A NEW COMBINING RULE FOR FLUID MIXTURES

José Alfredo GONZÁLEZ-CALDERÓN[1] and Fernando del RÍO[2,*]

Laboratorio de Termodinámica, Departamento de Física, Universidad Autónoma Metropolitana, Iztapalapa, San Rafael Atlixco 186, México, DF, 0934, Mexico;
e-mail: [1] jose_alfredogc@yahoo.com, [2] fdr@xanum.uam.mx

Received December 30, 2007
Accepted July 9, 2008
Published online February 23, 2009

Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

We present evidence for the regular behaviour of the Boyle temperature T_B in gaseous binary mixtures of small molecules with negligible multipolar moments. We use this regularity to construct a new combining rule for the prediction of the cross interaction $u_{12}(r)$ in those mixtures. The combining rule gives T_B of the cross interaction as the harmonic mean of the Boyle temperatures of the pure components. The validity of this harmonic rule is based on experimental data of 28 binary mixtures, whose T_B have been obtained from experimental data of the cross virial coefficient $B_{12}(T)$. In determining T_B we make use of non-conformal potentials that have been proven to represent very accurately the effective interactions of the molecules investigated. The new combining rule is used to give interaction parameters of several dozens of binary mixtures involving noble gases (Ne, Ar, Kr and Xe), diatomic molecules (N_2, O_2 and CO) and *n*-alkanes (from methane to *n*-octane). These interaction parameters lead to a prediction of cross virial coefficients $B_{12}(T)$ within experimental error. Electrostatic interactions, originating in permanent dipolar, quadrupolar, octupolar and hexadecapolar moments and exemplified by molecules of HCl, CO_2, CF_4 and SF_6, depart from the regular non-polar behaviour.
Keywords: Combining rules; Virial coefficients; Binary mixtures; Interactions; Polar and non-polar molecules; Boyle temperature; ANC potentials.

All classical theories of mixtures and solutions require knowledge of the interactions $u_{\alpha,\beta}$ between molecules of species α and β. The problem of incorporating adequate interaction models for $u_{\alpha,\beta}$ is usually divided into two steps: the first is to determine the pure-component interactions $u_{\alpha,\alpha}$, the step that can be carried out using information provided by quantum-mechanical *ab initio* calculations and/or inversion of thermodynamic data. The second step is to obtain the cross interaction $u_{\alpha\neq\beta}$ that in principle could be determined in the same way. Nevertheless, given the large number

Collect. Czech. Chem. Commun. 2009, Vol. 74, No. 2, pp. 363–391

doi:10.1135/cccc2007198

of possible systems and the scarcity of data, cross interactions in fluid mixtures are frequently predicted by means of combining rules expressing the parameters of the cross interaction in terms of the parameters characterizing the pure substances[1].

Ab initio quantum-mechanical calculations have increased significantly our knowledge of interaction potential surfaces not only between noble gas atoms but also between molecules of increasing complexity, as exemplified by recent work on N_2, CO_2 and Hg [2–5]. This type of work has also been done for interactions between different noble gas atoms[6–8] or molecules such as CH_4–N_2 [9] or fluorobenzene–argon[10]. Nevertheless, the same as with experimental determinations, the large number of binary systems of interest makes the calculation of every possible pair interaction unfeasible. This reinforces the need for developing adequate combining rules.

Combining rules are tied to the equation of state or to the interaction model used. Most interaction models involve two parameters: the first, ε, characterising the interaction energy and the second, δ, associated with the size or diameter of the molecules. The models more widely used are very simple potentials such as hard spheres and square wells or more realistic continuous functions, such as the popular Lennard–Jones potential with exponents 12 and 6 (LJ/12–6) or the Kihara potential with a spherical core[11]. Only very few studies have used three-parameter potentials such as the LJ/n–6 [12].

Attempts to derive combining rules from first principles have been based on the analysis of an approximate quantum-mechanical approach to the interatomic attraction, in particular those of London[13] and Kirkwood–Müller[14]. These theories give formulae for the attractive potential between two atoms that involve atomic or molecular attributes; polarisabilities and ionization energies for the London approach, and polarisabilities and diamagnetic susceptibilities for that of Kirkwood–Müller. When combined with a particular potential function and after some simplifications these formulae lead to the combining rules of Hudson–McCoubrey[15] and of Fender–Halsey[16]. Further simplification of the Hudson–McCoubrey rule gives the widely used Berthelot rule, although this was originally proposed even before the advent of quantum mechanics[17]. A second and semiclassical line of approach considers separating the repulsion or ‘distortion’ energy between two atoms as proposed by Sikora[18]. Again, new combination rules are obtained when this idea is used jointly with a specific interaction function[19]. All the combining rules obtained in either of these two ways contain different kinds of mean values (arithmetic, geometric or harmonic) of the molecular attributes and potential parameters. Díaz Peña and co-workers have studied systematically a large number of possible combination rules derived from the above arguments and used the LJ/12–6 potential and the Kihara potential with a spherical core[20]. They assess the combination rules by their ability to predict second virial coefficients and by the similarities of the parameters thus obtained with parameters derived from inversion of transport data. One of their conclusions is that there appears no systematic trend in classes of substances and that the simplest rules – the arithmetic mean for the diameters (Lorentz) and the geometric or harmonic mean for the energies (Berthelot[17] and Fender–Halsey[16]) – "are close to the rules giving the best results"[20].

The purpose of this paper is threefold. First, to introduce an empirical rule that holds for a large class of non-polar substances. This rule is independent of the particular type of potential function used. Second, to incorporate a three-parameter potential, which has proven to be very accurate in accounting for the thermodynamics of the fluids here considered, in the hope that a more accurate and systematic treatment of pure substances can lead to better results for their cross interactions. Third, to establish the limits of application of the empirical rule proposed and to determine which is the best set of rules – as far as simplicity and accuracy are concerned – for the non-polar substances here studied.

In the last decade a new family of three-parameter potential functions has been introduced and shown to account very accurately for the properties of pure fluids. These functions are termed approximate non-conformal (ANC) potentials and depend on the shape or form parameter s, besides the energy ε and diameter δ[21]. The ANC potentials have proven to be very successful in accounting for the second and third virial coefficients, $B(T)$ and $C(T)$, of many substances, leading to predictions in close agreement with experimental information[22]. They have also been used to predict critical temperatures for polar and non-polar fluids. A recent review is available for the reader interested in this topic[23].

Here we use the ANC potential functions in two ways. In the first case, as a tool for the determination of the Boyle temperature, T_B (defined by $B(T_B) = 0$), from experimental $B_{exp}(T)$ data in binary mixtures. It is very common that $B_{exp}(T)$ data for many substances are available only at temperatures well below T_B. This fact together with the uncertainties in $B_{exp}(T)$ leads to quite unreliable estimates of T_B for many substances of interest. The inherent robustness of the ANC approach makes up for a part of these difficulties and allows to determine the Boyle temperatures of the cross interactions of 28 mixtures involving 18 simple pure substances: the noble gases (He, Ne, Ar, Kr and Xe), diatomic molecules with small or negligible dipole moments (H_2, N_2, O_2 and CO) and n-alkanes (from CH_4 to n-C_8H_{18}). We also consider HCl, CO_2, CF_4 and SF_6 as examples of polar molecules. The values of T_B thus obtained and available information on $B_{12}^{exp}(T)$ allow us to establish that the Boyle temperature of the cross interaction, T_{12}^{B}, is very close to the harmonic mean of T_i^{B} for individual components, i. e.,

$$\frac{2}{T_{12}^{B}} = \frac{1}{T_1^{B}} + \frac{1}{T_2^{B}} . \qquad (1)$$

Since T_B in the ANC theory is expressed directly in terms of the substance interaction parameters ε, δ and s, Eq. (*1*) gives in essence a combining rule for these parameters.

In the second application of the ANC approach, we show that the above combining rule leads to a prediction of the cross interactions in systems different from those used to construct the rule. The knowledge of these effective interactions, together with the ANC potential functions and other two well known combining rules, gives very accurate second virial coefficients for close to 90 binary mixtures.

In the next section we introduce the ANC potential functions and quote the properties more relevant for our purposes. In the same section, we introduce the more traditional combining rules relevant to this work. Then we present our main results, namely, the empirical evidence supporting the rule in Eq. (*1*) and discusses its application in the prediction of the cross interactions of the binary systems here considered, and for which no empirical evidence is available or is insufficient. Finally, in the last section we advance a few conclusions.

THEORY

ANC Potential Functions

The family of non-conformal potentials used in this work is defined by[21]

$$u_{\mathrm{ANC}}(z,s) = \varepsilon\left\{\left[\frac{1-a}{\zeta(z;s)-a}\right]^{12} - 2\left[\frac{1-a}{\zeta(z;s)-a}\right]^{6}\right\} \qquad (2)$$

where $\zeta = (z^3/s + 1 - 1/s)^{1/3}$, $z = r/\delta$, r is the interparticle distance, a = 0.09574 and δ is the distance where the function (*2*) has its minimum

$u_{ANC}(z = 1) = -\varepsilon$. The form of $u_{ANC}(z)$ is determined by the dimensionless form factor s called the softness of the potential. For $s = 1.1215$ the function $u_{ANC}(z)$ is closely conformal to a LJ/12–6 potential. Decreasing s makes $u_{ANC}(z,s)$ steeper (or harder) so that for $s = 0$ Eq. (*2*) gives a hard-sphere potential. Any two potentials with the same s are conformal to each other and follow the principle of corresponding states; whereas potentials differing in s are not conformal to each other[22]. The reader can find a more detailed account of the ANC theory in a recent review[23].

An important property of ANC functions follows directly from their definition (*2*) and is expressed as a linear relationship between reduced second virial coefficients $B^*(T^*,s) = B(kT/\varepsilon,s)/(2\pi\delta^3/3)$ of two non-conformal systems. Here we set $T^* = kT/\varepsilon$. In particular, choosing as reference the system with $s = 1$, and writing $B_0^* \equiv B^*(T^*,s = 1)$, this linear property is[21]

$$B^*_{ANC}(T^*,s) = 1 - s + sB_0^*(T^*)\ . \tag{3}$$

This relation, exact for ANC potentials, is followed to very good approximation by the virial coefficients of many substances[22]. The reference virial coefficient $B_0^*(T^*)$ is known as a function of T^* and closely resembles the virial coefficient of argon[22]. Hence, from Eqs (*2*) and (*3*) the knowledge of the parameters ε, δ and s determines directly both the potential function and $B(T)$.

The Boyle temperature T_B where $B(T_B,s) = 0$ follows simply from Eq. (*3*) as

$$B_0^*(T_B^*) = (s-1)/s \tag{4}$$

which can be inverted numerically to obtain[22]

$$T_B^*(s) = 0.189754 + 2.09123s - 1.404325s^2 + \\ + 3.87119s^3 - 3.225s^4 + 1.27345s^5\ . \tag{5}$$

Combining Rules

The combining rules, which will be referred to in this work, were chosen from a wide selection[19,24–27], because of their simplicity and accuracy[18]. They are the rule of Lorentz for the molecular diameters

$$\delta_{12} = (\delta_1 + \delta_2)/2 \tag{6}$$

and for the energy the rules of Berthelot[15]

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \tag{7}$$

of Hudson–McCoubrey[15]

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}\ \frac{2\sqrt{I_1 I_2}}{I_1 + I_2}\ \frac{2\sqrt{\delta_1 \delta_2}}{\delta_{12}} \tag{8}$$

and the harmonic mean of Fender–Halsey[16]

$$\varepsilon_{12} = \frac{2\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\ . \tag{9}$$

In these equations, ε_i and δ_i are the interaction parameters that correspond to the pure components and ε_{12} and δ_{12} give the cross interactions in the mixture. Last, I_j are the (first) ionization energies of the molecules. In approaches using two parameters, the Lorentz rule Eq. (*6*) together with one of Eqs (*7*), (*8*) and (*9*) are sufficient to specify the cross interactions. Nevertheless, for three-parameter potentials such as $u_{\mathrm{ANC}}(z,s)$ one needs a third combining rule to determine the softness s_{12} of the cross interaction. Here we propose the harmonic combination of the Boyle temperatures,

$$T_{12}^{\mathrm{B}} = \frac{2T_1^{\mathrm{B}} T_2^{\mathrm{B}}}{T_1^{\mathrm{B}} + T_2^{\mathrm{B}}}\ . \tag{10}$$

Since $T_{ij}^{\mathrm{B}} = \varepsilon_{ij} T_{ij}^{*\mathrm{B}}/k$ and $T_{ij}^{*\mathrm{B}} = T^{*\mathrm{B}}(s_{ij})$ we can write Eq. (*10*) in terms of the interaction parameters ε_{ij} and s_{ij}:

$$\varepsilon_{12} T_{12}^{*\mathrm{B}}(s_{12}) = \frac{2\varepsilon_1 \varepsilon_2}{\varepsilon_1 T_1^{*\mathrm{B}}(s_1) + \varepsilon_2 T_2^{*\mathrm{B}}(s_2)}\, T_1^{*\mathrm{B}}(s_1) T_2^{*\mathrm{B}}(s_2)\ . \tag{11}$$

It is useful to combine Eqs (*7*), (*8*) and (*9*) with Eq. (*11*) to get the following relations for the cross interaction softness s_{12}:

$$T^{*\mathrm{B}}(s_{12}) = \frac{2\sqrt{\varepsilon_1 \varepsilon_2}}{\varepsilon_1 T^{*\mathrm{B}}(s_1) + \varepsilon_2 T^{*\mathrm{B}}(s_2)}\, T^{*\mathrm{B}}(s_1) T^{*\mathrm{B}}(s_2) \tag{12}$$

$$T^{*B}(s_{12}) = \frac{I_1 + I_2}{2\sqrt{I_1 I_2}} \frac{d_{12}}{\sqrt{d_1 d_2}} \frac{2\sqrt{\varepsilon_1 \varepsilon_2}}{\varepsilon_1 T^{*B}(s_1) + \varepsilon_2 T^{*B}(s_2)} T^{*B}(s_1) T^{*B}(s_2) \qquad (13)$$

and

$$T^{*B}(s_{12}) = \frac{\varepsilon_1 + \varepsilon_2}{\varepsilon_1 T^{*B}(s_1) + \varepsilon_2 T^{*B}(s_2)} T^{*B}(s_1) T^{*B}(s_2) \, . \qquad (14)$$

When used jointly with Eq. (*11*), Eqs (*12*), (*13*) and (*14*) are equivalents to the rules of Berthelot, Hudson–McCoubrey and Fender–Halsey, respectively. We have written explicitly that the factors T_{ij}^{*B} are functions of s_{ij}, which are given by Eq. (*5*).

RESULTS AND DISCUSSION

Harmonic Mean Rule for Boyle Temperatures

We present here the evidence regarding the validity of the harmonic mean rule (HMR) for the Boyle temperatures given by Eq. (*10*). It is reasonable to expect that the validity of a given set of combining rules depends on the type of molecular interaction involved. Here we focus our discussion on the cases where the short-range overlap and the London dispersion forces predominate. Thus we have selected 16 substances with negligible multipolar moments: the noble gases (He, Ne, Ar, Kr and Xe), three diatomic molecules (H_2, N_2 and O_2) and eight *n*-alkanes (from methane to *n*-octane). For brevity we shall refer to these molecules as non-polar; they were chosen for two reasons. First, their ANC interaction parameters and Boyle temperatures are well established, and second, there is experimental information about the cross virial coefficients of many of their binary mixtures. Further, the molecular properties (size, ionization energy I and polarisability α) of the noble gases and of the alkanes vary systematically within each group. Besides these substances and in order to explore the influence of electrostatic interactions, we have also considered five additional molecules: CO and HCl (dipolar), CO_2 (quadrupolar), CF_4 (octupolar) and SF_6 (hexadecapolar). Molecular properties of 21 selected substances are given in Table I. The ionization energies were taken from Vedeneev et al.[28] except for that of HCl that was taken from the NIST database[29].

All experimental data on $B(T)$ were obtained from the recent exhaustive compilation of Dymond et al.[30]. The possible binary mixtures of the substances here considered fall into three sets with respect to the existence and quality of $B_{exp}(T)$ data: set I, systems for which $B_{exp}(T)$ data are sufficient in number, temperature range and quality to determine T_B with reasonable accuracy. Set II, systems for which there are $B_{exp}(T)$ data, but these are only sufficient to give a qualitative estimate of the values of T_B, and set III, systems without $B_{exp}(T)$ data.

TABLE I
Interaction parameters of pure substances[a]

Substance	(ε/k), K	δ, nm	s	T_B, K	I, eV[b]
He	7.264	0.2982	1.1152	24.36	24.58
Ne	40.45	0.3054	1.0583	124.0	21.56
Ar	145.9	0.3685	0.9993	407.8	15.78
Kr	202.9	0.3985	0.9993	566.9	14.00
Xe	280.6	0.4333	0.9993	784.3	12.13
H_2	22.18	0.3669	1.3192	104.6	15.60
N_2	132.7	0.3889	0.9172	326.3	15.58
O_2	160.3	0.3620	0.9432	410.3	13.62
CO	145.3	0.3960	0.8876	340.8	14.01
SF_6	479.9	0.5037	0.6068	707.4	19.30
CH_4	210.5	0.3947	0.9073	509.4	12.99
C_2H_6	361.1	0.4627	0.8088	747.6	11.65
C_3H_8	515.0	0.4997	0.7008	893.2	11.08
n-C_4H_{10}	671.4	0.5330	0.6148	1003.9	10.63
n-C_5H_{12}	805.7	0.5673	0.5503	1071.1	10.55
n-C_6H_{14}	929.9	0.5993	0.5119	1149.0	10.48
n-C_7H_{16}	1059.2	0.6255	0.4693	1202.8	10.39
n-C_8H_{18}	1174.2	0.6515	0.4388	1251.9	10.24
CF_4	325.4	0.4496	0.6558	522.7	17.80
SF_6	479.9	0.5037	0.6068	707.4	19.30
CO_2	486.1	0.3830	0.5994	707.1	13.79
HCl	561.3	0.3823	0.4510	736.6	12.74

[a] Values of ANC parameters ε, δ and s, and Boyle temperatures T_B are those reported in ref.[22e] [b] Ionisation energies are from refs[28,29]

Analysis of the information provided for set I allows us to identify 28 mixtures satisfying the HMR for T_B. Tables IIA and IIB contain the information about these mixtures. The tables compare the value of T_B determined from the $B_{exp}(T)$ data – denoted T_B(exp) – with the value T_B(HMR) obtained from the combining rule, Eq. (*10*). The fourth column shows the percentage deviation $100 \times \delta T_B / T_B(\mathrm{exp})$, where $\delta T_B = T_B(\mathrm{exp}) - T_B(\mathrm{HMR})$. Determination of T_B from the $B_{exp}(T)$ data was made by interpolation or extrapolation of the same data. Of course, to be significant, a nonzero devi-

TABLE IIA
Binary mixtures obeying the HMR and involving noble gases and diatomic molecules

System	T_B, K		$100 \times \delta T_B$ $T_B(\mathrm{exp})^a$	$\delta B(\mathrm{eq})^b$ cm^3 mol^{-1}	$\delta B(\mathrm{exp})^c$ cm^3 mol^{-1}
	exp	HMR			
Ne–Ar	191.7	190.1	0.8	0.2	±3.0
Ne–Kr	204.9	203.4	0.7	0.2	±2.0
Ne–Xe	204.3	214.1	–4.6	–1.7	±3.0
Ar–Kr	476.5	474.3	0.5	0.2	±6.0
Ar–Xe	532.8[d]	536.5	–0.7	–0.4	±2.0
Kr–Xe	648.6	658.1	–1.4	–0.8	±6.0
Ne–N_2	168.7	179.7	–6.1	–1.9	±3.0
Ne–O_2	202.4	190.4	6.3	1.7	±2.5
Ne–CO	171.0	181.8	–6.0	–1.9	±1.0
Ar–N_2	363.0	362.5	0.1	0.1	±3.0
Ar–O_2	398.9	409.0	–2.5	–1.3	±2.5
Ar–CO	372.1	371.3	0.2	0.1	±4.0
Ar–HCl	522.6[d]	524.9	–0.4	0.2	±3.2
Kr–CO	426.7[d]	425.7	0.2	0.1	±1.0
Xe–N_2	467.4[d]	460.9	1.4	0.9	±2.0
Xe–CO	482.4	475.1	1.5	1.0	±4.0
N_2–CO	333.1	333.4	0.5	0.3	±1.0
N_2–O_2	371.7	363.5	2.3	1.0	±0.8

[a] δT_B is the deviation of T_B(exp) from the value obtained by the HMR. [b] δB(eq) is the equivalent deviation in $B(T)$ form experiment producing the observed deviation δT_B (see the text). [c] δB(exp) is an estimate of the experimental error in B at points close to T_B. [d] T_B obtained by extrapolation of $B_{exp}(T)$ data; the remaining values involve an interpolation of $B_{exp}(T)$.

ation δT_B has to be smaller than the error in determining T_B itself. On interpolation, the error in T_B is due to the error δB_{exp} ascribed to experimental points and their scatter. On extrapolation, there is an additional source of error, which depends on the extrapolating function and the distance of the experimental points to the $B = 0$ axis. For all systems of set I, the error in T_B(exp) was estimated to be smaller than 5%.

The deviation δT_B is thus a first indicator of the validity of the HMR for these mixtures: most systems in Tables IIa and IIB show deviations smaller than 3% and only a few deviate for as much as 4 or 6%, while systems in Tables IIIA and IIIB show deviations as large as 65%. In order to ascertain further that the HMR follows the experimental information on these systems we compare the experimental error of the $B_{exp}(T)$ data with $dB_{eq} = (\partial B/\partial T)dT_B$, which is the error in B that would be necessary to produce the observed error δT_B. The deviation δB_{eq} is shown in column 5 of the table and for the HMR to apply it should be smaller than the estimated experimental uncertainty of the data, δB_{exp}, contained in the last column. The magnitude of δB_{exp} was obtained from the same source as the $B_{exp}(T)$ data[30].

TABLE IIB
Binary mixtures obeying the HMR for T_B involving *n*-alkanes with noble gases and diatomic molecules. Explanation of the symbols is the same as in Table IIA

System	T_B, K		$100 \times \delta T_B / T_B(\mathrm{exp})$	δB(eq) cm^3 mol^{-1}	δB(exp) cm^3 mol^{-1}
	exp	HMR			
Ar–CH_4	454.1	452.9	0.3	–0.1	±1.5
Ar–C_2H_6	517.1[a]	527.7	–2.0	1.3	±0.6
Ar–C_3H_8	556.1[a]	559.9	–0.7	0.5	±1.0
Kr–CH_4	535.2	536.6	0.3	0.1	±1.5
Xe–C_2H_6	751.3[a]	765.5	–1.9	1.5	±16.0
N_2–CH_4	396.1[a]	397.8	–0.4	0.2	±0.5
N_2–C_2H_6	469.6[a]	454.3	3.4	–2.3	±2.0
N_2–C_4H_{10}	486.2[a]	492.5	–1.3	3.7	±6.5
O_2–CH_4	436.1[a]	454.3	–4.0	2.0	±1.0
CO–CH_4	415.8[a]	408.37	1.8	–1.0	±0.5

[a] T_B obtained by extrapolation of $B_{exp}(T)$ data; the remaining values involve an interpolation of $B_{exp}(T)$.

Analysis of the information gathered on δT_B shows very clearly which systems satisfy the HMR (Tables IIA and IIB) and which not (Tables IIIA and IIIB). The mixtures that follow the HMR for T_B are all those constituted by non-polar substances – except He, H_2 and to some extent Ne. Systems without *n*-alkanes are considered in Table IIA, and Table IIB contains systems with at least one alkane.

We first explain, with reference to Fig. 1, the procedure followed to determine T_B by interpolation or extrapolation using the ANC model for $B(T)$.

TABLE IIIA
Binary mixtures not obeying the HMR for T_B that contain He or H_2. Explanation of the symbols is the same as in Table IIA

System	T_B, K		$100 \times \delta T_B / T_B(\text{exp})$	$\delta B(\text{eq})$ $\text{cm}^3\ \text{mol}^{-1}$
	exp	HMR		
He–Ne	52.83	40.72	22.9	5.8
He–Ar	70.47[a]	45.97	34.8	13.4
He–Kr	83.18[a]	46.71	43.8	22.4
He–Xe	105.0[a]	47.25	55.0	65.9
He–H_2	29.64	39.52	–33.3	6.4
He–N_2	82.59	45.34	45.1	21.9
He–CO	86.10	45.47	47.2	24.2
He–O_2	99.57	45.99	53.8	27.8
He–SF_6	128.1[a]	47.13	63.2	58.0
H_2–Ne	96.87[a]	113.5	–17.1	3.0
H_2–Ar	223.7	166.7	25.6	8.9
H_2–Kr	253.0	176.6	30.2	12.3
H_2–Xe	265.2	184.6	30.4	13.8
H_2–CO	178.7	169.7	10.4	3.3
H_2–N_2	169.2	158.4	6.4	1.9
H_2–CH_4	198.4	173.6	14.3	3.6
H_2–C_2H_6	277.1	183.5	51.0	27.6
H_2–C_8H_{18}	295.1	193.1	52.8	39.6

[a] T_B obtained by extrapolation of $B_{\text{exp}}(T)$ data; the remaining values involve an interpolation of $B_{\text{exp}}(T)$.

The figure shows the cross second virial coefficients $B_{12}(T)$ of two systems: Ne–Ar and Kr–CO. For each mixture we show the experimental points $B_{exp}(T_i)$ and the curve fitted to them that was used to localize the Boyle point $B = 0$. This curve is given by the ANC model for $B(T; \varepsilon_{12}, \delta_{12}, s_{12})$, Eq. (*3*), with δ_{12} from the Lorentz rule and an initial value for the softness given by $s_{12}^0 = 2s_1s_2/(s_1 + s_2)$; then ε_{12} was determined by a least-square fit to the $B_{exp}(T_i)$ data. Usually this procedure leads to a fit well within the scatter of the experimental data. In the cases where this did not happen a new value of s_{12} was adopted and the procedure repeated again.

We now analyse Fig. 1 as example of the way in which the HMR is satisfied. The first mixture, Ne–Ar at the top in Fig. 1, has the Boyle point $B = 0$ at $T_B(\exp) = 191.7$ clearly interpolated by the fitting curve $B_{ANC}(T)$. The figure also shows the Boyle point obtained from the HMR: it sits almost precisely where the fitting curve crosses the $B = 0$ axis. The second mixture,

TABLE IIIB
Boyle temperatures for binary mixtures with significant electrostatic interactions. Explanation of the symbols is the same as in Table IIA

System	T_B, K		$100 \times \delta T_B / T_B(\exp)$	$\delta B(\mathrm{eq})$ cm^3 mol^{-1}
	exp	HMR		
CO_2–CH_4	622.41	592.2	5.1	–2.4
CO_2–C_2H_6	870.19	726.8	19.7	–7.8
HCl–C_3H_{10}	629.31	807.4	–22.1	28.1
HCl–Kr	434.91	640.7	–32.1	29.7
CO–C_3H_8	533.7	493.4	8.2	–2.0
CO–C_8H_{18}	602.4	535.8	11.1	–9.3
CH_4–CF_4	466.8	516.0	–9.5	–8.3
C_2H_6–CF_4	557.9	615.3	–9.3	10.2
SF_6–Ne	267.7[a]	211.0	28.2	11.1
SF_6–N_2	478.1[a]	446.6	7.1	5.3
SF_6–O_2	510.9[a]	519.4	–1.6	–1.1
SF_6–Ar	574.1[a]	517.3	9.9	5.7
SF_6–Kr	586.8[a]	629.4	–6.8	–5.2

[a] T_B obtained by extrapolation of $B_{exp}(T)$ data; the remaining values involve an interpolation of $B_{exp}(T)$.

Kr–CO at the bottom in Fig. 1, has its Boyle point outside the range of experimental data, nevertheless, the fitting curve nicely extrapolates and crosses the $B = 0$ axis very close to the HMR value. Figure 2 gives two examples of mixtures, N_2–CH_4 and CH_4–C_2H_6, containing an alkane and following the HMR. The fitting curves in both systems cross the $B = 0$ axis very close to the Boyle point determined by the HMR.

All systems in Tables IIA and IIB follow the same behaviour as the examples in Figs 1 and 2. The percentage deviations of T_B from the HMR are smaller than 3% for the large majority of systems, the equivalent errors δB_{eq} are all smaller than 4 $cm^3\ mol^{-1}$ and in most cases they are smaller than δB_{exp}. So the HMR clearly applies to these systems within experimental uncertainty.

The Boyle temperatures of the cross interactions for mixtures of the light gases, He and H_2, are given in Table IIIA. Examples of the anomalous behaviour of these systems are the He–Kr and Xe–H_2 mixtures whose $B(T)$ is shown in Fig. 3. In the first mixture the Boyle point is below the range of the data and the fitting curve crosses the $B = 0$ axis at a point 36 K above

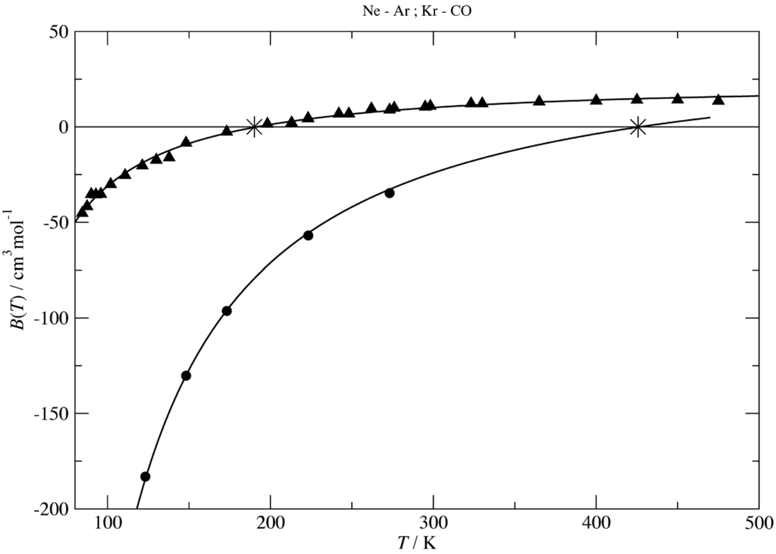

FIG. 1
Temperature dependence of the virial coefficients of the mixtures Ne–Ar (▲) and Kr–CO (●). The stars (✻) denote the Boyle temperatures according to the harmonic mean rule, MHR. The lines correspond to an ANC model. Both systems satisfy the MHR

the HMR value for T_B. In the latter mixture the Boyle point falls within the range of the data but these clearly point to a Boyle temperature quite different from that given by the HMR. Figure 4 gives two examples of mixtures, CF_4–CH_4 and Kr–HCl, that do not follow the HMR. The fitting curves in both systems cross the $B = 0$ axis far away from the Boyle point determined by the HMR.

The systems in Tables IIIA and IIIB do not follow the HMR. The deviations δT_B are significant, predominantly positive, in all cases but one larger than 10% and even as large as 63%. The equivalent errors δB_{eq} are correspondingly higher. A tentative explanation of the anomalies of systems in Table IIIA is in order. He and H_2 make an exception because their correct treatment should be based on quantum mechanics even if their virial coefficients are very well accounted for by ANC functions. Thus their anomalous behaviour *vis-à-vis* the combining rules could be tentatively ascribed to quantum-mechanical effects. A puzzling case is that of neon. While the mixtures of Ne with Ar, Kr, Xe, N_2, O_2 and CO all conform to the HMR (see Table IIA) the Ne–CH_4 mixture has its Boyle temperature clearly away from

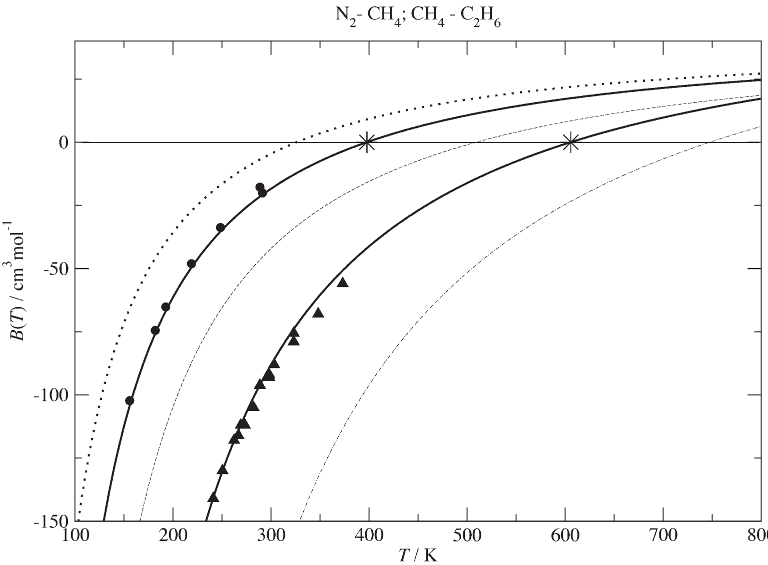

FIG. 2
Temperature dependence of the virial coefficients of the mixtures N_2–CH_4 (●) and CH_4–C_2H_6 (▲). The stars (✻) denote the Boyle temperatures according to the harmonic mean rule, MHR. The solid lines correspond to an ANC model and the dotted and dashed lines represent $B(T)$ of the pure components: N_2 (left), CH_4 (middle) and C_2H_6 (right). Both systems satisfy the HMR

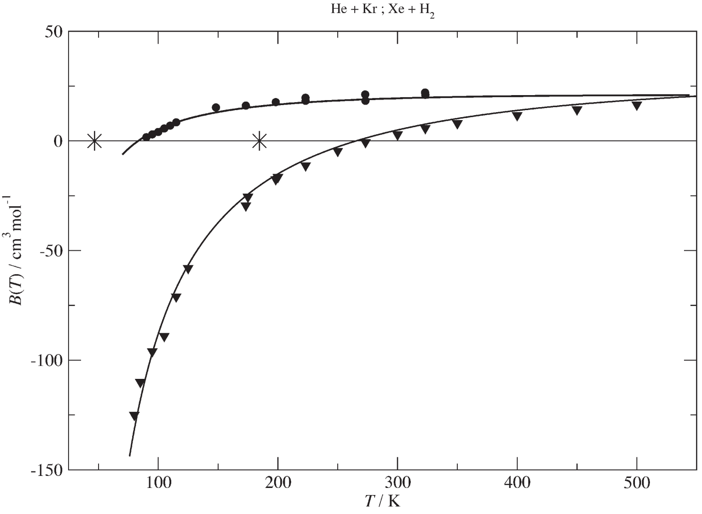

FIG. 3
Temperature dependence of the virial coefficients of the mixtures He–Kr (●) and Xe–H_2 (▼). The stars (✻) denote the Boyle temperatures according to the harmonic mean rule. These systems do not follow the rule

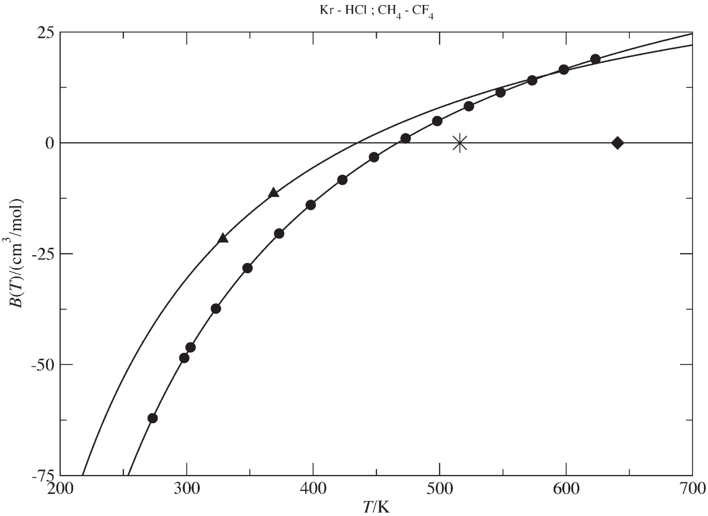

FIG. 4
Temperature dependence of the virial coefficients of the mixtures CF_4–CH_4 (●) and Kr–HCl (▲). The Boyle temperature according to the harmonic mean rule is denoted by a star (✻) for CF_4–CH_4 and by a diamond (◆) for Kr–HCl. These systems do not follow the HMR rule

the HMR value, a deviation that, accepting the reported errors in $B_{\mathrm{exp}}(T)$, cannot be ascribed to experimental uncertainties.

We find that mixtures where electrostatic interactions are not important follow also the HMR. This happens in particular in mixtures where the polar constituent – such as CO – has a small dipolar moment and the non-polar constituent is weakly polarisable. Tables IIA and IIB contain examples of this behaviour in systems formed by CO with Ne, Ar, Kr, Xe, N_2 and CH_4. It turns out that the mixture Ar–HCl has also a very small deviation $\delta T_B \approx$ 2.5 K from the HMR and has thus been included in this class; it seems that in spite of the high dipole moment of HCl the polarisability of argon is small enough to make the induction effects negligible.

The behaviour of T_B changes drastically with mixtures involving molecules with strong electrostatic interactions, which can be due to an increase in the electrostatic moment of one of the molecules in the mixture, or to the increased polarisability of the non-polar molecule, or to both factors combined. We already gave examples of this behaviour in Fig. 4. We first analyse the effect of increasing the polarisability of one component at a fixed dipole moment $\mu^* = \mu/\sqrt{\varepsilon\delta^3}$ of the second. We discuss the mixtures of CO as component 1 with Ar, Kr, Xe, N_2, CH_4, C_3H_8 and n-C_8H_{18} as component 2. In the order of increasing reduced polarisabilities $\alpha^* = \alpha\delta^3$, we have: $\alpha^* = 29.9$ (N_2), $\alpha^* = 32.4$ (Ar), $\alpha^* = 39.3$ (Kr), $\alpha^* = 41.2$ (CH_4), $\alpha^* = 49.4$ (Xe), $\alpha^* = 50.3$ (C_3H_8) and $\alpha^* = 55.7$ (n-C_8H_{18}). From the tables, we find that δT_B grows abruptly from almost zero for CO–N_2 (or Ar) to $\delta T_B \approx 67$ K for CO–n-C_8H_{18}. This means that δT_B increases with the polarisability of the non-polar component, which is what we could expect if deviations from the HMR were ascribed to the electrostatic induction forces between CO and its polarisable partner molecule given that these forces are proportional to $\alpha^*\mu^{*2}$. Consideration of the mixtures containing HCl leads to a similar conclusion: Whereas the HCl–Ar mixture has T_B very close to the HMR value, mixing HCl with the more polarisable C_3H_8 and Kr gives significant deviations, $\delta T_B \approx 176$ and 206 K (see Tables IIA and IIIB). In these cases, of course, deviations are much larger than for CO due to the higher dipole moment of HCl. Contributions from other electrostatic moments follow similar trends. The quadrupolar moment of N_2 does not appear to have any noticeable effect although we can assess the influence of the quadrupolar moment by looking at mixtures with CO_2: when mixed with CH_4 it gives $\delta T_B \approx 30$ K (Table IIIB) but, when mixed with the more polarisable C_2H_6, it has $\delta T_B \approx 143$ K. The octupolar interaction follows similar lines, as confirmed by two mixtures: CF_4–CH_4 and CF_4–C_2H_6 have deviations $\delta T_B \approx 49$

and 58 K, respectively. Lastly, introducing a hexadecapolar molecule, SF_6, again produces a departure from the HMR with $\delta T_B \approx 9$ K for SF_6–O_2 and $\delta T_B \approx 57$ K for SF_6–Ar.

The 28 systems whose T_B follows the HMR (Tables IIA and IIB) and the 31 systems that do not follow this rule (Tables IIIA and IIIB) are all the binary mixtures for which T_B can be determined with a reasonable accuracy of ca. 5%. All 31 systems but one, that do not conform to the HMR, contain a light molecule (He or H_2) or an induced electrostatic interaction between a fairly polarisable molecule and another one with a permanent multipolar moment. The only troublesome exception is the Ne–CH_4 mixture; it shows a deviation from the HMR, which even though small, cannot be explained easily by advocating the reported experimental uncertainties.

We shall focus next on the use of the HMR to predict the cross interaction virial coefficient $B_{12}(T)$ of all mixtures for which the rule can be assumed to hold. The comparison of this prediction with experiment brings a further proof of the validity of the HMR for mixtures of molecules with negligible electrostatic moments.

Prediction of Cross Interactions

Based on the results of the last subsection, we assume that the HMR holds for all mixtures of the non-polar molecules here considered with the exception of those involving He or H_2. In order to complete the set of combining rules, we assume the Lorentz rule for the diameters and one of the following rules: Berthelot, Hudson–McCoubrey and Fender–Halsey. With these rules, the pure-substance parameters in Table I and the ANC model for $B_{ANC}(T)$ (Eq. (*3*)), we can predict the second virial coefficient for any mixture and compare it with experiment. The results of these predictions are given in Tables IV for different types of molecules. The tables contain the diameter δ_{12} obtained from the Lorentz rule and, for each of the three combining rules considered, the tables give the energy ε_{12}, the softness s_{12} and the root-mean-square deviation Q of the model $B(T)$ from the experimental data. The comparison of the energy rules in the tables allows to assess the adequacy of each to predict $B_{12}(T)$.

We start by considering the mixtures of noble gases and diatomic molecules in Table IVA. Since these mixtures are not too asymmetric, with potential parameters of similar magnitude, all three energy rules give similar values of ε_{12} and s_{12}. They give also almost equally good predictions, with small deviations from the data. Nevertheless, on a closer look, we can regard the Fender–Halsey rule as slightly more accurate; not only because it

TABLE IVA
Predicted cross interaction parameters of binary mixtures assuming the HMR. Mixtures of noble gases and diatomic molecules with Lorentz rule for the diameters and different rules for the energy

System	Lorentz	Berthelot			Hudson–McCoubrey			Fender–Halsey		
	δ nm	εk^{-1} K	s	Q^a cm^3 mol^{-1}	εk^{-1} K	s	Q^a cm^3 mol^{-1}	εk^{-1} K	s	Q^a cm^3 mol^{-1}
Ne–Ar	0.3370	76.82	0.9214	2.6	73.92	0.9461	2.1	63.34	1.0451	1.5
Ne–Kr	0.3520	90.58	0.8595	5.1	83.95	0.9079	4.3	67.45	1.0482	3.1
Ne–Xe	0.3694	106.54	0.7897	3.4	93.36	0.8727	3.4	70.70	1.0506	4.0
Ar–Kr	0.3835	172.04	0.9906	2.2	170.94	0.9947	2.2	169.73	0.9993	2.3
Ar–Xe	0.4009	202.36	0.9656	5.4	196.71	0.9837	3.2	191.99	0.9993	1.4
Kr–Xe	0.4159	238.59	0.9909	5.4	236.73	0.9959	4.6	235.49	0.9993	4.1
Ne–N_2	0.3472	73.27	0.9155	3.3	69.23	0.9519	2.8	62.00	1.0226	2.3
Ne–CO	0.3507	76.65	0.8943	2.3	71.22	0.9413	2.1	63.27	1.0172	2.1
Ne–O_2	0.3337	80.52	0.8923	3.3	75.96	0.9296	3.5	64.59	1.0335	5.8
Ar–N_2	0.3787	139.2	0.9543	2.4	138.9	0.9557	2.4	139.0	0.9550	2.3
Ar–CO	0.3822	145.6	0.9408	2.4	144.8	0.9444	2.4	145.6	0.9408	2.4
Ar–O_2	0.3652	152.9	0.9713	2.3	151.9	0.9758	2.1	152.8	0.9720	2.1
Kr–CO	0.3972	171.6	0.9229	2.7	171.6	0.9229	2.7	169.3	0.9318	1.6
Xe–N_2	0.4111	193.0	0.8986	3.0	189.8	0.9092	2.0	180.2	0.9424	1.1
Xe–CO	0.4146	201.9	0.8894	3.6	200.1	0.8949	2.9	191.4	0.9235	1.2
N_2–CO	0.3924	138.9	0.9022	1.4	138.6	0.9033	1.4	138.7	0.9029	1.4
N_2–O_2	0.3754	145.9	0.9260	4.0	144.4	0.9324	4.3	145.2	0.9288	4.1

[a] Q is the root-mean-square-deviation of the predicted values of $B(T)$ from the experimental data.

TABLE IVB
Predicted cross interaction parameters of binary mixtures assuming the HMR. Mixtures of noble gases with *n*-alkanes. Explanation of symbols is as in Table IVA

System	Lorentz	Berthelot			Hudson–McCoubrey			Fender–Halsey		
	δ nm	εk^{-1} K	s	Q^a $cm^3\ mol^{-1}$	εk^{-1} K	s	Q^a $cm^3\ mol^{-1}$	εk^{-1} K	s	Q^a $cm^3\ mol^{-1}$
Ar–CH_4	0.3816	175.2	0.9495	4.9	173.8	0.9548	5.1	172.3	0.9602	5.3
Ar–C_2H_6	0.4156	229.5	0.8746	4.3	218.3	0.9066	2.5	207.8	0.9381	2.2
Ar–C_3H_8	0.4341	274.1	0.8000	2.9	251.8	0.8533	1.0	227.4	0.9184	5.1
Ar–*n*-C_4H_{10}	0.4508	313.0	0.7401	6.1	277.3	0.8148	13.3	239.7	0.9071	21.4
Ar–*n*-C_5H_{12}	0.4679	342.9	0.6965	24.2	292.6	0.7928	16.3	247.1	0.8995	15.2
Ar–*n*-C_6H_{14}	0.4839	368.3	0.6655	26.5	302.7	0.7835	10.4	252.2	0.8983	7.3
Ar–*n*-C_7H_{16}	0.4970	393.1	0.6348	16.5	312.6	0.7709	7.3	256.5	0.8952	18.8
Ar–*n*-C_8H_{18}	0.5100	413.9	0.6114	10.3	318.0	0.7664	15.2	259.6	0.8940	31.2
Kr–CH_4	0.3966	206.6	0.9525	1.3	206.5	0.9530	1.2	206.6	0.9526	1.3
Kr–C_2H_6	0.4306	270.6	0.8973	6.5	265.0	0.9107	5.1	259.8	0.9238	3.8
Xe–CH_4	0.4140	243.0	0.9386	1.1	241.3	0.9432	0.2	240.5	0.9452	0.3
Xe–C_2H_6	0.4480	318.3	0.9033	4.2	317.2	0.9055	3.6	315.8	0.9083	2.9

TABLE IVC
Predicted cross interaction parameters of binary mixtures assuming the HMR. Mixtures of diatomic molecules with *n*-alkanes. Explanation of symbols is as in Table IVA

System	Lorentz	Berthelot			Hudson–McCoubrey			Fender–Halsey		
	δ nm	εk^{-1} K	s	Q cm^3 mol^{-1}	εk^{-1} K	s	Q cm^3 mol^{-1}	εk^{-1} K	s	Q cm^3 mol^{-1}
N_2–CH_4	0.3918	167.1	0.8966	1.9	166.4	0.8993	1.8	162.8	0.9134	1.4
N_2–C_2H_6	0.4258	218.9	0.8099	7.2	211.8	0.8307	7.8	194.1	0.8859	9.5
N_2–C_3H_8	0.4443	261.5	0.7320	13.3	245.9	0.7694	16.3	211.1	0.8650	23.2
N_2–n-C_4H_{10}	0.4610	298.5	0.6710	8.3	272.2	0.7258	10.5	221.7	0.8529	15.9
N_2–n-C_5H_{12}	0.4781	327.0	0.6276	12.4	288.6	0.7002	13.7	227.9	0.8451	20.9
N_2–n-C_6H_{14}	0.4941	351.3	0.5964	12.3	299.8	0.6870	17.6	232.3	0.8431	28.9
N_2–n-C_7H_{16}	0.5072	375.0	0.5662	8.7	310.6	0.6720	18.3	235.9	0.8397	33.4
N_2–n-C_8H_{18}	0.5202	394.8	0.5432	5.6	317.0	0.6651	18.1	238.5	0.8381	35.8
O_2–CH_4	0.3783	183.7	0.9216	3.4	182.6	0.9254	3.3	182.0	0.9275	3.2
O_2–n-C_5H_{12}	0.4646	359.3	0.6715	19.9	306.8	0.7664	33.7	267.4	0.8521	44.4
O_2–n-C_6H_{14}	0.4806	386.1	0.6411	4.1	317.0	0.7579	24.9	273.4	0.8499	38.3
O_2–n-C_7H_{16}	0.4938	412.0	0.6109	1.4	327.1	0.7459	26.9	278.4	0.8460	43.5

TABLE IVD

Predicted cross interaction parameters of binary mixtures assuming the HMR for T_B. Mixtures of *n*-alkanes with *n*-alkanes. Explanation of symbols is as in Table IVA

System	Lorentz	Berthelot			Hudson–McCoubrey			Fender–Halsey		
	δ nm	εk^{-1} K	s	Q $cm^3\ mol^{-1}$	εk^{-1} K	s	Q $cm^3\ mol^{-1}$	εk^{-1} K	s	Q $cm^3\ mol^{-1}$
CH_4–C_2H_6	0.4287	275.7	0.8461	3.3	265.9	0.8689	5.3	270.1	0.8590	4.4
CH_4–C_3H_8	0.4472	329.2	0.7778	5.6	298.8	0.8383	12.1	314.8	0.8056	7.8
CH_4–n-C_4H_{10}	0.4638	375.9	0.7219	10.1	320.5	0.8200	20.5	349.6	0.7660	14.3
CH_4–n-C_5H_{12}	0.4809	411.8	0.6805	18.5	333.7	0.8080	31.4	371.3	0.7423	23.4
CH_4–n-C_6H_{14}	0.4970	442.4	0.6517	9.4	343.2	0.8043	31.4	386.3	0.7317	20.1
CH_4–n-C_7H_{16}	0.5101	472.1	0.6224	6.6	351.2	0.7987	27.7	400.7	0.7179	17.6
CH_4–n-C_8H_{18}	0.5231	497.1	0.6002	3.2	357.0	0.7958	67.1	409.6	0.7118	42.3
C_2H_6–C_3H_8	0.4812	432.1	0.7514	4.5	424.5	0.7610	6.9	429.2	0.7543	5.2
C_2H_6–n-C_4H_{10}	0.4979	492.4	0.7026	6.0	469.6	0.7309	14.8	484.6	0.7121	8.2
C_2H_6–n-C_5H_{12}	0.5150	539.4	0.6650	5.9	498.7	0.7112	29.3	522.2	0.6838	15.7
C_2H_6–n-C_6H_{14}	0.5310	579.5	0.6399	5.7	520.2	0.7029	36.9	550.4	0.6696	19.7
C_2H_6–n-C_8H_{18}	0.5571	651.1	0.5930	11.6	552.3	0.6869	32.3	595.4	0.6432	13.5
C_3H_8–n-C_4H_{10}	0.5163	588.0	0.6560	9.0	582.9	0.6611	12.3	586.1	0.6579	10.2
C_3H_8–n-C_5H_{12}	0.5335	644.1	0.6211	5.0	628.4	0.6352	17.5	636.2	0.6281	11.0
C_3H_8–n-C_6H_{14}	0.5495	692.0	0.5985	7.1	662.9	0.6226	25.4	674.9	0.6125	15.4
C_3H_8–n-C_7H_{16}	0.5626	738.6	0.5737	35.6	693.0	0.6087	16.6	710.8	0.5947	19.4
C_3H_8–n-C_8H_{18}	0.5756	777.6	0.5550	74.5	716.0	0.6000	37.3	737.2	0.5839	47.4
n-C_4H_{10}–n-C_5H_{12}	0.5501	735.5	0.5819	7.1	732.4	0.5842	10.3	733.34	0.5835	9.4
n-C_4H_{10}–n-C_6H_{14}	0.5661	790.1	0.5611	14.2	779.8	0.5683	9.5	782.0	0.5667	9.4
n-C_4H_{10}–n-C_8H_{18}	0.5923	887.9	0.5202	11.4	854.3	0.5404	19.2	861.4	0.5361	13.4
n-C_5H_{12}–n-C_6H_{14}	0.5832	865.5	0.5309	11.4	863.3	0.5322	12.9	863.6	0.5321	12.7
n-C_5H_{12}–n-C_7H_{16}	0.5964	923.8	0.5085	2.1	915.2	0.5133	9.4	917.1	0.5122	7.5
n-C_5H_{12}–n-C_8H_{18}	0.6094	972.6	0.4918	0.7	955.6	0.5007	18.5	958.6	0.4991	15.2
n-C_6H_{14}–n-C_8H_{18}	0.6254	1044.9	0.4746	7.9	1037.8	0.4779	3.1	1039.4	0.4772	2.1
n-C_7H_{16}–n-C_8H_{18}	0.6385	1115.2	0.4543	8.0	1113.7	0.4549	5.7	1113.8	0.4549	5.8

has a smaller overall deviation, but also because this rule is intrinsically better in dealing with conformal and nearly conformal systems. Indeed, it is the only rule to give an adequate answer in the limiting case of a conformal mixture, where both substances and the cross interaction should have equal softness. To exhibit this point we substitute $s_1 = s_2$ in Eqs (*12*), (*13*) and (*14*) to get, after simplification,

$$T^{*\mathrm{B}}(s_{12}) = \frac{2\sqrt{\varepsilon_1 \varepsilon_2}}{\varepsilon_1 + \varepsilon_2} T^{*\mathrm{B}}(s_1) \tag{15}$$

$$T^{*\mathrm{B}}(s_{12}) = \frac{I_1 + I_2}{2\sqrt{I_1 I_2}} \frac{d_{12}}{\sqrt{d_1 d_2}} \frac{2\sqrt{\varepsilon_1 \varepsilon_2}}{\varepsilon_1 + \varepsilon_2} T^{*\mathrm{B}}(s_1) \tag{16}$$

and

$$T^{*\mathrm{B}}(s_{12}) = T^{*\mathrm{B}}(s_1) \; . \tag{17}$$

It can be immediately seen that in the general conformal case ($\varepsilon_1 \neq \varepsilon_2$, $\delta_1 \neq \delta_2$, $s_1 = s_2$), only the third rule (Fender–Halsey) makes the cross interaction conformal to the other two ones. Table IVA contains three strictly conformal mixtures (with $s_1 = s_2 = 0.9993$): Ar–Kr, Ar–Xe and Kr–Xe. For them the Fender–Halsey rule prediction of $B(T)$ is the closest to $B_{\mathrm{exp}}(T)$ (it has the smallest Q).

We now consider systems involving alkanes. Their predicted interaction parameters are given in Tables IVB (mixtures with noble gases), IVC (mixtures with diatomic molecules) and IVD (mixtures with other alkanes). These parameters and the consequent mean deviation Q from $B_{\mathrm{exp}}(T)$ were obtained in the same way as those of noble gases in Table IVA. The three energy-combining rules give almost equal results for mixtures that are nearly conformal. These mixtures are those of CH_4 with a noble gas or a diatomic molecule, and those with two *n*-alkanes differing only in one carbon atom: CH_4–C_2H_6, C_2H_6–C_3H_8, C_3H_8–*n*-C_4H_{10}, *n*-C_4H_{10}–*n*-C_5H_{12}, *n*-C_5H_{12}–*n*-C_6H_{14}, *n*-C_7H_{16}–*n*-C_8H_{18}. In systems of higher *n*-alkanes with diatomic molecules or of two alkanes differing in two or more carbon atoms, the Berthelot rule is clearly superior to the other two ones; almost in all cases it gives smaller mean deviations than the Fender–Halsey or Hudson–McCoubrey rules. The exceptions seem to be C_3H_8–*n*-C_7H_{16} and C_3H_8–*n*-C_8H_{18}, and, to a lesser extent, n-C_4H_{10}–n-C_6H_{14} and n-C_6H_{14}–n-C_8H_{18}. The results for n-alkanes with noble gases in Table IVB, however, look little systematic: the Berthelot rule gives very good agreement for the mixtures of Ar–CH_4, Ar–C_4H_{10} and Ar–n-C_8H_{18}, and again for Kr–CH_4 and Xe–CH_4 mixtures. Nevertheless, this rule seems to give poor predictions for Ar–n-C_5H_{12}, Ar–n-C_6H_{14} and Ar–n-C_7H_{16}.

In order to determine the possible origin of a poor prediction by the Berthelot rule in the cases pointed out above we have first to look directly at the $B_{exp}(T)$ data. We consider first the mixtures of Ar with CH_4, C_2H_6, C_3H_8 and C_4H_{10}. Figure 5 shows $B_{exp}(T)$ for each of these systems together with the ANC predictions using the Berthelot rule, which agrees very well with the data. Next, in Fig. 6, we show the difficult cases of mixtures of Ar with n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16} and n-C_8H_{18} clearly showing that the disagreement of the theory with the data is due to the poor quality of the latter. The case of the mixtures C_3H_8–n-C_7H_{16} and C_3H_8–n-C_8H_{18} can similarly be ascribed to experimental data of very poor quality.

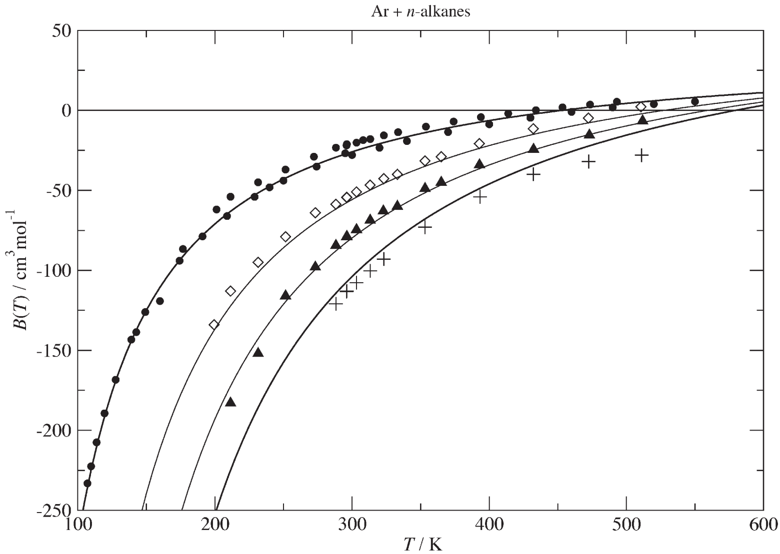

FIG. 5
Cross second virial coefficient in mixtures of Ar with n-alkanes. B_{12} experimental data of Ar with CH_4 (●), C_2H_6 (◇), C_3H_8 (▲) and n-C_4H_{10} (+). The lines are the ANC predictions using the HMR with the rules of Lorentz and Berthelot

All the above means that the Berthelot rule for the energy, the Lorentz rule for the diameters and the corresponding HMR for the softness constitute a set of combining rules which, when used jointly with the ANC potentials, gives a good prediction of all the 66 systems in Tables IV. Nevertheless, for mixtures of a noble gas with another noble gas or with a diatomic, the Fender–Halsey rule may be considered better. The results of the Hudson–McCoubrey rule are very close to those of the Berthelot rule.

As the final exercise we predict the cross interactions in systems with *n*-nonane, *n*-decane and *n*-dodecane. No direct measurements of $B(T)$ for these hydrocarbons have been reported in the literature. Nevertheless, there are data on several mixtures involving them, namely for *n*-C_9H_{20}, *n*-$C_{10}H_{22}$ and *n*-$C_{12}H_{26}$ mixed with Ar, N_2 and CH_4. Here we calculate $B_{12}(T)$ for these systems by a simple procedure. First, we obtain the ANC parameters for *n*-C_9H_{20}, *n*-$C_{10}H_{22}$ and *n*-$C_{12}H_{26}$ based on previous analyses of the ANC interactions of the first 8 alkanes. This analysis affords formulae $\varepsilon(n)$, $\delta(n)$ and $s(n)$ for the interaction parameters in terms of the number n of carbon

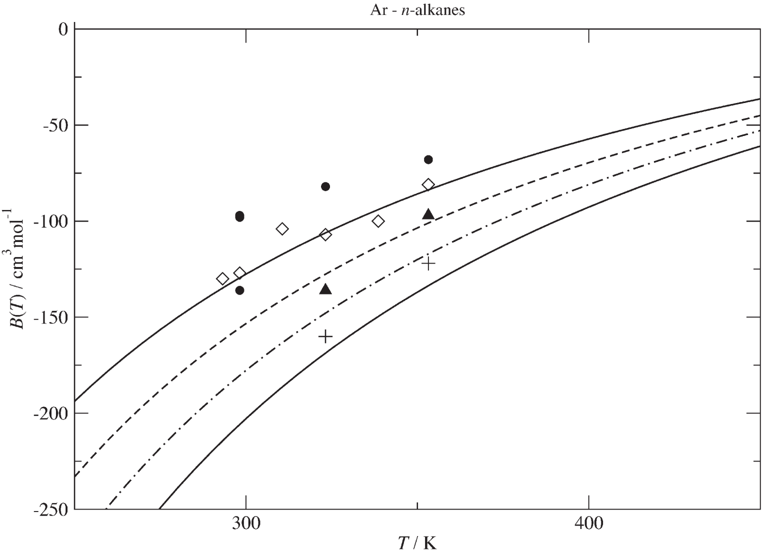

FIG. 6
Second virial coefficient in mixtures of Ar with *n*-alkanes. B_{12} experimental data of Ar with *n*-C_5H_{12} (●), *n*-C_6H_{14} (◇), *n*-C_7H_{16} (▲) and *n*-C_8H_{18} (+). The lines are the ANC predictions using the HMR with the rules of Lorentz and Berthelot for Ar–*n*-C_5H_{12} (solid line at the top), Ar–*n*-C_6H_{14} (dashed line), Ar–*n*-C_7H_{16} (dash-and-dotted line) and Ar–*n*-C_8H_{18} (solid line at the bottom)

atoms in the alkane[22]. The values of these parameters are given in Table V together with the calculated Boyle temperature for each substance. Second, we calculate the cross interaction parameters $\varepsilon_{12}(n)$, $\delta_{12}(n)$ and $s_{12}(n)$ for n = 9, 10 and 12 using the rules of Lorenz, Berthelot and HMR. Third, we calculate $B(T)$ from the ANC model. The resulting theoretical results $B_{ANC}(T)$ are then compared with experimental data in Figs 7 and 8 for mixtures with

TABLE V
Interaction parameters and Boyle temperatures T_B of the higher n-alkanes considered in this work

Substance	εk^{-1}, K	δ, nm	s	T_B, K
n-C_9H_{20}	1301.1	0.6791	0.4127	1311.8
n-$C_{10}H_{22}$	1414.7	0.7045	0.3902	1357.1
n-$C_{11}H_{24}$	1523.5	0.7290	0.3706	1397.9
n-$C_{12}H_{26}$	1627.5	0.7528	0.3535	1434.6

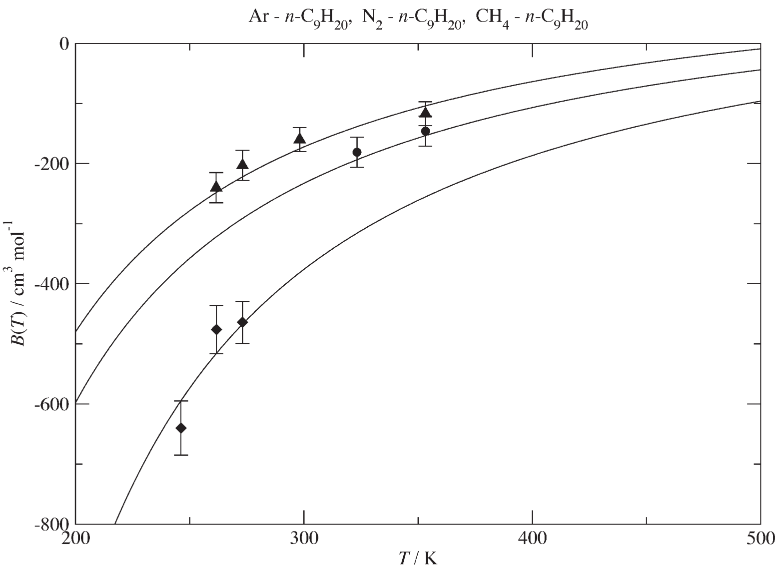

FIG. 7
Second virial coefficient in mixtures of n-nonane. B_{12} experimental data of n-C_9H_{20} with Ar (●), N_2 (▲) and CH_4 (◆). The lines are the ANC predictions using the HMR with the rules of Lorentz and Berthelot

n-C_9H_{20} and n-$C_{10}H_{22}$. The agreement of the theory with experiment is very good. However, in the mixture involving n-$C_{12}H_{26}$ for which $B_{12}^{\exp}(T)$ data are available, the prediction agrees poorly with the only two experimental points; the scarcity of the data does not permit to draw any firm conclusion.

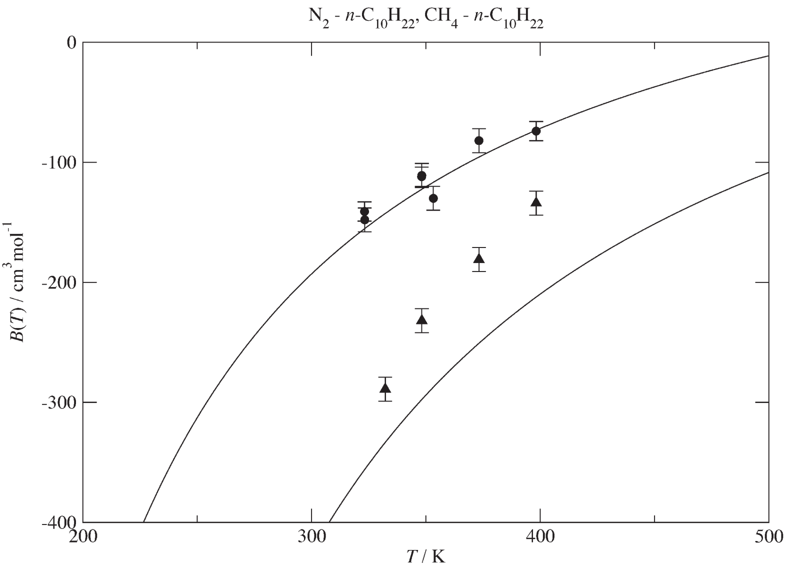

FIG. 8
Second virial coefficient in mixtures of n-decane. B_{12} experimental data of n-$C_{10}H_{22}$ with N_2 (●) and CH_4 (▲). The lines are the ANC predictions using the HMR with the rules of Lorentz and Berthelot

All the said above allows to use the HMR together with the Lorentz and Berthelot rules to predict the interaction parameters and virial coefficients for mixtures of non-polar substances, and in particular for the 50 binary mixtures of heavy noble gases, N_2 and O_2, and the first ten n-alkanes. The parameters of these interactions are not reported explicitly here since the reader can calculate them straightforwardly from the combining rules and parameters of pure compounds given in the present paper.

CONCLUSIONS

We have shown the existence of an empirical rule giving the Boyle temperature of the cross interaction as the harmonic mean of the T_B of the pure components. We have proven that this HMR is supported, with very good accuracy, by experimental $B(T)$ data for 28 binary mixtures. This rule should withhold in mixtures of non-polar molecules, except He and H_2, and for some polar molecules with not-too-high electrostatic moment mixed with not-too-polarisable molecules. Both quantum-mechanical effects and electrostatic interactions are factors explaining departures from the HMR.

The virial coefficients of non-polar substances can be predicted with good accuracy using the ANC potentials and the combining rules of Lorenz, Berthelot and the HMR. The prediction of cross interactions in systems containing *n*-alkanes with 9 and 10 carbons agrees very well with experiment.

SYMBOLS

a	hard-core diameter of the Kihara potential function
B	second virial coefficient
B_{12}	cross second virial coefficient
B_{ANC}	second virial coefficient of ANC system
B^*	reduced second virial coefficient
B^*_{ANC}	reduced second virial coefficient of ANC system
B^*_0	reduced reference second virial coefficient
B_{exp}	experimental value of the second virial coefficient
B^{exp}_{12}	experimental value of the cross second virial coefficient
C	third virial coefficient
I_j	ionization energy of *i*-th species
i, j	particle number
k	Boltzmann constant
Q	root-mean-square deviation
r	centre-to-centre distance
s	softness form parameter
s_i	softness of *i*-th species
s_{12}	softness of cross interaction
s^0_{12}	initial value of softness parameter
T	temperature
T^*	reduced temperature
T_{B}	Boyle temperature
$T^{*\mathrm{B}}$	reduced Boyle temperature
T^{B}_i	Boyle temperature of *i*-th species
T^{B}_{12}	Boyle temperature of cross interaction
u_{ANC}	ANC-type potential function
u_0	reference potential function
$u_{\alpha\beta}$	cross interaction potential (between dissimilar species)
z	dimensionless distance
α	molecular polarisability
α^*	reduced molecular polarisability
δ	mean molecular diameter
δ_{12}	cross mean molecular diameter

δB_{eq}	error in B equivalent to deviation δT_B
δB_{exp}	estimated experimental error in B
δT_B	deviation of experimental Boyle temperature from the mean harmonic rule
$\delta\rho_V$, $\delta\rho_L$	statistical errors in vapour and liquid densities
ε	attractive energy parameter
ε_i	energy parameter of i-th interaction
ε_{12}	energy parameter of cross interaction
μ	dipole moment
μ^*	reduced dipole moment
ζ	auxiliary variable

The authors wish to thank Dr O. Guzmán for insightful comments on this manuscript. This work was supported by the CONACYT (Mexico) project SEP-2003-43586. J. A. González-Calderón acknowledges a scholarship from CONACYT.

REFERENCES

1. Rowlinson J. S., Swinton F. L.: *Liquids and Liquid Mixtures*, 3rd ed. Butterworths, London 1980.
2. Cappelletti D., Vecchiocattivi F., Pirani F., Heck E. L., Dickinson A. S.: *Mol. Phys*. **1998**, *93*, 485.
3. Steinebrunner G., Dyson A. J., Kirchner B., Huber H.: *J. Chem. Phys*. **1998**, *109*, 3153.
4. Bukowski R., Sadlej J., Jeziorski B., Jankowski P., Szalewicz K., Kucharski S. A.: *J. Chem. Phys*. **1999**, *110*, 3785.
5. Munro L. J., Johnson J. K., Jordan K. D.: *J. Chem. Phys*. **2001**, *114*, 5545.
6. Aziz R. A., Slaman M. J.: *Mol. Phys*. **1986**, *58*, 679.
7. Barrow D. A., Aziz R. A.: *J. Chem. Phys*. **1989**, *89*, 6189.
8. Barrow D. A., Slaman M. J., Aziz R. A.: *J. Chem. Phys*. **1989**, *91*, 6348.
9. Schindler H., Vogelsang R., Staemmler V., Siddiqi M. A., Svejda P.: *Mol. Phys*. **1993**, *80*, 1413.
10. Cagide Fajín J. L., López Cacheiro J., Fernández B., Makarewicz J.: *J. Chem. Phys*. **2004**, *120*, 8582.
11. a) Kihara T.: *Rev. Mod. Phys*. **1953**, *25*, 831; b) Kihara T.: *Adv. Chem. Phys*. **1963**, *5*, 147.
12. Zarkova L., Hohm U., Damyanova M.: *Int. J. Thermodyn*. **2004**, *25*, 1775.
13. London F.: *Trans. Faraday Soc*. **1930**, *33*, 8.
14. a) Kirkwood J. G.: *Z. Phys*. **1932**, *33*, 57; b) Müller A.: *Proc. R. Soc. London, Ser. A* **1936**, *154*, 624.
15. Hudson G. H., McCoubrey J. C.: *Trans. Faraday Soc*. **1960**, *56*, 761.
16. Fender B. E. F., Halsey G. D., Jr.: *J. Chem. Phys*. **1962**, *36*, 1881.
17. Berthelot D.: *C. R. Acad. Sci*. **1898**, *126*, 1837.
18. Sikora P. T.: *J. Phys. B* **1970**, *3*, 1475.
19. a) Kong C. L.: *J. Chem. Phys*. **1973**, *59*, 968; b) Kong C. L.: *J. Chem. Phys*. **1973**, *59*, 1953; c) Kong C. L.: *J. Chem. Phys*. **1973**, *59*, 2464.
20. a) Díaz Peña M., Pando C., Renuncio J. A. R.: *J. Chem. Phys*. **1982**, *76*, 325; b) Díaz Peña M., Pando C., Renuncio J. A. R.: *J. Chem. Phys*. **1982**, *76*, 333.

21. a) del Río F., Ramos J. E., McLure I. A.: *J. Phys. Chem. B* **1998**, *102*, 10568; b) Ramos J. E., del Río F., McLure I. A.: *J. Phys. Chem. B* **1998**, *102*, 10576.
22. a) McLure I. A., Ramos J. E., del Río F.: *J. Phys. Chem.* **1999**, *103*, 7019; b) del Río F., Ramos J. E., McLure I. A.: *Phys. Chem. Chem. Phys.* **1999**, *1*, 4937; c) Ramos J. E., del Río F., McLure I. A.: *Phys. Chem. Chem. Phys.* **2000**, *2*, 2731; d) Ramos J. E., del Río F., McLure I. A.: *Phys. Chem. Chem. Phys.* **2001**, *3*, 2634; e) del Río F., McLure I. A., Chávez J., Ramos J. E., Ávalos E.: *Mol. Phys.* **2006**, *104*, 3757.
23. del Río F., Guzmán O., Ramos J. E., Ibarra-Tandi B. F.: *Phase Equilib.* **2007**, *259*, 9.
24. Thomaes G., van Steenwinkel R., Stone W.: *Mol. Phys.* **1962**, *5*, 301.
25. Smith F. T.: *Phys. Rev. A* **1972**, *5*, 1708.
26. Waldman M., Hagler A. T.: *J. Comput. Chem.* **1993**, *14*, 1077.
27. Delhommelle J., Millié P.: *Mol. Phys.* **2001**, *99*, 619.
28. Vedeneev V. I., Gurvich L. V., Kondratev V. N., Medvedev V. A.: *Bond Energies, Ionization Potential, and Electron Affinities*. Arnold, London 1966.
29. http://webbook.nist.gov/chemistry.
30. Dymond J. H., Marsh K. N., Wilhoit R. C., Wong K. C. in: *Virial Coefficients of Pure Gases and Mixtures* (M. Frenkel and K. N. Marsh, Eds), Group IV, Vol. 21, A & B. Landolt–Börnstein, Berlin Heidelberg 2002.