] also investigated Raman difference spectroscopy of CH_3CN/CD_3CN mixtures. While they found, in agreement with Laane *et al.*,[89] that resonance coupling accounts for most of the frequency shift on isotopic dilution, they suggested the additional term originates from an IE on polarizability, not molar volume. The explanation is acceptable and certainly plausible. We have already commented, in accord with Singh and Van Hook[20] and Bates and Wignall,[62] that the two effects share a common origin. The theory of dipolar resonant transfer in binary mixtures of isotopomers was originally developed by Logan.[91] The results of the Raman difference measurements afford strong confirmation of the present interpretation of excess isotope effects in isotopomer mixtures.

4. Conclusions

High-precision measurements of excess thermodynamic properties of isotopomer solutions for systems ranging from rare gases to polymers have been discussed in the context of the theory of isotope effects in condensed phases. Values for the excess Gibbs free energy are 2–3 orders of magnitude smaller than those typically found in binary mixtures of simple ordinary (*i.e.*, nonisotopic) molecules. Although small, the effects are additive, and for long-chain H/D-substituted polymers the excess free energies are large enough to cause demixing. Theoretical analysis clearly demonstrates the excess thermodynamic properties due to isotopomer mixing are vibrational in origin. Proper consideration of the volume dependence of vibrational properties of the component molecules is essential to the understanding of the mixtures. At first glance that conclusion is a little surprising, since these solutions should be among the simplest of solutions, *i.e.*, the most nearly ideal. It is an important conclusion, however, because many widely used theories of solution ignore vibration and vibrational interaction. The isotopomer results demonstrate this approach to be inadequate.

5. Acknowledgments

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