Second Cross Virial Coefficients for Interactions Involving Water. Critical Data Compilation

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Values of the second cross virial coefficients, B_{12}, and isothermal Joule−Thomson coefficients, φ_{12}, for interactions involving water are compiled and, as necessary, evaluated from existing experimental data including *PVT* properties of gas mixtures, measurements of the pressure dependence of the molar excess enthalpies of a gas mixture, and measurements of the solubility of the condensed phases of H_2O (liquid water or ice) in compressed gases. In all, there are data for interactions between water and 32 other compounds, and among these, nine interactions involve compounds with appreciable dipole moments. These B_{12} values, typically available over a limited temperature range, are extrapolated to high temperatures by means of the Tsonopoulos corresponding-states correlation. Finally, the temperature dependence of the second cross virial coefficients between water and solutes at temperatures up to 1200 K is approximated by an empirical polynomial equation, the coefficients of which are tabulated for each interaction.

Introduction

The nonideality of a gaseous phase is often expressed by the virial equation of state.[1] In the volume or density series

$$Z = PV/RT = 1 + B/V + C/V^2 + ... \qquad (1)$$

where Z is the compressibility factor, P stands for the pressure, V is the molar volume of a gas mixture, T is the absolute temperature, R is the gas constant, and B and C are the temperature-dependent second and third virial coefficients. In the pressure series

$$Z = PV/RT = 1 + B'P + C'P^2 + ... \qquad (2)$$

where $B = B'RT$ and $C = (B'^2 + C')(RT)^2$. For a mixture the composition dependence of the second virial coefficient is rigorously given by[1]

$$B = \sum_i \sum_j y_i y_j B_{ij} \qquad (3)$$

with B_{ij} designating the second virial coefficient between (like or unlike) interacting components of a mixture i and j, and where y stands for the mole fraction of a component in a gas mixture. The virial equation of state truncated at the second virial coefficient may be used at low to moderate densities, in favorable cases up to about one-half the critical density of a fluid.[1] Thermodynamic properties of multicomponent mixtures at these densities can be rigorously calculated provided that the second virial coefficients for all possible pairs of compounds i and j, B_{ij}, are known. Second virial coefficients for pure gases are experimentally measured[2] or can be reliably estimated using corresponding-states correlations.[3,4] However, considerably less information is available for the cross virial coefficients, representing interactions between unlike, i.e., $i \neq j$, compounds, for instance, between Ar and Kr, between H_2O and CO_2, and so forth.[5] Although it can be argued[6−8] that the theory of the second virial coefficients is one of the most rigorous theories of intermolecular interactions, accurate experimental data are still necessary, at least to check the intermolecular potential energy functions proposed.

Reliable experimental results for interactions involving water are scarce. These data would be of interest for a variety of applications, from industrial (design of combustion engines, air conditioners, cryogenic apparatus, humid air turbines, etc.) to thermodynamic (corrections for nonideality effects for aqueous mixture at low fluid density) to theoretical ones (testing the potential energy functions for orientation-dependent interactions where at least one of the compounds has an appreciable dipole moment and is able to form “hydrogen bonds”). Therefore, the objective of this work is to compile reliable second cross virial coefficients, B_{12}, for interactions involving water and many inorganic and organic compounds, including polar ones. Here and below, the index “1” stands for water and “2” stands for any other compound.

This presentation is organized as follows: first, we discuss experimental methods used to obtain B_{12} results, with emphasis on the problems and limitations of these methods when applied to interactions involving water. Second, we collect the second cross virial coefficients, B_{12}, and cross isothermal Joule−Thomson coefficients, φ_{12}, reported in the literature or, in many cases, calculated by us from published primary experimental data. The virial coefficients of pure compounds, B_{22}, employed in the data treatment are taken, as a rule, from the recommendations of Dymond et al.,[2] whereas values of the second virial coefficient of pure water, B_{11}, are taken from the IAPWS-95 formulation of thermodynamic properties of water.[9] Third, we use the Tsonopoulos corresponding-state method[3] to correlate simultaneously the B_{12} and φ_{12} data. Finally,

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the selected experimental data and predictions of the corresponding-states correlation at high temperatures are described by empirical temperature polynomials to provide estimates of B_{12} up to 1200 K. When this work was close to completion, Dymond et al.[5] published a valuable compilation of cross virial coefficients, including those for interactions with water, that has many similarities in scope to the present study. Nevertheless, our work adds some new B_{12} results evaluated mainly from solubility data, and it also incorporates another property, the cross isothermal Joule−Thomson coefficients for interactions involving water, thus significantly increasing the inventory of relevant data.

Sources of B_{12} Data

The following experimental methods to obtain B_{12} values are used in the literature: measurements of the *PVT* properties of gas mixtures, measurements of the pressure dependence of the molar excess enthalpies of a gas mixture, and measurements of the solubility of the condensed phases of water (liquid water or ice) in compressed gases. An additional method consists of measuring the speed of sound in gases;[10] however, to our knowledge, this method has not yet been employed to study aqueous mixtures. It has to be kept in mind that virial coefficients are not directly measured properties, and reported *B* values may depend on the method of data treatment, especially for calorimetric and speed-of-sound measurements.

PVT Measurements of Gas Mixtures. The most traditional method for the experimental determination of virial coefficients consists of accurate measurements of *P*, *V*, and *T* for a gas phase of known composition at low pressures. It is recommended[1,7] that higher terms of the virial series be included in the data treatment, using the following relation:

$$(Z - 1)V = B + C/V + ... \tag{4}$$

When experimental values of $(Z - 1)V$ are plotted against density, the intercept and the slope give *B* and *C*, respectively. Even if higher terms of the virial series may affect the slope, their effect on the intercept, *B*, is usually negligible. Knowledge of virial coefficients for water, B_{11}, and the other compound, B_{22}, allows determination of the cross virial coefficient, B_{12}, from the value of *B* of a binary mixture according to the relation

$$B_{12} = (B - {y_1}^2 B_{11} - {y_2}^2 B_{22})/(2y_1y_2) \tag{5}$$

High-precision *PVT* measurements are essential, making numerous high-temperature *PVT* data sets with an accuracy of (0.3 to 0.5)% in density useless for the purposes of virial coefficient determination.

It is recognized that the *PVT* measurements may bear considerable errors due to physical and chemical adsorption on the inner walls of the experimental vessel.[8] This problem is particularly severe for polar compounds and especially for aqueous mixtures at low temperatures due to the strong affinity between water and silica, the main component of laboratory glass. Some recent high-quality *PVT* measurements have been corrected for adsorption errors.[11−13]

Excess Molar Enthalpy Measurements of Gas Mixtures. Information about *B* of a mixture and its temperature dependence can be gained from excess molar enthalpy measurements. These measurements, obtained using a flow calorimeter, are free from adsorption errors. Practically all data of this kind for aqueous mixtures have been measured by Wormald and co-workers; a recent example is given by ref 14. These calorimetric data greatly increase the inventory of experimental results leading to second virial coefficient data for interactions involving water.

The pressure dependence of the isothermal excess molar enthalpy, H_m^E, of a binary gas mixture can be written as a series in pressure:[15]

$$H_m^E(P) = \alpha P + \beta P^2 + \gamma P^3 + ... \tag{6}$$

where α, the initial pressure slope (zero pressure limit), is given by

$$\alpha = y_1y_2(2\varphi_{12} - \varphi_{11} - \varphi_{22}) \tag{7}$$

with

$$\varphi_{ij} = B_{ij} - T(\mathrm{d}B_{ij}/\mathrm{d}T) \tag{8}$$

where φ is called, after Wormald and co-workers, the isothermal Joule−Thomson coefficient. It follows that accurate low-pressure H_m^E data can yield cross isothermal Joule−Thomson coefficients if the isothermal Joule−Thomson coefficients of the pure compounds are known. In practice, the value of α, determined by a fit of a limited number of experimental points along an isotherm, often has a large standard deviation. As an alternative procedure, Wormald and co-workers performed a global data fit assuming the functional form of the temperature dependence of the parameters α, β, and γ in eq 6 (see ref 16 for an example) or treated experimental data in the framework of a selected intermolecular potential energy function and particular mixing rules.[17] Although these methods of data treatment supply not only φ_{12} but B_{12} values as well, one can argue that such a selection of the approximating functions may affect the data treatment and distort the true temperature dependence of the second cross virial coefficients. In this sense, as one of the reviewers put it, B_{12} values calculated from calorimetric data “are much further from being real data” compared to φ_{12}. This is why we have used eq 6 in many cases to treat the published isothermal H_m^E data, thus avoiding any approximations about the temperature dependence of the isothermal Joule−Thomson coefficients. However, as a penalty, the calculated values of φ_{12} often have large uncertainty intervals. In general, the problems arising from the treatment of isothermal H_m^E data are very similar to problems encountered when reducing *PVT* data to evaluate the virial coefficients:[7] the numerical values of the zero pressure slope may depend on a number of terms in the polynomial series employed in the least-squares procedure, and they may be affected by unrealistic estimates of experimental uncertainties, particularly at low pressures, and so forth. For high-boiling compounds, for example, hexane and higher alkanes, the pressure range of applicability of the truncated virial equation of state appears small,[18] thus strongly complicating the data treatment.

In 1988 Wormald and Lancaster[17] reinterpreted earlier H_m^E data from that laboratory and published new sets of B_{12} and φ_{12}, which superseded older values. Therefore, we accept more recent values[17] in place of results reported by Wormald’s group before 1988.[19−22]

Measurements of the Solubility of Condensed Phases of H_2O in Compressed Gases. This method involves the measurements of the mutual solubility of condensed phases of H_2O (liquid water or ice, depending on temperature and pressure) and compressed gases, and it is of special importance, since it provides B_{12} data at low temperatures that are not accessible by the PVT or H_m^E methods. The treatment of data in a binary two-phase system (gas and liquid phases at equilibrium) starts with the condition that the chemical potentials of H_2O are equal in the coexisting phases, resulting in[1,23]

$$y_1\phi_1 P = (1 - x_2)P_1^{sat}\phi_1^{sat} \exp[\int_{P_1^s}^{P}(V_1/RT)\,dP] \tag{9}$$

where x stands for the mole fraction of a component in the condensed phase; ϕ_1 is the fugacity coefficient of water. Note that the solubility of gases in the condensed phases of water is so low that the activity coefficient of water can be set equal to one and the partial molar volume of water in solution is practically identical to the molar volume of pure water/ice. The exponential term is the Poynting correction for the pressure effect on the fugacity of a condensed phase, and V_1 stands for the molar volume of liquid water or ice. The superscript "sat" denotes the property at gas−solid or gas−liquid saturation, so that P_1^{sat}, for example, stands for the saturation water vapor pressure. For the case of equilibrium between a gas and liquid water, the term $P_1^s\phi_1^s \exp[\int_{P_1^s}^{P} (V_1/RT)\,dP]$ can be taken as the product of the total pressure and the fugacity coefficient of pure water at given T and P as calculated by the equation of state for pure water.[24] For the case of equilibrium of a gas with ice, eq 9 can be simplified by neglecting the solubility of gas in ice, the deviation from unity of the fugacity coefficient of saturated water vapor over ice (the error introduced is less than 0.05% everywhere below the triple point temperature[23]), and both compressibility and expansion of ice (the error in the molar volume of ice estimated for temperatures from (240 to 273) K is less than 0.5%,[25] which translates into an error of less than 0.2% in calculated B_{12} values) using the constant value of $V_1 = 19.65\ \mathrm{cm^3{\cdot}mol^{-1}}$:[25]

$$y_1\phi_1 P = P_1^{sat} \exp[V_1/RT] \tag{10}$$

From eqs 9 or 10 one can calculate ϕ_1, the fugacity coefficient of water in the gas phase, provided that the concentration of water vapor in a gas phase, y_1, is accurately known. On the other hand, the virial equation of state in the pressure form truncated after the second virial coefficient results in the following equation for ϕ_1 in a binary mixture:[1]

$$\ln \phi_1 = (2y_1B_{11} + 2y_2B_{12} - B)P/RT \tag{11}$$

Given values of ϕ_1, eq 11 can be used to calculate B_{12}. In most cases the concentration of water in the gas phase, y_1, is very small, so even rather large uncertainties in the values of second virial coefficients of pure water, B_{11}, will not introduce appreciable errors.

We have treated numerous literature data on water or ice solubility in compressed gases to extract B_{12} values. Where reported, experimental values of x_2, the gas solubility in liquid water, were used. Otherwise, x_2 values were calculated using the following relation:[1]

$$x_2 = (1 - y_1)\phi_2 P/(K_H(T) \exp[\int_{P_1^{sat}}^{P}(V_2^\infty/RT)\,dP]) \tag{12}$$

where $K_H(T)$ represents Henry's law constant and V_2^∞ stands for the partial molar volume of the dissolved gas. Values of $K_H(T)$ at temperatures from (273 to 450) K can be calculated from the relation

$$RT \ln K_H(T) = \Delta_h H^\infty(T_r) - T\Delta_h S^\infty(T_r) + \Delta_h C_p^\infty(T_r)[T - T_r - T \ln(T/T_r)] \tag{13}$$

where $\Delta_h H^\infty$, $\Delta_h S^\infty$, and $\Delta_h C_p^\infty$ stand for the infinite dilution partial molar enthalpy, entropy, and heat capacity of hydration of a solute, respectively; $T_r = 298.15$ K is the reference temperature. It is implicit when using eq 13 that values of $K_H(T)$ are calculated using the approximation that $\Delta_h C_p^\infty$ is constant. This approximation is considerably better than the often used approximation that $\Delta_h H^\infty$ is constant and is expected to give satisfactory results from at least (273 to 450) K. Over the same temperature range the approximation that $V_2^\infty = V_2^\infty$(298.15 K, 0.1 MPa) is expected to be sufficiently accurate. Values of $\Delta_h H^\infty$, $\Delta_h S^\infty$, $\Delta_h C_p^\infty$, and V_2^∞ at 298 K for many solutes are available in compilations,[26−28] although it should be noted that $\Delta_h S^\infty$ must be recalculated into the mole fraction concentration scale where necessary. In all cases considered, the solubility of gases in water is low even at relatively high pressures, and calculated values of B_{12} are insensitive to uncertainties of x_2 estimations.

A more important problem is the selection of an appropriate pressure range of solubility data for determining B_{12}. At high pressure, higher virial coefficients (first of all, C_{122}) may be important in the virial expansion of ϕ_1, and at low pressures, where deviations from the ideal gas behavior are insignificant, calculated values of B_{12} are extremely sensitive to even small experimental uncertainties. To avoid these problems, we used only data referring to the reduced density, ρ_r, range between 0.1 and 0.5. Because the solubility of water in compressed gases at $T < (400$ to $450)$ K is never large, ρ_r is calculated on the basis of a "dry" gas as $\rho_r = V_c/V_m$, where V_c stands for the critical volume of a pure gas. Nevertheless, accurate measurements of water concentrations in compressed gases are essential, because an error of (3 to 5)% in y_1 may result in an error of (10 to 20)% in the calculated value of B_{12}. Results of calculations are also sensitive to the selected values of the saturated vapor pressure over ice, taken from Wagner et al.,[29] and a change of P_1^{sat} within 1% may result in a change of B_{12} up to 4%.

It must be noted that the method described is applicable only for equilibrium between a gas solution and an aqueous solution (or pure ice). However, for many gases the formation of clathrates (gas hydrates) complicates the phase diagram (see ref 23 for a review). Therefore, in our treatment we employed data only at pressures below the pressures of clathrate formation, with the T−P coordinates of the corresponding equilibria quoted from Rabinovich and Beketov.[23]

Compilation of B_{12} Data

We have compiled literature data and in many cases evaluated second cross virial coefficients from various types of experimental information. The results obtained are tabulated and discussed in this section: first for nonpolar inorganic compounds (Ar, CO, etc); then for normal alkanes from methane, CH_4, to octane, C_8H_{18}; then for compounds that interact more strongly with water than nonpolar compounds of similar sizes (CO_2, ethylene, benzene, cyclohexane); and finally for compounds with appreciable dipole moments (NH_3, methanol, ethanol, HCl, CH_3Cl, etc).

B_{12} for Interactions between Water and Nonpolar Inorganic Compounds. Two sets of cross virial coefficients for H_2O + Ar interactions are reported in the

Table 1. Values of B_{12} for Inorganic Nonpolar Compound + Water Interactions, Evaluated in This Work (Standard Deviation Is Given in Parentheses)

T/K, B_{12}/cm^3·mol^{-1}	method	ref
Argon, Ar		
271.2, −41(3); 263.2, −36(2); 253.2, −55(7); 243.2, −57	solub	23
293.2, −32(4); 283.2, −32(1); 273.2, −52(3); 263.2, −62(2); 253.2, −78	solub	31
Hydrogen, H_2		
653.2, 1(11); 673.2, −4(12); 693.2, −3(9); 713.2, −4(10)	*PVT*	34
271.2, −1(2); 263.2, −2(1); 253.2, −3(2); 243.2, 3(5)	solub	23
293.2, −41(11);[a] 283.2, −45(15);[a] 273.2, −21(6);[a] 263.2, −22(5);[a] 253.2, −17(5);[a] 243.2, −33(9)[a]	solub	31
310.9, −11(5); 366.5, −3(3); 422.0, −2(6); 477.6, −7(3)	solub	36
323.2, −2(1)	solub	37
Nitrogen, N_2		
271.2, −45(4); 263.2, −42(3); 253.2, −54(4); 243.2, −51(4)	solub	23
700, 3; 750, 3; 800, 6; 850, 11; 900, 15; 950, 21; 1000, 25	*PVT*	44
293.2, −52(14); 283.2, −51(11); 273.2, −49(7); 263.2, −62(4)	solub	31
253.2, −73(6); 243.2, −93(5)	solub	36
310.9, −31(4); 366.5, −16(1); 422.0, −9; 477.6, −15(6)	solub	41
323.2, −46; 353.2, −31; 373.2, −5; 423.2, −2(6); 463.2, −7; 498.2, −5	solub	37
323.2, −25(2)		
Carbon Monoxide, CO		
310.9, −58(7); 366.5, −35(3); 422.0, −24(4); 477.6, −12(5)	solub	36

[a] These values are believed to be grossly in error and are excluded from further consideration.

Table 2. Values of φ_{12} for Nonpolar Inorganic Compound + Water Interactions, Evaluated in This Work from Isothermal H_m^E Data (Uncertainty at the 0.95 Confidence Level Is Given in Parentheses)

T/K, φ_{12}/cm^3·mol^{-1}	ref
Argon, Ar	
473.2, −65(70); 498.2, −79(20); 523.2, −30(14); 548.2, −19(62); 573.2, −29(16); 598.2, −18(12); 548.2, −20(8); 698.2, −22(6)	32
Hydrogen, H_2	
523.2, 23(48); 548.2, 13(44); 573.2, 57(20); 598.2, 30(24); 648.2, 19(14); 698.2, 10(40)	38
Nitrogen, N_2	
548.2, −59(64);[a] 573.2, −52(16); 598.2, −26(16);[a] 648.2, −21(12); 698.2, −25(4)[b]	38
Carbon Monoxide, CO	
473.2, −41(50); 523.2, −69(40); 573.2, −44(74); 623.2, −30(66); 648.2, −27(80); 673.2, −25(28); 698.2, −59(36)[c]	38

[a] Experimental value $P = 0.72$ MPa is excluded. [b] Experimental value at 1.48 MPa is excluded. [c] Including seven experimental H_m^E points from the Wilson and Brady (1983) report, as quoted by Wormald et al.[69]

literature. Rigby and Prausnitz[30] calculated B_{12} from their determinations of water solubility in compressed argon at four temperatures between (298.2 and 373.2) K, and Wormald and Lancaster[17] calculated both B_{12} and φ_{12} at six isotherms between (373.2 and 423.2) K from H_m^E results. In addition, we calculated B_{12} for the H_2O + Ar pair from two sets of data on the solubility of ice or water in compressed gaseous Ar, one measured by Kosyakov et al.[31] and another one by Iomtev et al., as tabulated elsewhere.[23] As discussed above, only data obtained at reduced argon densities between 0.1 and 0.5 were employed. The experimental data used refer to the gas + ice (water) equilibrium; that is, they are obtained below the pressure of argon hydrate formation. Calculated values of B_{12} are presented in Table 1, together with their standard deviations given in parentheses. It can be seen that the differences between the B_{12} values calculated from the solubility data[23,31] exceed the combined statistical uncertainties, suggesting that systematic errors are present in at least one set of the data, and the real uncertainties of B_{12} may be as large as (10 to 20) cm^3·mol^{-1}. Experimental H_m^E results for the H_2O + Ar gaseous mixture from (473 to 698) K (ref 32) were employed to evaluate the cross Joule−Thomson coefficients, φ_{12}, by the least-squares fit of isothermal data, as described above. The values of φ_{12} obtained and their uncertainties at the 0.95 confidence level are presented in Table 2 excluding cases where the corresponding statistical uncertainties are prohibitively large, in excess of (80 to 100) cm^3·mol^{-1}. Recently, values of B_{12} and φ_{12} at (100 to 2000) K were presented by Hodges et al.,[33] who constructed an accurate potential energy surface for the argon + water complex from scaled perturbation theory calculations. Results for Ar + H_2O interactions are presented in Figure 1, which shows the second cross virial coefficients, B_{12} (upper sets of symbols and lines), and the cross isothermal Joule−Thomson coefficients, φ_{12} (lower sets of symbols and lines) together in one plot. Vertical lines show the uncertainty brackets if they exceed the size of a symbol. The solid lines give results of simultaneous correlation of both B_{12} and φ_{12} data using the Tsonopoulos[3] corresponding-states correlation. The dashed lines show theoretical values obtained by Hodges et al.[33]

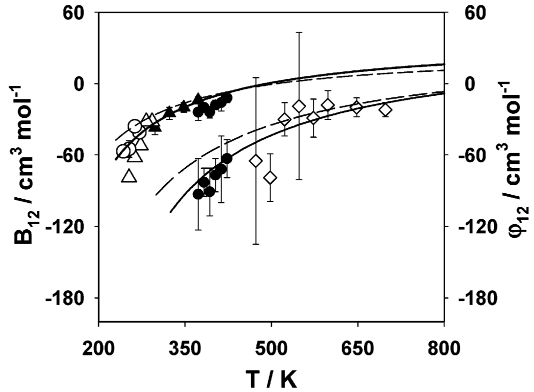

Figure 1. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for Ar + H_2O interactions: ▲, Rigby and Prausnitz;[30] △, Kosyakov et al.;[31] ●, Wormald and Lancaster;[17] ◇, Wormald and Colling;[32] ○, Rabinovich and Beketov;[23] —, Tsonopoulos correlation; - - -, Hodges et al.[33]

For $H_2 + H_2O$ interactions there are published values of both B_{12} and φ_{12} from (373.2 to 423.2) K, evaluated from H_m^E data.[17] In addition, we derived B_{12} from different sets of experimental data; see the discussion below. Seward et al.[34] calculated values of B, the second virial coefficients of the water + hydrogen mixtures, at four isotherms between (653.2 to 713.2) K from their *PVT* data. Values of the virial coefficients are given for mixtures with hydrogen concentrations, y_2, between 0.01 and 0.90. Values of B_{12} calculated by us show a large scatter with the mixture composition, especially at $y_2 \leqslant 0.09$ or $y_2 \geqslant 0.90$. Using results for six compositions, where $0.12 \leqslant y_2 \leqslant 0.80$, we obtained values of B_{12} that are given in Table 1. The necessary values of B_{22} at temperatures from (653.2 to 713.2) K are taken from Spycher and Reed,[35] because recommendations of Dymond et al.[2] for pure hydrogen are given up to 500 K. There are also four sets of data on the solubility of water in compressed hydrogen, at temperatures between (243 and 478) K;[23,31,36,37] see Table 1 for the B_{12} results calculated in this study. Low-temperature results[23,31] again show disagreement of about 20 $cm^3 \cdot mol^{-1}$. We note that the results[31] at (283.2 and 293.2) K diverge strongly from the expected temperature dependence. Experimental H_m^E results for the $H_2O + H_2$ gaseous mixture at high temperatures[38] were used to calculate the cross Joule–Thomson coefficients, φ_{12}, for corresponding interactions; see the results in Table 2. Many available values of B_{12} for hydrogen + water interactions appear to be of mediocre quality, and new accurate measurements for this mixture would be welcome.

There are many B_{12} data for $N_2 + H_2O$ interactions. Rigby and Prausnitz[30] calculated B_{12} from measurements of water solubility in compressed nitrogen at four temperatures between (298.2 and 373.2) K. Skripka[39] presented cross second virial coefficients from *PVT* measurements at (473 and 498 K). The latter results are much more negative than other published values or those calculated by us, suggesting that the experimental results[39] may be strongly affected by adsorption. Wormald and Lancaster[17] calculated both φ_{12} and B_{12} at temperatures between (373.2 and 423.2) K from H_m^E results. Abdulagatov et al.[40] evaluated the second cross virial coefficients for this system from *PVT* measurements at three isotherms between (523.2 and 663.2) K. In addition, we calculated B_{12} from the water solubility data at (243 to 498) K;[23,31,36,37,41] see Table 1. Our attempts to calculate B_{12} data from dew points measurements of the binary $N_2 + H_2O$ system[42,43] resulted in values that are scattered erratically and are in disagreement with other data. Gallagher et al.[44] presented a corresponding-states-based equation of state for homogeneous water + nitrogen mixtures at temperatures up to 1000 K. We decided to use this formulation to obtain estimates of B_{12} at (700 to 1000 K), but results at lower temperatures were not accepted because the calculated B_{12} values show an unrealistic increase with decreasing temperatures. To calculate B_{12}, the values of the infinite dilution partial molar volumes of nitrogen, V_2^∞, at low water densities, tabulated by Gallagher et al.,[44] are expanded, following O'Connell and Liu,[45] into the virial series

$$V_2^\infty/(\kappa RT) = 1 + 2\rho_1 B_{12} + {}^3/_2\rho_1^2 C_{112} + ... \qquad (14)$$

where ρ_1 and κ stand for the density and isothermal compressibility of pure water. Values of φ_{12} for this binary were evaluated by us from H_m^E results[38] and are given in Table 2. All the values of B_{12} for $N_2 + H_2O$ interactions are shown in Figure 2 (for clarity, values of φ_{12} are not shown, since they overlap with B_{12} results).

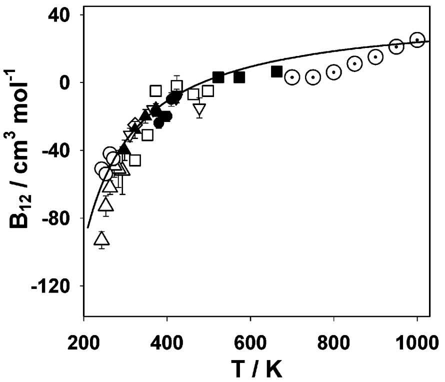

Figure 2. B_{12} for $N_2 + H_2O$ interactions: ◇, Bartlett;[37] □, Saddington and Krase;[41] ▲, Rigby and Prausnitz;[30] ▽, Gillespie and Wilson;[36] △, Kosyakov et al.;[31] ●, Wormald and Lancaster;[17] ⊙, Gallagher et al.;[44] ○, Rabinovich and Beketov;[23] ■, Abdulagatov et al.;[40] —, Tsonopoulos correlation.

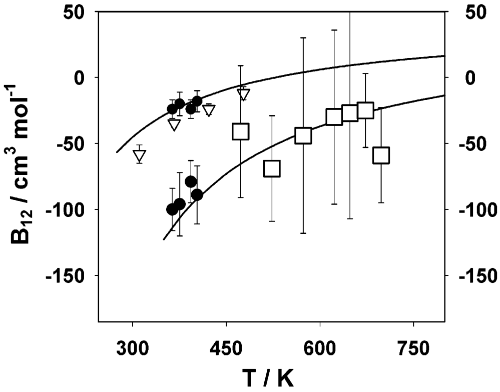

Figure 3. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $CO + H_2O$ interactions: ▽, Gillespie and Wilson;[36] ●, Wormald and Lancaster;[17] □, Lancaster and Wormald;[38] —, Tsonopoulos correlation.

The only literature values of B_{12} and φ_{12} for $CO + H_2O$ interactions are from (363.5 to 403.2) K and are obtained from calorimetric measurements.[17] In addition, we calculated the second cross virial coefficients from (310.9 to 477.6) K from solubility data[36] (see Table 1), and the isothermal cross Joule–Thomson coefficients from (473.2 to 698.2) K from H_m^E results[38] (see Table 2). All results are shown in Figure 3.

There are also B_{12} data for interactions between water and other nonpolar inorganic compounds. From results on the solubility of water in compressed gases, Coan and King[46] reported B_{12} values for $N_2O + H_2O$ interactions from (298 to 373) K. Hall and Iglesia-Silva[47] extracted second cross virial coefficients for $O_2 + H_2O$ interactions at (298.2 to 373.2) K from existing *PVT* data for moist air, and Wylie and Fisher[48] presented B_{12} for $O_2 + H_2O$ from 298 to 348 K from water solubility in compressed oxygen. Both sets of results are in satisfactory agreement.

Values of the second cross virial coefficients for He + H_2O interactions from 223 to 293 K may be obtained from water solubility data.[23,31] Unfortunately, there is a disagreement of more than 30 $cm^3 \cdot mol^{-1}$ between the two sets of results. The *PVT*-based[39] B_{12} values for the He + H_2O system (and for Ne + H_2O interactions) are unrealistically low, probably reflecting large errors due to adsorption phenomena. The most reliable values of the second cross virial coefficients between water and helium and between water and neon are due to Hodges et al.,[49,33] who constructed, from scaled perturbation theory calculations, an

Table 3. Values of B_{12} for Normal Alkane + Water Interactions, Evaluated in This Work (Standard Deviation Is Given in Parentheses)

T/K, B_{12}/cm^3·mol^{-1}	method	ref
Methane, CH_4		
323.2, −55; 348.2, −37; 423.2, −21(1); 477.6, −22(3); 533.2, −16(7)	solub	52
344.3, −51(5); 377.6, −32(2); 410.9, −27(1); 444.3, −19(4); 477.6, −26(7); 510.9, −23(11)	solub	51
Ethane, C_2H_6		
310.9, −104; 344.3, −79	solub	56
377.6, −66; 410.9, −53; 444.3, −49	solub	55

Table 4. Values of φ_{12} for Normal Alkane + Water Interactions, Evaluated in This Work from Isothermal H_m^E Data (Uncertainty at the 0.95 Confidence Level Is Given in Parentheses)

T/K, φ_{12}/cm^3·mol^{-1}	ref
Methane, CH_4	
498.2, −105(24); 523.2, −83(28); 548.2, −50(24); 573.2, −44(38); 598.2, −90(16); 648.2, −66(22); 698.2, −46(14)	38
Ethane, C_2H_6	
448.2, −155(28); 473.2, −106(36); 498.2, −101(16); 523.2, −108(74); 548.2, −84(24); 573.2, −95(14); 598.2, −82(6); 648.2, −79(6); 698.2, −67(4)	38
Propane, C_3H_8	
473.2, −237(74);[a] 498.2, −203(52); 523.2, −159(18); 573.2, −116(14); 598.2, −99(14); 648.2, −86(8); 698.2, −75(10)	38
Butane, C_4H_{10}	
498.2, −214(72); 523.2, −209(52); 573.2, −147(74); 598.2, −134(14); 648.2, −118(4); 698.2, −101(18)	38
Pentane, C_5H_{12}	
523.2, −212(80); 573.2, −163(20); 648.2, −136(14); 698.2, −135(24)	60
Hexane, C_6H_{14}	
598.2, −217(28); 623.2, −173(40);[b] 648.2, −194(32);[c] 673.2, −229(38); 698.2, −245(44)	18
Heptane, C_7H_{16}	
698.2, −226(58)	18
Octane, C_8H_{18}	
623.2, −261(54); 648.2, −283(52)[d]	61

[a] Experimental value at P = 0.79 MPa is excluded. [b] Experimental value at P = 1.13 MPa is excluded. [c] Experimental values at P = 1.03 and 1.79 MPa are excluded. [d] Experimental value at P = 0.51 MPa is excluded.

accurate potential energy surface for the water + helium and water + neon complexes, including first-order quantum corrections, and calculated B_{12} from (100 to 2000) K. Their results, which have small uncertainties, <3 cm^3·mol^{-1}, strongly suggest that the experimental data[23] on the solubility of ice in compressed helium are more reliable than those of Kosyakov et al.[31]

***B_{12}* for Alkanes from Methane, CH_4, to Octane, C_8H_{18}.** The normal alkanes, from methane, CH_4, to octane, C_8H_{18}, are nonpolar compounds with similar chemical properties but considerably different sizes.

There are many literature values of B_{12} for methane + water interactions evaluated from the solubility of water in compressed gaseous methane from (298 to 373 K)[30] or equilibrium between a gas solution and methane clathrates from (240 to 270 K),[50] H_m^E measurements[17] from (373 to 423) K, as well as *PVT* measurements from (523 to 653) K[40] or from (398 to 498) K[12] (precise results with correction for adsorption effects). We rejected *PVT*-based values from (473 to 523 K),[39] which are very negative. In addition to these published data, we calculated B_{12} values for CH_4 + H_2O interactions from results for water solubility in compressed methane in equilibrium with an aqueous solution (not methane clathrates) from (344 to 510) K[51] and from (323 to 533) K;[52] see Table 3. Water solubility results obtained in the field of stability of gas hydrates[53,54] were not used for B_{12} evaluation. Values of the isothermal cross Joule−Thomson coefficients, φ_{12}, from (498 to 698) K were calculated by us from H_m^E results.[38] Literature values and those evaluated in this work are shown in Figure 4. Note that the low-temperature B_{12} results[50] cannot be reproduced by the corresponding-states correlations. Although different explanations of these discrepancies are possible, we would like to emphasize the complicated procedure for treating experimental data involving equilibria with a clathrate phase, especially when not only B_{12} but also C_{122} virial coefficients are unknowns in the regression procedure.

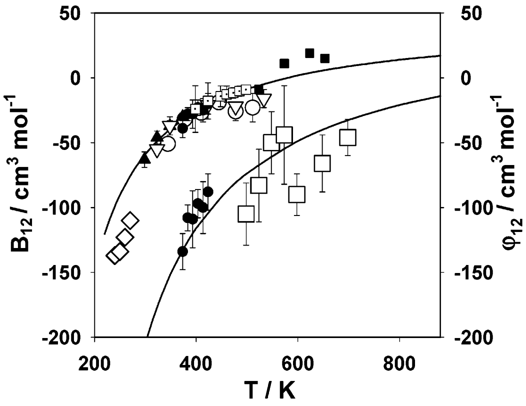

Figure 4. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for CH_4 + H_2O interactions: ○, Olds et al.;[51] ▲, Rigby and Prausnitz;[30] ◇, Aoyagi et al.;[50] ▽, Gillespie and Wilson;[52] ●, Wormald and Lancaster;[17] ⊡, Joffrion and Eubank;[12] □, Lancaster and Wormald;[38] ■, Abdulagatov et al.;[40] —, Tsonopoulos correlation.

For C_2H_6 + H_2O interactions, literature values of B_{12} are available from water solubility data[46] in the range (298 to 373) K, together with φ_{12} values from H_m^E data[17] from (363 to 393) K. In addition, we calculated second cross virial coefficients from water solubility in compressed ethane from (377.6 to 444.3) K[55] and from (310.9 to 410.9) K;[56] see Table 3. Experimental H_m^E values[38] were used to calculate φ_{12} from (448 to 698) K; see Table 4. Both B_{12} and φ_{12} data are shown in Figure 5.

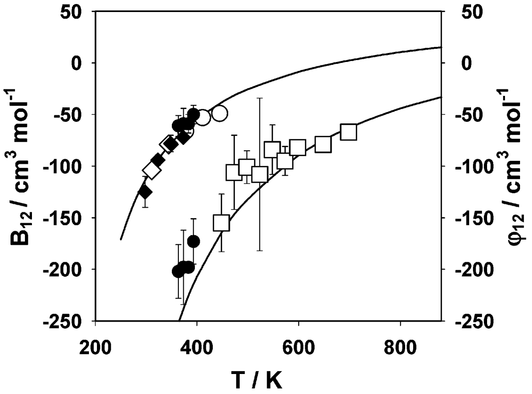

Figure 5. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $C_2H_6 + H_2O$ interactions: ○, Reamer et al.;[55] ◇, Anthony and McKetta;[56] ◆, Coan and King;[46] ●, Wormald and Lancaster;[17] □, Lancaster and Wormald;[38] —, Tsonopoulos correlation.

For higher alkanes there are experimental results on the solubility of water in the coexisting gaseous phase, for propane,[57,58] butane,[59] and pentane.[52] However, the calculated B_{12} values show unacceptable scatter (more than 100 cm^3·mol^{-1}), perhaps reflecting the experimental challenges of studying equilibrium relations between water and high-boiling hydrocarbons, and all the values of B_{12} for higher alkanes evaluated from water solubility studies were rejected. Because they are too negative, we rejected the *PVT*-based values[39] of B_{12} from (473 to 523) K for interactions between water and propane, hexane, and octane. The main sources of information on normal alkane + water interactions are the experimental measurements of excess molar enthalpies of gaseous mixtures, H_m^E, by Wormald and co-workers. Wormald and Lancaster[17] tabulated both B_{12} and φ_{12} from (363 to 423) K for all alkanes up to C_8H_{18}. In addition, we calculated values of φ_{12} up to 698 K from high-temperature H_m^E measurements;[18,60,61] see Table 4. As noted elsewhere,[18,61] the pressure range of applicability of the virial equation of state truncated after the third virial coefficient appears to be small for mixtures consisting of water and high-boiling hydrocarbons, which complicates the data treatment. This empirical finding is confirmed by the theoretical work of Harvey,[62] who demonstrated that the truncated virial expansion deteriorates at significantly lower densities as the solutes become larger. Calculated values of φ_{12} that have unacceptably large uncertainty brackets were rejected, explaining why the φ_{12} results in Table 4 are not given for every experimentally studied isotherm. Other sources of information for higher alkanes are the *PVT* studies by Abdulagatov et al.,[40,63] which give B_{12} for $C_5H_{12} + H_2O$ interactions at 647.05 K, for the $C_6H_{14} + H_2O$ system from (523 to 623) K, and for $C_8H_{18} + H_2O$ interactions at 623 K. Results for the propane + water, pentane + water, and octane + water systems are shown in Figures 6−8.

B_{12} for Interactions between Water and Some Multipolar Compounds. The third group consists of compounds that interact with water more strongly than alkanes. The more attractive character of interactions between these molecules and water molecules is revealed by values of the Gibbs energy of hydration at 298 K, which for cyclohexane and benzene are approximately (5 and 14) kJ·mol^{-1} less, respectively, than the Gibbs energy of hydration for hexane.[28] Compounds under consideration include CO_2, benzene, and ethene, that have zero or small dipole moments but appreciable quadrupole moments that may partially explain their more attractive interactions with water.

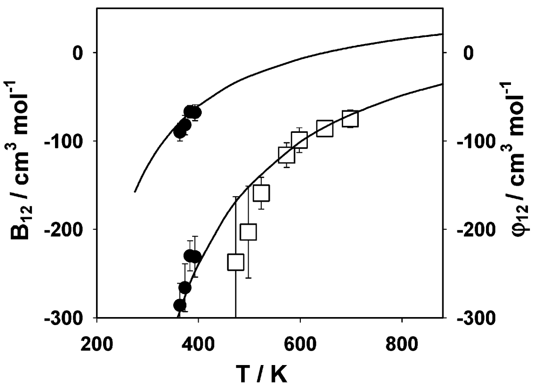

Figure 6. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $C_3H_8 + H_2O$ interactions: ●, Wormald and Lancaster;[17] □, Lancaster and Wormald;[38] —, Tsonopoulos correlation.

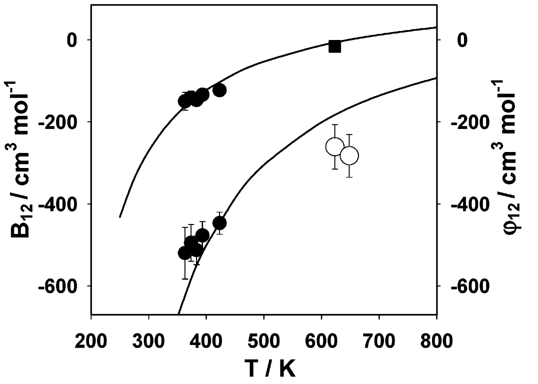

Figure 7. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $C_5H_{12} + H_2O$ interactions: ●, Wormald and Lancaster;[17] ○, Lancaster and Wormald;[60] ■, Abdulagatov et al.;[63] —, Tsonopoulos correlation.

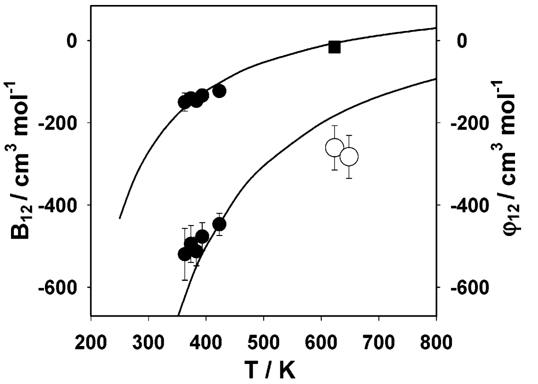

Figure 8. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $C_8H_{18} + H_2O$ interactions: ●, Wormald and Lancaster;[17] ○, Wormald and Al-Bizreh;[61] ■, Abdulagatov et al.;[40] —, Tsonopoulos correlation.

Many data are reported for $CO_2 + H_2O$ interactions. Coan and King[46] determined values of B_{12} from (298 to 373) K from the solubility of water in compressed carbon dioxide. Vanderzee and Haas[64] considered the four sets of literature data available at that time, including *PVT* measurements up to 1100 K, calculated second cross virial coefficients between carbon dioxide and water, and recommended reliable B_{12} values from (300 to 1100) K. Patel et al.[11] performed precise *PVT* measurements for $CO_2 + H_2O$ gaseous mixtures of different compositions from (348.15 to 498.15) K and calculated B_{12} for this system after a rather involved correction for adsorption effects. Wormald and Lancaster[17] tabulated B_{12} and φ_{12} from (363 to 393) K from

Table 5. Values of B_{12} for Multipolar Compound + Water Interactions, Evaluated in This Work (Standard Deviation Is Given in Parentheses)

T/K, B_{12}/cm^3·mol^{-1}	method	ref
Carbon Dioxide, CO_2		
288.7, −268; 298.2, −236; 304.2, −208; 348.2, −134(10); 366.5, −107(10); 394.3, −101(6); 422.0, −82(4); 477.6, −71(1)	solub	52
Ethene, C_2H_4		
310.9, −143(6); 344.3, −116(4); 377.7, −98(2); 410.9, −93(11)	solub	56
Benzene, C_6H_6		
647.05, −71(7)	*PVT*	71
Hydrogen Chloride, HCl		
500, −102; 550, −86; 600, −73; 650, −62; 700, −53; 750, −46	*PVT*	75
Ammonia, NH_3		
323.14,−762(67);[a] 373.12, −302(11); 423.12, −223(12);[b] 473.11, −164(7); 523.11, −119(5)	*PVT*	78
373.15, −340(18); 398.15, −269(11); 423.15, −227(7); 448.15, −193(5); 473.15, −165(3); 498.15, −135(2)	*PVT*	79

[a] Experimental values at $x_2 = 0.9725$ were excluded. [b] Experimental data at $x_2 = 0.9461$ were excluded.

Table 6. Values of φ_{12} for Multipolar Compounds + Water Interactions, Evaluated in This Work from the Isothermal H_m^E Data (Uncertainty at the 0.95 Confidence Level Is Given in Parentheses)

T/K, φ_{12}/cm^3·mol^{-1}	ref
Carbon Dioxide, CO_2	
473.2, −222(42); 498.2, −181(12); 523.2, −127(18); 548.2, −121(28); 573.2, −112(8); 598.2, −108(10); 648.2, −90(6); 698.2, −92(4); 698.2, −94(20);[a] 803, −41(16);[a] 913, −25(16)[a]	38
Ethene, C_2H_4	
473.2, −192(28); 498.2, −180(60); 523.2, −163(24); 548.2, −140(30); 573.2, −126(20); 598.2, −103(36); 648.2, −100(8)	38

[a] From experimental H_m^E data from the Wilson and Brady (1983) report, as by Wormald et al.[69]

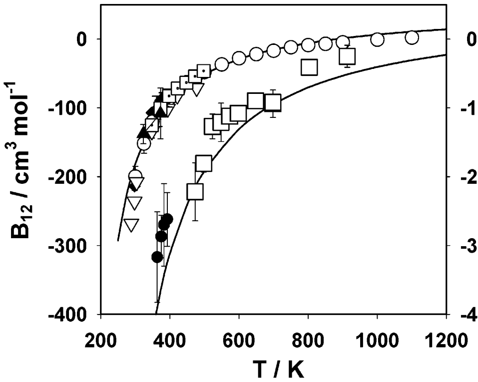

Figure 9. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $CO_2 + H_2O$ interactions: ◆, Coan and King;[46] ▲, Malezinska;[66] ○, Vanderzee and Haas;[64] ▽, Gillespie and Wilson;[52] ⊡, Patel et al.;[11] ●, Wormald and Lancaster;[17] □, Lancaster and Wormald;[38] —, Tsonopoulos correlation.

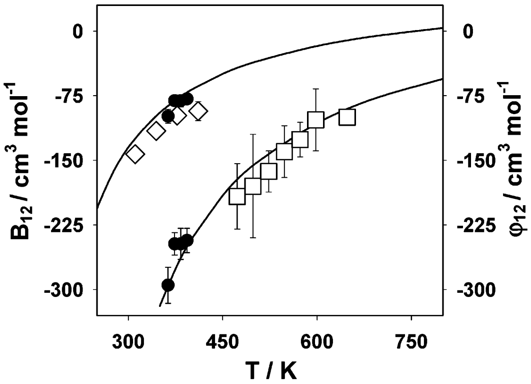

Figure 10. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $C_2H_4 + H_2O$ interactions: ◇, Anthony and McKetta;[56] ●, Wormald and Lancaster;[17] □, Lancaster and Wormald;[38] —, Tsonopoulos correlation.

H_m^E measurements. In addition to these results, we calculated B_{12} values for $CO_2 + H_2O$ interactions from (288.7 to 477.6) K from phase equilibria data;[52] see Table 5. All the second cross virial coefficients from the above-mentioned sources are in agreement, contrary to *PVT*-based B_{12} data from (473 to 523) K[39] and from (373 to 473) K,[65] which are more negative by as much as 100 cm^3·mol^{-1}. The latter data were rejected. We accepted B_{12} values at (323 and 373) K calculated by Malesinska[66] from phase equilibria studies[67,68] in the $CO_2 + H_2O$ system at pressures ≤ 100 atm. In Table 6 we give values of the cross Joule−Thomson coefficients for $CO_2 + H_2O$ interactions from (473 to 913) K; those from (473 to 698) K were evaluated from H_m^E data,[38] and those from (698 to 913) K, from H_m^E results of Wilson and Brady as recalculated and tabulated by Wormald and co-workers.[69] All the data are shown in Figure 9.

Results for $C_2H_4 + H_2O$ interactions (see Figure 10) consist of B_{12} and φ_{12} values from (363 to 393) K,[17] our evaluation of B_{12} from (310.9 to 410.9) K from data for water solubility in compressed ethene[56] (see Table 5) and isothermal cross Joule−Thomson coefficients from (473 to 648) K calculated in this work from experimental excess molar enthalpies[38] (see Table 6). For propene, there is only one set of calorimetric data, which were used to calculate B_{12} and φ_{12} values from (363 to 393) K.[17]

Most results for interactions between benzene and H_2O in the gaseous phase are available from calorimetric measurements by Wormald and co-workers,[17,70] who tabulated both B_{12} and φ_{12} from (363 to 698) K. The *PVT*-based value of $B_{12} = -25$ cm^3·mol^{-1} at 623 K[40] is about 65 cm^3·mol^{-1} more positive than the calorimetric values; however, the later *PVT* measurements of the water + benzene mixture with $x_2 = 0.439$, performed by the same group[71] at $T = 647.05$ K, are consistent with $B_{12} = -71 \pm 7$ cm^3·mol^{-1} (see Table 5) and are in good agreement with the calorimetric results. All the available data for $C_6H_6 + H_2O$ interactions are shown in Figure 11.

For methylbenzene (toluene) there is only one published set of B_{12} data, based on *PVT* measurements of gaseous toluene + water mixtures of variable composition with $0.22 < x_2 < 0.69$ from (400 to 525) K.[72] All the available data

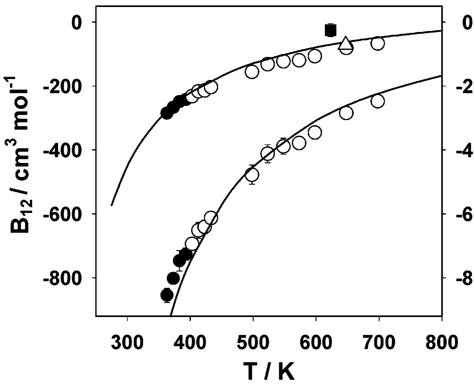

Figure 11. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $C_6H_6 + H_2O$ interactions: ●, Wormald and Lancaster;[17] ■, Abdulagatov et al.;[40] ○, Wormald et al.;[70] △, Abdulagatov et al.;[71] —, Tsonopoulos correlation.

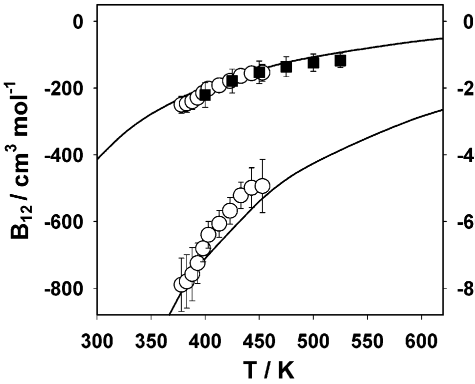

Figure 12. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $C_6F_6 + H_2O$ interactions: ■, Nopper et al.;[72] ○, Wormald and Wurzberger;[73] —, Tsonopoulos correlation.

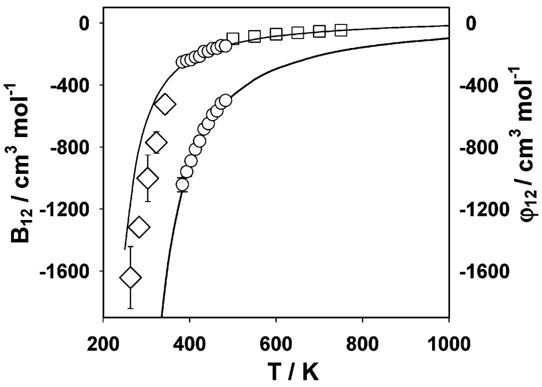

Figure 13. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $HCl + H_2O$ interactions: ◇, Kao;[74] □, Kindler et al.;[75] ○, Wormald;[76] —, Tsonopoulos correlation.

on cyclohexane $C_6H_{12} + H_2O$ interactions in the gaseous phase are due to the calorimetric measurements of Wormald and co-workers.[17,70] The second cross virial coefficients for hexafluorobenzene $C_6F_6 + H_2O$ interactions are calculated from *PVT* measurements from (400 to 525) K[72] and from calorimetric results from (378 to 453) K.[73] Both sets of data are in good agreement, as shown in Figure 12.

B_{12} for Interactions between Water and Polar Compounds. The final group we considered is compounds that possess appreciable dipole moments (more than 1 D, $D = 3.162 \times 10^{-25}$ (J·m^3)$^{1/2}$) and, therefore, interact particularly strongly with the water molecule, which also has a rather large dipole moment, 1.8 D. This group includes HCl, alcohols, ammonia, chlorinated alkanes, SO_2, and acetone.

There are several sources of experimental information on $HCl + H_2O$ interactions in the gaseous phase. Kao[74] measured the compositions of the coexisting liquid and gas phases in this system from (263 to 343) K at pressures up to 1.5 MPa, and they calculated from these data the B_{12} values for interactions between hydrogen chloride and water. One peculiarity of the vapor−liquid equilibrium data for the $HCl + H_2O$ system is the very high concentrations of HCl in the liquid phase, which strongly complicates reliable calculations of the fugacity of water in the coexisting phases. As a result, values of B_{12} calculated by Kao may bear larger uncertainties than those assumed by the author. Kindler et al.[75] performed a *PVT* study of the gas phase of this system with mole fractions of HCl between 0 and 0.23 from (460 to 780) K at pressures up to 15 MPa. This study was specifically oriented at obtaining accurate results for low density mixtures. All of the data, about 100 values, were fitted by Kindler et al.[75] with the following equation:

$$PV = RT + BP \tag{15}$$

with

$$B = b - a/RT^{1.5} \tag{16}$$

where b and a are assumed to be linear functions of the mole fraction of HCl, valid at y_2 between 0.04 and 0.23. Comparison of eq 15 with eqs 1 and 2 reveals that the parameter B of eq 15 is the second virial coefficient of a mixture, although the correct composition dependence should be quadratic rather than linear (in this case, the true dependence may be masked by the rather small range of compositions investigated). Nevertheless, we used the proposed relations[75] to calculate the second virial coefficient for the mixture for given compositions and evaluate the second cross virial coefficients between HCl and water; see Table 5 (during recalculations values of B_{11} were used as given by Kindler et al.[75]). Recently, Wormald[76] presented B_{12} and φ_{12} values for $HCl + H_2O$ interactions from (383 to 483) K obtained from calorimetric measurements. Results are shown in Figure 13. It appears that the data of Kao[74] suggest a stronger temperature dependence of B_{12} than that obtained from Wormald's[76] calorimetric measurements. However, the interpretation of the vapor−liquid equilibria data for the $HCl + H_2O$ system requires exceedingly accurate knowledge of the fugacity of water in the liquid phase, and consequently, calculated B_{12} data[74] may bear undetected systematic errors.

For the $NH_3 + H_2O$ system, Tillner-Roth and Friend[77] quoted two sources of vapor-phase *PVT* data.[78,79] In all, there are 250 data points at temperatures from (373.12 to 523.11) K[78] and 276 data points from (373.14 to 498.15) K,[79] as reported by Friend.[80] The *PVT* data at reduced densities < ~0.11 were used in this study to calculate B_{12} for $NH_3 + H_2O$ interactions at temperatures from (323 to 523) K; see Table 5. In addition, Wormald and Wurzberger[81] calculated B_{12} and φ_{12} from (383.15 to 493.15) K from their H_m^E measurements. All data are shown in Figure 14.

Bich et al.[13] reported B_{12} at 10 isotherms between 373 and 527 K for $CH_3OH + H_2O$ interactions after correction for adsorption of the previously published *PVT* data.[72] These results are shown in Figure 15. We are aware of only one source of B_{12} data for ethanol $C_2H_5OH + H_2O$ interactions from *PVT* measurements from (400 to 525) K.[72] These data were not corrected for adsorption; however, judging by the results for $CH_3OH + H_2O$ mixtures[13,72] from the same laboratory, we expect that the corrected values will

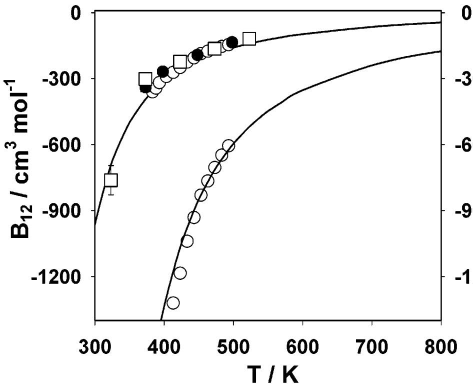

Figure 14. B_{12} and φ_{12} (upper and lower sets of symbols and lines) for $NH_3 + H_2O$ interactions: ●, Ellerwald;[78] □, Harms-Watzenberg;[79] ○, Wormald and Wurzberger;[81] —, Tsonopoulos correlation.

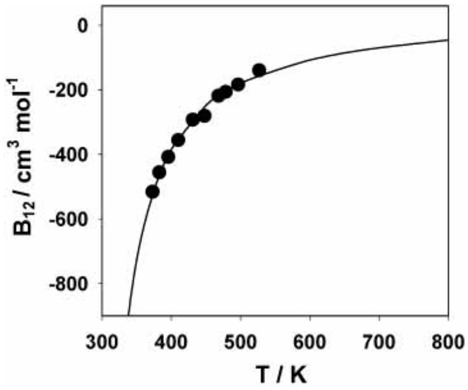

Figure 15. B_{12} results for $CH_3OH + H_2O$ interactions: ●, Bich et al.;[13] —, Tsonopoulos correlation.

be within the rather large uncertainty brackets (30 to 40 $cm^3·mol^{-1}$) of the uncorrected values.

The values of B_{12} and φ_{12} for interactions between water and the chlorinated alkanes CH_3Cl, $CHCl_3$, and C_2H_5Cl all come from the calorimetric measurements of Wormald and co-workers[17,82] over a temperature range from (353 to 423) K. Recently, Wormald reported B_{12} and φ_{12} values for water + acetone[83] and water + SO_2[84] interactions from gas-phase excess enthalpy measurements at temperatures from (383 to 443) and from (383 to 483) K, respectively.

This completes the list of accepted values of the second cross virial coefficients and the isothermal Joule−Thomson coefficients for interactions between water and other compounds. We rejected isolated literature values of B_{12} for water + dioxane,[85] water + diethylamine,[86] and water + tetrahydrofuran.[87] All of these values were obtained from *PVT* measurements at room temperature in glass apparatus, and the resulting values of B_{12} are on the order of >1000 $cm^3·mol^{-1}$ more negative than both B_{11} and B_{22}. These large negative B_{12} values suggest either unprecedented strength of water + solute interactions (compared to alcohols, ammonia, or HCl) or, more likely, the existence of large errors due to appreciable adsorption on the walls of the measuring devices. For $H_2S + H_2O$ interactions the values of B_{12} could be, in principle, calculated from the measured compositions of the coexisting vapor and liquid phases.[52] However, the simple method of data treatment, outlined above, cannot be used for the $H_2S + H_2O$ system because of the high mutual solubility of the components of this system in the coexisting phases.

Temperature Dependence of B_{12} Data

Summing up the compilation of the literature B_{12} data, we conclude the following:

Table 7. Values of the Mixture-Specific Parameter k_{12} for the Tsonopoulos Correlation

compd	a_{Ts}	N^d	T^e/K	k_{12}
Ar, argon		46	200−1200	0.352(27)
N_2, nitrogen		52	243−1000	0.296(11)
CO, carbon monoxide		19	311−698	0.251(30)
N_2O, nitrous oxide		4	298−100	0.17(4)
O_2, oxygen		7	298−348	0.40(3)
CH_4, methane		49	240−698	0.319(14)
C_2H_6, ethane		26	298−698	0.360(12)
C_3H_8, propane		15	363−698	0.433(13)
C_4H_{10}, *n*-butane		14	363−698	0.443(10)
C_5H_{12}, *n*-pentane		15	363−698	0.466(13)
C_6H_{14}, *n*-hexane		18	363−698	0.494(17)
C_7H_{16}, *n*-heptane		11	363−698	0.505(15)
C_8H_{18}, *n*-octane		13	363−648	0.517(15)
CO_2, carbon dioxide		59	289−1100	0.138(15)
C_2H_4, ethene		19	311−648	0.257(17)
C_3H_6, propene		8	363−393	0.32(3)
C_6H_6, benzene		32	363−698	0.282(11)
C_7H_8, toluene		6	400−525	0.27(3)
C_6H_{12}, cyclohexane		30	363−698	0.471(13)
C_6F_6, hexafluorobenzene		28	378−525	0.342(8)
HCl, hydrogen chloride	−0.011[a]	33	263−750	−0.224(14)
CH_3OH, methanol	0.0878[b]	10	373−527	0.012(8)
C_2H_5OH, ethanol	0.0878[c]	6	400−525	0.05(3)
NH_3, ammonia	−0.022[a]	37	373−523	−0.171(13)
CH_3Cl, chloromethane	−0.008[a]	14	363−423	0.16(3)
$CHCl_3$, chloroform	−0.003[a]	10	353−403	0.20(3)
C_2H_5Cl, chloroethane	−0.007[a]	14	363−423	0.21(3)
SO_2, sulfur dioxide	−0.009[a]	22	383−483	0.046(30)
C_3H_6O, acetone	−0.032[a]	26	383−443	−0.020(30)

[a] From our fit of B_{22} data recommended by Dymond et al.[2] [b] This a_{Ts} and b_{Ts} = 0.0525 are from ref 89. [c] This a_{Ts} and b_{Ts} = 0.0578 are from ref 89. [d] Total number of experimental B_{12} and φ_{12} data points. [e] The temperature range of available B_{12} and φ_{12} data.

1. There are data for 32 interactions between water and other compounds, including nine interactions involving compounds with a dipole moment higher than 1 D.
2. In most cases, where B_{12} results are available from various types of measurements, the agreement of different sets of data is satisfactory; see, as examples, Figures 2, 5, 9, 12, and 14.
3. Nevertheless, in the overwhelming majority of cases, the accuracy of available B_{12} and φ_{12} data and the limited temperature range where these values are measured do not allow meaningful determinations of the parameters of even simple intermolecular potential energy functions.

In light of this situation, the practical option is to use corresponding-state correlations to describe the temperature dependence of B_{12} and φ_{12} data. We employ for these purposes the widely used Tsonopoulos[3] correlation, which results in the expression:[3,88]

$$B(T) = \frac{RT_c}{P_c}(f^{(0)}(T_r) + \omega f^{(1)}(T_r) + a_{Ts}f^{(2)}(T_r) + b_{Ts}f^{(3)}(T_r)) \tag{17}$$

where $f^{(0)}(T_r)$, $f^{(1)}(T_r)$, $f^{(2)}(T_r)$, and $f^{(3)}(T_r)$ are universal functions of reduced temperature; ω stands for the acentric factor; the parameter a_{Ts} is necessary for polar compounds; and the parameter b_{Ts} is introduced for alkanols.[89] The recent test[90] of the Tsonopoulos correlation for argon showed that it may need revision at low and high reduced temperatures; however, we employ this correlation in its original form. For pure water we use a_{Ts} = −0.0109, as recommended by Tsonopoulos and Heidman.[91] For other polar compounds the optimal values of a_{Ts} were determined by the fit of the B_{22} data recommended by Dymond et al.,[2] and these values are given in Table 7. If all the necessary properties for pure compounds are known, then the ap-

Table 8. Values of the Parameters d_i of Eq 20 for Cross Virial Coefficients

compd	T/K	d_0	d_1	d_2	d_3	class
He, helium	100−2000	17.48	−3.829	−5.362	2.227	*a*
Ne, neon	100−2000	10.34	−15.26	−5.934	2.016	*a*
Ar, argon	100−2000	−28.89	−70.04	−13.56		*a*
H_2, hydrogen	243−713	1.01	−22.40	−9.94		*b*
N_2, nitrogen	243−1200	−34.79	−86.87	−5.15		*a*
CO, carbon monoxide	311−1200	−41.37	−95.97	−7.08		*a*
N_2O, nitrous oxide	298−1200	−179.54	−426.46	−232.44		*b*
O_2, oxygen	298−1200	−26.91	−84.07	−19.92		*a*
CH_4, methane	298−1200	−62.43	−193.78	−235.45	−187.80	*a*
C_2H_6, ethane	298−1200	−110.89	−239.90	−75.98		*a*
C_3H_8, propane	363−1200	−123.78	−261.62	−65.02		*b*
C_4H_{10}, butane	363−1200	−165.12	−343.92	−92.79		*b*
C_5H_{12}, pentane	363−1200	−185.66	−390.60	−106.97		*b*
C_6H_{14}, hexane	363−1200	−198.97	−412.40	−94.57		*c*
C_7H_{16}, heptane	363−1200	−233.95	−517.74	−164.73		*c*
C_8H_{18}, octane	363−1200	−251.02	−532.54	−136.75		*c*
CO_2, carbon dioxide	289−1200	−211.31	−729.48	−1064.54	−656.13	*a*
C_2H_4, ethene	311−1200	−131.77	−246.04	−50.96		*b*
C_3H_6, propene	363−1200	−183.79	−379.22	−131.57		*b*
C_6H_6, benzene	363−1200	−412.25	−769.03	−265.76		*b*
C_7H_8, toluene	400−1200	−535.97	−1128.45	−526.94		*c*
C_6H_{12}, cyclohexane	363−1200	−215.07	−370.24	−34.42		*b*
C_6F_6, hexafluorobenzene	378−1200	−388.58	−792.52	−297.92		*b*
HCl, hydrogen chloride	300−1400	−613.63	−2139.58	−3013.62	−1663.16	*d*
CH_3OH, methanol	373−1400	−1187.68	−4503.46	−6210.67	−3084.14	*c*
C_2H_5OH, ethanol	400−1400	−1186.85	−4391.86	−5966.82	−2967.59	*d*
NH_3, ammonia	323−1400	−1025.02	−4307.68	−6710.72	−3696.81	*c*
CH_3Cl, chloromethane	363−1200	−336.78	−900.72	−914.22	−442.92	*c*
$CHCl_3$, chloroform	353−1200	−692.83	−2627.15	−4034.41	−2387.31	*d*
C_2H_5Cl, chloroethane	363−1200	−394.39	−906.38	−490.79		*c*
SO_2, sulfur dioxide	383−1200	−520.83	−1620.29	−1966.46	−985.79	*b*
C_3H_6O, acetone	383−1400	−1721.83	−6783.94	−9864.78	−5137.07	*c*

[a] The expected accuracy of B_{12} is better than ± 10 $cm^3 \cdot mol^{-1}$ and better than ± 15 $cm^3 \cdot mol^{-1}$ at the lowest temperatures. [b] The expected accuracy of B_{12} is better than ± 20 $cm^3 \cdot mol^{-1}$ at the lowest temperatures. [c] The expected accuracy of B_{12} is better than ± 30 $cm^3 \cdot mol^{-1}$ at the lowest temperatures. [d] The estimates of accuracy appear unwarranted.

plication of this correlation to mixtures requires only one additional mixture-specific parameter, k_{12}, which appears in the combining rule for the critical temperature of a binary mixture, T_{c12}:

$$T_{c12} = (T_{c1}T_{c2})^{0.5}(1 - k_{12}) \tag{18}$$

Other mixture properties are estimated according to simple empirical combining rules given by Tsonopouolos.[3,88] In this study the determination of the optimal values of k_{12} was done by the minimization of the objective function

$$F = \sum((B_{calc} - B_{12})/\delta B_{12})^2 + \sum((\varphi_{calc} - \varphi_{12})/\delta\varphi_{12}) \tag{19}$$

where δ represents the assumed uncertainty of an experimental data point, and the subscript calc denotes the calculated value. Note that the accepted values of δ may differ from the error estimates given in parentheses in Tables 1−6, because the latter give only statistical errors and the real uncertainties may be considerably larger due to systematic errors of both the measurements and the data treatment. The necessary values of the critical properties and ω for pure compounds are taken from Poling et al.[88] For some compounds the values of the acentric factor are not given in that source and they are taken from ref 92. The optimal values of k_{12} are given in Table 7, together with their uncertainties in parentheses. If, for a particular interaction, data are only available from one laboratory over a limited temperature range, then the minimal uncertainty of k_{12} is taken to be 0.03. Otherwise, we accept the statistical value of the uncertainty interval at the 0.95 confidence level. In all cases, we considered the k_{12} parameter to be temperature independent. The corresponding-state correlations should not be used for interactions involving He, Ne, or H_2. In addition, the Tsonopoulos correlation cannot reproduce values of B_{12} for Ar + H_2O interactions within the small uncertainty brackets recommended[33] for the temperature range from (100 to 2000) K (however, these B_{12} can be described accurately by empirical temperature equations; see Table 8). The results[33] may suggest the necessity of more elaborate combining rules for interactions involving water. However, for other interactions, where data are available over more limited temperature ranges, inspection of Figures 1−15 reveals that in most cases the Tsonopoulos correlation describes available B_{12} and φ_{12} data satisfactorily. The current work gives the most extensive set of k_{12} values for interactions involving water for this popular corresponding-states correlation. Comparison with previously published values of k_{12} for the Tsonopoulos correlations,[3,89,91] based, as a rule, on smaller data sets, shows that k_{12} values agree within (0.01 to 0.03).

Finally, for data presentation purposes, it was decided to describe the temperature dependence of B_{12} by polynomials of the following type:

$$B_{12} = \sum_{i=0} d_i(T_0/T - 1)^i \tag{20}$$

where $T_0 = 298.15$ K. The d_i parameters were determined by the minimization of the objective function given by eq 19. Note that the temperature dependence of φ_{12} consistent with eq 20 is given analytically by the following equation:

$$\varphi_{12} = \sum_{i=0} d_i(T_0/T - 1)^{i-1}[(i + 1)T_0/T - 1] \tag{21}$$

We also included in the data set predicted values of B_{12} at temperatures up to 1200 K or up to approximately the

Boyle temperature for the corresponding B_{12}. However, no attempts to extrapolate B_{12} below the temperature of the availability of experimental values were undertaken. The resulting values of d_i are given in Table 8, together with the temperature range of the expected validity of eq 20. Naturally, these values of d_i are subject to revision as new experimental results are published. We also assign (presumably conservative) estimates of the expected uncertainties of B_{12} values (see the last column of Table 8), except for a few interactions where any estimates are unwarranted.

Conclusion

The goal of this work was to compile and, if necessary, evaluate from published experimental results the values of the second cross virial coefficients, B_{12}, and isothermal Joule−Thomson coefficients, φ_{12}, for interactions involving water. Methods of evaluation of B_{12} and φ_{12} from *PVT* properties and excess enthalpies of gas mixtures, and from solubility of water in compressed gases are outlined. The inventory of B_{12} values (or experimental data leading to B_{12} values) for each of the interactions considered is briefly discussed. In all, there are data for interactions between water and 32 other compounds, 9 of which have appreciable dipole moments. In most cases the temperature dependence of both B_{12} and φ_{12} can be satisfactorily described by the Tsonopoulos corresponding-states correlation. This correlation has been used to extrapolate B_{12} to high temperatures. Finally, the selected experimental data and predictions of the corresponding-states correlations at high temperatures are described by an empirical temperature polynomial equation that provides estimates of B_{12} up to 1200 K.

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Supporting Information Available:

Values of B_{12} and φ_{12}, both those from the literature and those evaluated in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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