

Interaction between Unlike Nonpolar Molecules: Correction of the Geometric Mean Rule

Part 2. Dilute Systems

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Equations for correcting the geometric mean rule are established from published values of the attraction coefficients for dispersion forces and experimental correction factors for unlike critical temperatures. For the 131 systems examined (composed of noble gases, hydrogen, nitrogen, oxygen, carbon monoxide, normal and branched alkanes, cyclohexane, aromatic hydrocarbons, carbon tetrafluoride, and monochlorodifluoromethane) it is possible to account for the correction factors with almost the same precision as the original data used.

The preceding paper¹ gave the basic formulae for correcting geometric mean rules for calculating interactions between unlike molecules from those between the like molecules involved. In this paper some more or less empirical correlations will be evaluated which enable us to calculate the geometric mean rule corrections for dilute (*i.e.* no correction for non-additivity of intermolecular forces is necessary) systems.

Numerical values of the attraction coefficients (k_{11}^o , k_{22}^o , and k_{12}) for dispersion forces are published by Dalgarno.² The systems are the like and the 28 unlike binary combinations of the noble gases He→Xe, hydrogen, nitrogen, and methane. From these data the products $f_I \cdot f_\alpha$ are obtained (Ref. 1, eqn. (3)).

Chueh and Prausnitz^{3,4} have compiled correction factors (which they call $1-k$) to the geometric means for critical temperatures. In this way experimental values of $f_I \cdot f_\alpha \cdot f_d^2 \cdot f_N \cdot f_c$ (Ref. 1, eqn. (27)) are available for 68 non-polar and weakly polar systems composed of normal and branched alkanes (C₁→C₈), cyclohexane, benzene, toluene, naphthalene, noble gases (He→Kr), hydrogen, nitrogen, oxygen, and tetrafluoromethane. Estimated and interpolated values are neglected together with systems involving ethylene, propylene, acetylene, carbon dioxide, and hydrogen sulphide, to ensure that dispersion forces alone are acting.

The same unlike critical temperature correction factors (called β) are determined by Brewer⁵ for 35 systems composed of noble gases (Ne→Xe), hydrogen, nitrogen, carbon monoxide, methane, propane, and monochlorodifluoromethane (F-22). Here, too, carbon dioxide systems are disregarded.

The correction factor f_d

f_d is defined in Ref. 1, eqn. (12); for d_{12} is used the arithmetical mean of d_{11}° and d_{22}° . These, in turn, are supposed to be proportional to the cube roots of the zero-point volumes, v° .

The correction factors f_N and f_c

In order to calculate f_N (Ref. 1, eqn. (13)), values of the repulsive exponents (n°) of the Lennard-Jones (6- n) potential functions are needed. Twenty-eight such values are taken from the tables 4-6 and 8-10 of Moelwyn-Hughes.⁶ (Carbon, metals, and hydrogen-bonded substances are neglected in establishing eqn. (1).) As $n^{\circ} > 6$, and as n° is assumed to increase with increasing molecular size, the data suggest

$$n^{\circ} = 6 + 0.145 \cdot v^{\circ} (\text{cm}^3/\text{mol}) \quad (1)$$

Even though this relationship (and/or the data used) needs more investigation (correlation coefficient=0.639) it will be used temporarily for the present purpose.

For the ten systems common to Dalgarno, and to Chueh and Prausnitz, and the twenty-one systems common to Dalgarno, and to Brewer, $f_1 \cdot f_{\alpha}$ and f_d^2 are eliminated, so that only $f_N \cdot f_c$ is left. It is seen from Ref. 1, eqns. (13), (24)-(26), and (28), that n_{12} is the only unknown quantity. After solving these equations with respect to n_{12} , the following empirical relationship is established

$$n_{12}^E \equiv n_{12} - \frac{1}{2}(n_{11}^{\circ} + n_{22}^{\circ}) = A(I) \cdot A(n^{\circ}/I)/3 \quad (2)$$

(correlation coefficient=0.957), where I is the ionisation potential and, e.g., $A(n/I) \equiv n_{11}^{\circ}/I_1 - n_{22}^{\circ}/I_2$.

The correction factors f_1 and f_{α}

Now the products $f_1 \cdot f_{\alpha}$ are available, immediately for Dalgarno's systems, but also for Chueh and Prausnitz' and Brewer's systems after eliminating $f_N \cdot f_c$ (with n_{12} from (2)) and f_d^2 .

From Ref. 1, eqns. (4) and (5), is seen that the unknown quantities are now the polarisability (α_1) of component 1 interacting with component 2, and the polarisability (α_2) of 2 interacting with 1.

Polarisabilities are related to refractive indices through the Lorentz-Lorentz equation, but to avoid defining molal volumes for a pair of isolated molecules, the zero-point volumes will be used and the resulting "refractive indices" denoted η . Thus for the pure substances

$$(\eta^{\circ})^2 = (2P + 1)/(1 - P); \quad P \equiv (4\pi/3) \cdot N_0 \cdot \alpha^{\circ}/v^{\circ} \quad (3)$$

Using the Lorentz-Lorenz equation simultaneously for α_i^0 and α_i one has

$$\alpha_i = \alpha_i^0 \frac{[\eta_i^2 - 1] \cdot [(\eta_i^0)^2 + 2]}{[(\eta_i^0)^2 - 1] \cdot [\eta_i^2 + 2]} \quad (i = 1, 2) \quad (4)$$

Macroscopic excess refractive indices are, to a first approximation and at least better than excess polarisabilities, parabolic and might be represented by $x_1 \cdot x_2 \cdot \text{constant}$, where x is the mole fraction. When the same approximation is used for η , one has for $x_1 = x_2 = \frac{1}{2}$ (as interactions between pairs of molecules are considered)

$$\eta_1 = \eta_1^0 - y \quad (5a)$$

$$\eta_2 = \eta_2^0 - y \quad (5b)$$

From the known values of $f_1 \cdot f_\alpha$, y was calculated for each of the 131 systems. It turns out that the following empirical relationship holds

$$y = \Delta(1/U) \cdot \Delta(\eta \cdot U) \cdot [0.0563 - 0.0883 \cdot (|\Delta\kappa|/(\kappa_1 + \kappa_2))^{1/3}] \quad (6)$$

Table 1. The data for the pure substances.

	κ	v^0 (cm ³ /mol)	$\alpha^0 \times 10^{24}$ (cm ³ /mol)	I (eV) ^d
He	2	20.93 ^c	.20364 ^f	24.581
Ne	6	13.07 ^c	.39256 ^f	21.559
Ar	6	21.86 ^c	1.6264 ^f	15.755
Kr	6	27.09 ^c	2.4559 ^f	13.996
Xe	6	34.71 ^c	3.9989 ^f	12.127
H ₂	2	13.4 ^b	.8023 ^f	15.427
N ₂	6	26.2 ^a	1.734 ^f	15.60
O ₂	8	21.8 ^a	1.561 ^f	12.21
CF ₄	24	42.3 ^b	4.02 ^h	17.8
F-22 ^m	20	45.7 ^a	(5.30) ^e	(10.8) ^e
CO	8	26.7 ^a	1.926 ^f	14.01
CH ₄	8	26.3 ^a	2.699 ^f	12.99
C ₂ H ₆	14	41.2 ^a	4.326 ^f	11.65
C ₃ H ₈	20	56.2 ^a	6.31 ⁱ	11.21
n-C ₄ H ₁₀	26	71.2 ^a	8.30 ⁱ	10.80
i-C ₄ H ₁₀	26	71.2 ^l	8.27 ⁱ	10.79
n-C ₅ H ₁₂	32	86.1 ^a	10.00 ⁱ	10.55
i-C ₅ H ₁₂	32	86.1 ^l	10.03 ^j	10.60
n-C ₆ H ₁₄	38	101.1 ^a	11.81 ⁱ	10.48
n-C ₇ H ₁₆	44	116.1 ^a	13.69 ⁱ	10.35
n-C ₈ H ₁₈	50	131.0 ^a	15.50 ⁱ	10.24
c-C ₆ H ₁₂	36	86.2 ^a	10.98 ^g	9.88
C ₆ H ₆	30	71.3 ^b	9.89 ^f	9.21
C ₆ H ₅ ·CH ₃	36	85.9 ^b	12.33 ^j	8.82
C ₁₀ H ₈	48	105.8 ^b	17.58 ^h	8.12

^a Sugden,⁷ eqn. (4). ^b Sugden⁸ from atomic and structural constants. ^c Grosse.⁹ ^d Vedenyev *et al.*¹⁰ ^e Estimated values. ^f Moelwyn-Hughes,⁶ p. 383. ^g Unpublished, result. ^h Watson *et al.*¹¹ ⁱ Landolt-Börnstein. ^j Selected values.¹² ^k Selected values.¹³ ^l The values for the corresponding n-alkanes are used. ^m F-22 is CHClF₂.

where $U = I \cdot \sqrt{\kappa}$, and κ is the number of electrons in the outer shells. The correlation coefficient is 0.615, but as y always appears together with η^0 , eqn. (5), the precision of η is about $\pm 1\%$.

AGREEMENTS AND COMMENTS

Using the data of Table 1, $f_I \cdot f_\alpha$ are calculated for the Dalgarno systems, and $f_I \cdot f_\alpha \cdot f_d^2 \cdot f_N \cdot f_c$ for Chueh and Prausnitz' and for Brewer's systems. The agreements are shown on Figs. 1–3.

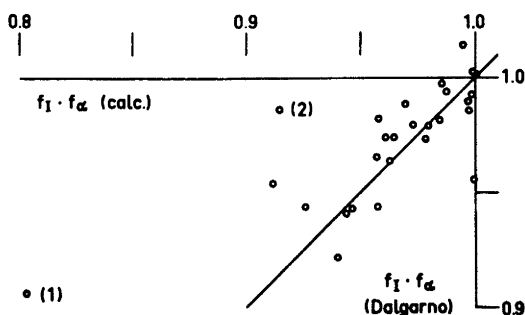


Fig. 1. Calculated correction factors to the geometric mean rule for dispersion forces compared to the data of Dalgarno.² (1): $H_2 + Ne$; (2): $He + Ne$.

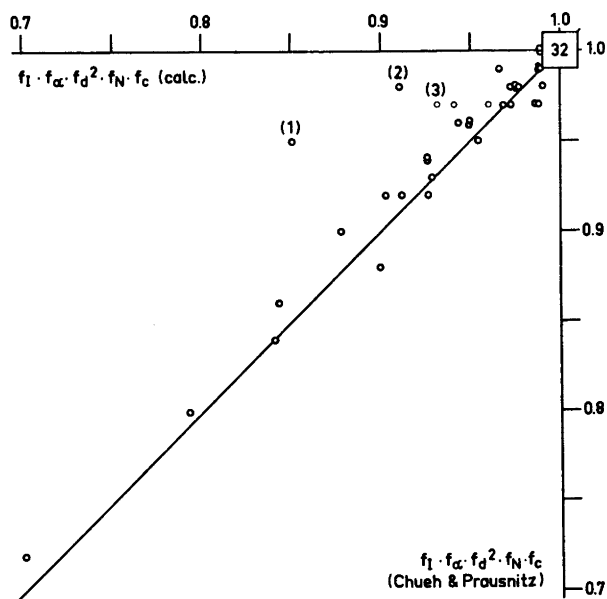


Fig. 2. Calculated correction factors to the geometric mean rule for unlike critical temperatures compared to the data of Chueh and Prausnitz.^{3,4} (1): $He + Ar$; (2): $CF_4 + N_2$; (3): $H_2 + CH_4$. 32 points appear in the upper right square.

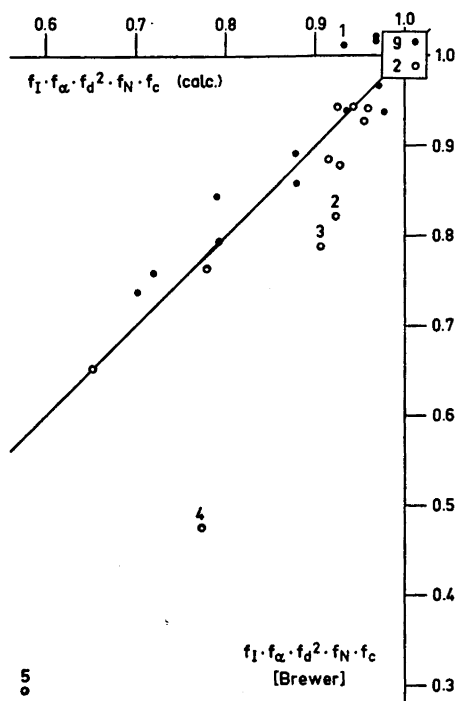


Fig. 3. Calculated correction factors to the geometric mean rule for unlike critical temperatures compared to the data of Brewer.⁵ (1): $\text{H}_2 + \text{CH}_4$; (2): $\text{F-22} + \text{N}_2$; (3): $\text{F-22} + \text{Ar}$; (4): $\text{F-22} + \text{H}_2$; (5): $\text{C}_3\text{H}_8 + \text{Ne}$. Systems with one or two of the gases Xe, F-22, and C_3H_8 (see text) are indicated by \circ . 9 (\bullet) + 2 (\circ) points appear in the upper right square.

Table 2. Correlation coefficients for $f[\text{total}]$ (Dalgarno, Chueh and Prausnitz, or Brewer) taken together with $f[\text{total}](\text{calc.})$ and with $f[\text{total}](\text{calc.})$, divided by each of the f -factors in turn.

Authors	Excluded systems (see text)	No. of systems	Correlation coefficients for $f[\text{total}]$ (D, CP or B) taken together with					
			$f[\text{total}](\text{calc.})$	$f[\text{total}](\text{calc.})$ divided by				
				f_1	f_α	f_d^2	f_N	f_c
Dalgarno ^a	$\text{He} + \text{H}_2$	27	0.744	0.027	0.636	—	—	—
Chueh and Prausnitz ^b	C_2H_4 , C_3H_8 , C_2H_2 , CO_2 , and H_2S	68	0.954	0.903	0.938	0.675	0.468	0.952
Brewer ^c	CO_2	35	0.890	0.906	0.771	0.801	0.571	0.892
Brewer ^c	CO_2 , Xe, F-22 and C_3H_8	21	0.952	0.873	0.931	0.959	0.469	0.957

^a Ref. 2. ^b Refs. 3–4. ^c Ref. 5.

The most serious disagreement occurs for $\text{He} + \text{H}_2$ ($f_1:f_\alpha$: Dalgarno: 0.94 and calc.=1.15). The reason might be “quantum effects”. This system is excluded from Fig. 1 and from the correlation coefficients.

The standard deviation for Dalgarno's systems is 2.9 %. This is the same order of magnitude as claimed by Dalgarno:¹ "With the possible exception of interactions involving Xe, in no case should the error exceed 10 % and it is usually much smaller."

Chueh and Prausnitz report their data (converted to f) with two significant figures, *e.g.*, $f = 0.98$, so that the precision is about ± 0.01 . This is in agreement with the standard deviation found (0.018).

The standard deviation of Brewer's systems is 0.043, calculated from his data, compared to 0.080 for the theory presented here. The standard deviation of Brewer reflects, however, only his reproducibility and curve fitting. Systematic errors caused by solubility of Xe, F-22, and C₃H₈ in particular in the manometer oil are stressed by Brewer. When the systems involving one or more of these three gases are excluded, the standard deviations are in better agreement: 0.024 (Brewer) and 0.031 (this work).

On the whole it appears possible, with the theory presented here, to account for corrections to the geometric mean rule with almost the same precision as the original data.

To examine the possibility that one of the correction factors could in general be so close to one that it can be safely ignored, correlation coefficients were calculated with one of the correction factors removed in turn from the calculated $f(\text{total})$. It is seen from Table 2 that only f_c can be ignored, but even in this case $\Delta(I)$ must not be too large. For Ne + CH₄, for example, $\Delta(I) = 8.6$, $f[\text{total}] = 0.72$ (Chueh and Prausnitz), and $= 0.70$ (calc.), but $f[\text{total}]/f_c = 0.65$. In general, f_c^{-1} increases approximately proportional to $(|\Delta I|)^3$.

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