

# Isotope effects on vapor phase 2nd virial coefficients

W. Alexander Van Hook,  
Luis Paulo N. Rebelo,  
Max Wolfsberg

**Abstract** Vapor phase 2nd virial coefficient isotope effects (VCIE's) are interpreted. A useful correlation is developed between  $-\Delta(\mathfrak{B}-b_o)/(\mathfrak{B}-b_o) = (-VCIE)$  and the reference condensed phase reduced isotopic partition function ratio  $[\ln(f_c/f_g)]^*$ .  $\mathfrak{B}$  is the second virial coefficient,  $b_o = 2\pi\sigma^3/3$ ,  $\sigma$  is the Lennard-Jones size parameter, and  $\Delta$  is an isotopic difference, light-heavy.  $[\ln(f_c/f_g)]^*$  can be obtained from vapor pressure isotope effects for  $T/T_{CRITICAL} < 0.7$ . Also  $(-VCIE) = \ln(f_p/f_g^2)$ , where  $\ln(f_p/f_g^2)$  is the reduced isotopic partition function ratio describing the equilibrium between monomers and interacting pairs. At temperatures well removed from crossovers in  $\ln(f_p/f_g^2)$  or  $[\ln(f_c/f_g)]^*$ ,  $\ln(f_p/f_g^2) = (0.4 \pm 0.2) [\ln(f_c/f_g)]^*$ .

**Key words** isotope effects • Lennard-Jones potential • reduced partition function ratio • vapor phase • vapor pressure isotope effects • virial coefficients

## Introduction

This paper reviews recent work on isotope effects (IE's) on intermolecular interaction in the vapor including comparison with condensed phase IE's [19]. It is well established that IE's on condensed phase molar volume (MVIE), vapor pressure (VPIE), virial coefficients (VCIE), and molecular polarizability (PIE) share a common origin in the vibrational properties of the interacting molecules. Even so, the details of the connections between PIE, MVIE, VCIE and VPIE have been argued for years, sometimes contentiously [1, 3, 4, 5-7, 17, 18]. The confusion arose because it is convenient to express virial coefficients (and VCIE's) in terms of the parameters of intermolecular potentials of the Lennard-Jones type and IE's thereon ( $\epsilon$ ,  $\sigma$ ,  $\Delta\epsilon/\epsilon$  and  $\Delta\sigma/\sigma$ ) [4, 8], but in the description of MVIE and VPIE one introduces a formalism which uses a set of vibrational frequencies, frequency shifts, and isotope dependences [2, 10]. In the worst case this can result in interpretations which violate the Born-Oppenheimer (BO) approximation. That approximation, of course, has been axiomatic in the theory of equilibrium isotope chemistry [11, 12, 20]. In the present development we compare free energy differences between condensed phase molecules or gas phase dimers, on the one hand, and the dilute gas phase reference on the other. The resulting correlation supports the conclusion that the two effects share a common origin.

W. A. Van Hook   
Chemistry Department, University of Tennessee,  
Knoxville TN 37996-1600, USA,  
Tel.: 865 974 5105, Fax: 865 974 3454,  
e-mail: avanhook@utk.edu

L. P. N. Rebelo  
Instituto de Tecnologia Químicas e Biológica, UNL,  
Apartado 127, 2780-901 Oeiras, Portugal

M. Wolfsberg  
Chemistry Department, University of California Irvine,  
Irvine CA 92697-2025, USA

Received: 25 June 2001

## Background

### The VPIE

Bigeleisen [2, 10] has shown the logarithmic isotopic vapor pressure ratio,  $\ln(P'/P)$ , is related to the reduced partition function ratio, condensed to gas,  $\ln(f_c/f_g)$ .

$$(1) \quad \ln(f_c/f_g) = \ln(P'/P) - \Delta(PV_c)/(RT) + (\mathfrak{B}'_0 P' - \mathfrak{B}_0 P)$$

$P'$  and  $P$  are equilibrium vapor pressures,  $\Delta(PV_c) = (P'V'_c - PV_c)$ , light-heavy.  $V'_c$  and  $V_c$  are condensed phase molar volumes,  $\mathfrak{B}'_0$  and  $\mathfrak{B}_0$  are virial coefficients. At low enough temperatures, say between  $T_{\text{TRIPLE}}$  and  $\sim 0.7 T/T_{\text{CRITICAL}}$ , the corrections (last two terms) are small, and  $\text{VPIE} \sim \ln(P'/P)$  defines the reference condensed phase isotopic partition function ratio,  $\ln(f_c/f_g)^*$ ,

$$(2) \quad \ln(f_c/f_g)^* = \ln(P'/P) = \text{VPIE}$$

Also,  $\text{VPIE} \sim \ln(P'/P)$  is the IE on the equilibrium constant,  $\ln(K'/K)$ , for the phase change (condensed = vapor)<sub>EQ</sub> [10]. In the harmonic oscillator rigid rotor approximation,

$$(3) \quad \ln(f_c/f_g)^* = A_c/T^2 + B_c/T$$

$A_c$  contains information on the force constants defining the external (lattice) frequencies of the molecule,  $A_c = (1/24)(hc/k)^2(\sum[(v_i'^2 - v_i^2)_c - (v_i'^2 - v_i^2)_g])$ . The sum is over low frequencies. Also  $B_c = (1/2)(hc/k)(\sum[(v_i'^2 - v_i^2)_c - (v_i'^2 - v_i^2)_g])$ ; this sum is over the  $(3n-6)$  high (internal) frequencies. Above  $T_{\text{CRITICAL}}$ , the reference condensed phase isotopic partition function ratio,  $\ln(f_c/f_g)^*$ , has no meaning in terms of comparisons with VPIE, but its numerical value still serves as an interesting reference when considering partition function ratios of interacting pairs in the theory of isotope effects on 2nd virial coefficients.

### The VCIE

The theory of the 2nd virial coefficient of gases,  $\mathfrak{B}$ , is well understood [8, 14, 16]. Classically

$$(4) \quad \mathfrak{B} = -2\pi N_A \int [\exp(-\phi_{(2)}(r)/kT) - \exp(-\phi_{(1)}(r)/kT)] r^2 dr$$

$\phi_{(2)}(r)$  is the potential of 2 atom interaction,  $\phi_{(1)}(r)$  is the 1 atom potential,  $N_A$  is Avogadro's number, and  $r$  is intermolecular distance. Using a statistical argument, Rice [16] has shown that Equation (4) can be reexpressed

$$(5) \quad \mathfrak{B} = (2/3)\pi\sigma^3 - K(T)$$

Here,  $2K(T)$  is the integrated excess probability of finding two atoms in the gas closer to each other than they would be in a random distribution with no two atom potential, and is equal to the equilibrium constant for dimer association (the factor 2 arises since two monomers form one dimer molecule). The first term,  $(2/3)\pi\sigma^3 = b_o$ , arises because the two body potential is repulsive at short range (distances less than  $\sigma$ ). In making the transition to quantum statistics it is necessary to replace the Boltzmann factors,  $\exp(-\phi_{(i)}(r)/kT)$ , by the corresponding normalized Slater sums

$$(6) \quad \sum \psi_n^*(r) [\exp(-(\mathbf{T} + \phi_1)/kT)] \psi_n(r)$$

The  $\psi_n(r)$ 's correspond to an orthonormalized complete set of functions.  $\mathbf{T}$  is the kinetic energy operator and the  $\phi_1(r)$  correspond to  $\phi_1(r)$  or  $\phi_2(r)$  of Eq. (4). We are led again to Eq. (5) except that now  $K$  is formulated quantum mechanically and is isotope dependent. In the model below, we consider  $K$  in the "harmonic approximation", replacing it by a bound dimer (pair) harmonic-rigid-rotor partition function divided by the square of the monomer partition function,  $\ln(f_p/f_g^2)$ .

Since  $b_o = (2/3)\pi\sigma^3$  is isotope independent ( $\sigma$  is the size parameter), one focuses the discussion of VCIE on  $(\mathfrak{B}-b_o)$  which is directly related to the association equilibrium constant  $K$ ,  $\ln(K'/K) = \ln(f_p^2/f_g)$  in precise analogy to Eq. (5). We define VCIE

$$(7) \quad \ln(K'/K) = -\ln(K'/K) = \ln(f_p/f_g^2) = -\ln[(\mathfrak{B}-b_o)'/(\mathfrak{B}-b_o)] = (-\text{VCIE}) = A_p/T^2 + B_p/T$$

The reason for the minus sign is that  $K$  involves the equilibrium (2 monomer = pair) but the vapor pressure equilibrium is (condensed phase monomer = vapor phase monomer). The sum in the expression for  $A_p$  for non-linear polyatomic molecules extends over twelve frequencies corresponding to the external degrees of freedom. In the monomers these are the rotations and translations of the two molecules, in the dimer they are the three rotations and three translations of the dimer molecule (null frequencies), plus six frequencies which correspond to one monomer-monomer stretch, and five other low lying frequencies (loose monomer-monomer bending modes or hindered internal rotations). The remaining internal frequencies of the  $n$ -atomic monomers map into internal frequencies of the dimer, slightly shifted from the monomer. These frequencies appear in the  $B_p$  term. The result is consistent with an earlier formalism [15].

The A contribution to  $\ln(f_c/f_g)^*$  or  $\ln(f_p/f_g^2)$  is necessarily positive and in the direction of a normal isotope effect (light > heavy). The B terms, on the other hand, involve the sum of dimer-monomer or condensed-vapor isotopic frequency differences, and can be either positive or negative. For monatomic species  $B_c = B_p = 0$  (there are no internal modes). For molecules with structure the situation is more complicated. If the net shift in internal modes on condensation/dimerization is to the blue, the A and B terms are both positive and reinforce one another. The IE will be positive and large. More often, the net shift in isotope sensitive internal frequencies is to the red (the ordinary case for noncomplexed H/D substitution) and B is of opposite sign to A. Over some range of temperature B/T may be, and often is, larger in magnitude than A/T<sup>2</sup>. In such cases the net isotope effect will be negative (inverse), it is a small difference between competing positive and negative terms with distinctly different temperature dependences. These matters have been thoroughly discussed so far as application to VPIE is concerned [2, 9, 10]. Similar considerations carry over to (-VCIE). That is the point of concern of the present paper.

### Comparing $\ln(f_c/f_g)^*$ and $\ln(f_p/f_g^2)$

The important features of the model are summarized in Figure 1. When a molecule is transferred from its ideal gas reference to dimer, or to the condensed phase, significant

changes occur in both internal and external degrees of freedom. We refer to a  $3n$  dimensional potential energy surface, PES, which describes how the molecular potential energy depends on the distortion of various atoms or groups of atoms (internal modes), and on the position or orientation of the molecule itself (externals). Fig. 1 represents the shifts in intermolecular potential energy and in the internal vibrational potential energy of a single normal mode, as two or more molecules vary their distance of intermolecular separation  $R_{\text{INTERMOL}} = R_{12}$ . A similar diagram can be constructed for each of the  $3n-6$  internal degrees of vibrational freedom. The upper curve,  $\alpha$ , sketches the transfer between the dilute gas reference state (on the right at large  $R_{12}$ ) and the complexed (dimerized) vapor molecule at the bottom of the upper well to the left. Similarly, the lower curve,  $\beta$ , shows transfer from dilute vapor to condensed phase. In the first case  $u(R_{12})$  represents the pair potential energy; and in the second, it represents the projection on the  $r$  axis of the intermolecular potential of a single molecule embedded in the field of  $(N-1)$  neighbors. That accounts for the significantly deeper and sharper well which describes condensation. During the change from dilute gas to condensed phase  $\text{PES}_{\text{INTERMOL}}$  shifts to lower energy, and, of at least equal importance, the curvature in the intramolecular dimension is perturbed by virtue of the coupling between internal and external degrees of freedom.

Figure 1 illustrates the truism that the intermolecular interactions accounting for  $\ln(f_p/f_g^2)$  (upper curve) and  $\ln(f_c/f_g^*)$  (lower curve) differ not in kind, but in degree. One concludes that  $[\ln(f_p/f_g^2)] = (-\text{VCIE})$  should be roughly proportional to  $\ln(f_c/f_g^*)$ , and the constant of proportionality should be less than unity (because of differences in the well depths and curvatures of the effective intermolecular potentials). The well depth for the gas-gas pair interaction

is “available” from fits of  $\mathfrak{B}$  for the parent molecule, and that for the condensed phase can be obtained by combining measured energies of vaporization with the zero point energies of the condensed and ideal vapor phases. Typically for attractive forces limited to the van der Waals dispersion interaction,  $\epsilon_{\text{DIMER}}/\epsilon_{\text{COND}} \sim 0.1$  [13]. In the condensed phase the average potential energy per molecule in a condensed system of  $N$  molecules becomes  $u(R_{12}) = (s_n C_{12}/R_{12}^n - s_m C_6/R_{12}^m)c/2$  where  $s_m$  and  $s_n$  are tabulated constants obtained from lattice or smeared lattice sums. With the (gas + gas = dimer) interaction as reference, the effect of condensation is to bring the molecules some 3 to 5% closer, and to increase the well depth by nearly an order of magnitude, at the same time increasing the curvature at the bottom of the intermolecular well (i.e. increasing force constants of the equivalent harmonic oscillators,  $\kappa_c > \kappa_d$ ), and shifting the associated external frequencies commensurately, ( $v_d/v_c \sim (1/2.7)^{1/2} \sim 0.6$ , and  $v_d^2/v_c^2 = (\kappa_d/\kappa_c)(\mu_c/\mu_d) \sim 0.4$ ). In the condensed state the average potential energy is greater than the near pairs value,  $(c/2) \epsilon_{\text{DIMER}}$  by 40 to 60 per cent or more [13]. In addition, and importantly for present purposes, one expects the zero point energy shifts to scale similarly.

The discussion, strictly interpreted, refers to intermolecular modes only. With modest generalization we expect similar arguments to apply to intramolecular modes as well. Most commonly the internal and external contributions to  $\ln(f_p/f_g^2)$  and  $\ln(f_c/f_g^*)$  are of opposite sign and are usefully described using the A, B formalism. The ratio  $[\ln(f_p/f_g^2)/\ln(f_c/f_g^*)] = [A_p/T^2 + B_p/T]/[A_c/T^2 + B_c/T]$ , is zero at the crossover temperature for  $(-\text{VCIE})$ ,  $T_{\text{CROSS,p}} = -A_p/B_p$ , and is unbounded at the crossover temperature for  $\ln(f_c/f_g^*)$ ,  $T_{\text{CROSS,c}} = -A_c/B_c$ . By crossover is meant that temperature at which one or the other isotope effect,  $\ln(f_p/f_g^2)$  or  $\ln(f_c/f_g^*)$ , goes through zero and changes sign. At temperatures near crossovers it is more useful to report ratios of A and B parameters separately, and not ratios of overall isotope effects.

ORTHOGONAL PLOT, LJ  $u(r_{12})$  vs.  $r_{12}$  and  $E_{\text{vib}}$  vs. oscillator amplitude for an internal mode

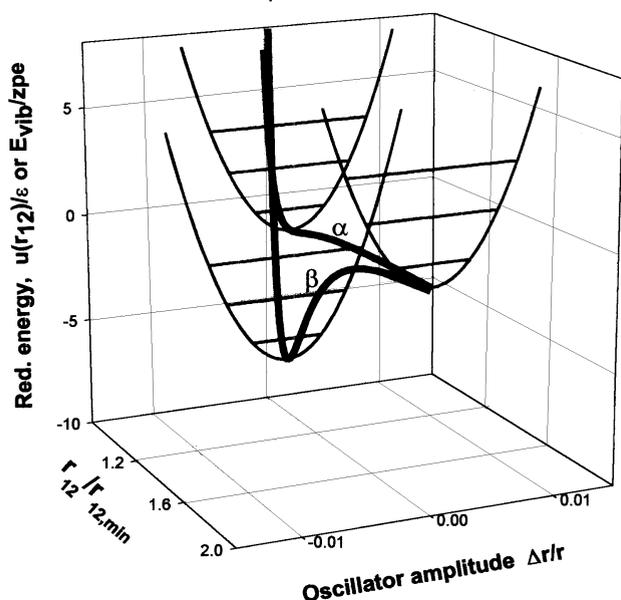


Fig. 1. Projection of  $3n$  dimensional (per molecule) potential surface for intermolecular interaction. The LJ PE of interaction is plotted against  $r$  in one plane, phase shifts in a representative internal frequency in a second plane. The upper curve represents the gas-gas “pair” interaction, the lower represents condensation. The lighter parabolic curves depict an internal vibration in dilute gas, dimer and condensed phase. Only a few vibrational levels are shown.

### Comparisons of VCIE and VPIE data

We have reviewed data for the 14 compounds (24 sets of isotopomer pairs) on which data for both VCIE and VPIE are available [19]. Another two pairs,  $\text{H}_2/\text{D}_2$  and  $\text{He}^3/\text{He}^4$ , are light. Their quantum corrections are large and the thermodynamics complicated by nuclear spin effects. They are not considered in present context.

In the comparisons one notes in almost every case that  $\ln(f_p/f_g^2)$  is of the same sign and smaller in magnitude, yet commensurate, with  $\ln(f_c/f_g^*)$ . VCIE’s are consistent with the correlation introduced above. VPIE and  $(-\text{VCIE})$ ,  $\ln(f_c/f_g^*)$  and  $\ln(f_p/f_g^2)$ , are subject to the same underlying principles. That is the point of concern of the present paper. In Table 1 we review (A, B) parameters of fit to Eq. (3) for averaged  $\ln(f_c/f_g^*)/\Delta M$  and  $\ln(f_p/f_g^2)/\Delta M$ . In spite of large uncertainties, the averaged ratios,  $\langle(A_p/A_c = A_{\text{VCIE}}/A_{\text{VPIE}})\rangle = 0.4 \pm 0.2$  and  $\langle(B_p/B_c = B_{\text{VCIE}}/B_{\text{VPIE}})\rangle = 0.4 \pm 0.1$ , are consistent with the expectations of the model. The large uncertainties are a consequence of experimental uncertainty in the VCIE data. Figure 2 shows another test of the correlation between

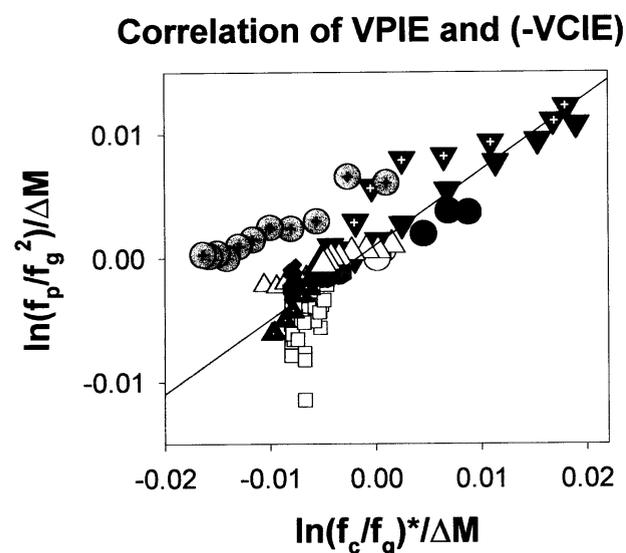
**Table 1.** A and B parameters for fits to (-VCIE) and VPIE for selected molecules (per  $\Delta M$  unit).

	VCIE		(-VCIE)/VPIE	
	A	B	A	B
$^{36}\text{Ar}/^{40}\text{Ar}$	10	–	$1.0 \pm 0.5$	–
$\text{CH}_4/\text{CH}_x\text{D}_{4-x}$	233	-2.34	$0.9 \pm 0.2$	$0.8 \pm 0.2$
$\text{C}_2\text{H}_4/\text{C}_2\text{H}_x\text{D}_{4-x}$	97	-0.91	$0.3 \pm 0.2$	$0.3 \pm 0.1$
$\text{C}_2\text{H}_6/\text{C}_2\text{D}_6$	53	-0.74	$0.4 \pm 0.1$	$0.3 \pm 0.1$
$\text{C}(\text{CH}_3)_4/\text{C}(\text{CD}_3)_4$	10.2	-0.51	$0.1 \pm 0.1$	$0.4 \pm 0.1$
$\text{NH}_3/\text{ND}_3$	2630	-5.43	$0.5 \pm 0.1$	$0.4 \pm 0.1$
$\text{CH}_3\text{NH}_2/\text{CH}_3\text{ND}_2$	1960	-2.70	$0.4 \pm 0.1$	$0.2 \pm 0.1$
$\text{H}_2\text{O}/\text{D}_2\text{O}$	4277	-6.14	$0.3 \pm 0.1$	$0.2 \pm 0.1$
Average			$0.4 \pm 0.2$	$0.4 \pm 0.1$

$\ln(f_c/f_g)^*$  and (-VCIE). It plots experimental values of  $[\ln(f_p/f_g^2)/\Delta M]$  vs.  $[\ln(f_c/f_g)^*/\Delta M]$ . An equation for the correlation is reported in the caption.

In the comparisons made in this paper it is important to keep several caveats in mind. To begin, Eq. (3), widely used for interpretation of VPIE data, is only valid at pressures low enough to ignore PV corrections. Similarly, the analogous equation for (-VCIE) is limited to pressures where contributions from third and higher virial coefficients are negligible. In present context we are comparing  $\ln(f_p/f_g^2)$  and  $\ln(f_c/f_g)^*$  at pressures and temperatures low enough to avoid PV complications. This we have accomplished by restricting the VPIE data used to define  $\ln(f_p/f_g^2)$  to low temperature and low to modest pressure, comparing with (-VCIE) at higher temperature, but still low to modest pressure. In no sense do we compare vapor pressures and VPIE's, with virial coefficients and VCIE's, at temperatures near or above the critical temperature, or at high pressure.

The ratio,  $[(\ln(f_p/f_g^2)/\Delta M)/(\ln(f_c/f_g)^*/\Delta M)] \sim 0.4 \pm 0.2$  is consistent with that expected from the model,  $\sim 0.2 \pm 0.1$ . Both  $\ln(f_c/f_g)^*$



**Fig. 2.** The correlation of  $\ln(f_p/f_g^2)$  with  $\ln(f_c/f_g)^*/\Delta M$  at the temperatures of the VCIE measurements. The correlation line is:  $\ln(f_p/f_g^2) = 0.49 \ln(f_c/f_g)^* + 1.2 \times 10^{-3}$ ,  $r^2 = 0.6$ . Open circles = argon, darkly shaded circles =  $\text{CH}_3\text{F}/\text{CD}_3\text{F}$ , small squares = methanes, lightly shaded triangles = ethanes, small diamonds = ethylenes, shaded hexagons = neopentanes, large inverted triangles = ammonia, large inverted crossed triangles = methyl amines ( $\text{CD}_3$ ), upright dotted triangles = methyl amines ( $\text{ND}_2$ ), upright open triangles = methyl amines ( $\text{CD}_3\text{ND}_2$ ), crossed shaded circles =  $\text{H}_2\text{O}/\text{D}_2\text{O}$ .

**Table 2.** LJ calculations of  $(A_p = A_{(-\text{VCIE})})/\Delta M$  and  $(A_c = A_{\text{VPIE}})/\Delta M$  compared with experiment [19].

Systems	$(\epsilon/k)K$	$\sigma/A$	$v_p/\text{cm}^{-1}$	$v_c/\text{cm}^{-1}$	$A_p/K^2$	$A_c/K^2$
$^{36}\text{Ar}/^{40}\text{Ar}$	118	3.4	26	47	1.6	12
Expt <sup>a</sup>			26	41	10	10
$\text{CH}_4/\text{CH}_x\text{D}_{4-x}$	148	3.82	$44.72^b$	$72.72^b$	288	238
Expt <sup>a</sup>				$75.75^b$	233	258
$\text{C}_2\text{H}_6/\text{C}_2\text{D}_6$	243	3.95	40	69	42	132
Expt					53	140

Remarks:

<sup>a</sup> See Ref. [19] for discussion of uncertainties.

<sup>b</sup> Frequencies are listed in the order: LJ pair frequency, hindered rotation in pair (vapor phase); or lattice translation, lattice libration (condensed phase).

and  $\ln(f_p/f_g^2)$  depend on temperature in a complicated fashion,  $\ln(R_{\text{VPIE or VCIE}}) = A/T^2 + B/T$ . In many cases A and B are of opposite sign but commensurate magnitude, in these cases  $\ln R$  amounts to a small difference between much larger terms. This difficulty, compounded by experimental uncertainty in the VCIE data, accounts for most of the uncertainty in the correlations above.

We have carried out more detailed calculations for  $^{36}\text{Ar}/^{40}\text{Ar}$ , the series of methane/deuteromethanes, and other molecules, developing a set of LJ force constants from the potential parameters, and demonstrating consistency between those parameters and VCIE, VPIE and independent spectroscopic observation (Table 2). Details may be found in the earlier report [19].

## Conclusion

Isotope effects on the vapor phase second virial coefficient and on vapor pressure share a common origin. They are approximately proportional,  $\ln(f_p/f_g^2) = (-\text{VCIE}) = (0.4 \pm 0.2) \ln(f_c/f_g)^*$ , provided the comparisons are made not too close to either crossover temperature. Both depend on temperature in a complicated fashion,  $\ln(f_c/f_g)^*$  or  $\ln(f_p/f_g^2) = A/T^2 + B/T$ . For many compounds, the A and B terms are of opposite sign but of commensurate magnitude, and in such cases  $\ln(f_c/f_g)^*$  or  $\ln(f_p/f_g^2)$  amounts to a small difference between much larger terms and may be either positive (normal) or negative (inverse). Ordinarily A results from quantization of the overall motions of the molecule of interest (external modes) upon transfer from the gas phase to the condensed phase or interacting pair, and is positive. The formalism developed in this paper treats the (vapor monomer = *n*-coordinated liquid) and (vapor monomer = vapor pair) equilibria analogously and focuses attention on their common origin.

Research at Univ. TN supported by the Ziegler Fund.

## References

- Bates FS, Keith HD, McWhan DB (1987) Isotope effect on the melting temperature of nonpolar polymers. *Macromolecules* 20:3065–3070
- Bigeleisen J (1961) Statistical mechanics of isotope effects on the thermodynamic properties of condensed systems. *J Chem Phys* 34:1485–1493
- Bigeleisen J, Wolfsberg M (1969) Comment on “Physical proper-

- ties of fluid  $\text{CH}_4$  and  $\text{CD}_4$ : theory". *J Chem Phys* 50:561
- Fang AY, Van Hook WA (1974) Isotope effects on the vapor phase second virial coefficients of the deuterated methanes. *J Chem Phys* 60:3513–3522
  - Grigor AF, Steele WA (1967) Physical properties of fluid  $\text{CH}_4$  and  $\text{CD}_4$ : theory. *J Chem Phys* 48:1038–1046
  - Grigor AF, Steele WA (1968) Physical properties of fluid  $\text{CH}_4$  and  $\text{CD}_4$ : experimental. *J Chem Phys* 48:1032–1037
  - Grigor AF, Steele WA (1969) Comment on "Physical properties of fluid  $\text{CH}_4$  and  $\text{CD}_4$ : theory". *J Chem Phys* 50:562
  - Hirschfelder JO, Curtiss CF, Bird RB (1954) *Molecular theory of gases and liquids*. Wiley, New York
  - Jancsó G, Rebelo LP, Van Hook WA (1993) Isotope effects in solution thermodynamics. Excess properties in solutions of isotopomers. *Chem Rev* 93:2645–2666
  - Jancsó G, Van Hook WA (1974) Condensed phase isotope effects (especially vapor pressure isotope effects). *Chem Rev* 74:689–750
  - Kleinman L, Wolfsberg M (1973) Corrections to the Born-Oppenheimer approximation and electronic effects on isotopic exchange equilibria. *J Chem Phys* 59:2043–2053
  - Kleinman L, Wolfsberg M (1974) Shifts in vibrational constants from corrections to the Born-Oppenheimer approximation. Effects on isotopic exchange equilibria. *J Chem Phys* 60:4749–4754
  - Moelwyn-Hughes EA (1957) *Physical chemistry*. Pergamon, New York
  - Munster A (1969) *Statistical thermodynamics*, vol. 1. Springer Verlag, Berlin
  - Phillips JT, Linderstrom-Lang CU, Bigeleisen J (1972) Liquid-vapor isotope fractionation from the triple point to the critical point. Mean Laplacian of the intermolecular potential in liquid argon. *J Chem Phys* 56:5053–5062
  - Rice OK (1967) *Statistical mechanics, thermodynamics and kinetics*. Freeman WH, San Francisco
  - Singh RR, Van Hook WA (1987) Excess free energies in solutions of isotopic isomers. Pt. 3: Solutions of deuterated and protiated polymers. *Macromolecules* 20:1855–1859
  - Steele WA (1961) Vapor pressure of nearly classical fluids. *J Chem Phys* 34:802–803
  - Van Hook WA, Rebelo LPN, Wolfsberg M (2001) An interpretation of the vapor phase second virial coefficient isotope effect: correlation of virial coefficient and vapor pressure isotope effects. *J Phys Chem* 105:9284–9297
  - Wolfsberg M (1969) Isotope effects. *Annual Review Phys Chem* 20:449–477