

Second Cross Virial Coefficients for Interactions Involving Water. Correlations and Group Contribution Values

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A simple method is presented for estimating the second cross virial coefficients for interactions involving water. It is based on the Tsonopoulos corresponding-states correlation and consists of a semiempirical equation for evaluating the mixture-specific parameter k_{12} of this correlation. The general structure of this equation is guided by a theory-based relation, which is valid for interactions between spherical nonpolar molecules. An empirical extension of this relation to interactions involving water was done by replacing the "energy" term with a function of the Gibbs energy of hydration of a compound at 298 K and 0.1 MPa. This correlation is supported by experimental B_{12} values for interactions between water and numerous compounds that differ greatly in size and strength of water–solute interactions. Limitations of this empirical correlation are briefly discussed. In addition, available B_{12} data for interactions between water and normal alkanes, from ethane to octane, strongly suggest the applicability of a group contribution method to predict the second cross virial coefficients between water and organic compounds. For interactions between water and large organic molecules, the group contribution approximation is the method of choice for B_{12} predictions. These findings were employed to predict the B_{12} values from (275 to 1200) K for interactions between water and many inorganic and small organic compounds (halogenated derivatives of methane and ethene), as well as for many functional groups of organic compounds.

Introduction

Values of the second virial coefficients for interactions involving water are needed for corrections of nonideality effects in aqueous mixtures at low densities. These data are of interest for industrial applications (design of combustion and humid air turbines, air conditioners, cryogenic apparatus, etc.), as well as for development of theory (testing the potential energy functions for orientation-dependent interactions where at least one of compounds, water, has an appreciable dipole moment and is able to form "hydrogen bonds"). Experimental results for interactions involving water are scarce. In a previous communication¹ we compiled and critically evaluated the experimental B_{12} data for the interactions between H₂O and 32 other compounds, greatly differing in size, polarity, and strength of water–solute interactions. In our nomenclature, B_{12} is the cross (unlike) second virial coefficient, the index 1 stands for water, and the index 2 designates any other compound. These results are examined now in an attempt to find ways to estimate B_{12} values for many interactions of interest, for which no experimental data are available. In particular, we propose a semiempirical method to estimate k_{12} , the mixture-specific parameter for the Tsonopoulos corresponding-states correlation.^{2–4} In addition, available B_{12} data for interactions between water and normal alkanes, from ethane to octane, strongly suggest the applicability of a group contribution method to predict

the second cross virial coefficients between water and organic compounds. These findings were employed to predict the B_{12} values from (275 to 1200) K for interactions between water and many inorganic and small organic compounds (halogenated derivatives of methane and ethene), as well as for many functional groups of organic compounds.

Estimation of Mixture-Specific Interaction Parameters for the Tsonopoulos Correlation

Tsonopoulos Corresponding-States Correlation. The Tsonopoulos expression for correlation of the second virial coefficient B for pure compounds is given by^{2,5}

$$B(T)P_c/RT_c = f^{(0)} + \omega f^{(1)} + a_{T_s} f^{(2)} + b_{T_s} f^{(3)} \quad (1)$$

where P_c and T_c are the critical pressure and temperature, respectively; $f^{(0)}$, $f^{(1)}$, $f^{(2)}$, and $f^{(3)}$ are universal functions of the reduced temperature, T/T_c ; ω is the Pitzer acentric factor; the parameter a_{T_s} is a function of the reduced dipole moment^{2,5} of a compound or a parameter specific for some classes of compounds (for water $a_{T_s} = -0.0109^3$); and b_{T_s} is another parameter needed for some classes of "hydrogen-bonded" compounds (alcohols).

The Tsonopoulos correlation can be extended to mixtures, or to unlike (cross) interactions. Although eq 1 remains valid, a set of combining rules is employed to evaluate P_c , ω , a_{T_s} , and b_{T_s} for a mixture.^{2,5} Only one mixture-specific parameter, k_{12} , is needed for each unlike binary interaction, and this new parameter appears in the combining rule for the critical temperature of a binary mixture:

$$T_{c12} = (T_{c1} T_{c2})^{1/2} (1 - k_{12}) \quad (2)$$

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We evaluated k_{12} for 29 interactions between water and other compounds.¹ Most of these compounds are nonpolar or have small dipole or quadrupole moments (for example, Ar, CO, C₂H₄, etc.), a few have appreciable dipole moments (chloromethane, for example), some exhibit relatively large dipole moments and form “hydrogen bonds” with water (alcohols and ammonia), and, finally, specific chemical forces are expected to come into play for interactions between H₂O and HCl. This inventory spans a wide range of solute–water interactions and provides a strong basis for a search for correlations to estimate the mixture-specific parameter k_{12} .

Approximate Theory of the k_{12} Parameter for Spherical Molecules. An approximate theory of the mixture-specific parameter k_{12} is available for the case of interactions between spherical nonpolar molecules of different sizes, where only dispersion forces contribute to the attractive branch of the intermolecular potential energy functions.^{6,7} The relation for T_{c12} can be written as

$$T_{c12} = (T_{c1}T_{c2})^{1/2}f(\text{energy})f(\text{size}) \quad (3)$$

where

$$f(\text{energy}) = \left\{ \frac{2(I_1I_2)^{1/2}}{I_1 + I_2} \right\} \quad (4)$$

where I is the first ionization potential of a molecule and

$$f(\text{size}) = \left\{ \frac{64(V_{c1}V_{c2})}{(V_{c1}^{1/3} + V_{c2}^{1/3})^6} \right\} \quad (5)$$

where V_c stands for the critical volume of a compound.

A comparison of eqs 2 and 3 shows that for the case of interactions between nonpolar molecules the following relation is valid:

$$(1 - k_{12}) = f(\text{energy})f(\text{size}) \quad (6)$$

Empirical Extension to Interactions Involving Water. The “energy term”, given by eq 4, is of no use for interactions involving water, where the contribution of dispersion forces is expected to be negligible in comparison with much larger contributions to the attractive part of the intermolecular potential energy due to electrostatic and specific chemical forces. Nevertheless, we accept the general form of eq 6, assuming that $(1 - k_{12})$ is equal to the product of two terms, the “energy term” and the “size term”. We also retain the analytical form of the “size term”, eq 5, assuming that the possible inadequacy of this term is of secondary importance. However, another approximation has to be proposed for the “energy term” for interactions involving water. Empirically, we found a correlation between the “energy term” and the standard Gibbs energy of hydration at 298.15 K and 0.1 MPa, $\Delta_h G^\circ$. The Gibbs energy of hydration contains contributions due to universal dispersion and repulsive forces, due to the different kinds of multipolar forces (dipole–dipole, dipole–quadrupole, dipole–induced dipole, etc.), and contributions due to “hydrogen bonds” and specific chemical forces.

This property, $\Delta_h G^\circ$, is not a perfect descriptor of the energetics of interactions between molecules of water and a solute in the gas phase, mainly because of the high density of water at ambient conditions and, as a result, much bigger contributions of repulsive forces. Still, one can defend the choice of $\Delta_h G^\circ$ as a descriptor to correlate k_{12} . For example, the difference in $\Delta_h G^\circ$ between the polar

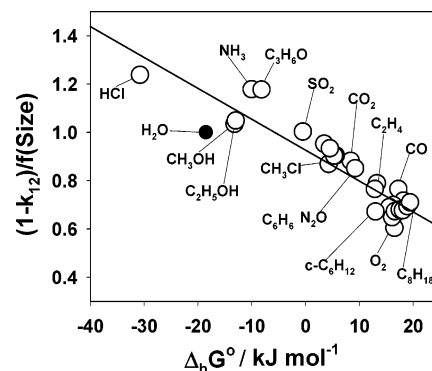


Figure 1. Values of $(1 - k_{12})/f(\text{size})$ (open circles) plotted against $\Delta_h G^\circ$; see text. The filled circle shows the corresponding value for water–water interactions. The solid line is given by eq 9. Note that not all compounds are labeled due to space limitations.

compound 1-butanol and its nonpolar homomorph butane is about 29 kJ·mol⁻¹.⁸ This number is notably larger than the increase in $\Delta_h G^\circ$ within homologous series of either normal alkanes or 1-alcohols when going from a compound with carbon number one to a compound with the carbon number 8 (approximately 5–6 kJ·mol⁻¹).⁸ Therefore, we expect that $\Delta_h G^\circ$ is much more sensitive to the polarity of the “building blocks” of a molecule than to the amount of these “building blocks”, despite the fact that the contribution of repulsive “hard-body” forces increases quickly with the size of a solute.⁷ We provide these arguments as a justification of our choice to use $\Delta_h G^\circ$ as a measure of the extent of attractive forces between water and other molecules: the more attractive the water–solute interactions are, the less (more negative) is the value of $\Delta_h G^\circ$.

In Figure 1 we plot the values of $(1 - k_{12})/f(\text{size})$, shown as open circles, against $\Delta_h G^\circ$. The values of the Gibbs energy of hydration of solutes at 298.15 K and 0.1 MPa are taken from literature compilations.^{8–11} Numerical values of $\Delta_h G^\circ$ depend on the standard state conventions adopted. In this communication the standard state adopted for an aqueous nonelectrolyte is the hypothetical state of the pure substance in water of unit activity at molality equal to one at any temperature and pressure; the standard state adopted for a gas is the ideal gas of unit fugacity at any temperature and a pressure of 0.1 MPa.¹² The Gibbs energy of hydration of pure water is equal to the standard Gibbs energy of vaporization of liquid water, $\Delta_{\text{vap}} G^\circ$, with the opposite sign, recalculated into the molality concentration scale: $\Delta_h G^\circ = -\Delta_{\text{vap}} G^\circ - RT \ln(1000/M_w) = -8.59 - 9.96 = -18.55$ kJ·mol⁻¹, where $M_w = 18.0152$ g·mol⁻¹ is the molar mass of water and the standard Gibbs energy of vaporization of liquid water is taken from the CODATA recommendations.¹² For the neutral ionic pair HCl_(aq)^o the value of $\Delta_h G^\circ = -30.8$ kJ·mol⁻¹ was calculated as follows:

$$\Delta_h G^\circ = \Delta_f G^\circ(\text{HCl}_{(\text{aq})}^\circ) - \Delta_f G^\circ(\text{HCl}_{(\text{g})}) \quad (7)$$

with

$$\Delta_f G^\circ(\text{HCl}_{(\text{aq})}^\circ) = \Delta_f G^\circ(\text{Cl}_{(\text{aq})}^-) - RT \ln K_{\text{ass}} \quad (8)$$

where the values of $\Delta_f G^\circ(\text{Cl}_{(\text{aq})}^-)$ and $\Delta_f G^\circ(\text{HCl}_{(\text{g})})$ are taken from the NBS tables.¹¹ The value of the association constant at 298.15 K and 0.1 MPa of HCl_(aq)^o, $K_{\text{ass}} = 10^{-0.90}$, is accepted from ref 13. This result is based on an empirical extrapolation to “pure water” of the values of K_{ass} of HCl in water–organic mixtures from conductance measurements, and it may bear an appreciable uncertainty, up to 1 log unit. We could not find experimental data

leading to $\Delta_h G^\circ$ of hexafluorobenzene, so k_{12} for the water–hexafluorobenzene interactions is not plotted in Figure 1. For He–water, H₂–water, and Ne–water interactions the corresponding-state correlations are not applicable,⁷ so k_{12} values for these interactions were not determined.

Examination of Figure 1 shows that there is a correlation between the “energy term”, $f(\text{energy}) = (1 - k_{12})/f(\text{size})$, for interactions involving water, and the Gibbs energy of hydration of a solute at 298.15 K and 0.1 MPa, $\Delta_h G^\circ$. The relation is approximately linear and is given by the solid line in Figure 1 consistent with the relation:

$$(1 - k_{12})/f(\text{size}) = f(\text{energy}) = 0.926 - (1.28 \times 10^{-2})\Delta_h G^\circ \text{ (kJ}\cdot\text{mol}^{-1}) \quad (9)$$

In our interpretation, there is a distinct separation of solutes according to the strength of their interactions with water. The first group, where $\Delta_h G^\circ > (12 \text{ to } 14) \text{ kJ}\cdot\text{mol}^{-1}$, includes nonpolar compounds, for example, Ar, normal alkanes, and so forth. Solute in the second group, with $(5 \text{ to } 7) < \Delta_h G^\circ < (12 \text{ to } 14) \text{ kJ}\cdot\text{mol}^{-1}$, typically have zero dipole moments in the gas phase but possess appreciable quadrupole electric moments (CO₂, C₂H₄, etc.) and, as a result, have lesser values of the Gibbs energy of hydration compared to those for nonpolar compounds of comparable sizes. The next group, with $0 < \Delta_h G^\circ < (5 \text{ to } 7) \text{ kJ}\cdot\text{mol}^{-1}$, includes compounds with somewhat stronger interactions with water because of (1) appreciable dipole moments (CH₃-Cl, for example, has a dipole moment of 1.9 D) or (2) weakly polar compounds able to form “hydrogen bonds” with water, for example, benzene.¹⁴ The next group includes polar compounds, such as alcohols, NH₃, H₂O, and HCl, which form strong “hydrogen bonds” with water and, therefore, have more negative values of the Gibbs energy of hydration, $(-40 \text{ to } -30) < \Delta_h G^\circ < (0 \text{ to } -10) \text{ kJ}\cdot\text{mol}^{-1}$.

Equation 9 reproduces the available k_{12} results satisfactorily (see Figure 1), suggesting that the Gibbs energy of hydration at 298.15 K and 0.1 MPa is an appropriate measure of the “energy term” for interactions between water and many other solutes. The “size term” is of secondary importance compared to the “energy term”; nevertheless, the “size term” definitely improves the fit of k_{12} data for interactions between water and normal alkanes, where experimental data are available from ethane to octane. Of the 29 values of k_{12} used to derive eq 9, the experimental and calculated values differ by more than 0.07 for only 4 of them (O₂, HCl, NH₃, acetone), and for 13 of the 29, this difference is less than 0.04. On the basis of these comparisons, we expect that eq 9 predicts k_{12} for most interactions within ± 0.05 and for most interactions between water and other “hydrogen-bonded” compounds within ± 0.10 .

Limitations of This Empirical Extension. First, the “size term” given by eq 5 is appropriate only for spherical nonpolar molecules and it is not expected to be accurate for molecules with nonspherical shapes. Evidence of that inadequacy can be seen in Figure 2 where predicted k_{12} results are used to calculate B_{12} for interactions between water and normal alkanes with carbon number up to 12. Calculated values are shown by dashed lines. (Solid lines show the group contribution values discussed below.) Up to octane, the predicted values of B_{12} are reasonably close to experimental results, which are given by circles. However, calculations predict an unrealistic increase of B_{12} at low temperatures for alkanes with carbon number above 7. Therefore, we suggest limiting the use of the proposed method of k_{12} estimation to the first few, maybe 3 or 4,

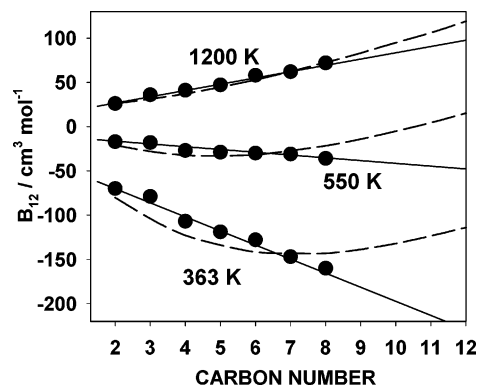


Figure 2. Values of B_{12} for interactions between water and normal alkanes at three temperatures from ref 1 (filled circles) plotted against carbon number: ---, values of B_{12} predicted using the proposed method of k_{12} estimation; —, values of B_{12} predicted using parameters for the CH₃ and CH₂ groups from Table 4.

members of homologous series of organic compounds, where inadequacies of the “size term” are not very severe.

Second, the corresponding-states principle states that it is impossible to have a two-term correlation that is applicable to all kinds of intermolecular interactions. Although the Gibbs energy of hydration is a complex function that contains contributions from different types of interactions, the principal limitations of two-term correlations are unavoidable.

Prediction of B_{12} for Interactions between Water and Inorganic Compounds and Halogenated Derivatives of Methane and Ethene

We employed the Tsonopoulos correlation in combination with eqs 5, 6, and 9 to estimate the cross second virial coefficients between water and some inorganic compounds. Results are presented in Table 1. The first column of the table gives the chemical formula of compound 2; compound 1 is always water. The Gibbs energy of hydration of a solute is given in the second column, if it was used to estimate the value of k_{12} according to eq 9. The estimated values of the parameter k_{12} are printed in the third column. The necessary auxiliary physical properties of compound 2 (T_c , P_c , V_c , μ , ω) are taken mainly from compilations^{5,15} or estimated⁵ where necessary. For convenience, the values of B_{12} , generated in this way at 275–1200 K, are fitted by a simple analytical relation valid for the square-well potential (SWP) given by

$$B_{12} = 2\pi N_A \sigma_{12}^3 / 3 \{ [1 - (\lambda_{12}^3 - 1) \exp\{\epsilon_{12}/k_B T\}] - 1 \} \quad (10)$$

where $N_A = 6.02214 \times 10^{23}$ stands for Avogadro’s number and k_B represents Boltzmann’s factor; σ_{12} is the collision diameter in Å (10^{-10} m), ϵ_{12}/k_B stands for the depth of the potential well; and λ_{12} is the well width in collision diameters.

As the correlated B_{12} values are approximate, it was found worthwhile to reduce the number of fitting parameters from three to two. This was accomplished using corresponding-states correlations to evaluate independently the λ parameter as a function of the Pitzer acentric factor, ω , and the dipole moment of a molecule, μ , see eqs A1–A3 in the Appendix. To extend correlations A1–A3 to estimate values of the potential width for cross interactions, λ_{12} , some combining rules have to be assigned to the cross acentric factor, ω_{12} , and the cross dipole moment, μ_{12} . In the absence of strong arguments to consider other relations, we adopted a simple mean relationship for the cross

Table 1. Results for Some Inorganic Compounds

compd 2	$\Delta_h G^\circ/\text{kJ}\cdot\text{mol}^{-1}$	k_{12}	λ_{12}	$10^{10}\sigma_{12}/\text{m}$	$(\epsilon_{12}/k_B)/\text{K}$
Ne ^a			1.454	2.533	61.6
Ar ^a			1.455	2.734	210.6
Kr	14.86 ⁹	0.28	1.454	3.21	253
Xe	13.45 ⁹	0.28	1.454	3.36	298
Rn	11.60 ⁹	0.28	1.458	3.49	337
SF ₆	20.62 ⁹	0.42	1.358	3.74	308
N ₂ ^a			1.436	3.17	202
H ₂ ^a			1.454	2.38	111
NF ₃	17.68 ⁹	0.33	1.351	3.36	317
D ₂	17.57 ¹⁶	0.30	1.533	2.94	91
N ₂ F ₄	17.51 ⁹	0.39	1.308	3.67	368
O ₂ ^a			1.443	3.10	185
CD ₄	16.30 ¹⁷	0.30	1.438	3.25	241
CO ^a			1.398	3.19	215
NO	15.49 ⁹	0.27	1.212	3.04	429
PH ₃	11.91 ⁹	0.26	1.356	3.25	418
AsH ₃	11.69 ⁹	0.24	1.401	3.38	410
NO ₂	11.4 ¹⁸	0.22	1.245	3.27	687
O ₃	10.9 ¹¹	0.23	1.294	3.23	447
COS	9.54 ⁹	0.25	1.328	3.33	492
N ₂ O ^a			1.345	3.21	459
CO ₂ ^a			1.355	3.19	468
Cl ₂	6.94 ¹¹	0.21	1.421	3.43	419
H ₂ Se	6.14 ⁹	0.19	1.380	3.25	482
H ₂ S	5.66 ¹²	0.17	1.324	3.10	554
NOCl	1.08 ¹¹	0.11	1.225	2.64	996
Br ₂	0.82 ¹¹	0.14	1.398	2.58	814
SO ₂ ^a			1.249	3.07	857
N ₂ O ₃	0.0 ¹⁸	0.19	1.193	3.20	834
N ₂ O ₄	0.0 ¹⁸	0.11	1.286	3.52	702
ClO ₂	-0.03 ⁹	0.11	1.216	2.80	1010
I ₂	-2.4 ¹⁹⁺¹²	0.12	1.401	2.49	1068
HCN	-6.06 ²⁰	0.06	1.183	2.72	1286
HN ₃	-6.3 ¹¹	0.07	1.183	2.80	1272
HNO ₂	-9.65 ²¹	-0.04	1.197	2.92	1296
NH ₃ ^a			1.248	2.04	1391
HF	-23.6 ¹¹	-0.22	1.209	2.48	1527
H ₂ O ₂	-28.46 ¹¹	-0.28	1.205	2.42	2052
HNO ₃	-28.6 ²²⁺¹¹	-0.20	1.140	3.11	1631
HCl ^a			1.298	2.61	958
N ₂ H ₄	-31.25 ¹¹	-0.21	1.226	2.28	1791

^a Values of B_{12} from ref 1 are used for the determination of σ_{12} and ϵ_{12}/k_B .

acentric factor

$$\omega_{12} = (\omega_1 + \omega_2)/2 \quad (11)$$

where for pure water $\omega_1 = 0.344$,⁵ and a simple geometric mean relationship for the cross dipole moment

$$\mu_{12} = (\mu_1\mu_2)^{1/2} \quad (12)$$

where for pure water $\mu_1 = 1.8$ D.⁵ Then the values of B_{12} from the Tsouopoulos correlation were fitted to the SWP relation, eq 10, with the fixed values of λ_{12} .

In Tables 2 and 3 we give the results of our predictions for halogenated derivatives of methane and ethene, respectively, for which we could find reliable values of the Gibbs energy of hydration at 298.15 K and 0.1 MPa.

Group Contribution Values for the Cross Virial Coefficients between Water and Organic Compounds

It is apparent in Figure 2 that the values of B_{12} for interactions between water and normal alkanes vary in a regular linear fashion with carbon number. The simplest explanation of this fact is the assumption that each of the alkanes is built-up from the CH₃ and CH₂ groups, which interact with water independently from each other, and the

Table 2. Results for Some Halogenated Derivatives of Methane

compd 2	$\Delta_h G^\circ/\text{kJ}\cdot\text{mol}^{-1}$	k_{12}	λ_{12}	$10^{10}\sigma_{12}/\text{m}$	$(\epsilon_{12}/k_B)/\text{K}$
CH ₄ ^a			1.449	3.29	230
CH ₃ F	7.02 ⁹	0.20	1.257	3.27	586
CH ₃ Cl ^a			1.267	3.15	710
CH ₃ Br	4.54 ⁹	0.20	1.258	3.15	737
CH ₃ I	4.21 ¹⁰	0.23	1.263	3.28	736
CH ₂ F ₂	6.62 ²³	0.20	1.232	3.29	667
CH ₂ Cl ₂	2.2 ²⁴	0.20	1.298	3.47	671
CH ₂ Br ₂	-0.90 ¹⁰	0.20	1.264	3.36	829
CH ₂ I ₂	-2.0 ²⁵	0.22	1.292	3.62	840
CH ₂ FCI	4.69 ⁹	0.21	1.264	3.42	663
CH ₂ ClBr	1.0 ²⁶⁺²⁷	0.19	1.253	3.31	827
CH ₂ ClI	0.3 ²⁵	0.22	1.261	3.40	815
CHF ₃	10.68 ⁹	0.26	1.244	3.33	538
CHCl ₃ ^a			1.273	3.36	775
CHBr ₃	-0.98 ¹⁰	0.25	1.294	3.65	752
CHF ₂ Cl	8.34 ⁹	0.26	1.261	3.42	573
CHCl ₂ Br	1.8 ²⁸	0.25	1.273	3.58	719
CHClBr ₂	0.2 ²⁸	0.24	1.273	3.45	824
CF ₄	20.97 ⁹	0.39	1.373	3.51	264
CCl ₄	8.1 ²⁹	0.33	1.367	4.01	463
CF ₃ Cl	17.73 ³⁰	0.38	1.309	3.58	372
CF ₃ Br	15.40 ¹⁰	0.36	1.301	3.63	412
CF ₂ Cl ₂	14.48 ³⁰	0.36	1.309	3.69	436
CFCl ₃	10.53 ²³	0.34	1.314	3.78	492

^a Values of B_{12} from ref 1 are used for the determination of σ_{12} and ϵ_{12}/k_B .

Table 3. Results for Some Halogenated Derivatives of Ethene

compd 2	$\Delta_h G^\circ/\text{kJ}\cdot\text{mol}^{-1}$	k_{12}	λ_{12}	$10^{10}\sigma_{12}/\text{m}$	$(\epsilon_{12}/k_B)/\text{K}$
C ₂ H ₄ ^b			1.413	3.46	332
C ₂ H ₃ Cl	7.63 ⁹	0.26	1.295	3.36	587
1,1-C ₂ H ₂ Cl ₂	8.2 ²⁸	0.30	1.249	3.49	649
1,1-C ₂ H ₂ F ₂	12.5 ³¹	0.30	1.286	3.38	463
1,2-C ₂ H ₂ Cl ₂	5.5 ²⁸	0.27	1.355	3.78	504
C ₂ HCl ₃	5.5 ³²	0.29	1.283	3.66	658
CF ₂ =CHCl	10.1 ²³	0.30	1.259	3.48	578
C ₂ F ₄	15.98 ⁹	0.35	1.354	3.66	342
C ₂ F ₃ Cl	12.6 ³¹	0.34	1.288	3.71	467
C ₂ Cl ₄	7.0 ³³	0.30	1.359	4.07	523

^a Values of B_{12} from ref 1 are used for the determination of σ_{12} and ϵ_{12}/k_B .

energetics of CH₃-H₂O and CH₂-H₂O interactions depend only on temperature but not on the nature of an alkane. This assumption is close to that often used in computer simulations where a molecule is approximated by a number of "sites", or centers of forces, that can interact with "sites" of another molecule independently of each other. With this in mind, Figure 2 can be seen as empirical evidence of the applicability of a group contribution approximation to the second cross virial coefficients between water and organic molecules. We would like to emphasize the high accuracy of the group contribution approximation in correlating experimental B_{12} values. For interactions between water and large organic molecules, the group contribution approximation appears to be a method of choice for B_{12} predictions. Assuming that the groups are independent of each other, we have chosen a first-order group contribution scheme. Note that similar first-order group contribution methods for second virial coefficients of like and unlike interactions were proposed earlier,³⁴⁻³⁸ however, not for interactions involving water. In the case where compound 1 is always water, the value of B_{12} is simply given by

$$B_{12}(T) = \sum_i n_i B_{1i}(T) \quad (13)$$

where n_i stands for the number of times the i -th group is present in the structure of an organic molecule 2 and B_{1i} is the value of the second virial coefficient for the interactions between water and the i -th group.

The simple group contribution approximation, given by eq 13, faces, of course, difficulties common to most additivity methods.³⁹ The first problem involves the empirical selection of groups, and the stoichiometry of groups chosen in this study is outlined below. Another problem is the inability of this simple method to distinguish between isomers, such as isobutylamine and *sec*-butylamine, for example. However, for such a poorly studied problem as B_{12} for interactions involving water, this deficiency seems of small importance. Finally, there is the problem of nearest-neighbor interactions (also called proximity effects or intramolecular bonding), when a molecule contains two or more functional groups in close proximity. As a result of additional electrostatic polarization, the properties of two neighboring groups differ from those of the same groups in states that are "isolated" from each other. An additional problem arises if a single water molecule may interact (bind) simultaneously with a number of functional groups, which are in close proximity within an organic molecule, rather than interact independently with each of them, as assumed by eq 13. The energetics of this interaction cannot, in general, be represented by the sum of separate interactions of water with each of the functional groups, and the simple additivity scheme under consideration will fail. In the framework of first-order group contribution schemes the usual method to account for proximity effects is to "construct" a new, larger group, which contains the interacting functional groups. As an example, to escape the potential "proximity effect" problems for small halogenated organic molecules, we decided not to use the group contribution approach for B_{12} of halogenated methanes and ethenes but to estimate properties for each of those compounds, where such an estimation is possible (see Tables 2 and 3).

The temperature dependence of B_{1i} , the second cross virial coefficients for interactions between water and the functional groups, was approximated by the analytical relation valid for the square-well potential given by eq 10. This approximation can be justified by the following heuristic argument. The square-well potential can be derived by approximating the molecule–water potential as either infinity, $-\epsilon_{12}$, or zero and then assigning the appropriate volumes (in the integration to get B_{12}) to the first two potential regions. Similarly, for a multifunctional molecule we can approximate the group–water interactions as either infinity, $-\epsilon_{1i}$, or zero and assign the appropriate volumes for the first two regions. In terms of σ_{1i} and λ_{1i} , the volumes are $V_{\infty,i} = 2\pi N_A \pi \sigma_{1i}^3 / 3$ and $V_{\epsilon,i} = V_{\infty,i} (\lambda_{1i}^3 - 1)$. As usual, in first-order functional group models, we ignore regions in space where water interacts simultaneously with two functional groups. In principle, second-order corrections could be made by adding a volume where the interaction is $(\epsilon_{1i} + \epsilon_{1j})$, but this has not been attempted. As done before for λ_{12} , the λ_{1i} parameter for functional group–water interactions was evaluated independently using eq A3 with values of μ_{1i} and ω_{1i} . In turn, μ_{1i} and ω_{1i} are determined from μ_i and ω_i with the combining rules given by eqs 11 and 12. This raises the problem of defining the dipole moment, μ_i , and the acentric factor, ω_i , for each of the groups in a situation where, in general, neither μ nor ω is an additive property. However, the acentric factor varies smoothly and approximately linearly with carbon number within a homologous series of organic compounds,

whereas the dipole moment is usually constant within a homologous series. Therefore, we approximated μ_i and ω_i of the group i by extrapolation to zero carbon number. Thus, the formalism of eqs A3, 11, and 12 can be empirically extended to determine the λ_{1i} parameter for many groups from the known properties of monofunctional organic compounds in the corresponding homologous series.

The SWP parameters of $\text{H}_2\text{O} + \text{CH}_3$ and $\text{H}_2\text{O} + \text{CH}_2$ interactions were determined by a global fit of B_{12} data recommended¹ for normal alkanes from ethane to octane. It was assumed that the SWP parameters of the $\text{H}_2\text{O} + \text{CH}_3$ and $\text{H}_2\text{O} + \text{CH}_2$ interactions are transferable even in the case of interactions between water and an organic compound containing strongly polar groups (carboxylic acid, amine, etc.). Parameters of the square-well potential for B_{1i} , where i represents many functional groups, were determined in the following way. First, we used eq 9 to determine the mixture-specific parameter k_{12} of the Tsoupoloulos correlation for two to four of the smallest members of a homologous series. Then, using estimated values of k_{12} , we calculated B_{12} values for these compounds at 275–1200 K, subtracted contributions of the $\text{H}_2\text{O} + \text{CH}_3$ and $\text{H}_2\text{O} + \text{CH}_2$ interactions, and obtained a number of B_{1i} values for each $\text{H}_2\text{O} + \text{group } i$ interaction. The averaged B_{1i} values were fitted to determine the SWP parameters, σ_{1i} and ϵ_{1i}/k_B , for a value of λ_{1i} , obtained by the method described above. The resulting values of the SWP parameters are given in Table 4 for interactions between water and many functional groups. For the OH, CO, CH_{ar} , C_{ar} , cyclic CH_2 , and Cl functional groups, we employed recommended¹ B_{12} values for interactions of water with methanol, acetone, benzene, toluene, cyclohexane, and chloroethane, respectively.

The necessary auxiliary physical properties of organic compounds are taken mainly from compilations.^{5,15} The usual sources of the Gibbs energy of hydration at 298 K are compilations;^{8–10} otherwise, we used numerous original publications of experimental values. For carboxylic acids, where experimental results have to be corrected for the presence of species other than monomers, we accepted the values of the critical parameters and acentric factors of carboxylic acid monomers evaluated by Jasperson et al.⁴⁰

Some comments concerning group selection and the problems encountered may be necessary. It was found that the calculated values of B_{1i} for interactions between water and the group C (the quaternary carbon) exhibit the physically unlikely behavior of having relatively large positive(!) values at low temperatures, which decrease (remaining positive) with temperature. This temperature dependence can be satisfactorily fitted by the SWP relation, eq 10, with a negative value of the σ_{12} parameter; see Table 4. One explanation is that the interactions between the quaternary carbon and water are effectively screened by the bulky methyl groups. So, we added the two new groups, $\text{C}(\text{CH}_3)_3$ and $\text{C}(\text{CH}_3)_2$, which can be used to represent compounds with the quaternary carbon, although the use of the group C (with the unphysical behavior of B_{1i}) seems to be a perfectly valid alternative. For aromatic hydrocarbons we use the following groups: HC_{ar} (benzene, for example), C_{ar} (alkylated benzenes, for example), the aryl–aryl bond $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}$ (necessary to "construct" biphenyl, for example, which is not identical to the sum of $10\text{HC}_{\text{ar}} + 2\text{C}_{\text{ar}}$ groups), and the fused carbon group in the polyaromatic hydrocarbons C_{fus} . It was decided to define as separate groups pairs of carbon atoms containing double or the triple bonds together with attached hydrogen atoms, for example, $\text{H}_2\text{C}=\text{CH}$, $\text{C}=\text{C}$, $\text{HC}\equiv\text{C}$, and others; see Table 4. We also

Table 4. Results for the Functional Groups of Organic Compounds

group <i>i</i>	λ_{1i}	$10^{10}\sigma_{1i}/\text{m}$	$(\epsilon_{1i}/k_B)/\text{K}$
CH ₃	1.430	2.788	283.8
CH ₂	1.430	2.226	271.4
CH	1.439	1.73	260 ^a
C	1.464	-2.421	265.7
C(CH ₃) ₂	1.420	2.957	261.4
C(CH ₃) ₃	1.394	3.668	304.0
H ₂ C=CH	1.348	2.96	446
HC=CH	1.341	2.51	525
H ₂ C=C	1.356	2.58	504
HC=C	1.348	1.89	702
C=C	1.368	1.54	753
C ₂ H ₂	1.368	3.39	404
HC≡C	1.304	2.72	662
C≡C	1.404	2.48	647
HC _{ar}	1.435	2.202	439
C _{ar}	1.376	1.63	859
C _{fus}	1.449	0.77	1419
C _{ar} -C _{ar}	1.430	0.52	1910
cyclic CH ₂	1.435	2.294	316
CF ₃	1.303	3.02	314
CCl ₃	1.285	3.28	647
CF ₂ Cl	1.327	3.19	375
CF ₂ Br	1.327	3.28	394
CFCl ₂	1.296	3.29	550
N	1.354	2.51	816
NH	1.295	2.68	928
NH ₂	1.276	2.70	988
O	1.308	2.49	780
HS	1.298	2.69	815
S	1.301	2.72	818
COO	1.253	2.94	920
F	1.330	2.34	515
Cl	1.327	2.50	814
Br	1.293	2.51	852
I	1.296	2.76	810
COH	1.236	2.85	1043
CO	1.232	2.76	1266
CN	1.206	2.75	1354
NO ₂	1.210	2.87	1231
CONH ₂	1.188	3.08	1829
CONH	1.190	3.14	1703
CON	1.220	3.08	1430
COOH (formate)	1.256	2.83	945
COOH (acid)	1.355	2.49	1136
H-COOH	1.369	2.31	1352
OH	1.182	2.56	1349

^a This value of ϵ_{12}/k_B was fixed in the fitting procedure.

define as separate groups CF₃, CCl₃, and CF₂Br (completely halogenated groups) to account for possible proximity effects. There are several possibilities for assigning groups for cyclic compounds. As an example, B_{12} can be considered as the sum of B_{1i} for the corresponding aliphatic groups and B_{1i} for the cyclic correction, specific for each ring geometry. However, as a first approximation to be used for cyclic compounds in the absence of experimental values, one can introduce just one cyclic CH₂ group and use "aliphatic" values for other groups constituting a cyclic compound; see Table 4.

It is difficult to judge objectively the accuracy of our estimates of B_{12} for water-organic compound interactions, because they are based on the semiempirical (at best) eqs 5, 6, and 9. We consider the values of the SWP parameters estimated in this paper as provisional for most interactions. The list of groups and the SWP parameters can be easily updated when new experimental B_{12} values become available.

Conclusions

An attempt is undertaken in this study to estimate the second virial coefficients for interactions between water and

many other compounds. The basis of the method is the semiempirical relation proposed for evaluating the mixture-specific parameter k_{12} of the Tsonopoulos corresponding-states correlation. The relation proposed, eq 9, can be viewed as an empirical extension of an approximate theory of interactions between spherical nonpolar compounds, where the "energy" term is replaced with a function reflecting the strength of intermolecular interactions between water and a solute. Although a number of possibilities may exist for choosing the appropriate functions, we selected the correlation with the Gibbs energy of hydration of a compound at 298 K and 0.1 MPa. This correlation is supported by the experimental B_{12} values for interactions between water and numerous compounds, greatly differing in size and the strength of the water-solute interactions. The limitations of this correlation are briefly discussed. In this way B_{12} values are estimated for many inorganic and organic compounds. As there is strong empirical evidence of the applicability of group additivity methods to B_{12} values, we used the proposed method to estimate group contribution values for the second virial coefficients between water and a number of functional groups of organic compounds. In all cases the SWP relations are used to describe the temperature dependence of the B_{12} values. We consider the values estimated in this paper as provisional and call for more experimental measurements of the second virial coefficients for interactions involving water.

Appendix. Corresponding-States Correlations for the λ Parameter of the Square-Well Potential

Values of the second virial coefficients, B , of more than 30 pure compounds, which are recommended over extended temperature ranges in the recent compilation by Dymond et al.,⁴¹ were employed to determine the parameters of the square-well potential for these substances. To extend the range of temperatures for some polar compounds up to at least 1000 K, we employed the Tsonopoulos^{2,5} correlation. The necessary values of the critical properties, μ and ω , are taken from Poling et al.⁵ For some compounds the values of the acentric factor are not given in that source and they are taken from ref 15. Results, including critical parameters of substances and temperature intervals of B , are given in Table 5. The numbers in parentheses show the 95% confidence limits of the last digit for the SWP parameters. These results are used in this study to search for corresponding-states correlations for the λ parameter of the square-well potential.

According to the principle of corresponding states,^{7,42} thermodynamic properties of heavier inert gases (Ar, Kr, Xe) and methane (small molecules with a spherically symmetrical force field) depend on only two variables. These are the so-called reduced potential energy and the reduced distance for the molecular variant of the corresponding states theory, or they may be chosen as the reduced volume and the reduced temperature for the macroscopic variant of this theory.⁷ As a consequence, when a three-parameter potential model (the square-well potential, SWP, in our case) is employed for these systems, only two parameters, σ and ϵ/k_B , are expected to be substance-specific. In addition, the connection between the macroscopic and molecular variants of the theory of corresponding states dictates that the ratios σ^3/V_c and $\epsilon/k_B T_c$ are constant and substance independent. The SWP parameters for Ar, Kr, Xe, and CH₄, calculated from second virial coefficient values, comply with these requirements of the theory. Indeed, the ratios σ^3/V_c and $\epsilon/k_B T_c$ are close to constant values of $(0.38 \pm 0.03) \times 10^{-24}$ mol and $0.68 \pm$

Table 5. Physical Properties and the SWP Parameters for Some Compounds

compd	T_c/K	P_c/bar	ω	μ/D	T_{range}/K	λ	$10^{10}\sigma/m$	$(\epsilon/k_B)/K$
Ar, argon	150.86	48.98	-0.002	0.0	81–1000	1.691 (13)	3.041 (15)	95.8 (25)
Kr, krypton	209.40	55.00	0.00	0.0	110–870	1.638 (7)	3.153 (18)	153.8 (25)
Xe, xenon	289.74	58.40	0.00	0.0	165–970	1.671 (15)	3.624 (18)	186.5 (57)
CH ₄ , methane	190.56	45.99	0.011	0.0	115–670	1.635 (8)	3.367 (8)	132.7 (22)
O ₂ , oxygen	154.58	50.43	0.022 ¹⁵	0.0	70–495	1.699 (47)	3.131 (31)	92.2 (88)
N ₂ , nitrogen	126.20	33.98	0.037	0.0	75–745	1.629 (16)	3.284 (19)	86.6 (28)
C ₂ H ₄ , ethene	282.34	50.41	0.087	0.0	200–470	1.561 (9)	3.836 (24)	215.2 (50)
C ₂ H ₆ , ethane	305.32	48.72	0.099	0.0	195–620	1.544 (15)	4.025 (40)	237.1 (91)
C ₃ H ₈ , propane	369.83	42.48	0.152	0.0	215–620	1.459 (38)	4.459 (38)	342.6 (64)
CF ₄ , tetrafluoromethane	227.51	37.45	0.177	0.0	175–770	1.516 (32)	4.136 (31)	175.3 (130)
C ₄ H ₁₀ , <i>n</i> -butane	425.12	37.96	0.200	0.0	245–585	1.412 (2)	4.845 (31)	435.5 (41)
SF ₆ , sulfur hexafluoride	318.72	37.60	0.208	0.0	200–545	1.395 (3)	4.398 (18)	335.4 (29)
C ₆ H ₆ , benzene	562.05	48.95	0.210	0.0	300–625	1.412 (15)	4.396 (188)	660.3 (196)
CO ₂ , carbon dioxide	304.12	73.74	0.225	0.0	220–770	1.397 (3)	3.416 (10)	327.8 (26)
C ₅ H ₁₂ , <i>n</i> -pentane	469.7	33.7	0.252	0.0	265–645	1.375 (2)	5.114 (26)	531.9 (30)
C ₆ H ₁₄ , <i>n</i> -hexane	507.6	30.25	0.300	0.0	300–660	1.298 (18)	5.27 (59)	705 (79)
C ₇ H ₁₆ , <i>n</i> -heptane	540.2	27.4	0.350	0.0	350–620	1.333 (10)	5.00 (20)	806 (24)
C ₆ F ₆ , hexafluorobenzene	516.73	32.75	0.396	0.0	305–620	1.248 (13)	4.50 (20)	966 (20)
C ₈ H ₁₈ , <i>n</i> -octane	568.7	24.9	0.399	0.0	340–620	1.265 (25)	5.36 (57)	951 (66)
C ₆ F ₁₄ , <i>n</i> -perfluorohexane	448.7	18.7	0.513	0.0	305–450	1.261 (8)	7.25 (27)	565 (33)
CO, carbon monoxide	132.85	34.94	0.045	0.1	125–570	1.638 (9)	3.339 (8)	88.9 (17)
N ₂ O, nitrous oxide	309.6	72.55	0.142	0.2	190–400	1.392 (4)	2.841 (46)	435.2 (67)
C ₆ H ₁₂ , cyclohexane	553.5	40.73	0.211	0.3	310–620	1.410 (10)	4.69 (16)	634 (18)
C ₃ H ₆ , propene	364.90	46.00	0.142	0.4	225–570	1.466 (5)	4.358 (31)	328.8 (55)
HCl, hydrogen chloride	324.69	83.1	0.132 ¹⁵	1.1	195–1000 ^a	1.409 (44)	3.17 (27)	380 (60)
CHCl ₃ , chloroform	536.5	55.0	0.222 ¹⁵	1.1	320–1500 ^b	1.363 (28)	4.52 (16)	637 (51)
NH ₃ , ammonia	405.4	113.53	0.257	1.5	240–595	1.295 (13)	2.493 (83)	727.1 (119)
CH ₃ OH, methanol	512.64	80.97	0.565	1.7	315–1500 ^c	1.095 (23)	2.95 (43)	1530 (80)
C ₂ H ₅ OH, ethanol	513.92	61.48	0.649	1.7	320–1500 ^c	1.081 (37)	3.35 (91)	1571 (230)
H ₂ O, water	647.14	220.64	0.344	1.8	273–1500 ^d	1.210 (13)	2.51 (12)	1307 (41)
C ₃ H ₆ O, acetone	508.1	47.0	0.307	2.9	300–1500 ^e	1.183 (8)	3.92 (35)	1116 (50)
CH ₃ NO ₂ , nitromethane	588.0	58.7	0.348	3.1	320–1500 ^f	1.166 (19)	4.16 (30)	1310 (19)

^a The Tsonopoulos correlation with $a_{TS} = -0.011$ was employed to estimate B from (500 to 1000) K. ^b The Tsonopoulos correlation with $a_{TS} = -0.003$ was employed to estimate B from (500 to 1500) K. ^c The Tsonopoulos correlation with a_{TS} and b_{TS} from ref 4 was employed to estimate B from (750 to 1500) K. ^d From the IAPWS-95 formulation.⁴³ ^e The Tsonopoulos correlation with $a_{TS} = -0.032$ was employed to estimate B from (500 to 1500) K. ^f The Tsonopoulos correlation with $a_{TS} = -0.047$ was employed to estimate B from (500 to 1500) K.

0.04, respectively, and the third parameter, λ , has a constant value of about 1.66 ± 0.03 ; see Table 5.

More complicated nonspherical, even nonpolar, molecules do not follow the two-parameter corresponding-states theory.^{7,42} Strongly polar, associated or hydrogen-bonded compounds do not follow it either. As a result, the ratios σ/V_c and $\epsilon/k_B T_c$, as well as the λ parameter, are not constant but become substance dependent. Following a widely used procedure, we plot values of λ from Table 5 versus ω , the Pitzer acentric factor, which can be considered as a measure of the nonsphericity of the force field of a molecule. To facilitate further analysis, data for nonpolar or slightly polar substances, with dipole moment magnitudes less than 0.5 D, are shown by open circles in Figure 3. The λ results for strongly polar compounds ($\mu > 0.5$ D) are shown in Figure 3 by filled circles. For both nonpolar and polar compounds, the values of λ (the relative width of the potential well) decrease with an increase of ω . This behavior is another illustration of the narrowing of the potential minimum (compared with that for simple fluids) of nonpolar and polar compounds, noticed and discussed by Pitzer in 1955.⁴² As values of λ for polar compounds are systematically lower than those for nonpolar compounds at similar values of the acentric factor ω (compare open and filled circles in Figure 3), the effect of narrowing of the potential minimum is expressed more strongly for polar substances.

Analytically, the dependence of λ on ω for nonpolar substances can be given by

$$\lambda = 1 + a_0 \exp[-b_0 \omega] \quad (\text{A1})$$

with $a_0 = 0.663$ (21) and $b_0 = 2.20$ (20), where the numbers

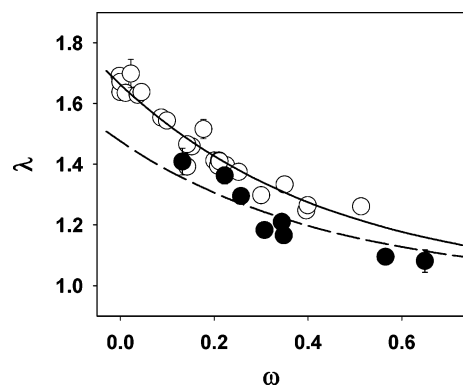


Figure 3. Values of the SWP parameter λ for pure compounds plotted against the acentric factor: \circ , nonpolar and slightly polar ($\mu < 0.5$ D) compounds; \bullet , compounds with $\mu > 0.5$ D; —, eq A1 for compounds with $\mu = 0$; - - -, eq A3 for compounds with $\mu = 1.7$.

in parentheses show the 0.95 confidence interval of the last digit. This relation satisfies two boundary conditions: (1) At $\omega = 0$ the value of λ must be equal to 1.66 ± 0.03 , that is, to the value empirically found for simple fluids (Ar, Kr, Xe, CH₄); see above. (2) $\lambda \rightarrow 1$ as $\omega \rightarrow \infty$, because the width of the potential well cannot be less than zero. Relation A1 is shown in Figure 3 by the solid line, and it is supposed to be valid for nonpolar compounds (open circles in Figure 3).

For polar compounds (filled circles in Figure 3) the relation giving λ as a function of ω must be modified to include the effect of polarity. From theoretical considerations, the appropriate parameter is the microscopic reduced dipole moment, defined as $\mu^2/\epsilon\sigma^3$, or, more conve-

niently, its macroscopic counterpart, the reduced dipole moment,^{2,5} $\mu_r = 10^5 \mu^2 P_c / (T_c)^2$. The following equation fits the data:

$$\lambda = 1 + a_0 \exp[-b_0 \omega - c_0 \mu_r] \quad (\text{A2})$$

with $c_0 = 2.38 (95) \times 10^{-3}$ and a_0 and b_0 retaining their values in eq A1. In addition, using the magnitude of the dipole moment (in D) as the sole characteristic of the polarity of a molecule gives an even slightly better fit:

$$\lambda = 1 + a_0 \exp[-b_0 \omega - d_0 \mu] \quad (\text{A3})$$

with $d_0 = 0.196 (41) \text{ D}^{-1}$ and a_0 and b_0 retaining their values in eq A1. Again, the numbers in parentheses show the 0.95 confidence interval of the last digit. Values of λ calculated by means of eq A3 for compounds with $\mu = 1.7 \text{ D}$, which is a representative value for many polar compounds in Table 5, are shown in Figure 3 by the dashed line.

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