# Dr. René Mora-Casal

The Second Virial Coefficients for Normal Fluids

Their Estimation, New Approach and Correlations
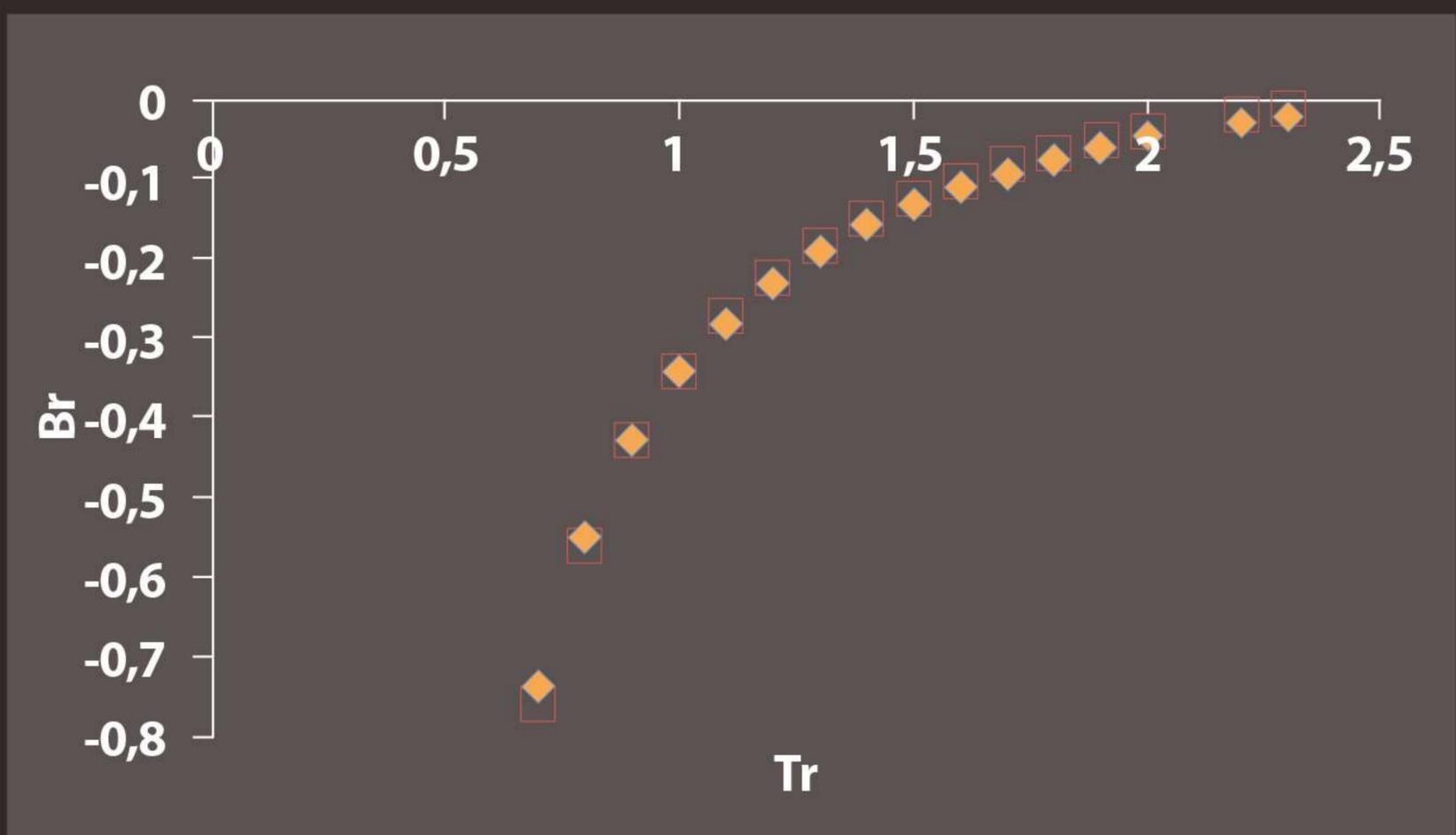
The Estimation of Second Virial Coefficients

for Normal Fluids:

New Approach and Correlations

René A. Mora-Casal

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© The Estimation of Second Virial Coefficients for Normal Fluids: New Approach and Correlations

René A. Mora-Casal
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To my grandmother,
Ester Morgan-Ulloa de Casal.

Scientific research consists in seeing what everyone else has seen,

but thinking what no one else has thought.

A. Szent-Gyorgyi.

ACKNOWLEDGMENTS

Thanks to God for allowing me to complete the Doctorate and this research project, on a subject that I began to be interested in almost twenty years ago.

Thanks to my wife for her love and continuous support during this journey.

Thanks to the National Institute of Standards and Technology (NIST) in the United States, for making available accurate second virial coefficients of many compounds thru the NIST SRD 134 Database. These data were fundamental for the development of this work

Thanks to the authors of the Infotherm database in Germany, for making available a lot of experimental data, among them critical constants and second virial coefficients that were not available in other sources.

Thanks to John H. Dymond for its continuous work, compiling and evaluating second virial coefficients during the last forty-five years. I understand his passion.

Thanks to all the remarkable researchers (Van der Waals, Berthelot, Pitzer, Tsonopoulos) that contributed, many years ago, to the advance of this very interesting area of research that touches many others. I owe to them very much.

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PRESENTATION

Two new correlations for the estimation of the second virial coefficient $B(T)$ were developed for normal fluids. A model-free strategy was followed for the determination of the required functions f_0 and f_1; their values were calculated directly, without any previous assumption about their mathematical form. Both correlations are based on the Corresponding States Principle using the acentric factor as the third parameter.

An analysis was made of seventeen models for $B(T)$, and mathematical specifications were defined for a general model in order to ensure the correct limits at low and high temperatures: three of those specifications are mandatory. It was found that many equations recommended in the Dymond et al. compilation (2002) do not comply with the specifications; in consequence, they exhibit wrong behavior.

For the development of the correlations 62 substances were used. They were divided in two groups: one of 42 non-polar substances, and the other one of 20 substances with slight dipole or quadrupole moments; at the end, no difference was found between both groups. Their critical properties and acentric factors were validated graphically, and the recommended $B(T)$ values by Dymond et al. were fitted to appropriate equations. For 16 substances, several sets of data were available covering a wide range of temperature, and reference equations were obtained from them. The equations for $B(T)$ developed by the Zarkova group in Europe could not be used because they predict the wrong temperature dependence (very steep) and Boyle temperatures (very low).

Boyle temperatures T_B were successfully used to extend the temperature range of the second virial coefficient equations for many compounds. In some cases, this property was estimated using the method of Iglesias-Silva et al. (2001).

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The obtained correlations provide good to excellent fits when compared to the recommended $B(T)$ values in the Dymond et al. compilation. The correlation based on RT_c/P_c is slightly better than the one based on V_c. The new correlations were compared graphically with the most relevant of the previous models, and in one case (f_1 reduced in V_c), the new curve is different from any previous model. The new correlations are less negative at low temperatures when compared with Tsonopoulos (1974) and other models; they are instead closer to Pitzer & Curl (1957).

Additionally, two correlations were obtained for the constant a_0, equal to the limit of the reduced B(T) at high temperature, and two correlations were obtained for the Boyle temperature T_B, all of them dependent of the acentric factor.

The results of the present research were successfully presented as the doctorial thesis to hold a Doctorate Degree in Chemical Engineering to the Atlantic International University, Hawaii, USA in 2014.

INTRODUCTION

The non-ideality of real gases should be considered during the calculation of vapor densities and fugacities, at low temperatures or high pressures, where the ideal gas assumption is not applicable (Prausnitz, 1959; Nagahama & Hirata, 1970). In vapor-liquid equilibrium processes involving pure substances or multi-component mixtures, the non-ideality of gases is an important issue, even at low pressures (Lee & Chen, 1998). If not taken into account, errors made could affect the design of mass transfer equipment. Examples of these processes are gas absorption and distillation.

The second virial coefficient is a relevant property when determining the effect of the non-ideality of real gases. It allows the fast calculation of fugacities at pressures above the atmospheric one, up to a value of about 15 atmospheres (Tsonopoulos, 1974); this includes the vast majority of existing chemical and industrial applications. Second virial coefficients are also used for the estimation of other properties, such as enthalpies, entropies and Joule-Thompson coefficients (Smith & Van Ness 1975; Boschi-Filho & Buthers 1997; O'Connell & Haile 2005).

Correlations for the second virial coefficient must be used to estimate this property in those cases when experimental information is scarce or non-existent, also for computer-aided calculations and simulation programs. Most of the recommended correlations (Tsonopoulos, Pitzer & Curl, among others) were developed more than forty years ago, when the existing experimental data about second virial coefficients were scarcer and less accurate. Thus, there is an interest in developing new correlations based on the latest available data.

For the calculation of fugacities and other functions for real gases, two approaches can be used (Prausnitz, 1959; O'Connell & Haile 2005):

   (a) Use of an equation of state, which may be specific for the substance or generic;

   (b) Use of the virial equation, which has the advantage of being theoretically rigorous and easily applicable to mixtures.

The virial equation was proposed originally by Thiessen in 1885 and later by Kammerlingh Onnes in 1901 (Rowlinson, 2002). It is written in terms of volume as follows:

(1) $$Z = \frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \cdots$$

It can also be written in terms of pressure:

(2) $$Z = 1 + B'P + C'P^2 + D'P^3 + \cdots$$

It can be demonstrated that $B' = B/RT$. For example, Figure 1 shows the variation of argon compressibility with pressure and temperature, up to 100 atmospheres and 1000 K; it is evident that Equation (2) can be used to fit the isotherms.

Figure 1.

Variation of argon compressibility with pressure, at several temperatures.

Data from Perry & Green (2007).
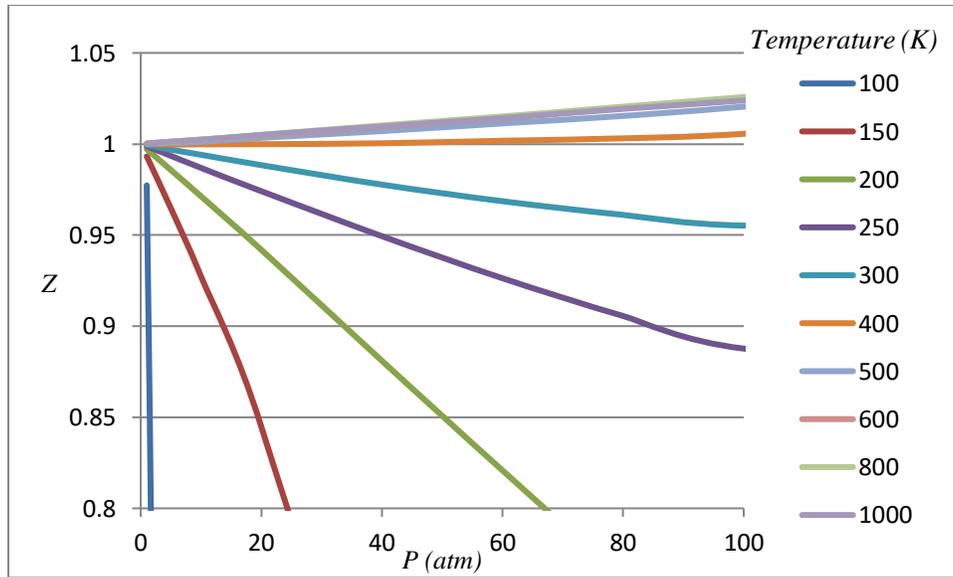
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Given the scarcity of information on virial coefficients beyond the second, and that the available data on critical pressures and temperatures are more reliable than the data on critical volumes, it is preferred to use the Equation (2) in practical applications, truncated after the second term (Tsonopoulos, 1974; Hayden & O'Connell, 1975):

(3A)
$$Z = 1 + B'P$$

(3B)
$$Z = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r}$$

There are many correlations for the estimation of *B(T)*, one of the most used is the Tsonopoulos correlation (Tsonopoulos, 1974), developed forty years ago. The improvement of these correlations is an active field of research, as new or more accurate *B(T)* information is available. Following the work of Pitzer & Curl (1957) and Schreiber & Pitzer (1988), correlations for *B(T)* in reduced terms have taken one of the following forms:

(4A)
$$\frac{B}{V_c} = B_{r1} = f_{01}(T_r) + \omega \cdot f_{11}(T_r)$$

(4B)
$$\left(\frac{BP_c}{RT_c}\right) = B_{r2} = f_{02}(T_r) + \omega \cdot f_{12}(T_r)$$

where ω is the acentric factor, a parameter which measures the asymmetry of the molecule, its deviation with respect to the spherical shape. Substances that satisfy equations (4A) or (4B) are called *normal fluids* (Pitzer et al. 1955b). In this document, the symbols B_r, f_0 and f_1 will be used instead of B_{r1}, f_{01}, f_{02}, etc. when referring to general characteristics shared by both correlations.

Equation (4B) has been the basis of several recent correlations for *B* (Zhixing, Fengcun & Yiqin 1987; Lee & Chen 1998; Vetere 2007), but other approaches have been recently tried, such as applying the square well and Stockmayer potentials (McFall et al. 2002; Ramos-Estrada et al. 2004), or using the Boyle temperature as the parameter (Iglesias-Silva & Hall 2001; Iglesias-Silva et al. 2010).

Problem Formulation and Systematization

In this study, a novel methodology to determine the functional shape of B_r for normal fluids will be proposed; this methodology has not been used so far for the estimation of second virial coefficients. It consists in plotting all the available B_r data at fixed T_r for different fluids, this is equivalent to choosing the acentric factor ω as independent variable. According to Equations (4A) and (4B) above, a graph of B_r versus ω at constant T_r should be a straight line for normal fluids. If

this procedure is repeated for each value of T_r where data is available, the values of $f_0(T_r)$ and $f_1(T_r)$ can be obtained *without making a prior assumption of the mathematical form of these functions*. This would be one of the main results of this study.

Figure 2.

Expected relationship between B_r and ω for a normal fluid.
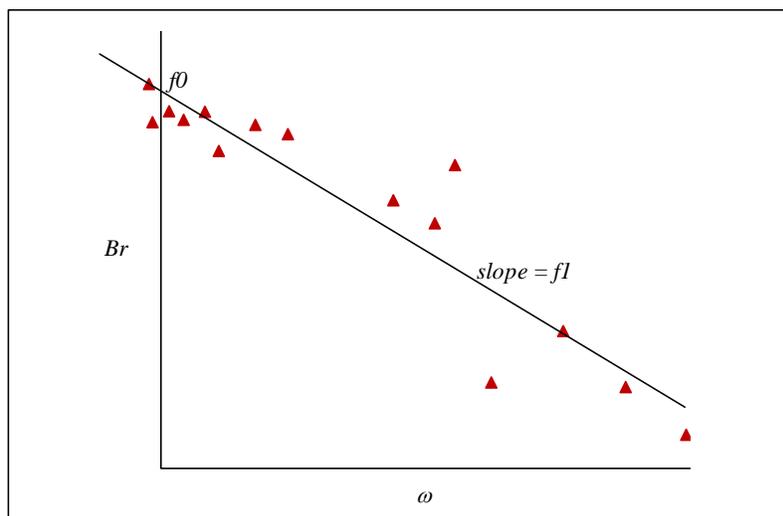
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The proposed study will address:

(1) An analysis of the requirements of a suitable model for *B(T)*, one with extrapolation capabilities;

(2) A critical analysis of the available *B(T)* data and fitting equations, specially the data and equations recommended in Dymond et al (2002);

(3) The expansion of the available range of *B(T)* data and fitting equations by the use of the experimental or estimated Boyle temperatures;

(4) The development of a new correlation for the second virial coefficient *B*, based on the above model-free strategy.

Research Rationale

As indicated above, the reasons for developing a new correlation for second virial coefficients are two: the existence of a growing set of experimental data for many substances, both of high quality and critically evaluated; and that the main correlations were developed many years ago, when this information was not available.

Another relevant reason to do this research is the possibility of studying the behavior of the functions $f_0(T_r)$ and $f_1(T_r)$ based on a direct calculation from the experimental data, without making assumptions about their mathematical form. A new correlation will be proposed, but its mathematical form (polynomial, exponential, other) will be defined according to the goodness-of-fit to the experimental values of the functions, and not vice versa.

A fourth reason is that both good equations and bad equations were found in the literature for estimating the second virial coefficient, their goodness based on the extrapolation capability. No attempt has been made before to establish minimum criteria that these fitting equations or correlations must obey, limiting the usefulness of these models.

This research will contribute to the Engineering field by providing better methods, and one improved correlation, for the estimation of second virial coefficients. Therefore, its general objective consists in developing a new and accurate correlation for the estimation of second virial coefficients in normal fluids, with good extrapolation characteristics, based on Equations (4A) and (4B) and applying a model-free approach to determine the values of the functions $f_0(T_r)$ and $f_1(T_r)$. The specific objectives of this study are:

a) To perform an analysis of the requirements of a suitable model for *B(T)*, based on theoretical and mathematical grounds, one with extrapolation capabilities for normal fluids;

b) To perform a critical analysis of the fitting equations in the compilation of Dymond et al (2002), determining which ones can be used and in which cases better equations should be obtained (fitted from the data or taken from the literature);

c) To combine the experimental *B(T)* data from Dymond et al. (2002), or from better sources, with the experimental or estimated information of Boyle temperatures, in order to obtain fitting equations for *B(T)* that cover a wider temperature range;

d) To obtain the numerical values of the functions $f_{01}(T_r)$, $f_{11}(T_r)$, $f_{02}(T_r)$ *and* $f_{12}(T_r)$ in Equations (4A) and (4B), by generating a table of values of reduced *B* versus two dependent variables, the reduced temperature T_r and the acentric factor ω.

e) To develop at least one new correlation for the second virial coefficient *B(T)*, applicable to normal fluids, based on the criteria established in objective (a), and test it against the experimental data.

The scope of this research will be restricted to the development of a correlation for second virial coefficients applicable to normal fluids, a group that mostly includes non-polar substances. Polar and associated substances shall not be considered; also the study of mixtures will be excluded from this research due to the following reasons:

1. The second virial coefficient of polar and associated compounds is usually modeled as the value of *B(T)* for a normal fluid, e.g. using Equations (4A) or (4B), plus a polar or association term. Therefore, the study of normal fluids is the first step.

2. The own interest in testing a model-free approach for obtaining the functional form of the second virial coefficient, without making any previous assumption.

3. The estimation of the second virial coefficient of mixtures is a step to be considered later, once a correlation has been developed. Mixing rules are already a separate subject of study.

This research will make use of the latest experimental and/or recommended second virial coefficients for a selected set of normal fluids, data already evaluated on its accuracy and reliability by other specialists. Accordingly, the experimental measurement of second virial coefficients as well as the evaluation of the existing experimental data to determine its accuracy and/or reliability will be outside the scope of this research.

Chapter I.
METHODOLOGICAL AND
THEORETICAL FRAMEWORK

1.1. METHODOLOGY

As a first step in this research, some recommendations will be made regarding the correct functional form of the second virial coefficient, one that has the correct asymptotic limits when the temperature is very low or very high. This is important in order to choose the mathematical form of the functions $f_0(T_r)$ and $f_1(T_r)$, once their values are obtained; this will allow the model to have extrapolation capabilities. An example of a good model for this sense is Pitzer & Curl (1957).

Examples of the opposite are the fitting equations included for individual compounds in the compilation of Dymond et al. (2002). Many of them have an incorrect behavior at the ends. A critical analysis of these equations will be the second step in this study; an important task because we will need fitting equations to develop a table of values of B_r with T_r and ω as dependent variables.

One note regarding the first two steps: for practical reasons, a positive value for the high-temperature limit of the second virial coefficient will be established, instead of the true limit which is zero; in this, most of the previous researchers are being followed. There are two reasons for this procedure: the true limit implies that there would be a maximum in *B(T)* at high temperature, that the model would need to reproduce; however, this maximum value of *B(T)* has been measured experimentally for a few substances only.

The third step in this study will be to develop a strategy to extend the range of applicability of the second virial coefficient fitting equations. Thus, the available *B(T)* information will be combined with the experimental or estimated Boyle temperature. There are several recent studies devoted to the accurate determination or estimation of this property (Iglesias-Silva et al. 2001, 2010; Ramos-Estrada et al. 2004; Estrada-Torres et al. 2007); an important result since it allows having the widest range of values of the reduced temperature.

A second note regarding the previous step: it is desirable to use different fitting equations for the calculation of the B_r values for the chosen fluids. There is one reason for that proposal: if we use the same model for all the fitting equations, it is possible that it influences the values of $f_0(T_r)$ and $f_1(T_r)$, so they will follow the same model. This kind of influence is to be avoided.

The fourth and last step of this research is the determination of the values of the functions $f_0(T_r)$ and $f_1(T_r)$. These functions will be fitted to a suitable model and then a verification of the accuracy of the resulting correlation will be made, by comparing the estimated values against the experimental ones.

This research will determine the numerical values of the functions $f_0(T_r)$ and $f_1(T_r)$ in Equations (4A) and (4B), without making any assumption about its mathematical form. If this determination is possible constitutes one of several leading questions of the project.

As a result of the present study, a new *B(T)* correlation for normal fluids will be proposed. What the desirable characteristics of a good model are and how to obtain the right model parameters from the experimental data are other relevant questions.

The Boyle temperature T_B will be used as an aid in extending the range of available *B(T)* data, and in obtaining extended fitting equations in those cases where this temperature is not included. If T_B can be used effectively as intended is a relevant question for this research.

This study is based on the following reasonable hypotheses:

a) The second virial coefficient of normal fluids follows a simple model, Equation (4A) or (4B).

b) As a consequence of (a), a graph of B_r versus the acentric factor will be a straight line.

c) A model for the second virial coefficient must comply with certain characteristics, i.e. specific asymptotic limits, in order to have good extrapolation capabilities.

Regarding the information sources, in recent years, many researchers have worked on the critical evaluation of the available experimental data, and the gathering of new high quality measurements, in order to establish its reliability (Dymond 1986; Tsonopoulos et al. 1989; Steele & Chirico 1993; Lemmon & Goodwin 2000; Owczarek & Blazej 2003, 2004, 2006); thereby ensuring access to the best information requested by the high technology industry and the scientific

community; a very relevant labor for the development of reliable estimation methods. As a result of these efforts, several databases exist worldwide, among them:

- The Thermodynamics Research Center (TRC) database (now at NIST, USA);
- The AIChE DIPPR 801 project database (USA);
- The Dortmund Data Bank (Germany);
- The DECHEMA Database (Germany);
- The NIST Webbook online database (USA, free access);
- The Infotherm database (Germany, free access);
- The CHERIC KDB database (Korea, free access);
- The AIST databases (Japan, free access).

For the current research, experimental information regarding the critical properties, acentric factors, second virial coefficients and Boyle temperatures will be required. The critical properties and acentric factors will be obtained from the literature (Steele & Chirico 1993; Lemmon & Goodwin 2000; Owczarek & Blazej 2003, 2004, 2006), and from the DIPPR compilation data available in *Perry's Chemical Engineers' Handbook* (Perry 2007) and the *CRC Handbook of Chemistry and Physics (Lide, 2009)*, among other sources. The aforementioned databases will be consulted if required.

Second virial coefficients will be obtained from the compilation of Dymond et al. (2002); however, this reference includes the data available up to 1998 only. After that date, a significant number of articles have been published with experimental data of second virial coefficients (Hurly 1999, 2000a, 2000b, 2002, 2003, 2004; Hurly et al. 1997, 2000; Zhang et al 2001), or with recommended values and fitting equations (Zarkova et al. 1996, 1998, 1999, 2000a, 2000b, 2003, 2005, 2006; Zarkova & Pirgov 1997; Zarkova & Hohm 2002, 2009; Harvey & Lemmon, 2004; Hohm & Zarkova 2004; Hohm et al. 2006, 2007; Damyanova et al. 2009, 2010); all this literature will be considered.

Boyle temperatures will be obtained from the literature available: there are several recent articles devoted to methods of obtaining this property from experimental *B(T)* data or from reference equations of state (Iglesias-Silva et al. 2001, 2010; Ramos-Estrada et al. 2004; Estrada-Torres et al. 2007). In cases when an experimental value is not available, there are three estimation methods, which are Danon & Pitzer 1962; Tao & Mason 1994 and Iglesias Silva et al. 2001.

The first step of this study will have strong theoretical and mathematical foundations, as several models for the second virial coefficient will be analyzed in order to identify desirable features to include in the *B(T)* model. Among the models to be analyzed are: hard-sphere, square-well, Lennard-Jones, Berthelot, Pitzer-Curl, Tsonopoulos, among others.

For the remaining steps, the research will involve the analysis of experimental data and the use of numerical methods, the main one will be the least-squares method for the fitting of linear models to the *B(T)* data. The theory of least-squares is widely known and it will not be discussed here; there is already computer software available with regression capabilities included, i. e. Excel from Microsoft. Excel has the option to perform the polynomial regression of a set of data inside a graphic, including also the regression equation and the coefficient of determination R^2. This will be used extensively during the study, as testing of several possible models is rapidly allowed, as well as the visual verification of the goodness-of-fit of the model. Some numerical differentiation of data will also be done in order to calculate the derivatives of the argon second virial coefficient; a relevant comparison when discussing a simple model that reproduces *B(T)* and its derivatives for argon.

The validation of the fitting equations will be made by means of the coefficient of determination as well as visually in order to detect cases of overfitting (there are several cases in the Dymond compilation). The validation of the final model for *B(T)* will be done by comparing the calculated values versus the experimental ones for selected compounds.

1.2. THEORETICAL FRAMEWORK

1.2.1. Corresponding States Principle

Any generalized correlation of *B(T)*, as most Engineering correlations, is based on the Corresponding States Principle (CSP), one of the simplest but most powerful principles in Physics. It can be expressed as follows: *all fluids can be represented by a universal function in reduced variables* (Guggenheim 1945, Glasstone 1949, Xiang 2005). The universal function can be an equation of state or an intermolecular potential, dependent of a few characteristic reduced parameters; for example, many equations of state can be written as follows:

$$(5) \qquad\qquad P/P_c = F(T/T_c , V/V_c)$$

The CSP was first established by Van der Waals in 1880, it can be demonstrated on a statistical thermodynamic basis (Xiang 2005). The conditions for Equation 5 to be applicable are very strict and were established first by Pitzer (1939) and later by Guggenheim (1945) as follows:

(i)   classical statistical mechanics applied (i.e. no quantum effects);

(ii)   spherical symmetry;

(iii)   intramolecular vibrations the same in the liquid and gas states;

(iv)   additivity of intermolecular forces, and

     (v)   the potential energy can be expressed as a universal function $A\Phi(r/r_0)$ (the Lennard-Jones potential being an example).

The formulation above is called *two-parameter CSP* and it is only applicable to simple, spherical molecules such as the noble gases (Guggenheim 1945). For gases with quantum effects like helium, hydrogen and neon, a third parameter Λ^* must be added; these gases are usually taken out of second virial coefficient correlations, with one exception (Meng & Duan 2007). More important was the development of a *three-parameter CSP* for describing the behavior of normal fluids around 1950, being the acentric factor ω and the critical compressibility Z_c examples of the third parameter (Pitzer 1955b, Leland 1966). Polar and associating compounds require a *four-parameter CSP* in order to reproduce their behavior, several fourth parameters have been proposed (e.g. Halm & Stiel 1971, Tsonopoulos 1974, Xiang 2005). For each additional parameter, there is an increase in complexity and a loss of generality in the CSP correlations, as it is difficult for one model to describe all substances, unless specific parameters are used. In this study the three-parameter CSP will be used, based on the acentric factor ω defined by Pitzer et al. (1955b).

1.2.2. The Second Virial Coefficient
1.2.2.1.   Definition of Second Virial Coefficient

The second virial coefficient *B(T)* can be defined in two ways:

1. As the coefficient of the second term in Equation (1), the virial equation;
2. According to Statistical Thermodynamics, *B(T)* represents the contribution of two-molecule interactions or collisions to the compressibility Z. It can be calculated rigorously as follows:

(6) $$B(T) = -2\pi N_A \int_0^\infty \left(e^{-U(r)/kT} - 1\right) r^2 \, dr$$

where N_A is the Avogadro number and $U(r)$ is the intermolecular potential function, a measure of the potential energy between two molecules. A typical graph of *B* vs *T* is shown in Figure 3 below, based on argon data (Kestin et al. 1984). For a few gases, such as helium and neon, a maximum in the *B(T)* curve has been observed; this is also predicted from Equation (6).

Figure 3.

Typical graph of *B* vs. *T* for argon.
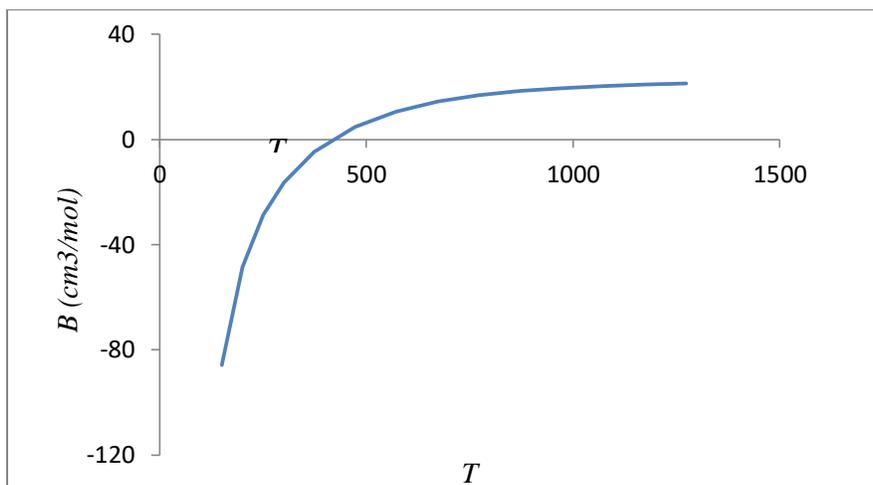
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The temperature at which *B(T)* becomes zero is called *Boyle temperature* T_B. From the graph above, it can be noted that the *B(T)* curve has a hyperbolic shape, so it is interesting and also very useful to graph this property against the inverse of the absolute temperature, as the resulting curve is flatter and some of its properties become evident for fitting purposes. This type of graph will be used extensively for this research, and a typical example is shown in Figure 4, this time based on nitrogen data (Dymond et al. 2002).

Figure 4.

Typical graph of *B* vs *1/T* for nitrogen.
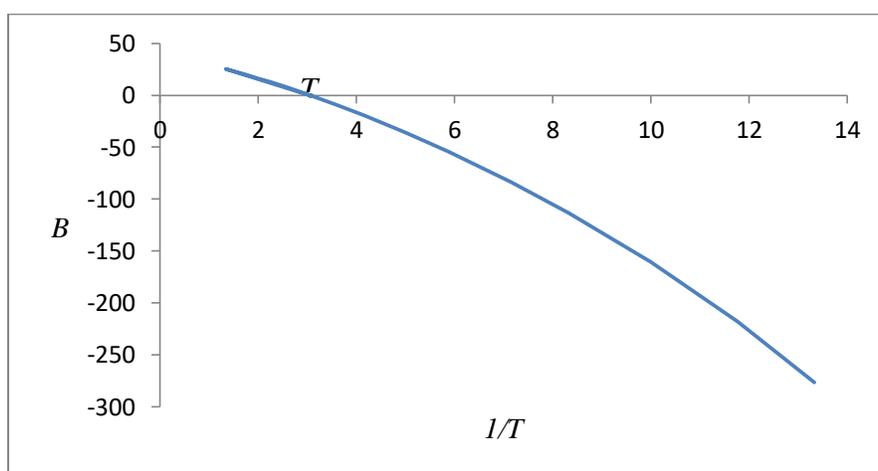
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The first and second derivatives of the second virial coefficient are required for the calculation of other properties, such as the Joule-Thomson coefficient and the effect of pressure on the specific heat (Pitzer 1957; Smith & Van Ness 1975; O'Connell & Haile 2005). Fitting of the derivatives is a stringent test for any $B(T)$ model; values of the derivatives can be obtained numerically from experimental data or high-accuracy theoretical data. In Figures 5 and 6 the first and second derivatives of argon are shown, as calculated numerically from the highly accurate values recommended by NIST (from a model by Aziz, 1993).

Figure 5.

The first derivative of *B(T)* for argon.
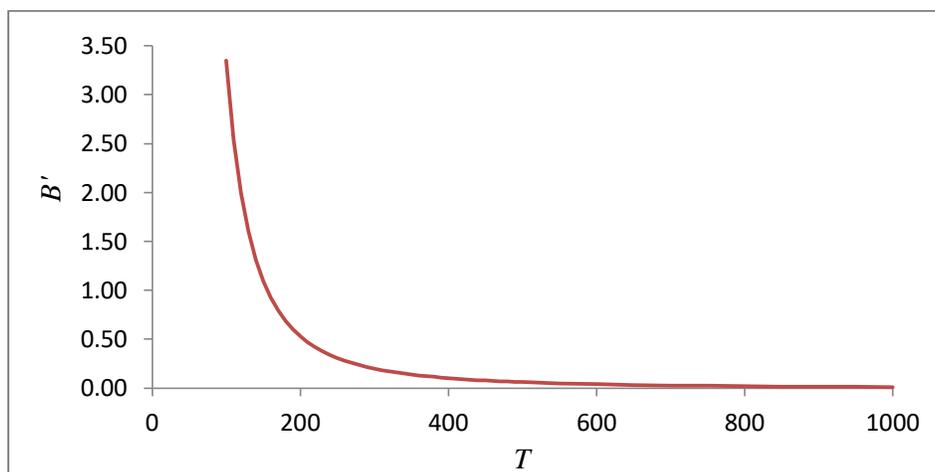
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Figure 6.

The second derivative of *B(T)* for argon.
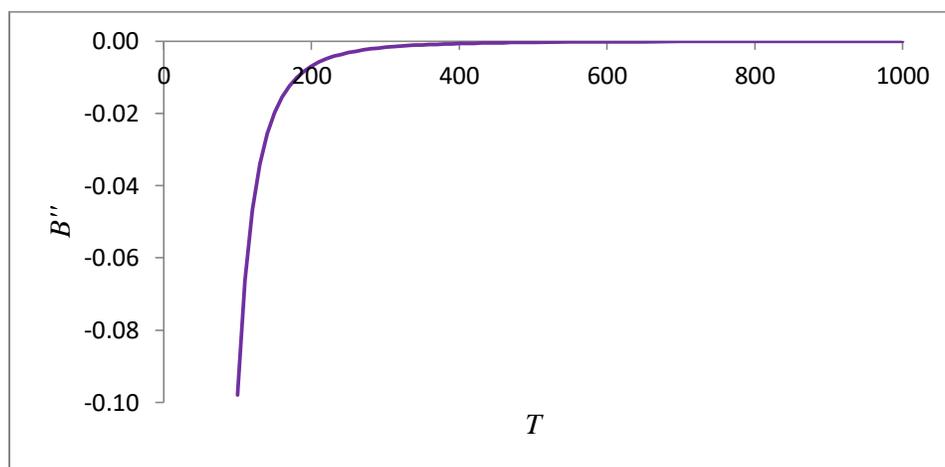
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1.2.2.2. Relationship between the Second Virial Coefficient and Other Properties

The thermodynamic properties of real gases can be estimated with the knowledge of the second virial coefficient (Pitzer 1957, Smith & Van Ness 1974; Dymond et al. 2002; O'Connell & Haile 2005). They are obtained by applying fundamental thermodynamic relationships to the truncated virial equation (3A). Some of these properties are:

Residual volume:

(7) $$\Delta V' = B$$

Residual internal energy:

(8) $$\frac{\Delta U'}{RT} = \frac{P}{R}\frac{dB}{dT}$$

Residual enthalpy:

(9) $$\frac{\Delta H'}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right)$$

Residual entropy:

(10) $$\frac{\Delta S'}{R} = -\frac{P}{R}\frac{dB}{dT}$$

Residual Gibbs energy (or chemical potential or fugacity):

(11) $$\frac{\Delta G'}{RT} = \frac{\mu_i - \mu_i^0}{RT} = \ln\left(\frac{f_i}{P}\right) = \frac{B_i P}{RT}$$

Joule-Thomson coefficient at zero pressure:

(12A) $$\eta_0 = \frac{1}{C_P^0}\left(T\frac{dB}{dT} - B\right)$$

(12B) $$\eta_0 = -\frac{1}{C_P^0}\frac{d(B/T)}{d(1/T)}$$

Variation of specific heat, at constant temperature, with pressure:

(13) $$\lim_{P\to 0}\left(\frac{\partial C_P}{\partial P}\right)_T = -T\frac{d^2 B}{dT^2}$$

The Equation (13) was used by Pitzer and Curl (1957) as a test for their correlation for *B(T)*, with successful results.

1.2.2.3. Experimental Determination of B

The experimental determination of second virial coefficients is based on several methods, the most fundamental of them is the analysis of *PVT* data, where equations (1) or (2) are used and *B(T)* is calculated as a limit when the pressure vanishes or the volume goes to infinity. Several possible limits can be used:

(14)
$$B(T) = \lim_{1/V \to 0} V(Z - 1)$$

(15)
$$B(T) = \lim_{1/V \to 0} \frac{\partial Z}{\partial (1/V)}$$

(16)
$$B'(T) = \lim_{P \to 0} \frac{(Z-1)}{P}$$

(17)
$$B'(T) = \lim_{P \to 0} \frac{\partial Z}{\partial P}$$

(18)
$$B(T) = \lim_{P \to 0} \frac{RT(Z-1)}{P}$$

(19)
$$B(T) = \lim_{P \to 0} (V - \frac{RT}{P})$$

One problem with this method is the fluid adsorption from the container walls, which affects the accuracy of the results. Other methods, such as calorimetric and speed-of-sound measurements, have been developed and are described elsewhere (Dymond et al. 2002).

1.2.2.4.   Some Theoretical Models for the Second Virial Coefficient

An expression for the second virial coefficient can be obtained if a chosen intermolecular potential formula is substituted into Equation (6). There are many possible *B(T)* models, but only three of them will be considered for the purposes of this research: the hard spheres, the square well and the Lennard-Jones models. They are important for several reasons: all are simple models; the first one (hard spheres) is the basis of the others; and the second and third models have been used successfully to fit, and even extrapolate, second virial coefficient data (Kunz & Kapner 1971; Nothnagel et al. 1973; Zhang et al. 2001; McFall et al. 2002; Nasrifar & Bolland 2004).

Hard-spheres Model

This model considers that the fluid particles are rigid spheres, so the intermolecular potential is infinite if the distance between centers is less than the particle diameter, and it is zero for greater distances, as follows (Prausnitz et al. 1999):

(20)
$$U(r) = \begin{cases} \infty \ if \ r \leq \sigma \\ 0 \ if \ r > \sigma \end{cases}$$

Figure 7.

Hard-spheres potential.
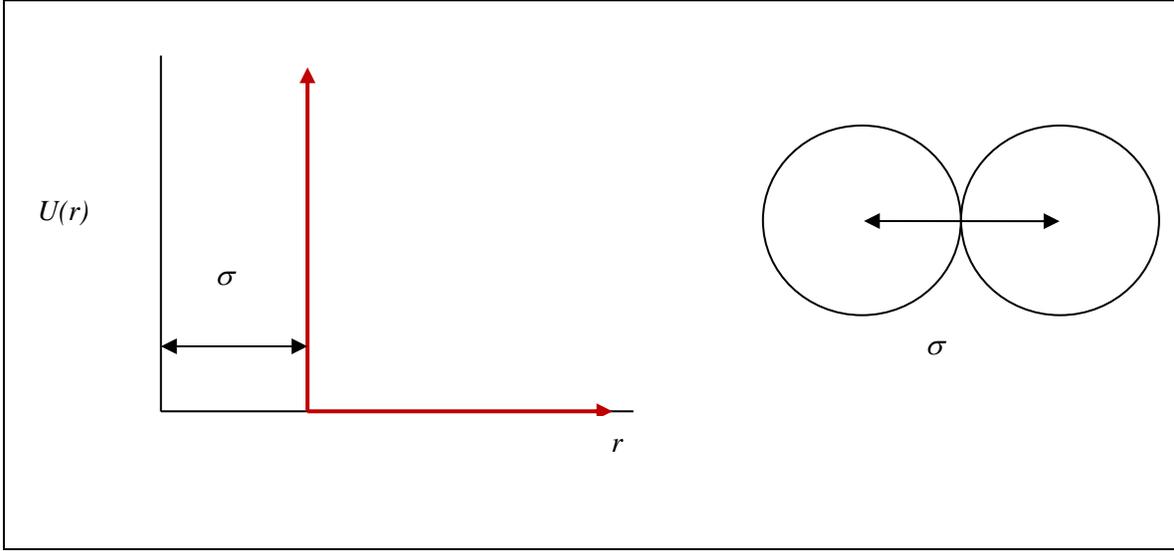
Own source

By the substitution of this potential into Equation (6), the following result is obtained:

$$B = -2\pi N_A \int_0^{\sigma} \left(e^{-\infty/kT} - 1\right)r^2 dr - 2\pi N_A \int_{\sigma}^{\infty} \left(e^{-0/kT} - 1\right)r^2 dr$$

$$(21) \qquad \boldsymbol{B = b_0 = (2/3)\pi N_A \sigma^3}$$

The constant b_0 is called the *hard-spheres second virial coefficient*, and it is a good approximation of *B(T)* at high temperature, as the distance between molecules is large and their attraction is negligible (Prausnitz et al. 1999); also b_0 will be a reference value for the constant term magnitude when fitting models to experimental *B(T)* data, as it will be discussed later.

Square-well Model:

The square-well potential can be considered an improvement over the hard spheres model, where an attractive region of magnitude $-\epsilon$ is added between $r = \sigma$ and $r = \lambda\sigma$, as follows (Huang 1998; Prausnitz et al. 1999):

$$(22) \qquad U(r) = \begin{cases} \infty \; if \; r < \sigma \\ -\epsilon \; if \; \sigma \leq r < \lambda\sigma \\ 0 \; if \; r \geq \lambda\sigma \end{cases}$$

Figure 8.

Square well potential.
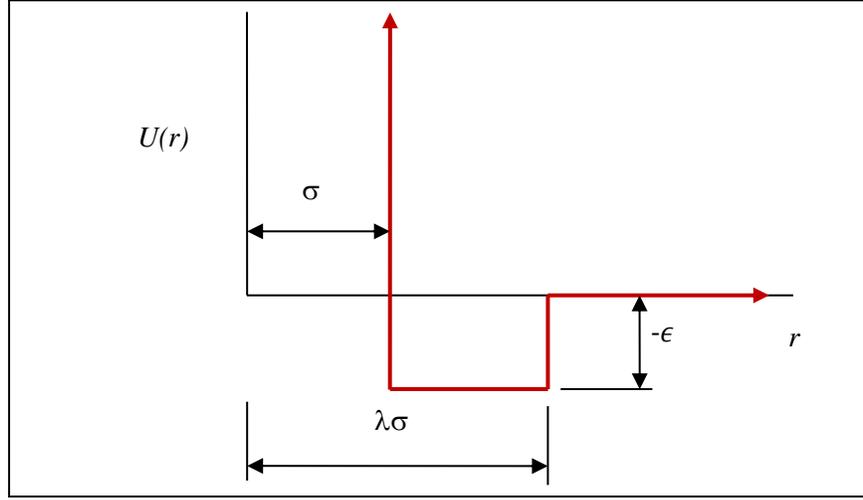
Own source

By the substitution of this potential into Equation (6), the following result is obtained:

$$B = -2\pi N_A \int_0^{\sigma} \left(e^{-\infty/kT} - 1\right)r^2 dr - 2\pi N_A \int_{\sigma}^{\lambda\sigma} \left(e^{\epsilon/kT} - 1\right)r^2 dr - 2\pi N_A \int_{\lambda\sigma}^{\infty} \left(e^{-0/kT} - 1\right)r^2 dr$$

$$B = -2\pi N_A \int_0^{\sigma} (0 - 1)r^2 dr - 2\pi N_A \int_{\sigma}^{\lambda\sigma} \left(e^{\epsilon/kT} - 1\right)r^2 dr - 2\pi N_A \int_{\lambda\sigma}^{\infty} (1 - 1)r^2 dr$$

$$B = \frac{2}{3}\pi N_A \sigma^3 - 2\pi N_A \left(e^{\epsilon/kT} - 1\right)\left(\frac{\lambda^3 \sigma^3 - \sigma^3}{3}\right) - 0$$

(23A)
$$\boldsymbol{B = b_0\left[1 - \left(e^{\epsilon/kT} - 1\right)\left(\lambda^3 - 1\right)\right]}$$

(23B)
$$\boldsymbol{B = b_0\left[\lambda^3 - \left(\lambda^3 - 1\right)e^{\epsilon/kT}\right]}$$

This is an exponential function that can be expanded as an infinite series in powers of T^{-1}. This fact will be used in Chapter 4 in order to analyze this model, and explain why its characteristics ensure the correct behavior at the temperature limits.

Lennard-Jones Potential

This potential was proposed for the first time by Lennard-Jones in 1924, and it is the simplest one of the realistic potentials. It is represented by the following function:

(24)
$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

Figure 9.

Lennard-Jones potential.
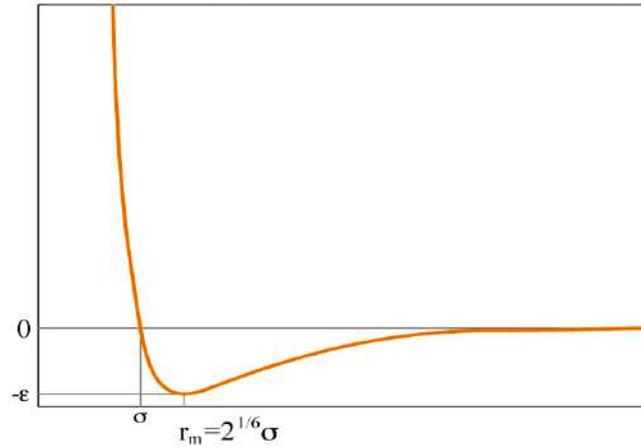
Own source

Substitution of this potential in Equation (6) produces an infinite series with no simple formula (there are some closed expressions in terms of complex functions, e.g. Vargas et al. 2001); it can be represented in reduced form as follows:

(25A) $$B^*(T^*) = B(T)/b_0$$

(25B) $$B^*(T^*) = -\sum_{j=0}^{\infty} \left(\frac{2^{j+1/2}}{4j!}\right) \Gamma\left(\frac{2j-1}{4}\right) \left(\frac{1}{T^*}\right)^{\frac{2j+1}{4}}$$

(25C) $$B^*(T^*) = \left(\frac{1}{T^*}\right)^{1/4} \left[\beta_0 + \beta_1 \left(\frac{1}{T^*}\right)^{1/2} + \beta_2 \left(\frac{1}{T^*}\right) + \cdots\right]$$

where $T^* = kT/\epsilon$ and b_0 is the hard spheres second virial coefficient. A graph of $B^*(T^*)$ is shown in Figure 10 below.

Figure 10.

Lennard-Jones reduced second virial coefficient.
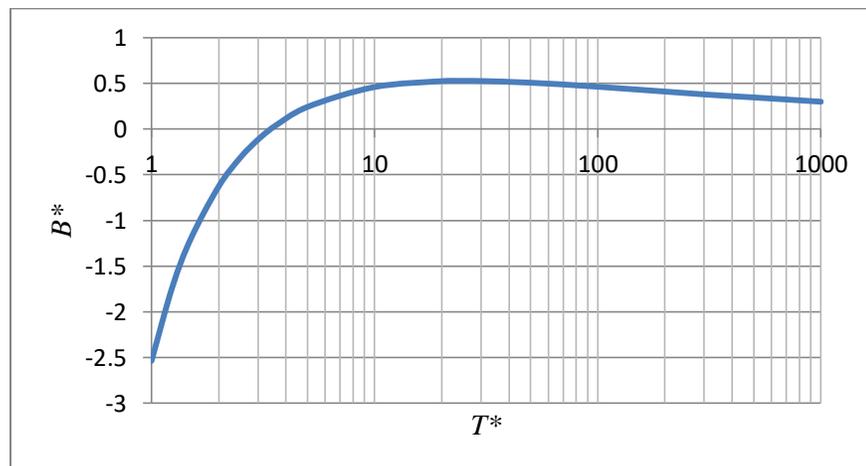
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$B^*(T^*)$ has a Boyle temperature of $T_B^* = 3.418$ and a maximum value of about $0.53\, b_0$ at $T^* \approx 25$, descending towards zero as T^* approaches infinity. As an example, the L-J constants for argon are $b_0 = 54.03$ cm³/mol and $\epsilon/k = 118.13$ K (Tee et al. 1966), so the Boyle temperature is $(3.418)(118.13) = 403.7$ K and the maximum value of the second virial coefficient is $B = (0.52)(54.03) = 28.6$ cm³/mol at $T = (25)(118.13) = 2953$ K. These observations are useful when selecting and comparing models for $B(T)$, based on real data.

1.2.2.5.   Estimation of the Second Virial Coefficient

Correlations for $B(T)$ are necessary for its estimation when there are no data available, as well as for computer-based calculations and process simulations. Simple correlations are used for rapid calculations or when high accuracy is not required; otherwise, more complex correlations have to be used. All correlations are based on two approaches, somehow related:

A. THE "INTERMOLECULAR POTENTIAL" APPROACH, which consists in assuming the form of the intermolecular potential, e.g. square-well, Lennard-Jones or other, and determining the second virial coefficient $B(T)$ from the force constants of the substances. Constants are obtained by consulting tables, by direct calculation from data, or with empirical correlations (Tee et al. 1966). This approach has been used by Kunz & Kapner (1971), Halm & Stiel (1971), and McFall et al. (2002), among others.

B. THE "EMPIRICAL EQUATION" APPROACH, which consists in guessing the form of the $B(T)$ function, dependent from certain characteristic parameters of the substance $(T_c, P_c, V_c, \omega, \dots)$. This has been the approach used by most researchers, such as Pitzer & Curl (1957), Black (1958), Tsonopoulos (1974) and others. Sometimes the equation is based on a particular potential; for example, exponential fits can be related to the square well potential (Nothnagel et al. 1973; McFall et al. 2002). Some researchers have performed intermolecular potential calculations to determine the shape of the empirical function (Hayden & O'Connell 1975, Ramos-Estrada et al. 2004). One of the methods (Nothnagel et al. 1973) defines an equation of state, from which an empirical formula for B is proposed, and then this result is associated to the square well potential.

1.2.2.6.   Classification of Empirical Equations for the Second Virial Coefficient

A classification of the existing second virial coefficient correlations is presented in Table 1, based on their mathematical characteristics. The list is not exhaustive. When f_0 and f_1 are mentioned, these are the functions in the Equations (4A) and (4B).

TABLE 1.

A classification of second virial coefficient correlations.

TYPE	EXAMPLES
Two-term model: $$\frac{B}{V_c} \text{ or } \frac{BP_c}{RT_c} = a - \frac{b}{T_r^n}$$	Berthelot 1907 ($n = 2$). Abbott 1973 ($n = 1.6$). Mathias 2003 ($n = 1 + e$). All cubic equations of state, such as: Van der Waals 1873 ($n = 1$). Redlich-Kwong 1949 ($n = 1.5$).
Quadratic in $1/T$: $$\frac{B}{V_c} = a_0 + \frac{a_1}{T_r} + \frac{a_2}{T_r^2}$$	McGlashan & Potter 1962.
Cubic in $1/T$: $$\frac{B}{V_c} \text{ or } \frac{BP_c}{RT_c} = a_0 + \frac{a_1}{T_r} + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3}$$	Pitzer and Curl 1957 (function f_0). Zhixing et al. 1987 (both f_0 and f_1). Weber 1994 (both f_0 and f_1).
Fourth-order in $1/T$: $$B\rho_b = a_0 + \frac{a_1}{\theta} + \frac{a_2}{\theta^2} + \frac{a_3}{\theta^3} + \frac{a_4}{\theta^4}$$	Eslami (2000). $\theta = T/T_b$
Higher order in 1/T: $$\frac{B}{V_c} \text{ or } \frac{BP_c}{RT_c} = a_0 + \frac{a_1}{T_r} + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3} + \cdots + \frac{a_m}{T_r^m}$$ $$(m = 6, 8 \text{ or } 9)$$	Pitzer and Curl 1957 (function f_1). Tsonopoulos 1974. McCann & Danner 1984. Schreiber & Pitzer 1988, 1989. Lee & Chen 1998. Meng et al. 2007. Vetere 2007.

Other approaches:
 	
    Square well (exponential)
    Lennard-Jones
    Empirical functions.
    Four-parameter functions.
	Kunz & Kapner 1971 (Lennard-Jones).
	Halm & Stiel 1971.
	Nothnagel et al. 1973 (Square-Well).
	Hayden & O'Connell 1975.
	Martin 1984.
	Iglesias-Silva & Hall 2001.
	McFall et al. 2002 (modified Square-Well).
	Xiang 2002.
	Ramos-Estrada et al. 2004.
	Iglesias-Silva et al. 2010.

Own source

1.2.3. Review of the Literature

Table 2 is a non-exhaustive list of the most relevant correlations for *B(T)*, included due to their use, historical reasons, or because they represent an interesting approach.

TABLE 2.

List of relevant correlations for the second virial coefficient.

AUTHOR	YEAR	COMMENT
Berthelot	1907	The first empirical equation proposed for *B*. Used for many years to estimate "gas imperfection", also the basis of more accurate correlations (e.g. Pitzer & Curl 1957; Black 1958; Kunz & Kapner 1971; Martin 1984). Interest has revived for this equation recently (Mathias 2003).
Pitzer & Curl	1957	The most important correlation for normal fluids, empirical with a solid theoretical background. The basis of most of the later correlations.
Black	1958	A good correlation for all fluids, based on an empirical modification to the Van der Waals equation. Revised in 1970 by Nagahama & Hirata.
McGlashan & Potter	1962	An empirical equation developed for alkanes and α-olefins, up to C_8. Recently applied to polymethyl compounds (Barbarin-Castillo 1993, 2000).
Kunz & Kapner	1971	A very elegant approach: they developed a group contribution method to calculate the Lennard-Jones force constants, from which *B* is calculated. It uses the "chemical theory" (Prausnitz, 1959) to calculate the correction of *B* for the case of associated compounds (alcohols).
Halm & Stiel	1971	Empirical correlation based on the acentric factor ω and a polar factor *x*.
Abbott	1973	A very simple and practical correlation, similar to Berthelot's.
Nothnagel et al.	1973	A correlation based on the "chemical theory" of association for molecules. Applicable to all kinds of compounds.
Tsonopoulos	1974	One of the most important and used correlations. Based on Pitzer & Curl correlation. Applicable to all kinds of compounds.
Hayden & O'Connell	1975	Empirical equation with theoretical ground; not based on acentric factor but on radius of gyration. Applicable to all compounds. Often used.
McCann & Danner	1984	Coefficients of *B* (instead of B_r) are calculated directly, using a group contribution method. One equation only, neither f_0 nor f_1. It applies only to organic compounds.
Zhixing, Fengcun & Yiqin	1987	Using minimum squares and statistical criteria, they arrive at simple functions f_0 and f_1 that fit all the available B data from normal fluids.
Schreiber & Pitzer	1988	An improved version of the Pitzer-Curl correlation for normal fluids.

TABLE 2. (CONT)

List of relevant correlations for the second virial coefficient.

AUTHOR	YEAR	COMMENT
Weber	1994	A modification of Tsonopoulos, applicable to polar refrigerants.
Lee & Chen	1998	An empirical correlation, with new formulae except that they retain the f_0 function of Pitzer & Curl for simple fluids. Applicable to all fluids.
Eslami	2000	A reduced equation in terms of the normal boiling point.
Iglesias-Silva & Hall	2001	An empirical equation, based on the Boyle temperature.
Xiang	2002	Empirical correlation based on the acentric factor ω and a new factor θ.
McFall et al.	2002	An empirical modification of the square-well equation for B.
Ramos-Estrada et al.	2004	An empirical correlation based on the Stockmayer potential.
Vetere	2007	A modification of the Pitzer-Curl correlation.
Meng et al.	2007	New equations to replace Pitzer-Curl, Weber and Tsonopoulos.
Iglesias-Silva et al.	2010	An empirical method based on the Boyle temperature.

Chapter 2.

ANALYSIS OF MODELS FOR *B(T)*

2.1. Preliminaries: Fluid Data, Selection of Substances

One of the preliminary activities is the search of information regarding the critical constants, acentric factors and additional relevant information. Another activity is the selection of a set of substances for the analysis and the development of the results according to the objectives.

Critical Constants

The critical constants for 42 substances were taken from the DIPPR database, as reported in *Perry's Chemical Engineers' Handbook* (Perry & Green 2007). In this reference, the critical pressures were calculated from the critical temperatures and the vapor pressure equations recommended by DIPPR in order to ensure consistency. Critical constants for 15 substances, not included in the first reference, were taken from the *CRC Handbook of Chemistry and Physics* (Lide 2009). Critical constants for three substances (cyclo-C_6F_{12}, MoF_6, WF_6) were found in the Infotherm online database. The critical constants for trimethyl gallium were taken from the *NIST SRD 134 Database*. The critical constants for uranium hexafluoride were taken from the monograph of Anderson et al. (1994). The total of substances considered was sixty-two (62).

A validation was made for families of compounds by plotting each critical constant against the molecular weight in order to ensure a smooth variation with increasing molecular weight. This is especially important for the critical volume, the property with greater uncertainty. Based on this exercise, a correction was made to the critical volume of two substances (n-C_6F_{14} and cyclo-C_6F_{12}). The plot of the critical volume against the molecular weight is shown in Figure 11.

Figure 11.

Validation of the critical volume data.
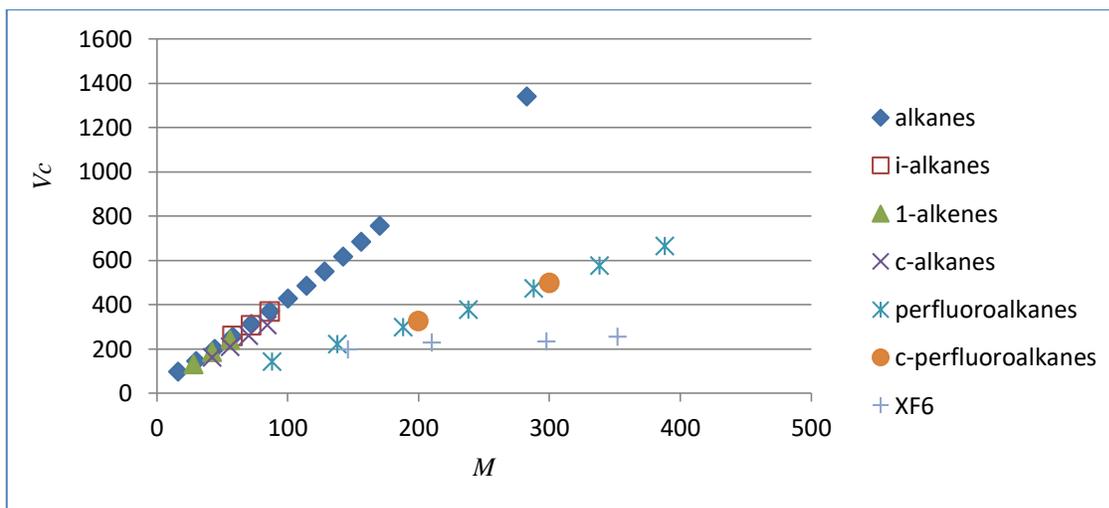
Own source

Initially, the method of Schreiber and Pitzer (1988) was considered for the calculation of an "optimum" critical volume, based on a linear relationship between the critical compressibility Z_c and the acentric factor. However, during the validation stage, it was concluded that this relationship is valid for n-alkanes only, and no definite trend was identified for other families of compounds.

Acentric Factors

The acentric factors for 40 substances were taken from the DIPPR database, as reported in *Perry's Chemical Engineers' Handbook* (Perry & Green 2007). The acentric factors for eleven substances were taken from the *NIST Chemistry Webbook* (webbook.nist.gov). The acentric factors for seven substances were calculated from vapor pressure data as reported by Perry & Green (2007). The acentric factors for three substances (n-C_6F_{14}, C_2F_4, C_6F_6) were taken from the Infotherm database. The acentric factor for trimethyl gallium was calculated from vapor pressure data, as reported in the *NIST SRD 134 Database*.

Dipole and Quadrupole Moments

The dipole moment information is relevant for this study because the normal fluids are constituted by non-polar compounds; however, there are slightly polar compounds that show normal fluid behavior (CO, NO, N_2O). Also the hydrocarbon family, usually classified as non-polar, contains slightly polar (e.g. propane and heavier n-alkanes) and polar (e.g. propene, 1-butene, cis-2-butene, isobutene, toluene) compounds. For our purposes, a compound will be non-polar if it has a dipole moment between zero and 0.1 Debyes.

The quadrupole moment information was also considered relevant because there are many non-polar compounds with zero dipole moment but a non-zero quadrupole moment; typical examples are carbon dioxide and benzene. This could have an effect in the second virial coefficient, to be verified during the study. For the purposes of this research, substances with a quadrupole moment lower than $5 \cdot 10^{-40}$ Cm^2 are considered non-quadrupolar.

The dipole moment data were taken from the report NSRDS-NBS 10 from the National Bureau of Standards (Nelson et al. 1967). The quadrupole moment data were taken from the compilation of Gray and Gubbins (1984). For some substances, the dipole and quadrupole information was estimated from similarity with other ones: for example, the dipole moments for some perfluoroalkanes were estimated from data of the corresponding alkanes.

The following tables contain all the information discussed above for the fluids to be included in this study; they were divided in two groups for reasons to be discussed below.

TABLE 3.
Relevant properties for selected fluids. Group A.

Substance	M	Tc	Pc	Vc	Zc	w	dipole	quadrupole
Ar	39.948	150.86	48.96	74.59	0.2911	-0.00219	0	0
Kr	83.798	209.48	55.25	91	0.2887	-0.0009	0	0
Xe	131.293	289.733	58.42	118	0.2862	0.00363	0	0
N2	28.013	126.2	33.91	89.21	0.2883	0.0377	0	-4.7
O2	31.999	154.58	50.21	73.4	0.2867	0.0222	0	-1.3
F2	37.997	144.12	51.67	66.547	0.2870	0.053	0	2.5
CH4	16.042	190.564	45.9	98.6	0.2856	0.0115	0	0
C2H6	30.069	305.32	48.52	145.5	0.2781	0.0995	0	-2.2
C3H8	44.096	369.83	42.14	200	0.2741	0.1523	0.084	
n-C4H10	58.122	425.12	37.7	255	0.2720	0.2002	0.05	
n-C5H12	72.149	469.7	33.64	313	0.2696	0.2515	0.1	
n-C6H14	86.175	507.6	30.45	371	0.2677	0.3013	0.1	
n-C7H16	100.202	540.2	27.19	428	0.2591	0.3495	0.1	
n-C8H18	114.229	568.7	24.67	486	0.2536	0.3996	0.1	
i-C4H10	58.122	407.8	36.3	259	0.2773	0.1835	0.132	
i-C5H12	72.149	460.4	33.66	306	0.2691	0.2279	0.13	
2-methyl C5	86.175	497.7	30.44	368	0.2707	0.2791	0.05	
C(CH3)4	72.149	433.74	31.96	307	0.2721	0.196	0	0
C2H4	28.053	282.34	50.32	131	0.2808	0.0862	0	5.0
trans-2-C4H8	56.106	428.6	41	238	0.2738	0.2176	0	
1,3-butadiene	54.09	425	43.03	221	0.2691	0.195	0	
c-C3H6	42.08	398	55.4	162	0.2712	0.1278	0	5.3
c-C5H10	70.133	511.7	45.13	260	0.2758	0.1949	0	
c-C6H12	84.159	553.8	40.94	308	0.2738	0.2081	0	
CF4	88.004	227.51	37.42	143	0.2829	0.179	0	0
C2F6	138.011	293.03	30.48	222	0.2777	0.257	0	
C3F8	188.019	345.1	26.8	299	0.2793	0.317	0.014	
n-C4F10	238.027	386.4	23.23	378	0.2733	0.374	0.05	
n-C5F12	288.035	420.59	20.45	473	0.2766	0.423	0.1	
n-C6F14	338.042	448.77	18.68	576	0.2884	0.51181	0.1	
C2F4	100.015	306.5	39.4	172	0.2659	0.2254	0	
CCl4	153.823	556.35	45.44	276	0.2711	0.1926	0	0
c-C4F8	200.03	388.46	27.84	324	0.2793	0.3553	0	
c-C6F12	300.045	457.2	22.37	497	0.2925	0.44562	0	
Si(CH3)4	88.224	448.6	28.21	361.6	0.2735	0.241	0	0
SiF4	104.079	259	37.48	202	0.3516	0.3858	0	0
SF6	146.055	318.69	37.71	198.52	0.2825	0.2151	0	0
MoF6	209.951	485.2	49.7	229	0.2821	0.21498	0	0
WF6	297.831	452.7	45.8	233	0.2835	0.20709	0	0
UF6	352.02	503.3	46.1	256	0.2820	0.32809	0	0
SiCl4	169.898	508.1	35.93	326	0.2773	0.21838	0	0
Ga(CH3)3	114.827	510	40.4	211	0.2010	0.20773	0	0

Own source

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TABLE 4.

Relevant properties for selected fluids. Group B.

Substance	M	Tc	Pc	Vc	Zc	w	dipole	quadrupole
Ne	20.18	44.4	26.53	41.7	0.2997	-0.0396	0	0
CO2	44.1	304.21	73.83	94	0.2744	0.2236	0	-14
CS2	76.141	552	79	160	0.2754	0.1107	0	12
Cl2	70.906	417.15	77.93	124	0.2786	0.0688	0	12
BF3	67.806	260.8	49.8	115	0.2641	0.40176	0	13
C2H2	26.037	308.3	61.38	112	0.2682	0.1912	0	20
isobutene	56.106	417.9	40.04	239	0.27541	0.1948	0.503	-8.34
C3H4 propadiene	40.064	394	52.18	165	0.2628	0.1041	0	15
benzene	78.112	562.05	48.75	256	0.2671	0.2103	0	-29
p-xylene	106.165	616.2	35.01	378	0.2583	0.3218	0	
C6F6	186.054	516.73	32.73	335	0.2552	0.3958	0	32
CO	28.01	132.92	34.99	94.4	0.2989	0.0482	0.112	-9.5
N2O nitrous	44.013	309.57	72.45	97.4	0.2742	0.1409	0.167	-10
NO nitric	30.006	180.15	65.16	58	0.2523	0.5829	0.153	-4.4
C3H6	42.08	364.85	45.99	185	0.2805	0.1376	0.366	
1-C4H8	56.106	419.5	40.21	241	0.2778	0.1845	0.34	
cis-2-C4H8	56.106	435.5	42.38	234	0.2739	0.2019	0.3	
toluene	92.138	591.75	40.8	316	0.2620	0.264	0.36	
BCl3	117.17	455	38.7	239	0.2445	0.12314	0	14
NF3	71.002	234	45	118.75	0.2747	0.126	0.235	

Own source

The colors and highlights in the tables are explained as follows:

- Data in black are taken from Perry & Green (2007).

- Data in blue are taken from Lide et al. (2010).

- Data in red are taken from the Infotherm database.

- Data in brown are taken from the NIST Webbook and NIST databases.

- Data highlighted in dark green are calculated from vapor pressure data.

- Data highlighted in light green are corrected or estimated values.

- Data highlighted in yellow are taken from Anderson et al. (1994).

The selected 62 substances were divided in two groups: a first group of 42 substances that were classified as non-polar, according to the criteria discussed above (Group A), and a second group of 20 substances that may follow normal fluid behavior but have a non-negligible dipole moment, quadrupole moment or both (Group B). The first group will be used primarily for this research, while the second group will be used as a control group for verification of the correlation.

Boyle Temperatures

The Step 3 of this research explores the usefulness of the Boyle temperature for extending the range of *B(T)* fitting equations; therefore, experimental values of this property are needed, or else good estimates. We will take advantage of recent studies regarding or including the Boyle temperature (Ramos-Estrada et al. 2004; Estrada-Torres et al. 2007; Iglesias-Silva et al. 2010), and studies of second virial coefficients in a wide range of temperatures, where this property is one of the results (Hurly 1999, 2000a, 2000b, 2002, 2003, 2004; Hurly et al. 1997, 2000; Zarkova et al. 1996, 1998, 1999, 2000a, 2000b, 2003, 2005, 2006; Zarkova & Pirgov 1997; Zarkova & Hohm 2002, 2009; Hohm & Zarkova 2004; Hohm et al. 2006, 2007; Damyanova et al. 2009, 2010).

Boyle temperatures for 37 substances were taken from the study of Estrada-Torres et al. (2007), who reported this property for 81 substances. Other important sources of information were Iglesias-Silva et al. (2010), Tao & Mason (1994) and the articles by Zarkova, cited above. For eleven substances (1,3 butadiene, cyclopropane, perfluoropropane, perfluoro-hexane, cyclo-perflorohexane, hexafluorobenzene, carbon disulfide, acetylene, propadiene and p-xylene), there was not available information of this property; for these compounds, the Boyle temperature was estimated with an equation developed by Iglesias-Silva et al. (2001), which has good accuracy according to Estrada-Torres et al. (2007). There are other available equations (e. g. Danon & Pitzer 1962; Tao & Mason 1994), but the chosen equation gave results closer to the experimental values for most compounds.

The following table shows the main sources for the Boyle temperatures used in this research. The total of substances is more than 61 because the Boyle temperature for the same substance can be reported by several sources.

TABLE 5.
Sources for the Boyle temperatures.

SOURCE	SUBSTANCES
Estrada-Torres et al. 2007	37
Iglesias-Silva et al. 2010	16
Tao & Mason 1994	12
Iglesias-Silva estimated	11
Zarkova articles	10
Hurly articles	6
Nasrifar & Bolland 2004	5
Ihm, Song & Mason 1991	4
Lisal & Aim 1999	1
Other sources (experimental)	4

Own source

2.2. Analysis of Models for the Second Virial Coefficient

In the following sections, we will analyze the main existing models for the second virial coefficient, both theoretical and empirical, in order to determine general criteria that can be applied to the development of new models, with correct limits at the extremes of temperature and with extrapolation capabilities. We will also show examples of bad models, usually fitting equations for a particular substance, in order to relate the bad behavior of that model to one or more of the criteria developed here.

Reduced in Terms of Pressure or Volume?

Perhaps one of the first relevant questions is which variable will be used to obtain a reduced second virial coefficient: the critical pressure (and temperature) or the critical volume. The reason behind such question is due to some of the correlations for the second virial coefficient being developed for B/V_c, the correct form from a theoretical point of view, while others have been developed for BP_c/RT_c, which is more practical from an Engineering viewpoint. The existence of more accurate data for the critical pressure and temperature than for the critical volume has motivated, along the years, the choice of one set of variables (P_c, T_c) over the other (V_c).

There is a relationship between the two approaches and they are not interchangeable, as it will be demonstrated soon:

$$(26) \qquad \frac{BP_c}{RT_c} = Z_c \cdot \frac{B}{V_c}$$

The critical compressibility Z_c is a constant for the simple fluids only (i.e. the noble gases). For other families of fluids, Z_c is a function of the acentric factor ω (Schreiber & Pitzer 1988, 1989). If we consider both B/V_c and Z_c linear functions of ω, then BP_c/RT_c would be a quadratic function of ω, as follows:

$$(27A) \qquad Z_c = \alpha + \beta\omega$$

$$(27B) \qquad \frac{B}{V_c} = \delta + \gamma\omega$$

$$(27C) \qquad \frac{BP_c}{RT_c} = (\alpha + \beta\omega)(\delta + \gamma\omega)$$

$$(27D) \qquad \frac{BP_c}{RT_c} = \alpha\delta + (\alpha\gamma + \beta\delta)\omega + \beta\gamma\omega^2$$

On the contrary, if we consider both BP_c/RT_c and Z_c linear functions of ω, then B/V_c would be a rational function of ω, as follows:

(27A) $$Z_c = \alpha + \beta\omega$$

(28A) $$\frac{BP_c}{RT_c} = \delta + \gamma\omega$$

(28B) $$\frac{B}{V_c} = \frac{\delta + \gamma\omega}{\alpha + \beta\omega}$$

Therefore, if one of the two reduced expressions B/V_c or BP_c/RT_c is chosen to develop a correlation in the form of Equations (4A) or (4B), then a correlation in terms of the other reduced expression will be linear in ω only as an approximation. Based on this fact, it will be necessary to test both expressions when plotting the experimental data in reduced terms, and when developing the new correlation, in order to determine which expression produces the best fit.

The Square-Well Model

The square-well model, Equation (23B), is an effective model for second virial coefficients, since it has been used as the basis of several correlations (Nothnagel et al. 1973; McFall et al. 2002). The exponential term can be expanded as an infinite series, as follows:

(23B) $$B = b_0\left[\lambda^3 - \left(\lambda^3 - 1\right)e^{\epsilon/kT}\right]$$

$$B = b_0\lambda^3 - b_0\left(\lambda^3 - 1\right)\sum_0^\infty \frac{1}{j!}\left(\frac{\epsilon}{kT}\right)^j$$

(29) $$B = b_0 - b_0\left(\lambda^3 - 1\right)\left(\frac{\epsilon}{kT} + \frac{1}{2}\frac{\epsilon^2}{k^2T^2} + \frac{1}{6}\frac{\epsilon^3}{k^3T^3} + \frac{1}{24}\frac{\epsilon^4}{k^4T^4} + \cdots\right)$$

According to the above equation, the high-temperature limit of B for this model is b_0 and the higher order terms all have negative coefficients, provided that $\lambda > 1$. These higher-order coefficients have also decreasing magnitude because of the factor $1/j!$; although a value of $\epsilon/k > 1$ can determine an increase of the first coefficients, for some value of j they will start to decrease.

As a practical application of this result, we will put numerical values to the model and expand it in terms of powers of T^{-1}. In Section 3.5 of the *Kaye & Laby Tables of Chemical and Physical Constants* (www.kayelaby.npl.co.uk), it is reported that the following equation fits the second virial coefficients of simple fluids:

(30) $$BP_c/RT_c = 0.599 - 0.467\exp(0.694T_c/T)$$

Expanding the exponential term, the following result is obtained:

$$\frac{BP_c}{RT_c} = 0.599 - 0.467 \sum_{0}^{\infty} \frac{1}{j!} \left(\frac{0.694T_c}{T} \right)^{j}$$

$$\frac{BP_c}{RT_c} = 0.599 - 0.467 \left[1 + \frac{0.694}{T_r} + \frac{1}{2}\left(\frac{0.694}{T_r}\right)^2 + \frac{1}{6}\left(\frac{0.694}{T_r}\right)^2 + \cdots \right]$$

(31)
$$\frac{BP_c}{RT_c} = 0.132 - \frac{0.324}{T_r} - \frac{0.1125}{T_r^2} - \frac{0.026}{T_r^3} - \cdots$$

This expression will be compared later to the Pitzer and Curl model for simple fluids (1957). If we consider that for simple fluids $Z_c = 0.29$, then we can use Equation (26) and obtain another expression for B:

(32)
$$\frac{B}{V_c} = 0.455 - \frac{1.117}{T_r} - \frac{0.388}{T_r^2} - \frac{0.0897}{T_r^3} - \cdots$$

This expression will be compared later to the McGlashan and Potter model (1962). Both Equations (31) and (32) comply with the characteristics of the square-well model, regarding the positive constant and negative decreasing coefficients. Comparing Equations (29) and (32), an estimation of b_0 would be obtained with the expressions $0.455\ V_c$ or $0.132RT_c/P_c$.

The Lennard-Jones Model

The Lennard-Jones model for the second virial coefficient has been used only once (Kunz & Kapner 1971), perhaps due to the difficulties in handling an infinite series in the past. However, it is a realistic model so it is important to analyze its characteristics.

Based on Equation (25B), the coefficients of $B^*(T^*)$ can be calculated following the recurrence below:

(33)
$$\beta_j = \begin{cases} +1.7330010 \ if \ k = 0 \\ -2.5636934 \ if \ k = 1 \\ \frac{(2j-5)}{j(j-1)} \beta_{j-2} \ for \ all \ other \ k \end{cases}$$

The following table displays the first 20 coefficients of Equations (25B) or (25C):

TABLE 6.

Coefficients of Equations (25B) and (25C).

j	β_j
0	1.7330010
2	-0.8665005
4	-0.2166251
6	-0.0505459
8	-0.0099287
10	-0.0016548
12	-0.0002382
14	-0.0000301
16	-0.0000034
18	-0.0000003
20	-3.16E-08
1	-2.5636934
3	-0.4272822
5	-0.1068206
7	-0.0228901
9	-0.0041329
11	-0.0006387
13	-0.0000860
15	-0.0000102
17	-0.0000011
19	-0.0000001

Own source

The coefficients in the table are arranged the even ones first, followed by the odd ones because the recurrence determines two groups, one depending on β_0 and the other on β_1. Looking at these coefficients, the following observations can be made:

A. There is not a constant term b_0.

B. The high-temperature limit is $B^*(T^*) = 0$.

C. There is a maximum of $B^*(T^*)$ for some T^*.

D. The first coefficient β_0 only is positive; all the other β_j's are negative.

E. The coefficients decrease at a very fast rate;

The coefficient β_o will determine the high-temperature behavior, while the negative coefficients determine the behavior when $T^* \to 0$. This model has correct asymptotic limits, as demonstrated in the following example. Table 7 and Figure 12 contain the second virial coefficient data for argon, as recommended by NIST (determined from the potential of Aziz 1993), along with the calculated values using Equation (25C) and a set of optimum force constants, estimated by the method of Kunz and Kapner (1971), i. e. $b_0 = 50.9462$ cm³/mol, $\epsilon/k = 122.054$ K.

TABLE 7.
Comparison of $B(T)$ values for argon, against L-J potential.

T (K)	B (NIST)	B (L-J opt)
80	-272.30	-269.46
100	-181.99	-182.57
150	-85.99	-89.55
200	-47.89	-50.95
250	-27.69	-30.03
300	-15.30	-16.99
400	-1.033	-1.79
500	6.785	6.67
600	11.623	11.97
700	14.851	15.54
800	17.117	18.08
900	18.768	19.95
1000	20.003	21.36

Own source

Figure 12.
Graphical comparison of $B(T)$ values for argon, against L-J potential.
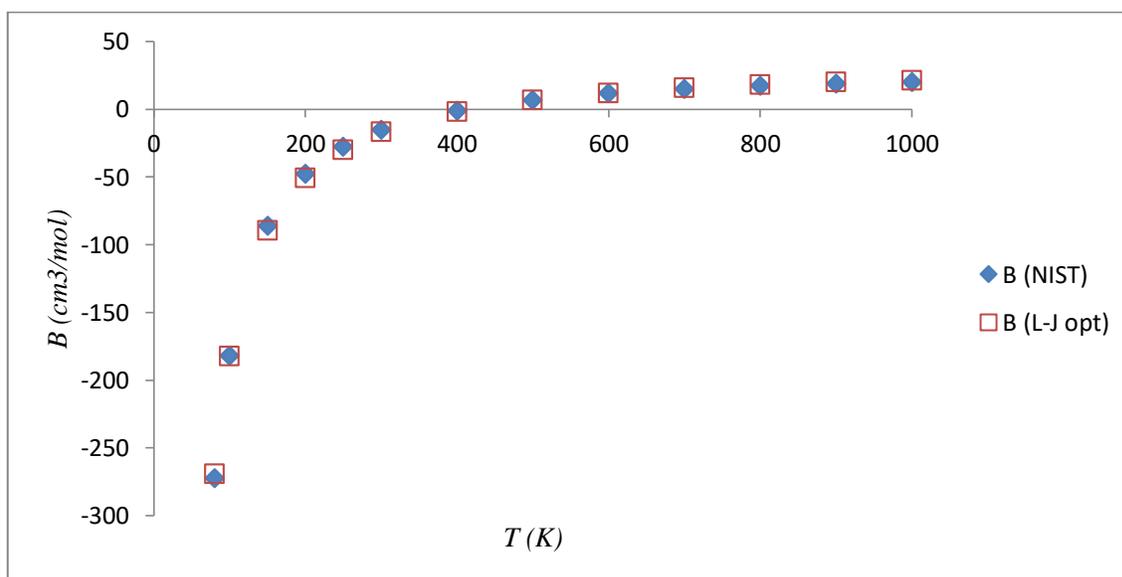
Own source

Two-Term Models

These are the simplest models for estimation of the second virial coefficient; all of them are originated from cubic equations of state. Except for the Van der Waals correlation, all of them have been used to estimate *B(T)* for a broad class of substances. They can give also guidance for the high-temperature behavior and extrapolation of this property, and they allow the evaluation of theoretical and empirical correlations (Mathias 2003). We will consider four models of this type:

Van der Waals (1873):

$$(34) \qquad \frac{BP_c}{RT_c} = \frac{1}{8} - \frac{27}{64}T_r^{-1}$$

Berthelot (1907):

$$(35) \qquad \frac{BP_c}{RT_c} = \frac{9}{128} - \frac{27}{64}T_r^{-2}$$

Redlich-Kwong (1949):

$$(36) \qquad \frac{BP_c}{RT_c} = 0.08664035 - 0.42748023T_r^{-3/2}$$

Coefficients obtained from $b = c/3$, $a = (9c)^{-1}$ where $c = 2^{1/3} - 1 = 0.25992105$.

Abbott (1973), function B^0:

$$(37) \qquad B^0 = \frac{1}{12} - \frac{27}{64}T_r^{-8/5}$$

Equation (37) is the only one from the above that is part of a generalized correlation in terms of the acentric factor and Equation (4B); it is also the only one that is recommended and included in textbooks (Smith & Van Ness 1975; Poling et al. 2001). Its companion equation B^1 will be discussed among the higher-than-cubic equations.

Recently, it was stated that the Redlich-Kwong expression for the second virial coefficient, Equation (36), is still a valid and effective correlation, with an exponent of T^{-n} equal to $n = 1 + e$ (Mathias 2003). It is interesting to examine the dependency of *B(T)* against the inverse reduced temperature: it can be shown that $n = 1.5$ gives an almost linear relationship, while other exponents such as $n = 2$ not, as shown in Figure 13. Probably this plot determined that Redlich and Kwong chose $n = 1.5$ for the temperature dependency of *B(T)* in their equation. Although an exponent $n = 2$ gives a poor fit for a wide range of temperature, it still provides an excellent fit at low temperatures, an explanation for the extended success of the Berthelot equation.

From a mathematical viewpoint, all the above equations share a positive constant term and a negative temperature-dependent term. These are characteristics shared with the previous models analyzed, i. e. square-well and Lennard-Jones.

Figure 13.

Dependency of B with reduced temperature. Argon data.
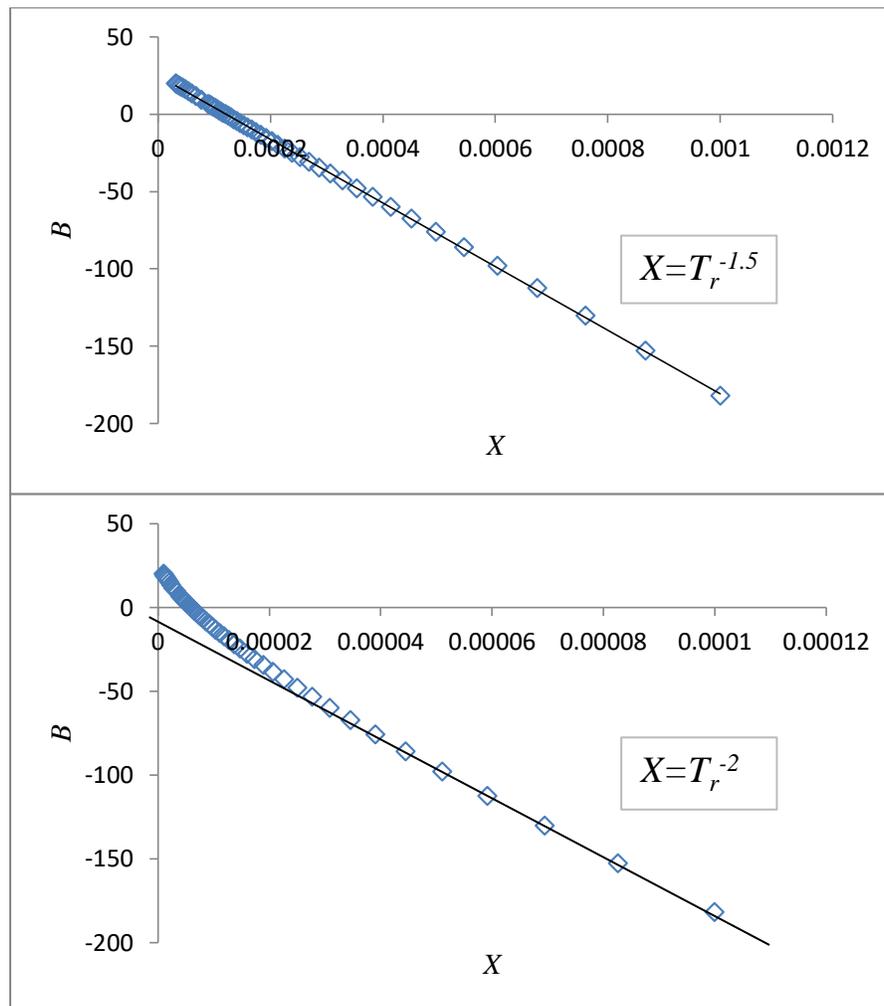
Own source

Models Quadratic in 1/T

There is only one model in this category, but an important one. In 1962, McGlashan and Potter proposed the following equation to represent the second virial coefficient of simple fluids:

(38A) $$B/V_c = 0.430 - 0.866T_r^{-1} - 0.694T_r^{-2}$$

For n-alkanes and α-olefins, they found that an additional term must be added to the above, it becomes a higher-than-cubic equation:

(38B) $$B/V_c = 0.430 - 0.866T_r^{-1} - 0.694T_r^{-2} - 0.0375(n-1)T_r^{-4.5}$$

In the last equation, n is the number of carbon atoms. This model is applicable to many compounds, except the alcohols; recently it was applied to polymethyl silanes, where n is the number of methyl groups (Barbarin-Castillo 1993, 2000). The coefficients in Equation (38A) are

slightly different from the ones obtained for Equation (32), from the square-well model. As it will be shown in a later chapter, the best fit for *B(T)* data of many non-polar compounds is quadratic in T^{-1}, a higher-order fit is not justified; an example of this is given by oxygen, as shown below.

Figure 14.

Comparison of Eq. (38A) against oxygen *B(T)* data (Dymond et al. 2002).
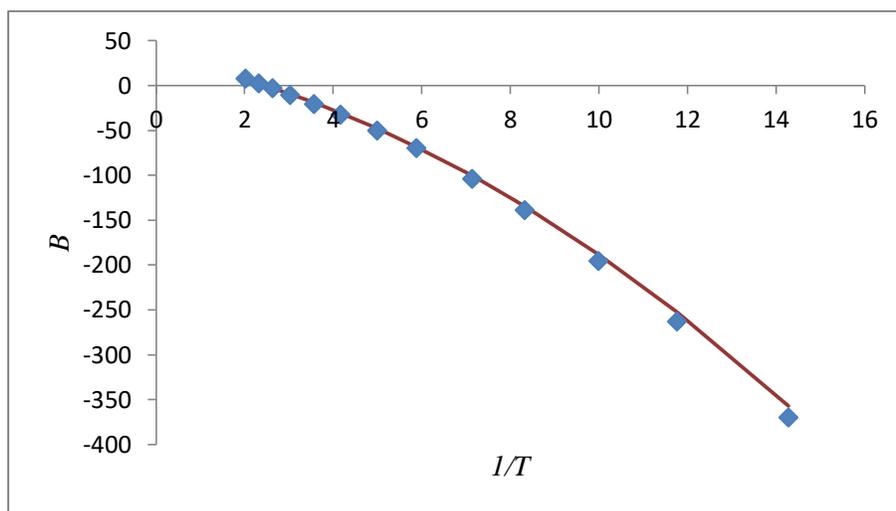
Own source

As all the previous models, this one has a constant positive term, and several temperature-dependent terms, all decreasing and negative. This structure allows the model to have correct limits and good extrapolation characteristics, and it explains the success of Equation (38B) to fit the second virial coefficient data for alkanes and α-olefins (McGlashan & Potter 1962).

Models Cubic in 1/T

Several researchers have proposed generalized models for *B(T)* that are cubic in terms of T^{-1}, or at least one of their functions is cubic. Four models will be considered:

Pitzer & Curl (1957), also Weber (1994) and Lee & Chen (1998), function f_{02}:

$$(39) \qquad f_{02}(T_r) = 0.1445 - 0.330T_r^{-1} - 0.1385T_r^{-2} - 0.0121T_r^{-3}$$

Zhixing et al. (1987):

$$(40A) \qquad f_{02}(T_r) = 0.1372 - 0.3240T_r^{-1} - 0.1108T_r^{-2} - 0.0340T_r^{-3}$$

$$(40B) \qquad f_{12}(T_r) = 0.9586 - 2.9924T_r^{-1} + 3.5238T_r^{-2} - 1.5477T_r^{-3}$$

Weber (1994), function f_{12}:

$$(41) \qquad f_{12}(T_r) = 0.0637 + 0.331T_r^{-2} - 0.423T_r^{-3}$$

The Zhixing et al. and Weber correlations are purely cubic, while the Pitzer-Curl and Lee-Chen correlations are cubic for the function f_{02}. Weber deleted the higher-order term in the function f_{12} of Tsonopoulos correlation; for f_{02} he used the Pitzer-Curl equation, as Lee & Chen did. Weber wrote than he used Tsonopoulos' function f_{02} but he made a mistake in his equation (2a), as he forgot that Tsonopoulos added a high-order term to the f_{02} of Pitzer & Curl.

Zhixing et al. fitted new equations using selected accurate data for *B(T)*, and statistical criteria to stop adding temperature-dependent terms; these authors concluded that terms higher than T_r^{-3} are not justified. Equation (40A) is slightly different from Equation (39), and it could be considered an update of the Pitzer & Curl's function f_{02}. On the contrary, Equation (40B) is very different than Pitzer & Curl's f_{12}.

In general, all the f_{02} functions above follow the pattern of previous models, having a positive constant term and negative, decreasing temperature-dependent terms. Weber and Zhixing et al. f_{12} functions contain a positive term dependent of T_r^{-2}, so the value of *B(T)* calculated with Equation (4B) has a contribution from a positive, temperature-dependent term. However, the terms in T_r^{-1} and T_r^{-3} (last term) are negative, these are the relevant ones to determine the low-temperature and high-temperature limits, as it will be discussed later in this chapter.

Several researchers (Zhixing et al. 1987; Meng et al. 2004) have explained that the low-temperature values of the second virial coefficient, as calculated with the Tsonopoulos correlation, are too negative. The reason for that is the lower accuracy and reliability of the older data from the low-temperature region. The main experimental source of error for these data would be the adsorption effect, which produces more negative values for B and perhaps affected Tsonopoulos correlation.

Models Quartic in 1/T

Eslami (2000) has proposed a quartic model of *B(T)* for normal fluids, which claims good accuracy for hydrocarbons. The model is made of one equation only, not dependent on the acentric factor, and differs also from other correlations because it is not reduced in terms of the critical temperature and volume, but in terms of the normal boiling point temperature and density as shown:

$$(42)\ B_2\rho_{bp} = 1.033 - 3.0069\left(\frac{T_{bp}}{T}\right) - 10.588\left(\frac{T_{bp}}{T}\right)^2 + 13.096\left(\frac{T_{bp}}{T}\right)^3 - 9.8968\left(\frac{T_{bp}}{T}\right)^4$$

This model contains the positive term $13.096\left(T_{bp}/T\right)^3$; however, the term in $\left(T_{bp}/T\right)$ and the last term in $\left(T_{bp}/T\right)^4$, both negative, are the relevant ones to determine the low-temperature and high-temperature limits. According to Eslami, this correlation is recommended for petroleum.

There is another quartic model worth of consideration, the Black correlation (1958), which is a modification of the Van der Waals equation with good capabilities to predict fluid behavior. The second virial coefficient for non-polar compounds is represented in the following way:

$$\frac{BP_c}{RT_c} = \frac{1}{8} - \frac{27}{64}\frac{\xi^0(T_r)}{T_r}$$

$$\xi^0(T_r) = 0.396 + 1.181T_r^{-1} - 0.864T_r^{-2} + 0.384T_r^{-3}$$

(43) $\quad \frac{BP_c}{RT_c} = 0.125 - 0.16706T_r^{-1} - 0.49823T_r^{-2} + 0.3645T_r^{-3} - 0.162T_r^{-4}$

This model was updated by Nagahama and Hirata in 1970, who fitted individual constants for 28 non-polar and 40 polar compounds; however, an attempt to generalize the results was not achieved.

Models with Higher Terms in 1/T

Seven models will be considered in this section; some of them are modifications of the Pitzer & Curl's and Tsonopoulos' models, also included here. First we will analyze the simplest of these generalized models proposed by Abbott (1973):

(44A) $\qquad\qquad B^1 = \frac{441}{1280}\left(T_r^{-8/5} - T_r^{-18/5}\right)$

(44B) $\qquad\qquad B^1 = 0.139 - 0.172T_r^{-4.2}$

The function B^0 for this model is Equation (37), discussed above. Abbott proposed two different expressions for B^1: the first one is from the original article, while the second one is given in a textbook (Smith & Van Ness 1975). Figure 15 is a plot of the two expressions for B^1; they differ in that Equation (44A) is less negative than Equation (44B) at lower temperatures. Besides the former goes to zero while the later goes to a constant value at high temperature. Equation (44A) is relevant because it does not have a constant term; it is a possible choice for the new correlation. The exponent of the temperature-dependent term in Equation (44B) can be compared to the last term in Equation (38B), i. e. -4.2 vs. -4.5.

Figure 15.

Comparison between the two expressions for B^1.
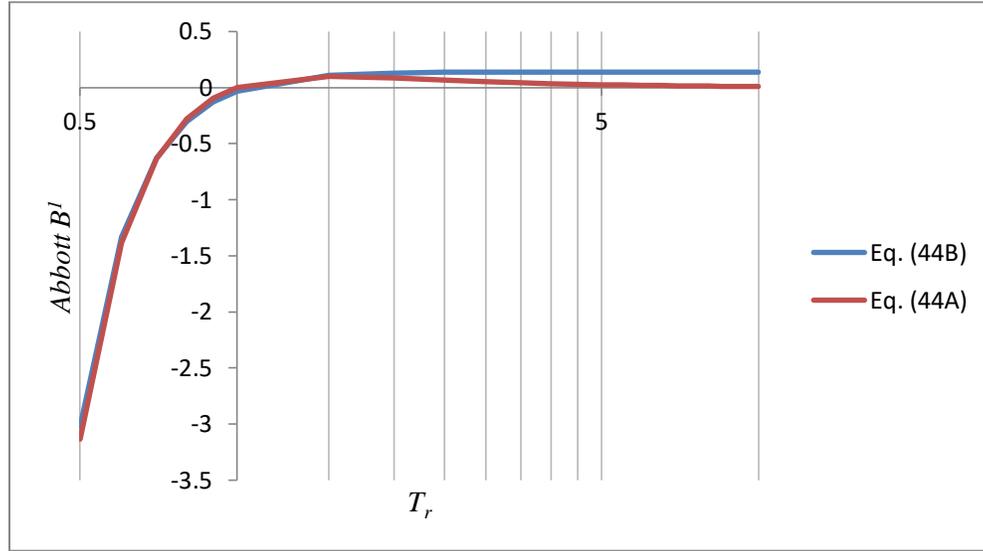
Own source

Model of Pitzer and Curl (1957), function f_1:

The function f_{02} for this model is Equation (39), cubic in *1/T*.

(45) $f_{12}(T_r) = 0.073 + 0.46T_r^{-1} - 0.50T_r^{-2} - 0.097T_r^{-3} - 0.0073T_r^{-8}$

Model of Tsonopoulos (1974):

Tsonopoulos added a higher-order term to Equation (39) of Pitzer & Curl; he also eliminated the T_r^{-1} term and adjusted the coefficients of the f_{12} function from Pitzer & Curl.

(46A) $f_{02}(T_r) = 0.1445 - 0.330T_r^{-1} - 0.1385T_r^{-2} - 0.0121T_r^{-3} - 0.000607T_r^{-8}$

(46B) $f_{12}(T_r) = 0.0637 + 0.331T_r^{-2} - 0.423T_r^{-3} - 0.008T_r^{-8}$

Model of McCann & Danner (1984):

(47) $B = a + bT_r^{-1} + cT_r^{-3} + dT_r^{-7} + eT_r^{-9}$

This is the only model of order 9 in T_r^{-1}, which is a non-reduced model with coefficients specific for each substance, calculated by a group contribution method. Equation (47), or a variant of it, has been used as the basis for fitting second virial coefficient data in the DIPPR 801 database.

Model of Schreiber and Pitzer 1988, 1989:

(48A) $B^0/V_c = 0.442259 - 0.980970T_r^{-1} - 0.611142T_r^{-2} - 0.00515624T_r^{-6}$

(48B) $B^1/V_c = 0.725650 + 0.218714T_r^{-1} - 1.24976T_r^{-2} - 0.189187T_r^{-6}$

These equations are an update of the Pitzer & Curl model, made by Pitzer himself. The model differs from the others in that it is reduced in terms of the critical volume. Also the higher-order temperature term is T_r^{-6} instead of T_r^{-8}; this determines that the variation of *B(T)* is less steep at low temperatures. According to the authors, this model is very accurate for normal fluids.

Model of Lee & Chen (1998):

The function f_{02} for this model is Equation (39), cubic in *1/T*.

(49) $\quad f_{12}(T_r) = 0.0943 - 0.0142T_r^{-1} + 0.3001T_r^{-2} - 0.3970T_r^{-3} - 0.0112T_r^{-8}$

Model of Meng et al (2004):

These equations can be considered an update of the Pitzer & Curl model.

(50A) $f_{02}(T_r) = 0.13356 - 0.30252T_r^{-1} - 0.15668T_r^{-2} - 0.00724T_r^{-3} - 0.00022T_r^{-8}$

(50B) $f_{12}(T_r) = 0.17404 - 0.15581T_r^{-1} + 0.38183T_r^{-2} - 0.44044T_r^{-3} - 0.00541T_r^{-8}$

As with previous models, all the f_{02} functions above follow the pattern of having a positive constant term and negative, decreasing temperature-dependent terms; the f_{12} functions not necessarily follow that pattern. All the f_{12} functions, with two exceptions, contain a positive term dependent of T_r^{-2}, so the comment made for previous models is applicable here too.

In the case of the two models by Pitzer, the f_1 functions have a positive term dependent of T_r^{-1}; this may result in a positive slope at high temperature in the graph *B* vs. *1/T* for a high enough value of the acentric factor. This means that *B(T)* would *decrease* towards a constant value for high temperature, an undesirable result for this kind of models (we want *B* to *increase* towards a constant for high *T*). This would happen at $\omega > 0.717$ for the Pitzer-Curl correlation; therefore, it would predict an incorrect behavior for hexadecane ($\omega = 0.7486$) and heavier substances. The corresponding value for the Schreiber-Pitzer correlation is $\omega > 4.485$ which is a very high value, greater than the acentric factor of any known substance.

Some researchers (Zhixing et al. 1987; Weber 1994) have concluded that the higher-than-cubic terms included in the Pitzer-Curl, Tsonopoulos & other correlations are not really required for normal fluids. After studying the above models, one can argue than this is true for the function f_0 but not necessarily for the function f_1.

A graphical comparison of the functions f_0 and f_1 can be made. In the following figure, seven different expressions for f_0 are plotted versus $1/T_r$ for the range $0.5 < T_r < 20$, the selected range is equal to about 75-3000 K in the case of argon. All the curves are very similar at high temperature; their differences show up at low temperature, where the Pitzer-Curl and McGlashan-Potter equations are the least negative, while the Black equation is the most negative, followed by the Tsonopoulos one, and the more recent correlations falling between those ones.

The McGlashan-Potter and Schreiber-Pitzer equations were multiplied by $Z_c = 0.29$, according to Equation (26), for this comparison. It is remarkable that the McGlashan and Potter equation, which is the simplest of the plotted models, does a good job in representing *B(T)* over most of the temperature range, being similar to the Pitzer and Curl one.

Figure 16.

Graphical comparison of different f_0 functions.
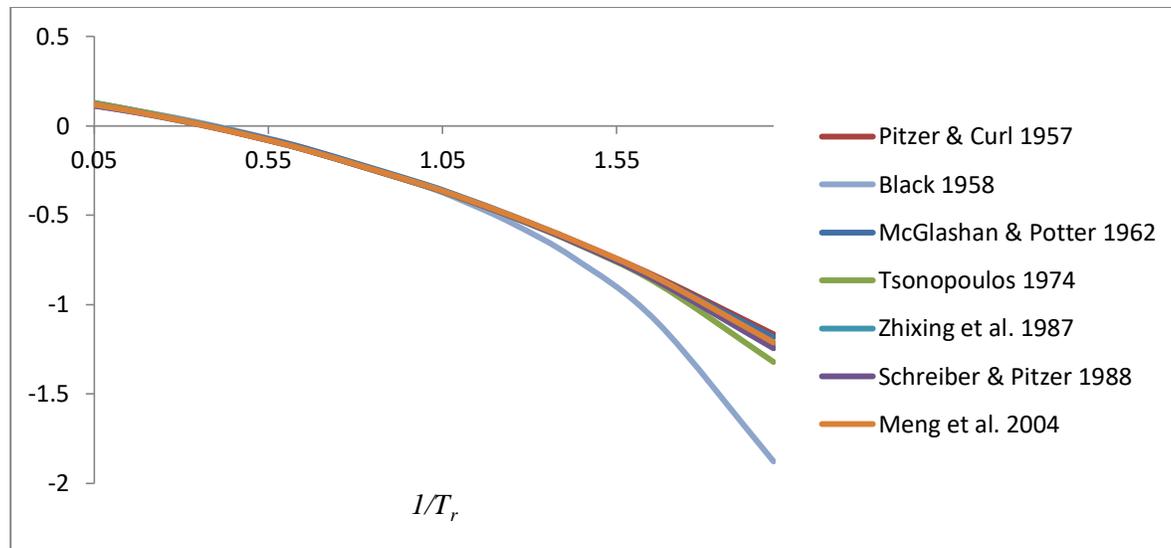
Own source

In Figure 17 below, eight different expressions for f_1 are plotted versus $1/T_r$ for the range $0.5 < T_r < 20$. The Schreiber-Pitzer equation was multiplied by $Z_c = 0.29$, according to Equation (26), for it to be compared with the other models. These curves show greater variability, particularly at the lower temperatures where the Schreiber-Pitzer and Lee-Chen equations are the most negative and the Weber equation is the least negative. The Zhixing et al. equation presents an inconsistent behavior, increasing at high temperature towards a constant value (0.9586) much higher than the other equations. The Abbott model represents the simplest one and it does a good job. It is not possible to conclude which is the best model from the graph alone.

Figure 17.

Graphical comparison of different f_1 functions.
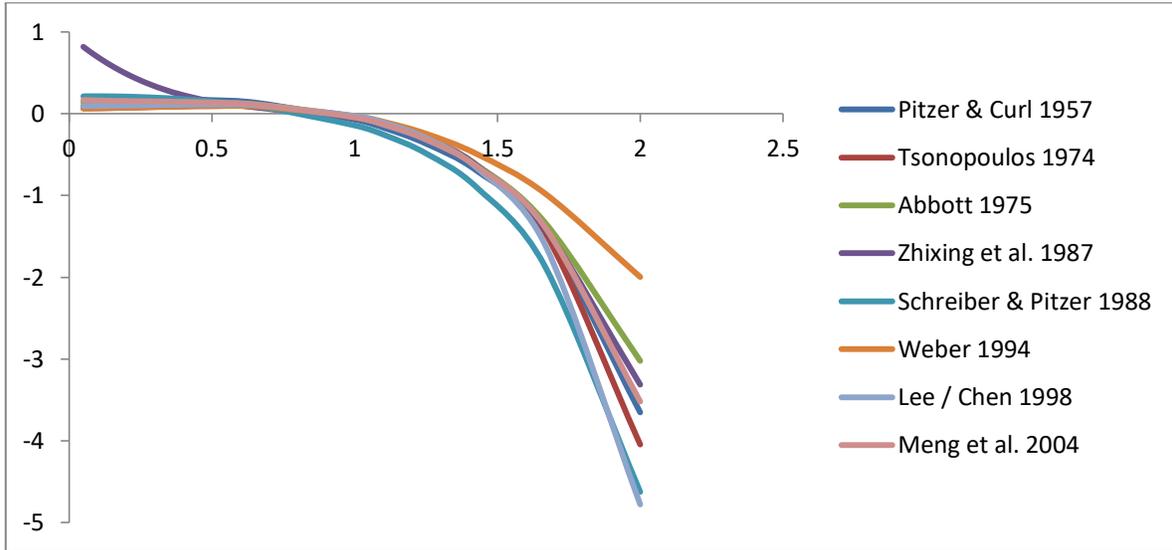
Own source

Other Models

There are several other models for *B(T)* in the literature, different from the ones included in this chapter, which will not be studied nor discussed here. The most relevant ones are models based on the square-well potential (Nothnagel et al. 1973; McFall et al. 2002), on the Lennard-Jones potential (Kunz & Kapner 1971), or on the inclusion of a fourth parameter (Halm & Stiel 1971; Xiang 2002). There is also one model based on a two-step square-well model (Kreglewski 1969).

We will only mention the model of Iglesias-Silva and Hall (2001), as an example of an equation based on a different approach; it is reduced in terms of the Boyle temperature:

(51) $$B/b_0 = \theta^m\left(1 - \theta^l\right)\exp(b_1\theta^n) \text{ where } \theta = T_B/T$$

Characteristics of a good model

After reviewing eighteen models, general criteria or specifications can be established about the characteristics of a good model for *B(T)*. Some of these criteria will be mandatory, while others will be just desirable; a list of them is displayed below while then each one will be explained.

Mandatory specifications:

a. Constant term positive.

b. Term in T_r^{-1} negative.

c. Term with highest order T_r^{-m} negative.

Desirable (non-mandatory) specifications:

    d.   Other temperature-dependent terms negative.

    e.   No more than one positive term, different from the constant.

    f.   Decreasing magnitude of successive coefficients, after the constant.

    g.   Small coefficients, magnitude less than unity in reduced form.

    h.   Constant (non-reduced) of the same order of b_0 for hard spheres or Lennard-Jones.

    i.   Function f_0: constant in the range $0.07 \ldots 0.145 RT_c/P_c$.

    j.   Function f_0: constant in the range $0.43 \ldots 0.455 V_c$.

    k.   Function f_1: constant in the range $0.073 \ldots 0.175 RT_c/P_c$.

    l.   Function f_1: constant in the range $0.726 \ldots 1.033 V_c$.

    m.   B varies like $T_r^{-1.5}$ approximately for simple fluids.

    n.   B varies more than cubic for normal fluids, $n \approx -4.5$.

    o.   Small order of the model (quadratic or cubic for f_0).

       A *B(T)* model that complies with the above criteria will be well-behaved, that means it will be a *monotonic* function (always increasing with *T*), avoiding oscillatory behavior and/or points of inflection; it will also have a correct asymptotic behavior at high and low temperatures.

       The model for *B(T)* can have positive and negative coefficients, but there are some restrictions. The constant term must always be non-negative, otherwise the fluid would not have a Boyle temperature; this includes the option of a zero constant term, such as in the Lennard-Jones model. For most of the models analyzed above (the exception being Lennard-Jones), *B(T)* is an *increasing* function at high temperature; this fact implies that the coefficient of T_r^{-1} must always be negative. This can be seen at a graph of *B(T)* vs. $1/T$, the slope near the origin is represented by the coefficient of T_r^{-1}. The specifications (a) and (b) are related: a fit of experimental data with positive constant will usually have a negative term in T_r^{-1}. This behavior can be seen in Figure 18 below.

Figure 18.

Expected behavior of *B(T)*, oxygen data (Dymond et al. 2002).
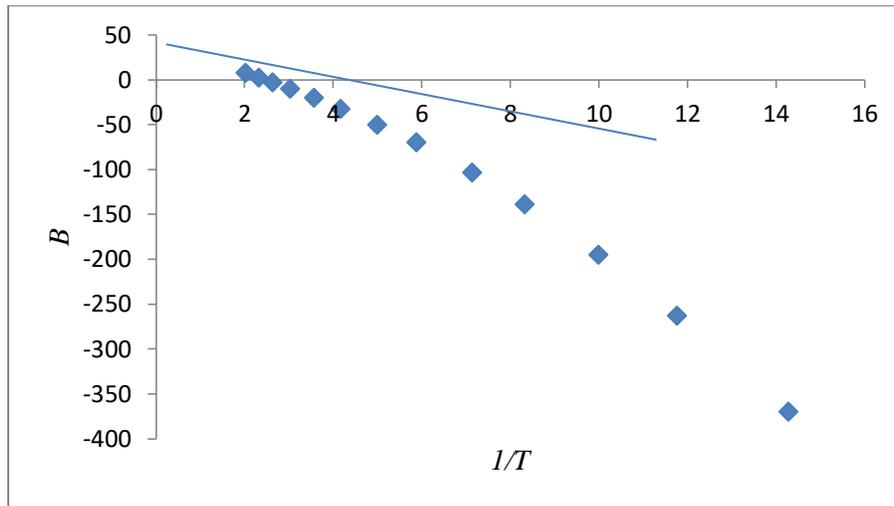
Own source

There is a reason for the last term of *B(T)* models being always negative to be realistic: for a sum of terms in T_r^{-1}, T_r^{-2}, ... T_r^{-m}, the most negative exponent will dominate the behavior at low temperature $(T \rightarrow 0)$. The sum will approach $+\infty$ if its coefficient is positive, and $-\infty$ if its coefficient is negative. As the correct limit is $-\infty$, it results in specification (c).

When one or more positive terms are introduced in a model, the possibility of oscillatory behavior and inflexion points increase, not observed in real fluids. The worst case could happen with alternating sign coefficients, as shown in the following plot of cyclopentane data from Dymond et al. (2002), the Boyle temperature is from Estrada-Torres (2007).

Figure 19.

Oscillatory behavior and inflexion point.

$$y = -296.64x^3 + 2134x^2 - 5134.2x + 3339.7$$
$$R^2 = 1$$
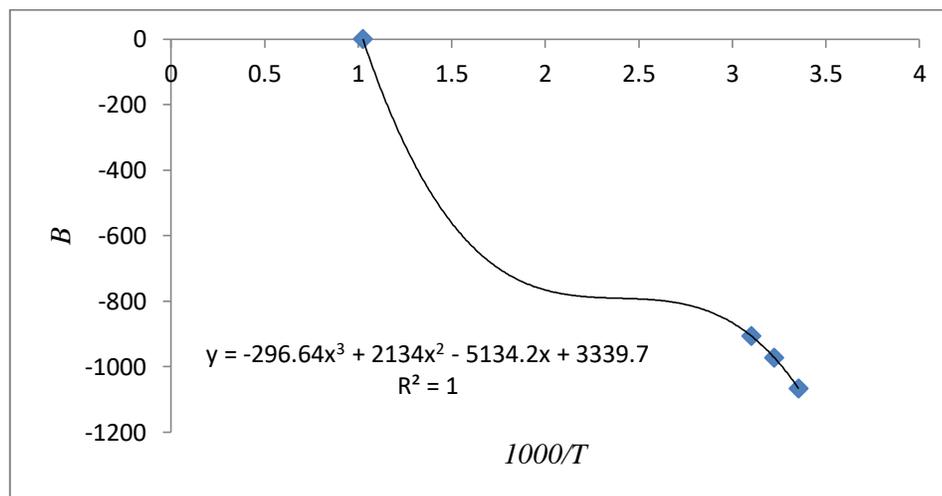
Own source

The figure above illustrates also the problem of *data overfitting*: in this case, a third-grade model was fitted to data which are linear or quadratic at most. In addition to the oscillatory behavior and the inflection point, the manifestations of overfitting include the presence of very high coefficients that cancel each other, as seen in the above figure. That, as well as the analysis of the previous models, are the reasons of specifying that the coefficients must be small and of decreasing magnitude, specifications (f) and (g). Overfitting does not improve the accuracy of a model; therefore it has always to be avoided. There are some statistical tests to determine the maximum order of a model; one of them (*F-test*) will be used when fitting experimental data later.

It is convenient to compare the constants of the fitting equations for *B(T)* against the values of the hard spheres second virial coefficient b_0. Table 8 and Figure 20 compare three sets of data: values of the Lennard-Jones b_0 from methane to octane, smoothed and/or interpolated from the data of Tee et al. (1966); constants from cubic equations fitted to recommended *B(T)* values for the same substances, and the corresponding constants from fourth-order equations fitted to the same data. The *B(T)* equations were adjusted by the use of the Boyle temperature, as it will be discussed later. The constants from the cubic fit are approximately equal to $0.5825b_0$ while the constants from the fourth-order fit are approximately equal to $0.2547b_0$. As discussed previously, the maximum value of *B(T)* for the L-J model is about $0.53b_0$, which is similar to the cubic fit constant. Later results (Chapter 7) point to the fourth-order fit as closer to the optimum value for the constants.

Figure 20.

Plot of constants from Lennard Jones and *B(T)* fits for n-alkanes.
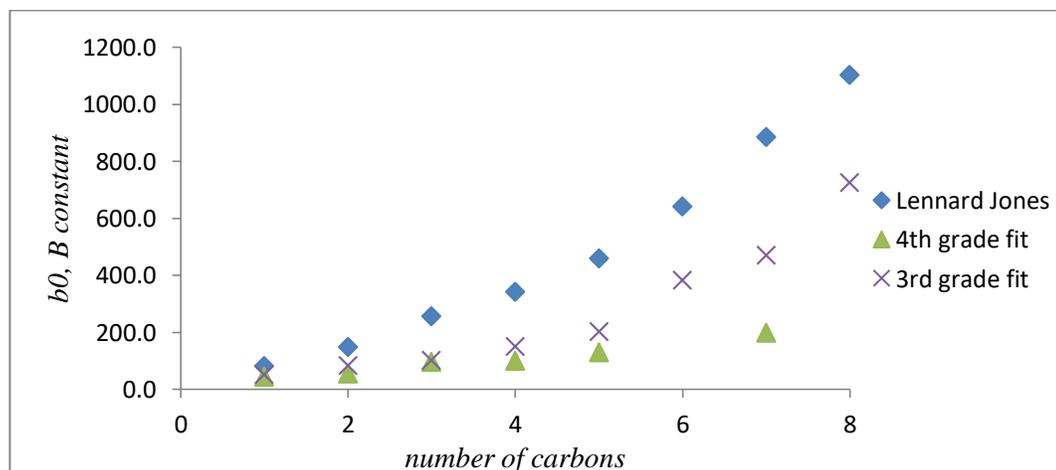
Own source

TABLE 8.

Comparison of Lennard Jones constants and *B(T)* data fits.

SUBSTANCE	LENNARD JONES b_0	4TH GRADE FIT a_0	3RD GRADE FIT a_0
CH4	81.2	44.344	52.29
C2H6	149.5	55.629	83.754
C3H8	256.4	95.825	102.21
n-C4H10	342.1	99.895	149.713
n-C5H12	458.8	130.283	203.412
n-C6H14	640.5		382.873
n-C7H16	884.1	199.27	469.55
n-C8H18	1102.3		725.79

Own source

Some Examples of Incorrect Behavior

The following are examples of equations, or models, fitted to second virial coefficient data sets, which violate one or more of the mandatory specifications established in a previous section. All the examples are taken from Dymond et al. (2002). These authors included the warnings that their equations do not have physical meaning, and that they are not intended to be used outside of the range of the experimental data; however, there are clear mistakes in their recommended values (e. g. inflection points, negative constants in the equations) that could have been avoided if they would have made a graph.

First, a compact form to report a fitting equation for *B(T)* has to be defined because there will be many equations in the following chapters. Dymond et al. (2002) fitted the experimental data to the following model, from which they calculated their recommended values:

$$(52) \qquad B = a_0 + a_1 T^{-1} + a_2 T^{-2} + a_3 T^{-3} + a_4 T^{-4} + a_5 T^{-5} + a_6 T^{-6} + \cdots$$

Most of the substances will have four non-zero coefficients; some substances will require the coefficient a_4 and only a few substances (usually highly accurate data) will require the coefficients a_5 and a_6. The constants of this model for a particular substance, the minimum and maximum temperatures of application, and the calculated Boyle temperature, will be reported in the following format, taking argon as an example:

ARGON

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
34.162	-1.21E+04	-7.67E+05	-1.96E+07		76	1000	411.730

The first example to be considered is 2-methylbutane. The equation proposed by Dymond et al. violates specifications (a) and (b), as it has a negative constant and a positive coefficient in T^{-1}. Red color indicates which coefficients are wrong. As seen in the graph below, the curve never touches the horizontal axis; this means there is not a Boyle temperature for this model.

2-METHYL BUTANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-202.33	1.85E+05	-1.23E+08	-2.31E+09		260	585	n.a.

Figure 21.

2-methyl butane, data and fit by Dymond et al. (2002).
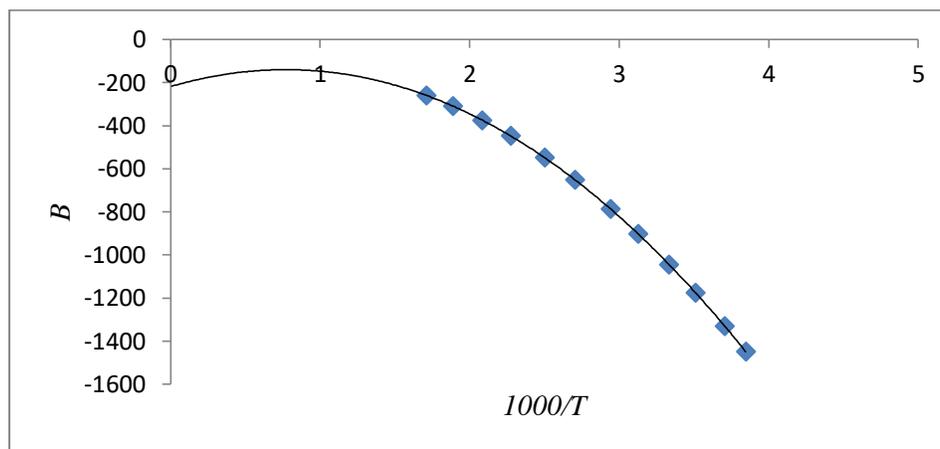
Own source

The second example to be considered is silicon tetrafluoride. The equation proposed by Dymond et al. violates specification (b), as it has a positive coefficient in T^{-1}. Additionally, the powers of 10 in the coefficients were wrong: 48.41 instead of 4.841 for a_0, and 3.09E+03 instead of 3.09E+04 for a_1. As seen in the graph below, the curve crosses the horizontal axis and looks "almost" normal; however, the slope when it touches the vertical axis is small, but positive. These data only accept a linear fit.

SILICON TETRAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
48.41	3.09E+03	-2.20E+07			295	350	646.24

Figure 22.

Silicon tetrafluoride, data and fit by Dymond et al. (2002).
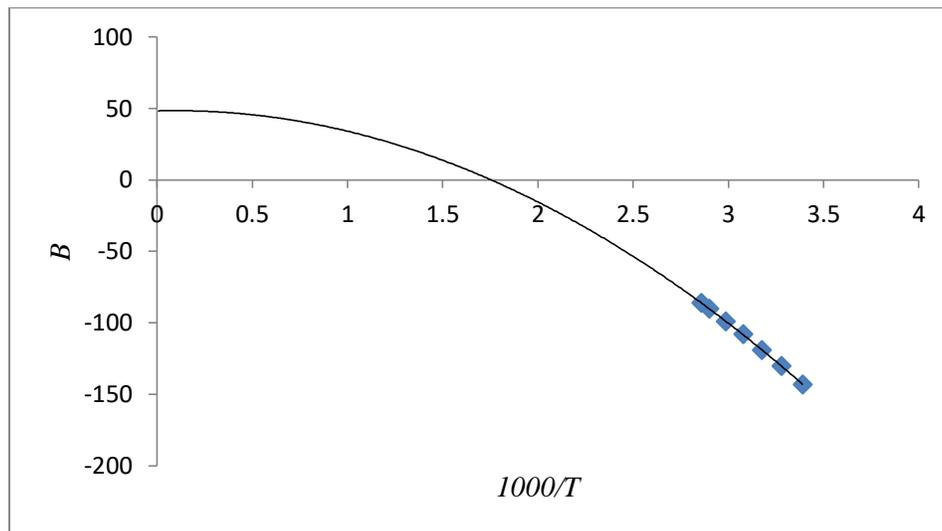
Own source

The third example to be considered is decafluorobutane. The equation proposed by Dymond et al. violates specification (c), as it has a positive coefficient in T^{-2}, the last term. As seen in the graph below, the curve starts to increase at the lower temperatures, an unphysical behavior. The constant of the model is also very high, which is a reason to suspect of the fit. These data only accept a linear fit.

DECAFLUOROBUTANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
2087.4	1.22E+06	-9.75E+07			285	370	490.74

Figure 23.

Decafluorobutane, data and fit by Dymond et al. (2002).
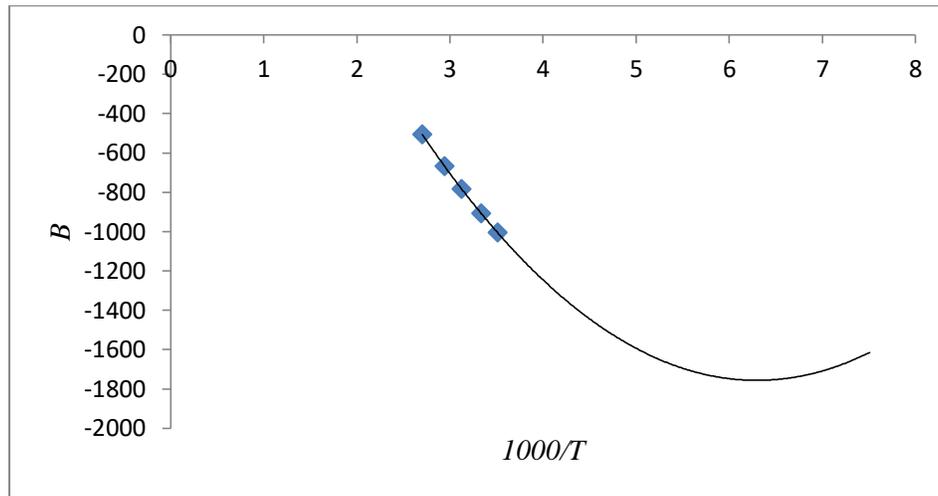
Own source

The fourth and last example to be considered is uranium hexafluoride. The equation proposed by Dymond et al. violates all three specifications (a), (b) and (c): three of its four coefficients have the wrong sign. As seen in the graph below, this determines that the curve has an incorrect behavior both at low and high temperatures, not having a Boyle temperature. Reducing the grade of the fit does not help, because a quadratic fit also violates specifications (a) and (b); these data only accept a linear fit.

URANIUM HEXAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-1697.7	1.87E+06	- 7.70E+08	7.78E+10		330	465	n.a.

Figure 24.

Uranium hexafluoride, data and fit by Dymond et al. (2002).
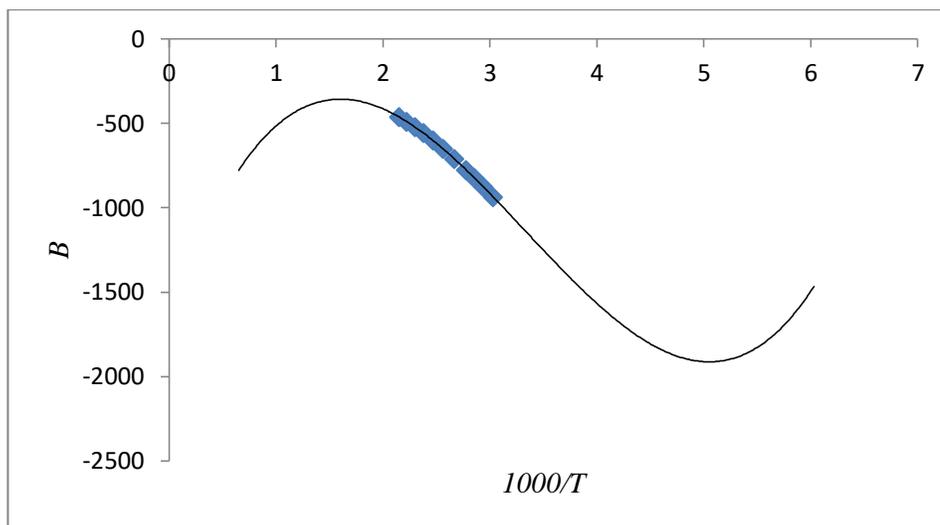
Own source

A Very Good Model for Argon

During the course of this investigation, a very good model for argon was found, a model that could open new lines of research about modeling second virial coefficients. The initial finding was that the second derivative of $B(T)$, when plotted against T^{-4}, is almost a straight line, with a value of R^2 of 0.9994; this result could be also obtained from the Berthelot model, Equation (35):

Figure 25.

Second derivative of B for argon (data from NIST).
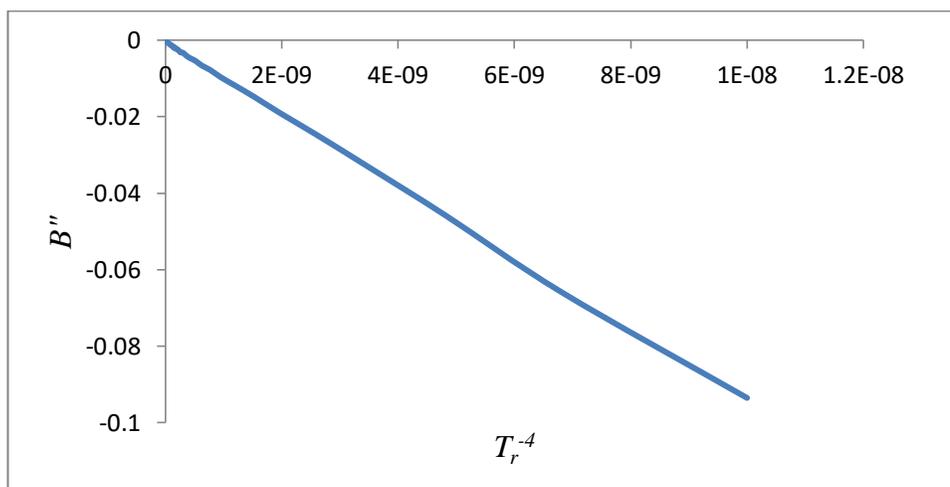
Own source

An improvement of the fit is obtained if we add a term in T^{-2}, with the value of R^2 increasing to 0.9998 and a F-test value of 32. However, if this result be correct, the model for $B(T)$ would contain a logarithmic term, as follows:

$$\frac{d^2B}{dT^2} = -\frac{A}{T^2} - \frac{B}{T^4}$$

$$\frac{dB}{dT} = +\frac{A}{T} + \frac{B}{3T^3}$$

(53) $$B = A\,ln(T) - B/6T^2 + C$$

The model above did not provide a good fit of the argon data, a quadratic fit was better; however, it was found that a cubic fit combined with the logarithmic term was much better than a five-order fit. This is shown in the following table, where the R^2 values are tabulated for different fits of the argon second virial coefficient data, taken from NIST for their high accuracy:

TABLE 9.
Coefficients of determination for different models of argon *B* data.

Type of fit	R^2
linear fit in 1/T	0.98297518
quadratic fit	**0.99997622**
third-order fit	0.99997888
fourth-order fit	0.99999733
fifth-order fit	0.99999944
third-order + ln(T)	**0.99999992**

Own source

The fitting procedure was not continued after the fifth-order model because it violated the specification (c) established here; that is, the highest order term in $1/T$ had a positive coefficient. From the table above, it can be concluded that a quadratic fit is already very good, as it explains the 99.998% of the variability represented by the coefficient of determination R^2. If the order of the model is increased, the adjustment improves but the number of coefficients of the model also increases. The fact that the last model containing the $ln(T)$ term reduces the variability in the order of about 10, when compared with the previous fifth-order model, is remarkable because the number of coefficients is being *reduced* by one. This last model explains the 99.999992% of the variability of the argon second virial coefficient data from NIST.

If R^2 represents the explained variability, then $(1 - R^2)$ represents the non-explained variability; it is possible to get an idea of the improvement obtained with the following calculations:

Reduction ratio of $(1 - R^2)$ when adding the ln(T) term to the third-order model:

$$\frac{1 - 0.99997888}{1 - 0.99999992} = 268$$

Reduction ratio of $(1 - R^2)$ when going from the 5-th order model to the best model:

$$\frac{1 - 0,99999944}{1 - 0.99999992} = 7.04$$

The resulting model, Equation 54, reproduces the second virial coefficient of argon; it is also able to reproduce the first and second derivatives of *B(T)*, as shown in Figures 26 to 28.

(54) $B = 51.19634 - 114.249T_r^{-1} - 10.1290T_r^{-2} - 11.8618T_r^{-3} - 7.24678\ln(T_r)$

Figure 26.

Argon data from NIST, fitted to Equation (53).
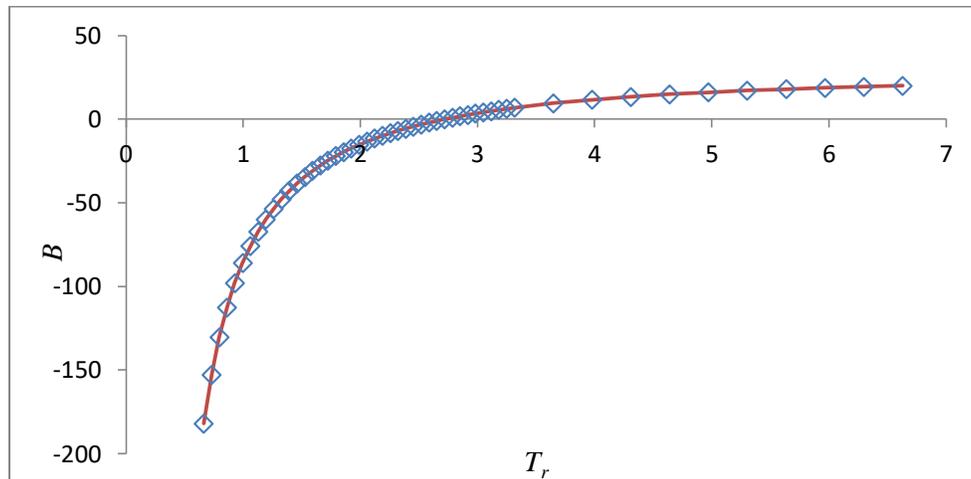
Own source

Figure 27.

dB/dT_r for argon, fitted to derivative of Equation (53).
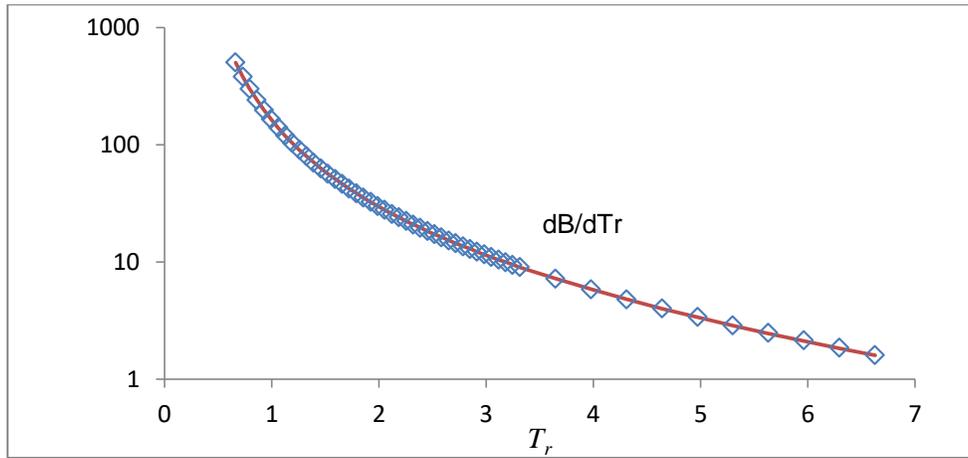
Own source

Figure 28.

d^2B/dT_r^2 for argon, fitted to second derivative of Equation (53).
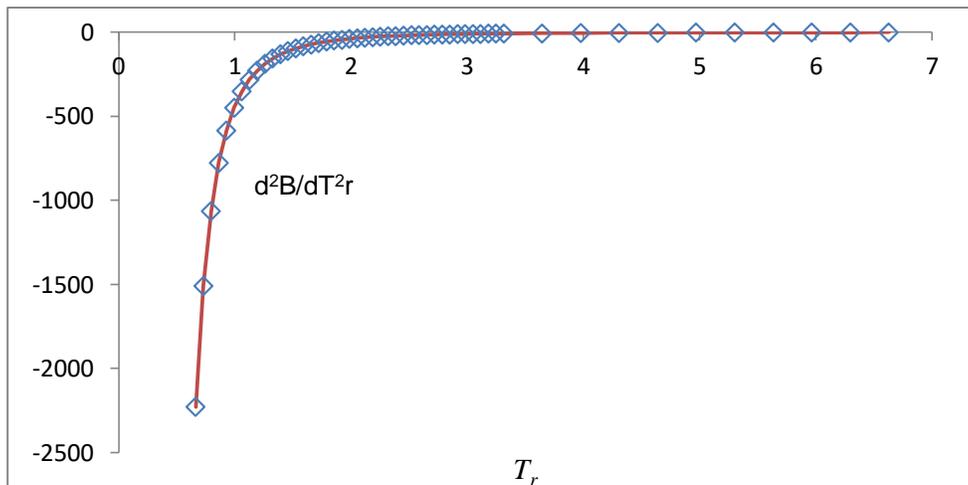
Own source

Chapter 3.
CRITICAL ANALYSIS OF SOURCES

Following, a critical analysis of the sources of second virial coefficient data and equations will be done in order to identify not only the best sources, but also the flaws that some of them have. One of the reasons is to reduce the number of substances when refitting the data with equations that do not follow the specifications defined in Chapter 4; also because it is recommendable to use the best data and equations when they are available. Among the several sources chosen are:

a) <u>Compilation of Dymond et al., third edition (2002)</u>: This is the primary reference for this research to be considered the authoritative source of second virial coefficient data since its first edition in 1969. It provides recommended values of *B(T)* for hundreds of substances, based on an analysis of all the available information up to 1998; for each substance, a fitting equation is also given for interpolation purposes. However, as it will be shown below, the recommended data and equations have flaws (e.g. inflection points, overfitting); this is due, in some cases, to the few data available for some substances.

b) <u>Highly-accurate data and equations from L. Zarkova and its group</u>: In recent years, a group of European researchers have studied more than 30 substances from the point of view of a new, temperature-dependent Lennard-Jones type potential (Zarkova, Hohm & Damyanova 2006; Hohm, Zarkova & Stefanov 2007; Zarkova & Hohm 2002, 2009; Damyanova, Zarkova & Hohm 2009). They have obtained the potential parameters and calculated a set

of consistent properties for each substance, taking into account all the experimental information available. The second virial coefficient was included in these studies, and their results are highly accurate (within experimental error) and cover a wide range of temperatures. They also have provided fitting equations for each substance: the equations for 23 substances will be included in this study.

c) <u>High-accurate data from NIST</u>: The National Institute of Standards and Technology (USA) has many online databases, among them the Standard Reference Database 134, *Database of the Thermophysical Properties of Gases Used in the Semiconductor Industry*. This database includes highly accurate second virial coefficients for 15 of the substances included in this research. Most of these data come from careful experiments done after 1999, using the latest experimental techniques, such as speed of sound measurements (Estela-Uribe & Trustler 2000; Hurly 1999, 2000a, 2000b, 2000c, 2002a, 2002b, 2003). The data obtained from this source were fitted to equations in order to be included in this study.

d) <u>Equations from DIPPR DIADEM database</u>: the DIADEM database was developed by the DIPPR (Design Institute for Physical Properties), as part of their DIPPR 801 project. It contains comprehensive information for two-thousand compounds in their latest release. Their open-access, demo version contains information of 58 compounds, among them 25 substances included in this research. They provide a fitting equation and coefficients for the second virial coefficient of these substances, based on the McCann-Danner model, Equation (46). A comparison was made between the values predicted by this model, which is of order 9, and the other available models or experimental data. Based on this comparison, it was decided not to use the DIPPR data or equations because they tended to predict a different temperature dependence from the other models, more steep or negative at low temperatures (consistent with a higher-order model). Also, about half of the equations violated one or more of the specifications established in Chapter 4 for a good *B(T)* model.

All the equations reported below will follow Equation (52), introduced in Chapter 4:

$$B = a_0 + a_1 T^{-1} + a_2 T^{-2} + a_3 T^{-3} + a_4 T^{-4} + a_5 T^{-5} + a_6 T^{-6} + \cdots$$

Equations from Dymond et al.

The compilation of Dymond et al. provides equations for 57 of the 62 substances included in this study. The equations for only 13 substances comply with the specifications established in Chapter 4 and they predict the Boyle temperature correctly; therefore they are accepted:

ARGON

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
34.162	-1.21E+04	-7.67E+05	-1.96E+07		76	1000	411.73

KRIPTON

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
38.03	-2.00E+04	-1.48E+06	-1.35E+08		240	870	600.04

NITROGEN

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
40.286	-9.34E+03	-1.42E+06	6.13E+07	-2.72E+09	75	745	327.01

FLUORINE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
33.609	-1.06E+04	-6.08E+05	-2.28E+07		85	295	369.96

CARBON MONOXIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
48.826	-1.56E+04	-2.76E+05	-4.77E+07		125	570	344.42

CARBON DIOXIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
57.4	-3.88E+04	4.29E+05	-1.47E+09		220	770	715.86

METHANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
44.344	-1.66E+04	-3.54E+06	2.98E+08	-2.34E+10	115	670	509.44

PROPANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
109.71	-8.47E+04	-8.12E+06	-3.44E+09		215	620	893.83

PROPENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
101.01	-7.57E+04	-7.95E+06	-2.80E+09		225	570	875.77

SULFUR HEXAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
133.13	-9.49E+04	4.38E+06	-3.68E+09		200	545	720.55

MOLYBDENUM HEXAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
164.53	-4.49E+04	-7.88E+07			300	450	841.94

TUNGSTEN HEXAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
338.48	-2.81E+05	-7.98E+06			315	460	857.85

BORON TRIFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
91.039	-5.91E+04	1.05E+07	-3.05E+09		275	475	550.31

The following four equations in Dymond et al. (2002), although they seem to comply with the required specifications, show an unphysical inflection point so they are rejected. These equations tend to predict a lower value for the Boyle temperature; look also the high values of the constant a_0.

1,3-BUTADIENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
17027	-1.66E+07	5.34E+09	-5.88E+11		285	360	430.23

CARBON DISULFIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
2841.5	-2.90E+06	9.58E+08	-1.25E+11		285	470	555.92

NITRIC OXIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
97.54652	-6.26E+04	1.18E+07	-1.08E+09		240	475	415.73

PROPADIENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
2666.4	-2.28E+06	6.10E+08	-6.01E+10		225	350	469.80

A clear example of the inflection point is given in Figure 29, where the second virial coefficient data of nitric oxide is plotted, taken from Dymond et al. (2002).

Figure 29.

***B(T)* data for nitric oxide, taken from Dymond et al. (2002).**
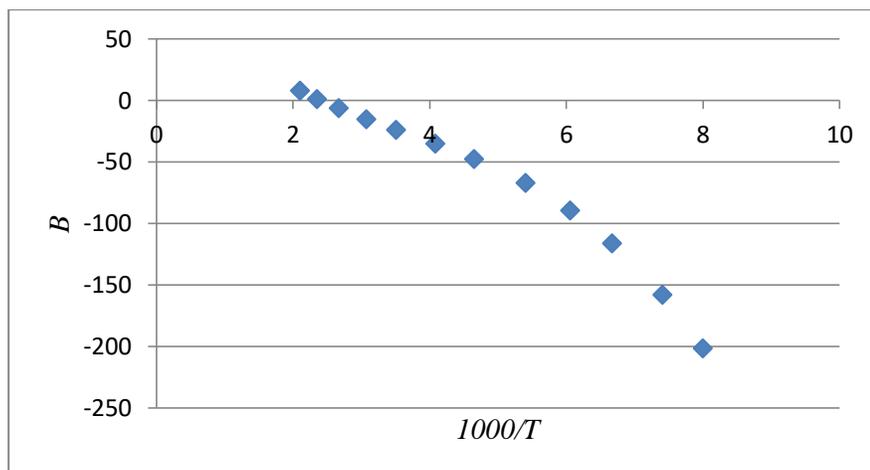
Own source

The following six equations in Dymond et al. (2002) violate specification (c), i.e. the highest-order coefficient is positive, so they are rejected. The wrong coefficient is highlighted in red color. Although some of these equations predict the Boyle temperature correctly (e.g. xenon, oxygen), they need an adjustment in order to comply with the specifications.

NEON

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
15.89	-9.94E+02	-1.26E+05	2.27E+06		50	870	119.22

XENON

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
67.836	-5.32E+04	2.22E+06	-1.39E+09	5.85E+10	165	970	773.79

OXYGEN

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
42.859	-1.77E+04	5.20E+05	-1.64E+08	5.09E+09	70	495	404.47

TETRAFLUOROMETHANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
82.106	-3.09E+04	-5.99E+06	9.59E+06		175	770	517.19

N-DECAFLUOROBUTANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
2087.4	-1.22E+06	9.75E+07			285	370	490.74

1-BUTENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
1844.9	-2.48E+06	1.15E+09	-2.45E+11	1.66E+13	205	520	688.06

The following two equations in Dymond et al. (2002) violate specification (b), that is, the coefficient a_1 is positive. The wrong coefficient is highlighted in red color. These equations overpredict the Boyle temperature.

CHLORINE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
13.171	5.11E+03	-2.94E+07	-5.04E+08		300	1070	1322.42

SILICON TETRAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
4.841	3.09E+04	-2.20E+07			295	350	646.24

The following seven equations in Dymond et al. (2002) violate specifications (a) and (b), that is, coefficient a_0 is negative and coefficient a_1 is positive. The wrong coefficients are highlighted in red color. For several of these equations, the calculated Boyle temperature is very different from the real one, as they never cross the horizontal axis (B is always negative).

2-METHYL BUTANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-202.33	1.85E+05	-1.23E+08	-2.31E+09		260	585	1363.25

2-METHYL PENTANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-704.89	7.74E+05	-3.25E+08			300	545	839.10

TRANS-2-BUTENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-1288.8	8.63E+05	-2.07E+08			245	330	479.84

CIS-2-BUTENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-2461	1.64E+06	-3.32E+08			255	340	406.02

ISOBUTENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-1553.6	2.63E+06	-1.66E+09	4.26E+11	-4.19E+13	245	545	696.53

N-TETRADECAFLUOROHEXANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-379.91	6.19E+05	-3.50E+08			305	450	1130.27

TETRACHLOROMETHANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-1309.4	9.91E+05	-3.20E+08			320	415	645.15

DODECAFLUOROCYCLOHEXANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-50.538	2.29E+05	-2.15E+08			355	450	1330.07

The following three equations in Dymond et al. (2002) violate specifications (a), (b) and (c), that is, coefficient a_0 is negative, coefficient a_1 is positive and the highest-order coefficient is positive. The wrong coefficients are highlighted in red color. These equations also predict the wrong Boyle temperature, as they never cross the horizontal axis (B is always negative).

CYCLOPROPANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-1225.1	1.34E+06	-5.13E+08	5.65E+10		300	400	525.67

URANIUM HEXAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-1697.7	1.87E+06	-7.70E+08	7.78E+10		330	465	623.13

ACETYLENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
-789.31	5.20E+05	-1.02E+08	1.20E+09		200	310	374.68

The following four substances have neither data nor equations in Dymond et al. (2002); however, highly accurate data are available from other sources:

BORON TRICHLORIDE

NITROGEN TRIFLUORIDE

SILICON TETRACHLORIDE

TRIMETHYL GALLIUM

The following substance has no equation, only data, in Dymond et al. (2002):

CYCLOPENTANE

This completes the analysis of the equations reported in Dymond et al. (2002).

Equations from Zarkova et al.

The work of Zarkova et al. has produced tables of consistent properties and fitting equation for 32 substances. The following 23 equations comply with all the specifications established here previously, so they are accepted. The source of the coefficients is indicated in parenthesis. In some cases, the equation is an alternative to another one; this is also indicated.

METHANE (Zarkova, Hohm & Damyanova 2006) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
46.515	-2.02E+04	-1.71E+06	-6.18E+07		100	1200	510.69

CHLORINE (Damyanova, Zarkova & Hohm 2009)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
81.58	-8.26E+04	1.92E+06	-2.94E+09		200	1000	1023.38

FLUORINE (Damyanova, Zarkova & Hohm 2009) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
34.74	-1.12E+04	-5.53E+05	-1.98E+07		70	1000	368.37

There is an error in the source article, concerning the sign of the last coefficient.

BORON TRIFLUORIDE (Zarkova & Hohm 2002) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
121.23	-6.92E+04	3.96E+06	-9.44E+08		200	900	536.91

TETRACHLOROMETHANE (Zarkova & Hohm 2002)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
331	-5.64E+05	1.34E+08	-3.91E+10		200	900	1485.24

TETRAFLUOROMETHANE (Zarkova & Hohm 2002)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
97.43	-4.77E+04	-4.20E+05	-5.59E+08		170	1000	518.89

TETRAMETHYL SILANE (Zarkova & Hohm 2002)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
516	-5.31E+05	1.16E+08	-3.16E+10		200	900	849.88

SILICON TETRAFLUORIDE (Zarkova & Hohm 2002)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
126.3	-6.26E+04	-4.14E+06	-1.16E+08		200	900	557.49

SILICON TETRACHLORIDE (Zarkova & Hohm 2002)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
563	-7.27E+05	2.21E+08	-5.36E+10		200	900	992.42

SULFUR HEXAFLUORIDE (Zarkova & Hohm 2002) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
162.8	-1.05E+05	1.10E+05	-2.35E+09		170	1000	677.24

MOLYBDENUM HEXAFLUORIDE (Zarkova & Hohm 2002) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
440	-5.45E+05	1.82E+08	-4.18E+10		200	900	895.77

TUNGSTEN HEXAFLUORIDE (Zarkova & Hohm 2002) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
365	-3.90E+05	1.04E+08	-2.79E+10		200	900	836.22

URANIUM HEXAFLUORIDE (Zarkova & Hohm 2002)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
1033	-1.46E+06	6.20E+08	-1.17E+11		200	900	876.10

1-BUTENE (Zarkova & Hohm 2009)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
231.29	-1.74E+05	-1.43E+07	1.34E+09	-1.38E+12	200	1000	830.06

ISOBUTENE (Zarkova & Hohm 2009)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
205.07	-1.54E+05	-2.55E+07	4.52E+09	-1.86E+12	200	1000	875.62

CIS-2-BUTENE (Zarkova & Hohm 2009)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
601.3	-5.55E+05	1.51E+08	-3.10E+10		200	1000	662.01

TRANS-2-BUTENE (Zarkova & Hohm 2009)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
394.33	-2.83E+05	5.65E+06	2.14E+09	-2.47E+12	200	1000	703.33

CYCLOPROPANE (Zarkova & Hohm 2009)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
190.26	-1.55E+05	7.84E+06	-3.14E+09	-1.59E+11	200	1000	790.12

HEXAFLUOROETHANE (Hohm, Zarkova & Stefanov 2007) (alternative to Hurly)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
161.6145	-8.75E+04	-8.63E+06	-8.55E+07	-2.03E+11	175	1000	632.41

OCTAFLUOROPROPANE (Hohm, Zarkova & Stefanov 2007)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
356.83	-2.01E+05	-1.26E+07	3.27E+09	-1.60E+12	175	1000	614.32

DECAFLUOROBUTANE (Hohm, Zarkova & Stefanov 2007)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
417.87	-1.35E+05	-1.33E+08	4.20E+10	-7.96E+12	175	1000	646.00

DODECAFLUOROPENTANE (Hohm, Zarkova & Stefanov 2007)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
517.83	-1.32E+05	-2.42E+08	8.11E+10	-1.50E+13	175	1000	690.12

TETRADECAFLUOROHEXANE (Hohm, Zarkova & Stefanov 2007)

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
698.39	-6.57E+05	2.12E+08	-1.47E+11	3.66E+13	-5.31E+15	175	1000	807.40

Several of the equations above are a refit of the equations reported in the references, in order to adjust them to the model represented by Equation (51) because the data were fitted to a different model in those references.

Nine substances studied by Zarkova and its group are being excluded: ethane, ethene, propane, propene, n-butane, i-butane, n-pentane, i-pentane and 2,2-dimethyl propane. The corresponding data and equations tend to predict lower Boyle temperatures than other methods considered (e.g. Estrada-Torres, Iglesias-Silva, DIPPR). Also these substances are well represented in the compilation of Dymond et al. However, the authors claim that their results are within experimental error, and they go up to 1000 K (Zarkova, Hohm & Damyanova 2006; Zarkova & Hohm 2009). These data and equations would be considered later, depending of the results obtained in Step 4. i.e. which data and equations provide a better fit[1].

Equations from NIST

The NIST Standard Reference Database 134 includes highly accurate second virial coefficients for 15 of the substances included in this study. For each substance a fitting equation was developed, as shown below. The source of the data is indicated in parenthesis. In some cases, the equation is an alternative to another one; this is also indicated.

ARGON (Aziz 1993) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
30.62	-8.67E+03	-1.86E+06	1.21E+08	-6.07E+09	100	1000	410.60

NITROGEN (Estela-Uribe & Trustler 2000) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
40.289	-9.21E+03	-1.49E+06	7.33E+07	-3.43E+09	77	1000	327.06

OXYGEN (NIST)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
34.536	-1.17E+04	-9.09E+05	-2.19E+07	-1.42E+06	200	1000	408.46

CARBON MONOXIDE (Saville et al. 1987) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
46.063	-1.34E+04	-8.54E+05	1.45E+07	-3.01E+09	75	1000	344.52

CARBON DIOXIDE (NIST) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
50.140	-2.70E+04	-7.00E+06	4.91E+08	-1.70E+11	-2.01E+12	200	1000	722.16

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[1] In fact, all of Zarkova equations had to be discarded later.

CHLORINE (Hurly 2002) (alternative to Zarkova et al.)

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
60.978	-5.30E+04	-1.33E+07	3.98E+08	-2.81E+11	-8.59E+12	240	1000	1070.73

NITROUS OXIDE (Hurly 2003)

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
51.878	-3.29E+04	-4.86E+06	-4.02E+08	-2.77E+10	-3.23E+12	200	1000	770.50

NITRIC OXIDE (Hurly 2003)

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
32.154	-1.01E+04	-1.20E+06	-6.70E+07	-8.42E+09	-6.13E+10	200	1000	418.36

TETRAFLUOROMETHANE (Hurly 1999) (alternative to Zarkova et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
82.004	-3.16E+04	-6.15E+06	2.96E+08	-5.43E+10	150	1000	520.67

HEXAFLUOROETHANE (Hurly 1999)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
133.038	-5.85E+04	-1.83E+07	1.43E+09	-3.37E+11	170	1000	637.76

SULFUR HEXAFLUORIDE (Hurly et al. 2000) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
115.278	-6.01E+04	-1.68E+07	1.09E+09	-3.33E+11	223	1000	714.90

TUNGSTEN HEXAFLUORIDE (Hurly 2000) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
91.194	-2.29E+04	-9.27E+07	1.94E+10	-3.67E+12	205	1000	1056.55

BORON TRICHLORIDE (Hurly 2000)

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
133.647	-1.14E+05	-2.98E+07	-1.65E+09	-2.82E+11	-1.21E+14	290	1000	1074.10

NITROGEN TRIFLUORIDE (Hurly 2002)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
72.068	-3.53E+04	-2.60E+06	-2.23E+08	-4.30E+09	200	1000	564.40

TRIMETHYL GALLIUM (Hurly 2002)

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
265.381	-7.04E+05	5.87E+08	-3.01E+11	6.58E+13	-7.12E+15	200	1000	1695.28

The following two sets of coefficients represent accurate *B(T)* data for their respective substances, they are included here because they were published and/or recommended by NIST; the sources of the data are indicated in parenthesis.

XENON (Sifner & Klomfar 1994) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
63.269	-4.48E+04	-2.64E+06	-2.39E+06	-6.93E+10	161.36	800	765.69

FLUORINE (Prydz & Straty 1970) (alternative to Dymond et al.)

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
28.968	-8.80E+03	-8.22E+05	-1.52E+07		80	300	381.79

A brief of the relationship between the different sets of equations presented above is shown in Table 10 below. A total of 38 equations are already available for the Step 4 of this research. Alternative equations are indicated by "alt".

TABLE 10.
Available equations from several sources.

| Dymond	Zarkova	Hurly /	Other
Ar		Ar alt	
Kr			
			Xe
N_2		N_2 alt	
		O_2	
F_2	F_2 alt		F_2 alt
	Cl_2	Cl_2 alt	
CO		CO alt	
CO_2		CO_2 alt	
		N_2O	
		NO	
CH_4	CH_4 alt		
C_3H_8			
C_3H_6			
SF_6	SF_6 alt	SF_6 alt	
MoF_6	MoF_6 alt		
WF_6	WF_6 alt	WF_6 alt	
	UF_6		
BF_3	BF_3 alt		
		NF_3	
		BCl_3	
		$Ga(CH_3)_3$	
	trans-2-C_4		
	1-butene		
	isobutene		
	cis-2-C_4		
	cyclo-C_3		
	CF_4	CF_4 alt	
	C_2F_6 alt	C_2F_6	
	C_3F_8		
	C_4F_{10}		
	C_5F_{12}		
	C_6F_{14}		
	CCl_4		
	$Si(CH_3)_4$		
	SiF_4		
	$SiCl_4$		

Own source

Extended-Range, High Accuracy Equations

During the process of developing the correlation for *B(T)*, it was noted that most of the available data covered a narrow range of reduced temperatures, around 0.5 to 4.2 in most cases. For the correlation to cover an extended range, 0.2 to 20, a way to obtain the required *B(T)* data was necessary. Therefore, reference equations were developed for those substances with available and accurate data in the required temperature range. For these substances, there were accurate data of *B(T)* up to 3273 K available in most cases, based on theoretical calculations (Kestin et al. 1984; Bousheri et al. 1987). The development of the equations will be illustrated with ethane.

The equation for ethane was based on three different sources of data, as shown in Figure 30 below:

a.   Dymond et al. (2002) provided recommended second virial coefficient data for ethane for the range 195 - 620 K;

b.   Bücker and Wagner (2006) provided calculated second virial coefficient data for ethane at very low temperatures (71-200 K);

c.   Bousheri et al. (1987) provided calculated second virial coefficient data for ethane up to very high temperatures (250 – 2273.15 K).

Figure 30.

Available *B(T)* data for ethane.
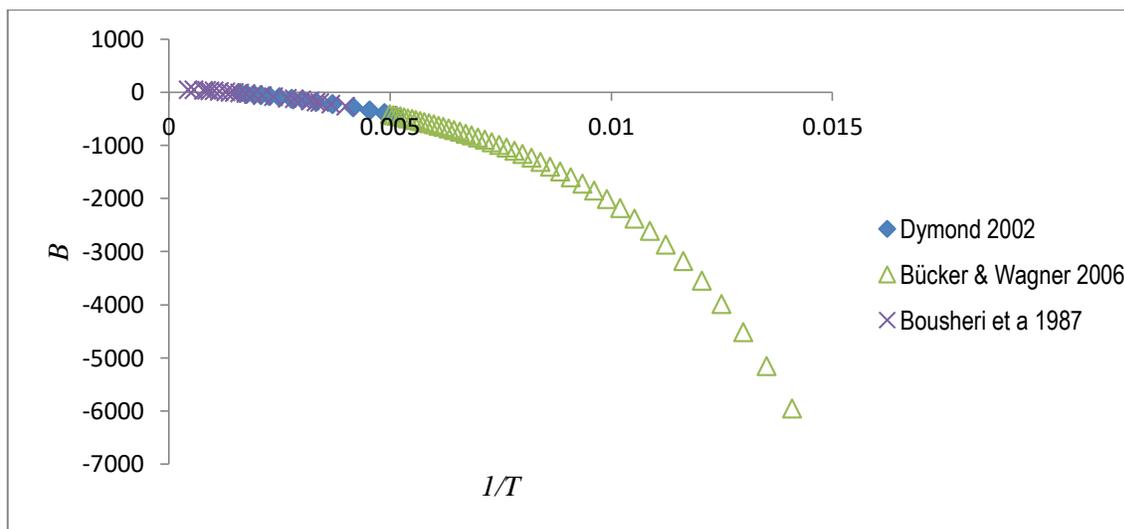
Own source

Combining the three sets of data, it is possible to develop an equation for the second virial coefficient of ethane, valid for a wide range of temperature (71-2273.15 K), and able to fit well all the data. The result is less accurate using the DIPPR/TRC recommended values.

ETHANE

a0	a1	a2	a3	a4	a5	a6	Tmin	Tmax	Tboyle
70.6022	-3.64E+04	-1.43E+07	1.51E+09	-2.87E+11	1.56E+13	-5.47E+14	71	2273.15	755.03

The extended-range equations for other 15 substances are shown below:

ARGON

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
29.842	-8.75E+03	-1.58E+06	5.68E+07	-2.44E+09	50	3273.15	411.707

KRYPTON

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
36.6697	-1.76E+04	-2.06E+06	-1.77E+08	1.61E+10	-6.99E+11	50	3273.15	587.62

XENON

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
49.4329	-3.45E+04	-2.89E+06	-1.24E+09	1.48E+11	-7.04E+12	50.00	3273.15	803.54

METHANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
40.0199	-1.12E+04	-5.49E+06	5.45E+08	-3.32E+10	100	3273.15	503.87

NITROGEN

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
38.0628	-6.94E+03	-2.06E+06	1.25E+08	-4.92E+09	75	1773.15	322.61

FLUORINE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
27.5220	-4.68E+03	-2.36E+06	1.75E+08	-7.52E+09	80	1000	363.59

ETHENE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
51.9509	-1.77E+04	-1.71E+07	2.36E+09	-2.38E+11	200	2273.15	720.57

TETRAFLUOROMETHANE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
70.7153	-1.07E+04	-1.70E+07	2.46E+09	-1.99E+11	150	3273.15	511.05

SULFUR HEXAFLUORIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
102.4426	-2.26E+04	-3.99E+07	6.17E+09	-7.03E+11	147.52	3273.15	683.00

NEON

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
15.7546	-9.25E+02	-1.43E+05	3.52E+06	-2.98E+07	50	870	119.78

CARBON MONOXIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
40.5587	-8.75E+03	-2.01E+06	1.24E+08	-6.56E+09	75	1773.15	339.33

CHLORINE

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
60.9778	-5.30E+04	-1.33E+07	3.98E+08	-2.81E+11	-8.59E+12	240	1000	1070.73

NITROUS OXIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
36.5710	-1.00E+04	-1.80E+07	2.98E+09	-3.55E+11	190	3273.15	788.14

CARBON DIOXIDE

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
38.4595	-7.83E+03	-1.78E+07	3.05E+09	-3.99E+11	220	3273.15	719.64

NITRIC OXIDE

a0	a1	a2	a3	a4	a5	Tmin	Tmax	Tboyle
31.2185	-8.65E+03	-1.88E+06	1.80E+07	3.39E+09	-2.44E+12	124	2273.15	418.34

Relationship between Constant a_0 and the Lennard–Jones b_0

In the previous chapter, a first analysis was made of the relationship between the constant a_0 in Equation (51) and the hard-spheres second virial coefficient b_0, which is equal to one of the constants of the Lennard-Jones potential. Another approach to determine this relationship will be followed here, by trying to determine optimum values of a_0 for several substances.

Several researchers have calculated values of the second virial coefficient at high temperatures (Kestin et al 1984., Bousheri et al. 1987). These values can help in determining the correct high-temperature limit for the fitting equations, that is the value of a_0. This can be done by calculating the ratio of the constant a_0 to the predicted value of $B(T)$ at 3273.15 K, or 2273.15 K, depending of the available data; this ratio is multiplied by the calculated value of $B(T)$ at high temperature, in order to obtain the "optimum" or "expected" value for constant a_0.

When comparing the estimated "optimum" values of a_0 versus the Lennard-Jones constants b_0 for several substances, it is found again that the optimum value should be around $0.50b_0$, as it is indicated in Table 11 and Figure 31.

TABLE 11.

Optimum values of a_0 vs. Lennard-Jones b_0.

SUBSTANCE	L-J b_0	B(3273 K)	a_0 ESTIM
Ar	54.03	24.55	27.005
Ne	26.2	11.87	13.77
Kr	71.76	29.24	34.9418
Xe	86.93	35.71	46.0659
N_2	63.58	30.38	32.8104
NO	40	26.65	29.5815
O_2	57.75	25.47	28.5264
CO	67.222	30.38	33.7218
N_2O	122	31.24	39.05
CH_4	81.33	33.63	38.3382
CO_2	85.05	33.52	42.2352
CF_4	131	64.21	73.1994
SF_6	211.1	93.3	112.893
C_2H_4*	109.88	38.59	47.8516
C_2H_6*	149.5	47.93	58.9539

* B at 2373 K.

Own source

Figure 31.

Comparison between optimum values of a_0 vs. Lennard-Jones b_0.
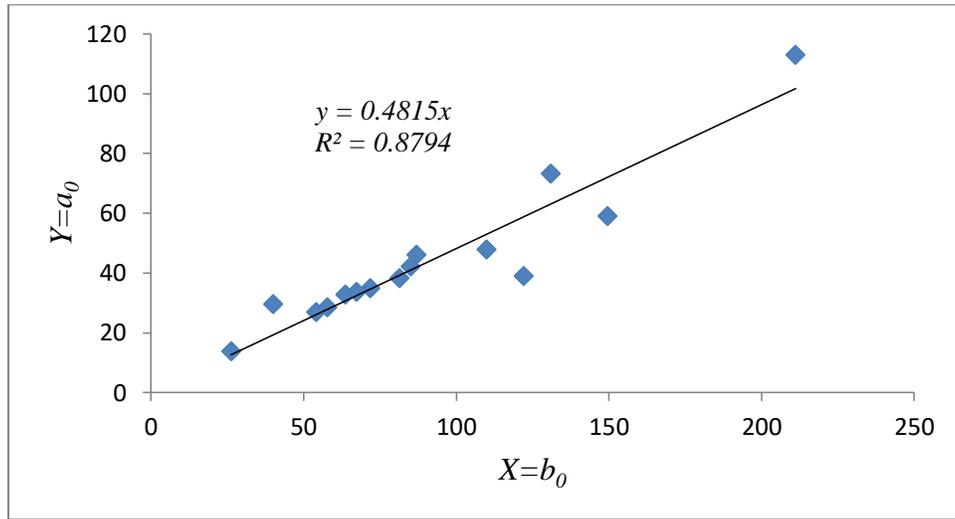
Own source

Chapter 4.

BOYLE TEMPERATURES

AND EQUATIONS FOR *B(T)*

In this chapter, the working equations to estimate the second virial coefficient of 25 substances will be developed. Combined with the 38 substances whose equations were selected in the previous chapter, this completes the list of 62 substances included in this study. Xenon is included also in this group because a suitable equation can be obtained from the data of Dymond et al. (2002). These equations are required to develop a generalized correlation for *B(T)*.

In order to extend the range of applicability of the equations, the Boyle temperatures of most of these substances have been compiled from different sources but estimated in some other cases. These data will be presented for each substance when it is required. Some methods and equations will be also introduced as required, such as the statistical F test and the equations to estimate the Boyle temperature.

Xenon

The unwanted coefficient is eliminated by *reducing* the order of the equation with minor changes in the other coefficients and the predicted Boyle temperature. The resulting equation is:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
63.1482	-4.57E+04	-1.70E+06	-5.72E+08		165	970	773.58

Neon

The unwanted coefficient is eliminated by *increasing* the order of the equation with minor changes in the other coefficients and the predicted Boyle temperature. The resulting equation is:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
15.8994	-9.80E+02	-1.29E+05	2.49E+06	-5.45E+06	50	870	119.11

n-Butane

The following are estimated Boyle temperature values for this substance:

1017.7	Estrada-Torres 2007
1019.2	Estrada-Torres 2007
1031.3	Estrada-Torres 2007
1034.4	Estrada-Torres 2007
1003.5	Iglesias-Silva 2010
1022.9	Tao & Mason 1994
1023.836	DIPPR calc

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
99.53762	-3.92E+04	-7.15E+07	9.81E+09	-1.99E+12	245	1021.848	1021.85

In the following figure, the improvement in the data fitting when including the Boyle temperature is shown. This result is similar for many of the substances considered.

Figure 32.
Result of including T_B for n-butane.
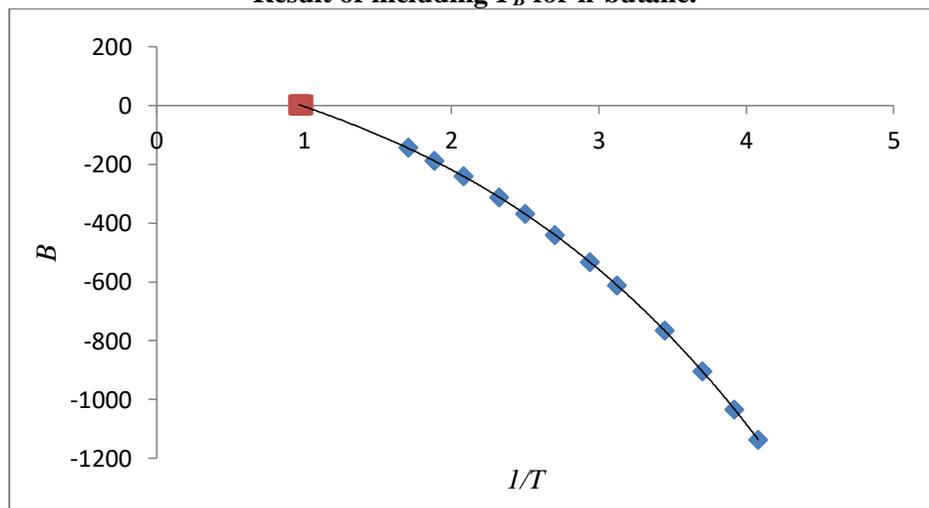
Own source

Two fits are possible, one of grade 3 and the other one of grade 4. The coefficients of determination are $R^2 = 0.99998843$ and 0.99999377. An F-test was made to determine if the increase in R^2 was significant based on the R^2 information and the number of data $N = 18$:

Model	R^2	F Test
Grade 3	0.99998843	
Grade 4	0.99999377	11.1428571

The statistic F is defined as the ratio between the explained variability and the unexplained variability, and is calculated as follows (Nagpaul, 1999):

(55) $F = \dfrac{(R_2^2 - R_1^2)/(n-m)}{(1-R_2^2)/(N-n-1)} = \dfrac{(0.99999377 - 0.99998843)/(4-3)}{(1-0.99999377)/(18-4-1)} = 11.142$

The 99% probability of F with degrees of freedom (1,13) is 8.99 so there is less than 1% probability for F = 11.142. Thus, it must be concluded that the fourth-grade model is significant.

n-Pentane

The following are estimated Boyle temperature values for this substance:

1113.5	Estrada-Torres 2007
1113.1	Estrada-Torres 2007
1110.4	Estrada-Torres 2007
1130.4	Estrada-Torres 2007
1081.6	Iglesias-Silva 2010
1103.71	DIPPR calc

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
131.1759	-6.63E+04	-9.69E+07	1.38E+10	-3.99E+12	265	1108.92	1108.92

Two fits are possible, one of grade 3 and the other one of grade 4. The coefficients of determination are $R^2 = 0.99998416$ and 0.99999043. The number of data is $N = 18$. The result of the F-test is as follows:

Model	R^2	F Test
Grade 3	0.99998416	
Grade 4	0.99999043	8.51724138

The probability of F with degrees of freedom (1,13) being lower or equal to 8.5172 is of 98.83%. Thus, it must be concluded that the fourth-grade model is significant.

n-Hexane

The following are estimated Boyle temperature values for this substance:

1185.5	Estrada-Torres 2007
1185.6	Estrada-Torres 2007
1174	Estrada-Torres 2007
1156.11	DIPPR calc

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
386.9717	-6.05E+05	2.48E+08	-8.24E+10		300	1169.70	1169.70

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

n-Heptane

The following are estimated Boyle temperature values for this substance:

1252.3	Estrada-Torres 2007
1246	Estrada-Torres 2007

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
199.2696	-6.39E+04	-3.02E+08	1.12E+11	-2.93E+13	350	1249.12	1249.12

Two fits are possible, one of grade 3 and the other one of grade 4. The coefficients of determination are $R^2 = 0.99999048$ and 0.99999909. The number of data is $N = 14$. The result of the F-test is as follows:

Model	R^2	F Test
Grade 3	0.99999048	
Grade 4	0.99999909	85.1538462

The 99.5% probability of F with degrees of freedom (1,9) is 13.3 so there is less than 0.5% probability for F = 85.154. Thus, it is concluded that the fourth-grade model is highly significant.

Octane

The following are estimated Boyle temperature values for this substance:

1311.6	Estrada-Torres 2007
1300.6	Estrada-Torres 2007
1296.1	Estrada-Torres 2007
1314.78	DIPPR calc

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
720.5847	-1.38E+06	7.62E+08	-2.41E+11		340	1304.74	1304.73

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

2-Methyl propane

The following are estimated Boyle temperature values for this substance:

984.54	Estrada-Torres 2007
984.53	Estrada-Torres 2007
992.14	Estrada-Torres 2007
978.16	Estrada-Torres 2007
990.1	Tao & Mason 1994

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
150.8506	-1.41E+05	8.97E+05	-8.57E+09		255	986.28	986.28

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

2-Methyl butane

The following are estimated Boyle temperature values for this substance:

1107.2	Estrada-Torres 2007
1101.5	Estrada-Torres 2007

When these values are included, the resulting equation has an inflection point. One or more recommended values by Dymond et al. seem to be more negative for the highest temperatures. In order to obtain a suitable equation, a comparison between the values calculated with the model by Zarkova, Hohm & Damyanova (2006) for isopentane and the recommended values by Dymond et al. was made, that in order to find a path between one model to another, as shown below.

Figure 33.

Comparison between $B(T)$ values of Zarkova et al. versus Dymond et al.
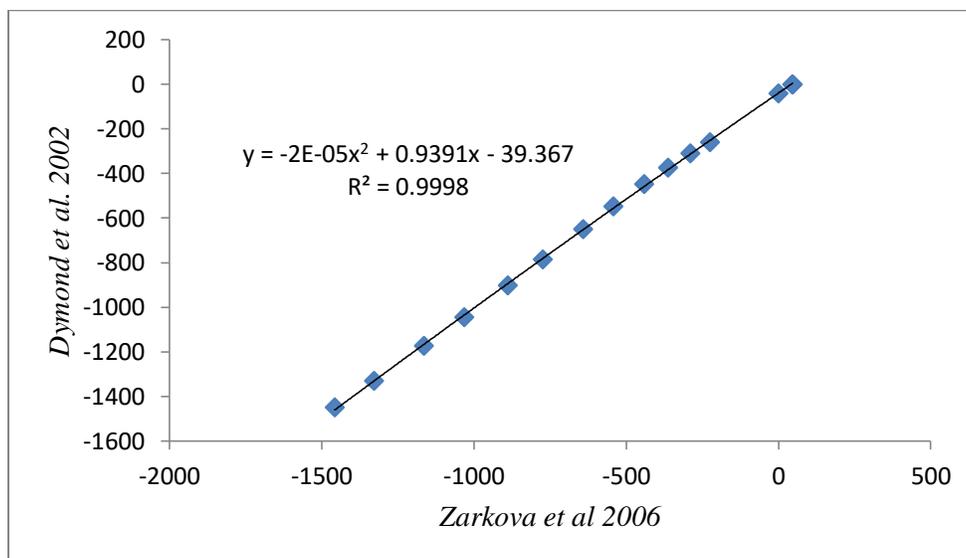
Own source

A quadratic fit was required as a minimum to reproduce the Boyle temperatures of Estrada-Torres (2007). After comparing several fits and making some adjustments, the equation obtained provides a satisfactory fit to the data:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
305.312	-3.95E+05	8.89E+07	-2.73E+10		260	1104.94	1104.94

2-Methyl pentane

The following is the estimated Boyle temperature value for this substance:

1171.6	Estrada-Torres 2007

When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
93.9577	-1.03E+03	-1.26E+08			300	1164.45	1164.45

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4. The original data by Dymond et al. could only be fitted to a linear model; that would mean that the high-temperature data from this reference are more positive. In order to obtain a better suitable equation, the Corresponding States Principle was applied in the following way:

− The equation for 2-methyl butane was put in reduced form;

− It is assumed that the same equation applies to 2-methyl pentane;

− The equation is put back in non-reduced form, using the critical constants of 2-methyl pentane;

− A set of data was calculated and compared to the recommended values of Dymond et al. (2002), similar to Figure 33 above;

− The final equation was obtained from that comparison and a small adjustment.

Applying the procedure above, it is concluded that the data of Dymond et al. (2002) from 440 to 545 K are more positive, as shown in Figure 34.

Figure 34.

Comparison between the obtained equation for $i - C_6$ and Dymond et al.
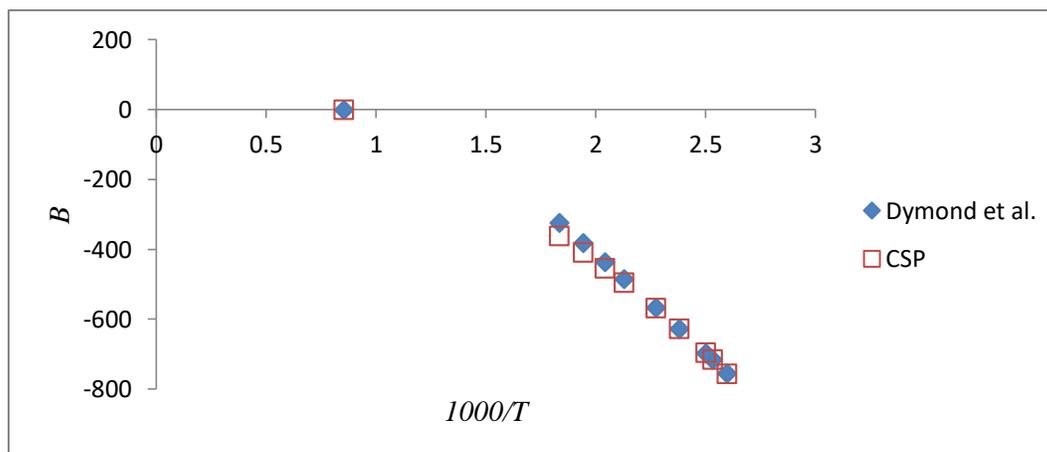
Own source

The following equation provides a satisfactory fit to the data:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
333.6433	-4.59E+05	1.12E+08	-3.7E+10		300	1171.60	1171.60

2,2-dimethylpropane

The following is the estimated Boyle temperature value for this substance:

1029.1	Estrada Torres 2007

When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
189.2486	-1.80E+05	-4.77E+06	-1.06E+10		275	1026.42	1026.42

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

Ethene

The following are estimated Boyle temperature values for this substance:

724.33	Estrada-Torres 2007
723.27	Estrada-Torres 2007
724.63	Estrada-Torres 2007
722.39	Estrada-Torres 2007
720.19	Bousheri et al 1987

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
48.11561	-1.27E+04	-1.93E+07	2.77E+09	-2.65E+11	200	722.88	722.88

Two fits are possible, one of grade 3 and the other one of grade 4. The coefficients of determination are $R^2 = 0.9999935$ and 0.9999982. The number of data is $N = 18$. The result of the F-test is as follows:

Model	R^2	*F Test*
Grade 3	0.9999935	
Grade 4	0.9999982	33.944

The 99% probability of F with degrees of freedom (1,13) is 8.99 so there is less than 1% probability for F = 33.944. Thus, it must be concluded that the fourth-grade model is significant.

1,3-Butadiene

For this substance, the data are scarce (6 points), it shows an inflection point and the Boyle temperature is not available. The first step to follow is the estimation of the Boyle temperature; there are three possible equations that can be used, all of them depending on the critical temperature (T_c =425 K) and the acentric factor (ω =0.195). These are:

Danon & Pitzer (1962):

(56) $$T_B = 2.656 T_c/(1 + 1.028\omega) = 940.3 \ K$$

Tao & Mason (1994):

(57) $$T_B = T_c(2.6455 - 1.1941\omega) = 1025.4 \ K$$

Iglesias-Silva et al. (2001):

(58) $$T_B = T_c[2.0525 + 0.6428\exp(-3.6167\omega)] = 1007.3 \ K$$

The correlation of Iglesias-Silva et al. (2001) will be used in this study, for two reasons:

a) it was recommended by Estrada-Torres et al. (2007), after a comparison with values of the Boyle temperature calculated with reference equations of state;

b) when compared with the compiled Boyle temperature data, it gives the closest estimates, while the Danon & Pitzer correlation tends to give smaller values;

When the estimated value of T_B is included, the resulting third-grade equation has an inflexion point. A quadratic fit is not suitable, as it violates specifications (a) and (b) defined before. The six points of Dymond et al. can only be fitted to a linear model; the addition of the Boyle temperature excludes this model. The recommendation in this case is to simplify the model: instead of using Equation (52), the Berthelot model or a variant of it will be used, that is Equation (35). The procedure will be to look for a dependence on T^{-2}, and a graph of *B(T)* against this variable is almost linear, as shown in the following figure.

Figure 35.

Temperature dependence of B(T) for 1,3-butadiene.
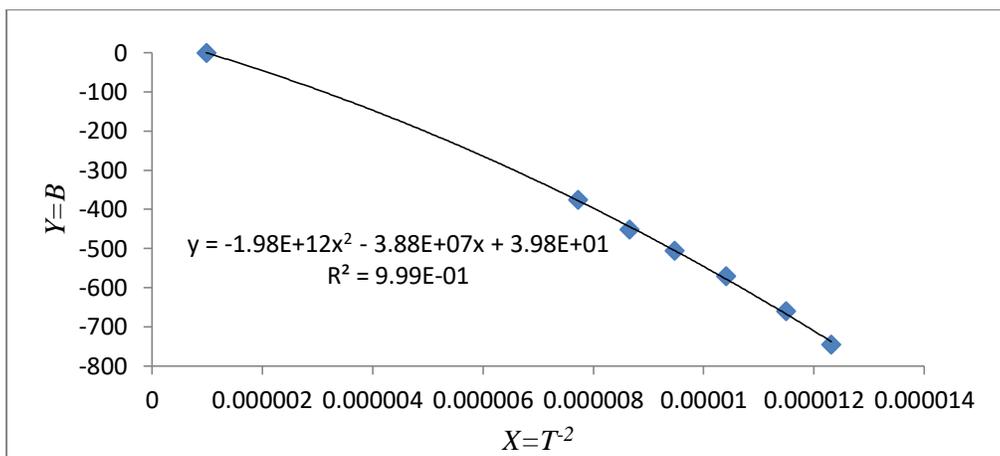
Own source

Based on the considerations above, the following equation is obtained, and it provides a satisfactory fit:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
39.773	0	-3.88E+07	0	-1.98E+12	285	1011.98	1011.98

Cyclopentane

This substance is a special case because only three points were included in the compilation of Dymond et al. (2002), and no equation was calculated (the three points fall on a straight line in T^{-1}). There is one value of the Boyle temperature available, as follows:

975.72	Estrada-Torres 2007

When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
169.69	-7.68E+04	-8.67E+07			298.16	975.82	975.82

No attempt to fit a higher order model was made because there are not enough data.

Cyclohexane

The following are estimated Boyle temperature values for this substance:

1314.4	Estrada-Torres 2007
1302.5	Estrada-Torres 2007
1306.5	Estrada-Torres 2007

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
226.1523	-3.25E+05	6.85E+07	-3.97E+10		310	1308.43	1308.43

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

Tetrafluoroethene

There are only five points available for this substance in the compilation of Dymond et al. (2002). The Boyle temperature is not available, so it will be estimated using the correlation of Iglesias-Silva et al. Equation (58); the resulting value is $T_B = 716.28 \, K$.

When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
118.8282	-8.34E+04	-1.25E+06			275	716.30	716.30

Two fits are possible, one of grade 1 (linear) and the other one of grade 2 (quadratic). The coefficients of determination are $R^2 = 0.9999651$ and 0.9999979. The number of data is $N = 6$. The result of the F-test is as follows:

Model	R^2	F Test
Grade 1	0.9999651	
Grade 2	0.9999979	46.8571

The 99% probability of F with degrees of freedom (1,3) is 40.5 so there is less than 1% probability for F = 46.8571. Thus, it must be concluded that the quadratic model is significant.

Octafluorocyclobutane

The following is the estimated Boyle temperature value for this substance:

827.02	Estrada Torres 2007

When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
283.1	-2.88E+05	7.68E+07	-2.55E+10		295	821.43	821.43

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

Dodecafluorocyclohexane

There are only six points available for this substance in the compilation of Dymond et al. (2002). The Boyle temperature is not available so it will be estimated using the correlation of Iglesias-Silva et al. Equation (58); the resulting value is $T_B = 997.05\ K$.

When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
141.3029	-1.09E+04	-1.16E+08	-1.35E+10		355	997.05	997.05

Trying a quadratic fit results in the violation of specification (b) defined in Chapter 4. Instead, the data was fitted to a variant of the Berthelot model, Equation (35) with good results; therefore, an alternative equation was obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
143.5288	0	-1.4E+08	0	-2.3E+12	355	997.05	996.85

Carbon disulfide

The recommended data by Dymond et al. (2002) present an inflection point. The Boyle temperature is not available so it will be estimated using the correlation of Iglesias-Silva et al. Equation (58); the resulting value is $T_B = 1364.54\ K$. When this value is included, the inflection point persists. In order to identify what the problem would be, the data was adjusted to a variant of the Berthelot model, Equation (35), in a similar way to the procedure followed with 1,3-butadiene. The resulting curve is like the one shown in Figure 35, and the following auxiliary equation obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
27.65	0	-5.01E+07	0	-2.28E+12	285	1362.45	1362.45

The equation and the plot of the data indicate that the point at 430 K is more positive in 20 cm3/mol, while the point at 470 K is more positive in 53 cm/mol. Removing these two points, the standard fitting procedure followed with other substances can be done and the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
67.8612	-9.72E+04	2.21E+07	-2.16E+10		285	1362.45	1363.72

Acetylene

According to Dymond et al. (2002), the available second virial coefficients for acetylene cover a limited temperature range, from 200 to 310 K. All data come from two references, one from 1937 and the other one from 1958. The Boyle temperature is not available so it will be estimated using the correlation of Iglesias-Silva et al. Equation (58); the resulting value is $T_B = 732.04\ K$. When this value is included, the resulting equation is very sensitive to the order of the model. In order to check the quality of the data, a plot of B versus T^{-2} similar to the one shown in Figure 35 was made, in order to flatten the data and apply a variant of the Berthelot model, Equation (35). The following auxiliary equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
13.2283	0	-5.57E+06	0	-7.53E+11	200	727.30	727.30

The equation and the plot of the data indicate that the points at 290, 300 and 310 K are more negative, being the difference 2.5 cm3/mol at 290 K and 10 cm3/mol at 310 K. According to Dymond et al. (2002), the accuracy of the data in that range is 5 cm3/mol and they correspond to the data measured in 1958. When these points are removed, the standard fitting procedure followed with other substances can be done, and the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
47.7703	-6.15E+04	3.18E+07	-9.04E+09		200	734.33	732.20

A verification of the validity of this equation can be made by applying one of the results found in previous chapters: the constant of this equation is approximately equal to half the hard-spheres coefficient of acetylene, which is about 100 cm3/mol.

Propadiene

According to Dymond et al. (2002), the available second virial coefficients for propadiene cover a limited temperature range, from 225 to 350 K. All data come from two references, one from 1940 and the other one from 1953. Also the data show an inflection point. The Boyle temperature is not available so it will be estimated using the correlation of Iglesias-Silva et al., Equation (58); the resulting value is $T_B = 982.49\ K$. When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
51.054	-1.75E+04	-3.30E+07			225	993.44	993.44

Two fits are possible, one of grade 2 (quadratic) and the other one of grade 3. The coefficients of determination are $R^2 = 0.9989$ and 0.9994. The number of data is $N = 9$. The result of the F-test is as follows:

Model	R^2	F Test
Grade 2	0.9989	
Grade 3	0.9994	4.1667

The 95% probability of F with degrees of freedom (1,5) is 6.42 which is greater than the calculated value F = 4.1667. Thus, it must be concluded that the third grade model is not significant, and the quadratic model is retained.

Benzene

The following are estimated Boyle temperature values for this substance:

1326.5	Estrada Torres 2007
1340.3	Estrada Torres 2007
1347	Iglesias Silva 2001
1339.7	Tao & Mason 1994
1328.48	DIPPR calc

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
130.19	-1.04E+05	-1.10E+08	2.91E+10	-8.90E+12	300	1335.53	1335.53

Two fits are possible, one of grade 3 and the other one of grade 4. The coefficients of determination are $R^2 = 0.9999828$ and 0.9999965. The number of data is $N = 17$. The result of the F-test is as follows:

Model	R^2	F Test
Grade 3	0.9999828	
Grade 4	0.9999965	46.97

The 99.5% probability of F with degrees of freedom (1,12) is 11.8 so there is less than 0.5% probability for F = 46.97. Thus, it must be concluded that the fourth-grade model is highly significant.

Toluene

The case of toluene is very relevant because the data by Dymond et al. (2002) had to be discarded in favor of other, more reliable data, as it is explained below.

The original data from Dymond et al. (2002) cover the range 345 – 580 K and showan inflection point, suspicious since the value of the constant is too high ($a_0 = 1900.7$). The following values of the Boyle temperature were obtained from several sources:

1403.1	Estrada Torres 2007
1401.5	Estrada Torres 2007
1361.6	Iglesias-Silva 2001
1379.8	Tao & Mason 1994
1310.68	DIPPR calc

When these values are included, the resulting equation also has an inflection point. In order to obtain a suitable equation, the equation of benzene was modified according to the Corresponding States Principle (CSP), following the same procedure as with 2-methyl pentane. The following auxiliary equation was obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
160.703	-1.35E+05	-1.51E+08	4.20E+10	-1.35E+13	363	1406.10	1406.10

When this equation is compared with the data in Dymond et al. (2002), it is found that a significant adjustment is required to transform one set of data into the other, specifically:

$$Dymond = 1.2716 * CSP + 117.15$$

Considering the small difference in acentric factors between benzene ($\omega = 0.2103$) and toluene ($\omega = 0.264$), this adjustment is considered excessive, from the point of view of the compliance with the Corresponding States Principle. Therefore, the toluene data from Dymond et al. (2002) were considered suspicious and subject to verification from another source.

Searching in the Infotherm database for second virial coefficient data for toluene, a data set was found (Akhundov & Abdullaev 1977) that was more similar to the values calculated from the CSP. These data were used by Goodwin (1989) for the development of a reference equation of state for toluene, this author provided a fitting equation. In the following table and figure the values from Dymond et al. (2002), from the CSP and from Akhundov & Abdullaev (1977) are compared.

TABLE 12.

Toluene *B(T)* data from different sources.

T	Dymond et al. 2002	CSP estim	Akhundov & Abdullaev 1977
345	-1723	-1428.9	-1469.1
355	-1579	-1328.5	-1370.8
370	-1398	-1197.9	-1242.1
390	-1204	-1053.3	-1098.7
420	-987	-883.3	-928.3
450	-828	-753	-795.7
490	-672	-620.6	-658.4
530	-555	-520.3	-551.4
580	-440	-424.7	-445.5

Own source

Figure 36.
Toluene *B(T)* data from different sources.
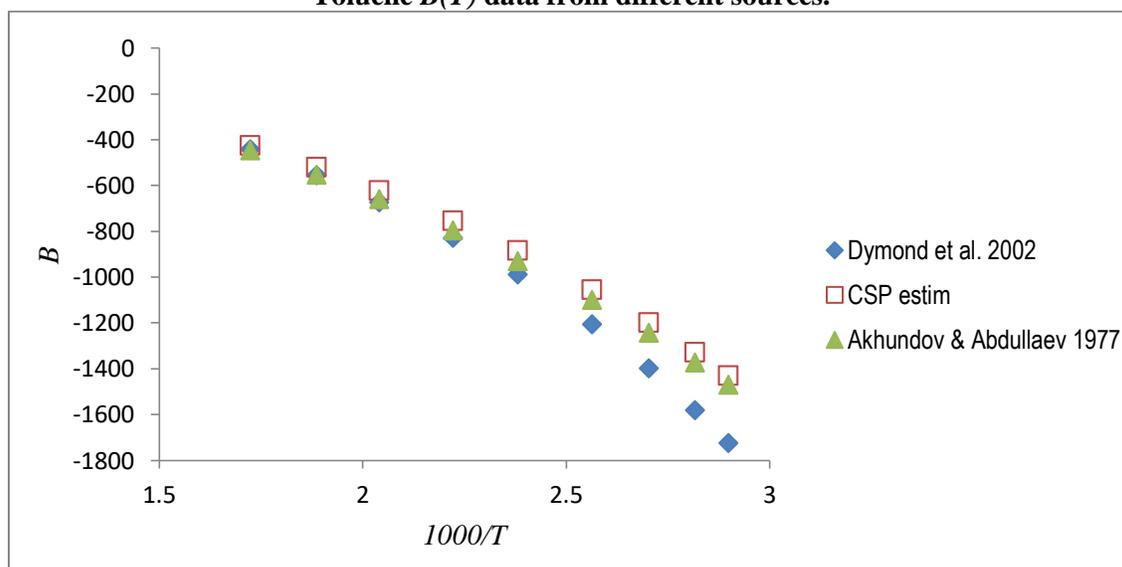
Own source

From the comparison above, it must be concluded that the data of Dymond et al. (2002) are more negative at low temperature; therefore, the data from Akhundov & Abdullaev (1977) is taken as reference. The following equation was provided by Goodwin (1989):

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
0	3.77E+05	-6.07E+08	1.89E+11	-2.93E+13	298	1260.10	1260.10

This equation seems to violate one of the specifications established for *B(T)* models previously, as it has a positive linear coefficient (in T^{-1}). However, it has also a constant equal to zero, and it can be demonstrated that the coefficient of T^{-1} must be positive in this case, for the equation to have a Boyle temperature; otherwise, and in graphical terms, it would never cross the horizontal axis. If an equation with non-zero constant is desired, the following one provided a satisfactory fit to the data:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
267.7527	-9.96E+04	-2.97E+08	1.02E+11	-2.03E+13	298	1115.44	1115.44

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

p-Xylene

The Boyle temperature is not available for this substance. There are two estimated values:

- one from the correlation of Iglesias-Silva et al. (2001), the resulting value is $T_B = 1388.44\ K$.

- the other from the DIPPR second virial coefficient model, the resulting value is $T_B = 961.63\ K$.

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
207.7749	-2.57E+05	1.18E+08	-1.26E+11		350	1188.512	1188.512

Trying to remove any of the estimated Boyle temperatures result in an inflection point. Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

Hexafluorobenzene

The recommended data by Dymond et al. (2002) present an inflection point. The Boyle temperature is not available so it will be estimated using the correlation of Iglesias-Silva et al. Equation (58); the resulting value is $T_B = 1139.96\,K$. When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
248.37	-2.37E+05	-7.51E+07	4.50E+10	-2.25E+13	305	1139.47	1139.47

Trying to fit a lower order model results in an inflection point. Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

During the development of the correlation for *B(T)*, the following four substances were included in this chapter because the corresponding equations from the Zarkova group had to be discarded, and alternative equations had to be developed from the experimental data and the Boyle temperatures.

Cyclopropane

The Boyle temperature is not available so it will be estimated using the correlation of Iglesias-Silva et al. Equation (58); the resulting value is $T_B = 978.04$ K. When this value is included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
68.912	-3.83E+04	-2.84E+07			300	977	976.94

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

n-Decafluorobutane

There are only five points available for this substance in the compilation of Dymond et al. (2002), they follow a linear trend in T^{-1}. The Boyle temperature is available from Estrada Torres (2007), its value is $T_B = 913.39\,K$. The data were fitted to a variant of the Berthelot model, Equation (35) with good results, the following equation was obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
123.429	0	-9.15E+07			285	860.93	860.93

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

1-Butene

The following are estimated Boyle temperature values for this substance:

1008.30	Estrada-Torres 2007
1047.26	DIPPR calc

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
206.69	-2.72E+05	8.33E+07	-2.36E+10		205	1032.51	1032.51

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

Cis-2-butene

The following are estimated Boyle temperature values for this substance:

1049.4	Estrada-Torres 2007
909.51	DIPPR calc

When these values are included, the following equation is obtained:

a0	a1	a2	a3	a4	Tmin	Tmax	Tboyle
331.65	-4.67E+05	1.79E+08	-3.98E+10		255	982.312	982.312

Trying to fit a higher order model results in the violation of one or more of the specifications defined in Chapter 4.

Chapter 5.

MAIN RESULTS AND CORRELATIONS

Following the individual equations developed in Chapters 5 and 6 are used to develop the correlations for *B(T)*. First they have to be put in reduced form, for that there are two possibilities:

a) in terms of V_c, Equation (4A), or

b) in terms of the combination RT_c/P_c, Equation (4B).

Once the equations are in reduced form, a table or matrix can be generated (in MS Excel, for example), where each row represents one value of acentric factor, and each column represents one reduced temperature. Fitting Equation (4A) or (4B) to the data in one column, a pair of values of f_0 and f_1 can be obtained.

Initial comparisons between the substances in Group A and Group B showed similar trends; therefore, it was decided to combine both groups and using the 62 substances to develop the correlations. As explained in Chapter 5, most of the available data covers a limited, "middle" range; data from reference substances was fitted to equations that cover the whole temperature range. These equations became very relevant at low and high temperatures. The following is a list of the reference substances and their *reduced* temperature range.

TABLE 13.

Reference substances and their T_r range.

Substance	T_r min	T_r max
Argon	0.331	21.697
Kripton	0.239	15.625
Xenon	0.173	11.297
Methane	0.525	17.176
Nitrogen	0.594	14.050
Fluorine	0.555	6.939
Ethene	0.708	8.051
Ethane	0.233	7.445
CF4	0.659	14.387
SF6	0.463	10.271
Neon	1.126	19.595
Carbon monoxide	0.376	24.625
Chlorine	0.575	2.397
Nitrous oxide	0.614	10.573
Carbon dioxide	0.723	10.760
Nitric oxide	0.688	12.618

Own source

An unexpected result was that all of the Zarkova equations had to be discarded, as they do not follow the right temperature trend. Four of the substances in this subgroup could be recovered by fitting an equation to the Dymond et al. plus Boyle temperature data. Other substances (fluorine, chlorine, methane, CF_4, SF_6) could be fitted to reference equations. This was not possible for the rest of substances of the subgroup, usually because the few data available did not have the right temperature trend.

The main results from this study will be developed and presented in this chapter, most of them by graphical means. Specifically, two correlations for $B(T)$ will be obtained, as well as two correlations for the constant a_0 and two correlations for the Boyle temperature T_B.

5.1. Correlation in V_c

This correlation is based on the application of Equation (4A), as explained above:

(4A) $$B_{r1} = B/V_c = f_{01}(T_r) + \omega \cdot f_{11}(T_r)$$

A plot of the 62 reduced constants a_0 versus the acentric factor shows a trend, but also high data dispersion, as seen in Figure 37. Three points (silicon tetrachloride, uranium hexafluoride, cis-2-butene) had to be discarded because they were very large or very small, "outliers". A linear trend is obtained but the slope is very large, as shown in the figure below: the black line is the obtained trend, while the blue line is the trend predicted by using the reference substances only, and by the generalized correlation.

Figure 37.

Plot of a_0 reduced on V_c versus ω, all substances.
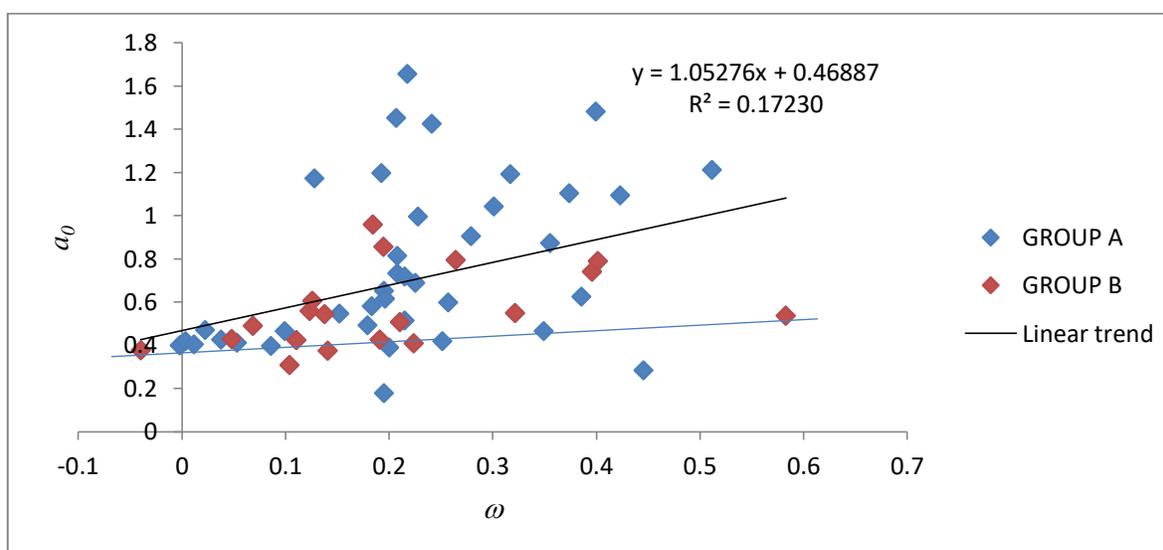
Own source

A linear trend with a much lower slope was obtained using the reference substances only; this trend was later found to be the correct one, it is represented in Figure 38 and by the following equation:

(59) $$a_0 = 0.2312\omega + 0.4106$$

Figure 38.

Plot of a_0 reduced on V_c versus ω, reference substances.
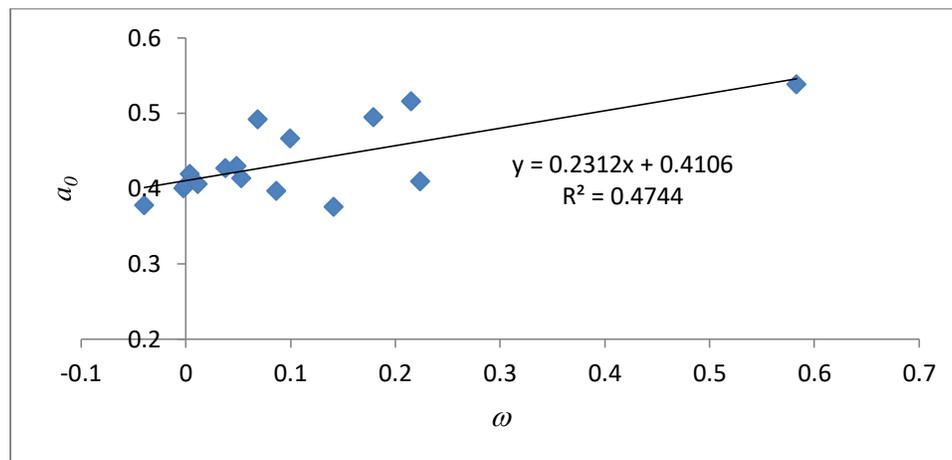
Own source

Equation (59) could be useful to adjust the constants of the individual equations, in case a further refinement of the generalized correlation is desired; also for estimating the constants of the f_0 and f_1 functions, if the tabular data are fitted to equations.

A table of B_{r1} for the 62 values of ω and 60 values of T_r was generated. A plot of B_{r1} versus the acentric factor at each constant T_r were made, and a linear fit of the data was calculated. In all cases a linear trend could be identified, although there were some data dispersion; this could be seen in the following figures, covering selected T_r values from the range 0.2 to 20.

Figure 39.

B_{r1} versus acentric factor at $T_r = 0.2$.
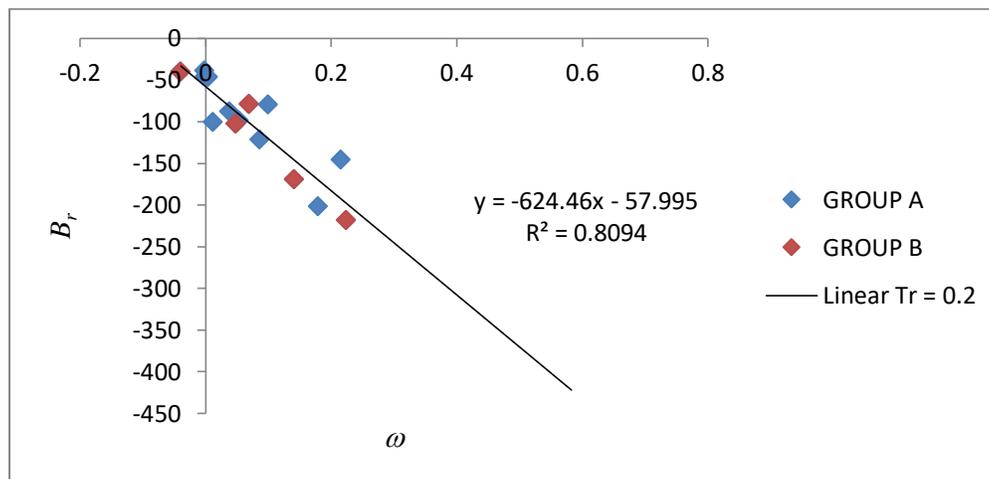
Own source

Figure 40.

B_{r1} versus acentric factor at $T_r = 1$.
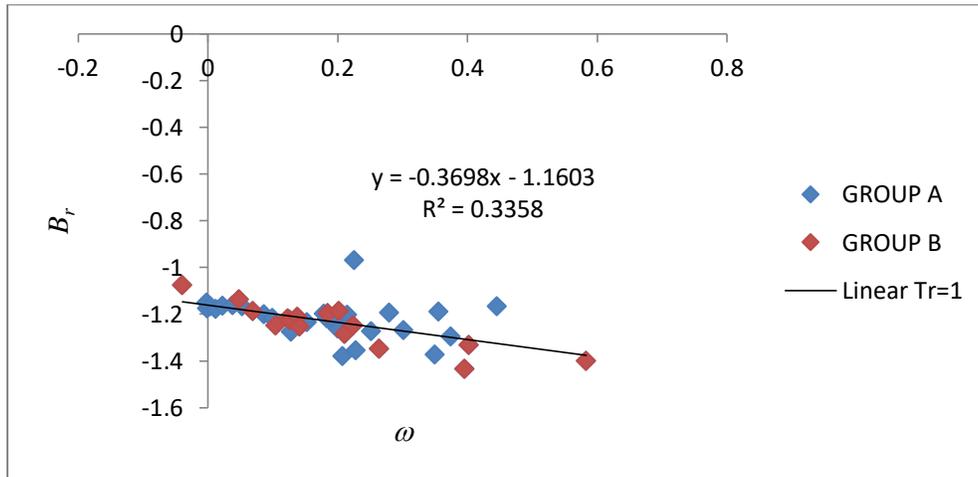
Own source

Figure 41.

B_{r1} versus acentric factor at $T_r = 2$.
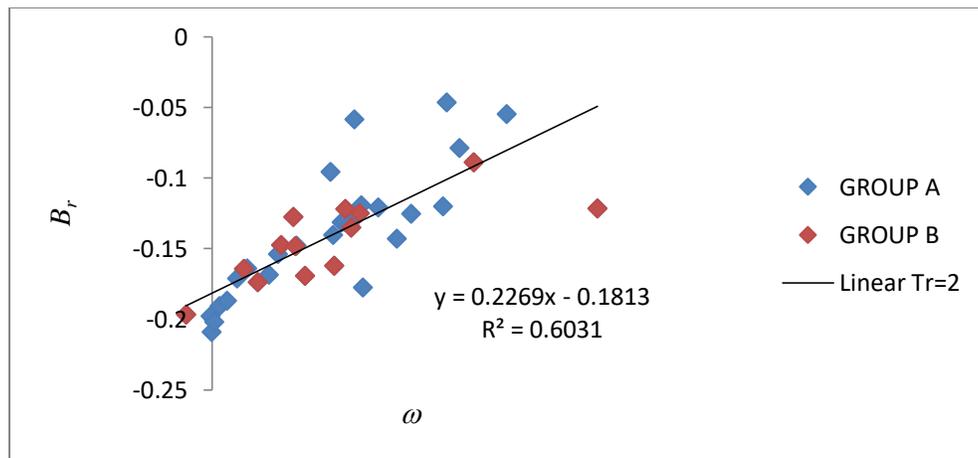
Own source

Figure 42.

B_{r1} versus acentric factor at $T_r = 20$.
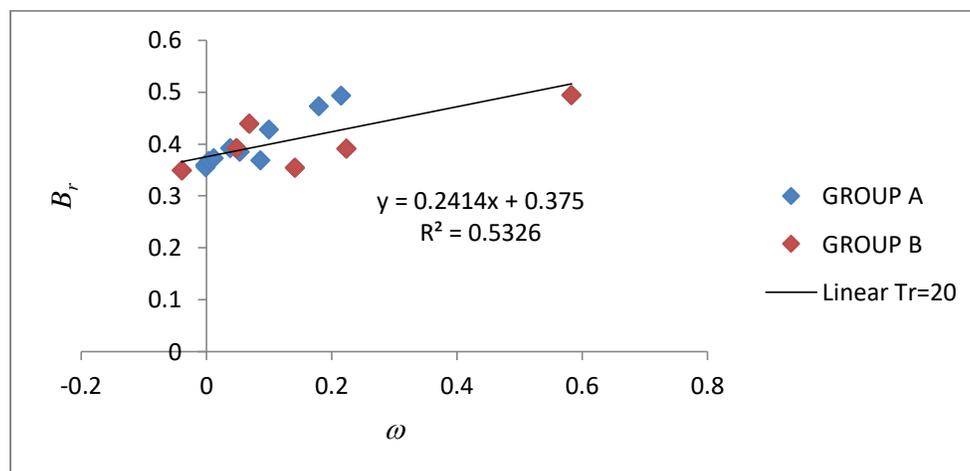
Own source

As it can be seen from the figures, there are more points at intermediate temperatures, and fewer points at the highest and lowest temperatures: basically the later are the values from the reference equations, which were very relevant at these temperature ranges.

Eighteen compounds were taken out during the study because their temperature trends were different than the general trend. They were carbon tetrachloride, cyclopentane, 1,3-butadiene, trimethyl gallium, trans-2-butene, silicon tetrachloride, tetramethylsilane, hexafluoroethane, octafluoropropane, uranium hexafluoride, silicon tetrafloride, n-dodecafluoropentane, cycloperfluorohexane, n-tetradecafluorohexane, sulfur disulfide, ethyne, isobutene and p-xylene. They were more negative at one temperature end and more positive at the other end, or vice versa; they could also be consistently more negative or positive at all temperatures. This was identified by the presence of "outliers" in the plots, points that affected the linear trend.

Among the discarded compounds there are many fluorinated ones which were added to the last edition of Dymond et al.; also some compounds with recent and accurate data (such as trimethyl gallium and hexafluoroethane). This negative selection was possible because there were still 44 compounds from which the generalized correlation could be obtained. As to be shown later, the generalized correlation is able to fit well most of these compounds.

During the fitting procedure and analysis of the B_{r1} plots, there were two basic requirements to identify and discard outliers:

a) The line intercepts ($\omega = 0$) must fall near the points representing the noble gases, ideally between argon ($\omega = -0.00219$) and xenon ($\omega = +0.00363$);

b)

c) The line slopes must fall over the points of the reference substances, such as N_2, CO, F_2, C_2H_6, Cl_2, among others. These compounds have low acentric factor, so they follow the Corresponding States Principle closely, and their data are also known with high accuracy for a wide temperature range.

The Table 14 contains the numerical values of the f_{01} and f_{11} functions for 60 values of T_r, covering a range from $T_r = 0.2$ to $T_r = 20$. Taking argon as an example, it represents a temperature range from 75 to 3000 K approximately. The f_{01} and f_{11} functions are also represented in several ways in Figures 43 to 48.

Figure 43.

Function f_{01} versus T_r for correlation in V_c.
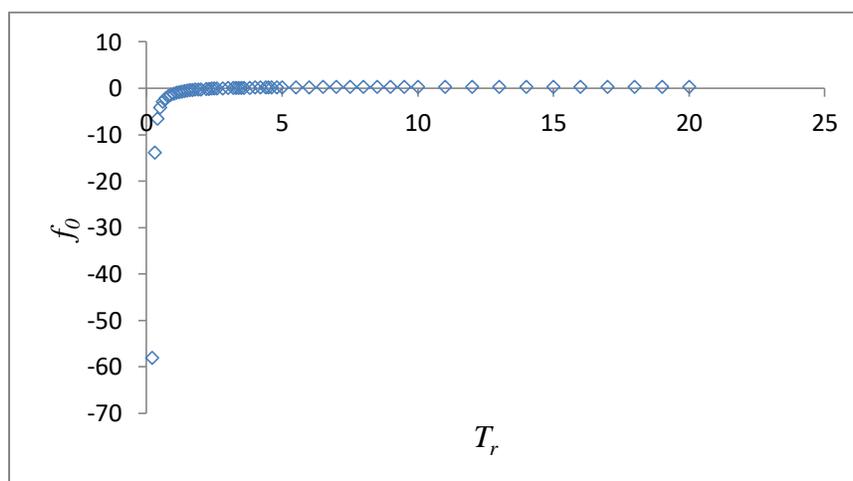
Own source

Figure 44.

Function f_{11} versus T_r for correlation in V_c.
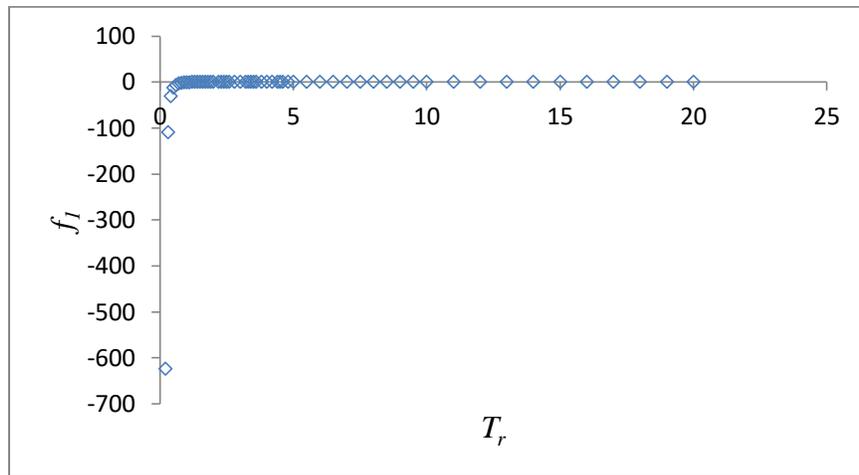
Own source

Figure 45.

Function f_{01} versus $1/T_r$ for correlation in V_c.
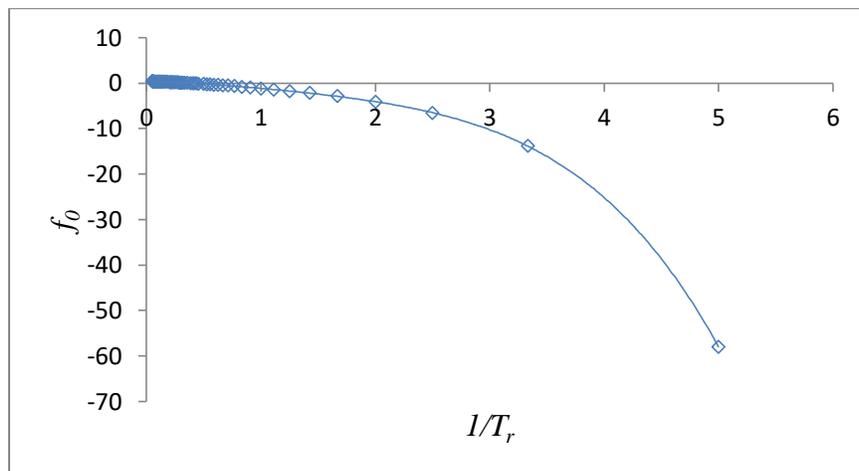
Own source

TABLE 14.
Values of f_{01} and f_{11} for correlation in V_c

T_r	f_{01}	f_{11}	T_r	f_{01}	f_{11}
0.2	-57.995	-624.46	3.6	0.1431	0.2504
0.3	-13.848	-108.71	3.8	0.1615	0.2520
0.4	-6.5484	-30.790	4.0	0.1778	0.2533
0.5	-4.1107	-12.038	4.2	0.1923	0.2542
0.6	-2.8248	-6.4702	4.4	0.2022	0.2508
0.7	-2.1933	-3.0533	4.5	0.2081	0.2509
0.8	-1.7650	-1.4078	4.6	0.2137	0.2510
0.9	-1.4190	-0.7016	4.8	0.2241	0.2511
1.0	-1.1603	-0.3698	5.0	0.2335	0.2511
1.1	-0.9585	-0.1543	5.5	0.2535	0.2508
1.2	-0.7995	-0.0191	6.0	0.2696	0.2501
1.3	-0.6705	0.0628	6.5	0.2830	0.2492
1.4	-0.5637	0.1173	7.0	0.2931	0.2514
1.5	-0.4740	0.1549	7.5	0.3024	0.2509
1.6	-0.3978	0.1817	8.0	0.3103	0.2503
1.7	-0.3328	0.2025	8.5	0.3172	0.2498
1.8	-0.2761	0.2179	9.0	0.3233	0.2493
1.9	-0.2251	0.2167	9.5	0.3286	0.2487
2.0	-0.1813	0.2269	10	0.3333	0.2482
2.2	-0.1066	0.2290	11	0.3414	0.2472
2.3	-0.0770	0.2253	12	0.3479	0.2463
2.4	-0.0495	0.2223	13	0.3533	0.2455
2.5	-0.0255	0.2235	14	0.3579	0.2447
2.6	-0.0027	0.2291	15	0.3618	0.2441
2.8	0.0365	0.2361	16	0.3651	0.2434
3.0	0.0715	0.2413	17	0.3681	0.2429
3.2	0.0977	0.2452	18	0.3707	0.2423
3.3	0.1103	0.2468	19	0.3730	0.2419
3.4	0.1220	0.2482	20	0.3750	0.2414
3.5	0.1329	0.2493			

Own source

Figure 46.

Function f_{11} versus $1/T_r$ for correlation in V_c.
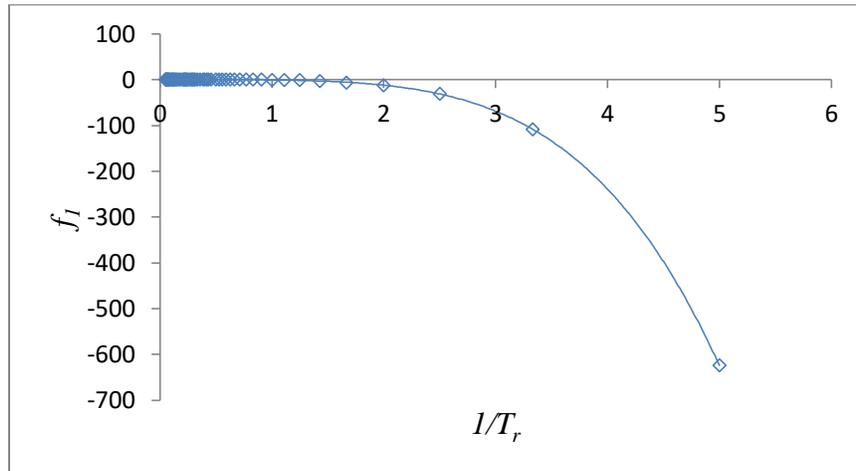
Own source

Figure 47.

Close-up of Figure 41.
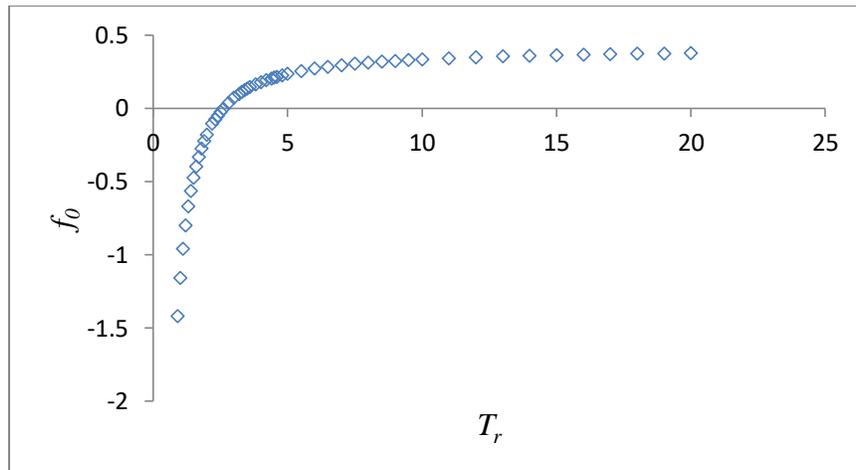
Own source

Figure 48.

Close-up of Figure 44.
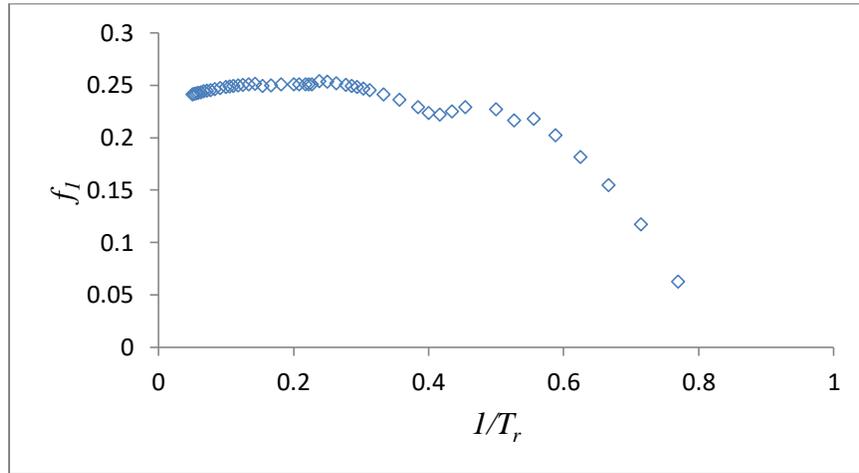
Own source

As seen from the figures above, f_{01} is a well behaved, i.e. continuous monotonic function; the curve is very similar to that of argon and other noble gases. In this correlation there is not attempt to reproduce the maximum that neon and other gases show at high enough temperature. The function f_{01} is easily adjusted to a 4th-order polynomial in $1/T_r$:

$$(60)\ f_{01} = 0.406009 - 0.598188T_r^{-1} - 1.40674T_r^{-2} + 0.595012T_r^{-3} - 0.151387T_r^{-4}$$

The data of f_{11} are much more difficult to fit to an equation because the curve has a "flat" region and then it slowly descends at high temperatures; they are also not as smooth as the f_{01} data. The following equation provides an acceptable fit of the data, and the highest power of T_r is equal to -4.5, similar to the Abbott (1975) and McGlashan & Potter (1962) correlations:

$$(61)\qquad f_{11} = 0.2359310 + 0.2894730T_r^{-1.5} - 0.5318495T_r^{-3} - 0.4017655T_r^{-4.5}$$

Figure 49 is a comparison between the values of f_{11} calculated with Equation (61) and the original values. The recommended procedure, until best-fit equations are developed, is to use directly the tabulated values in calculations, or to interpolate for values of T_r not in Table 14.

Figure 49.

Function f_{11}, Equation (61) versus original values.
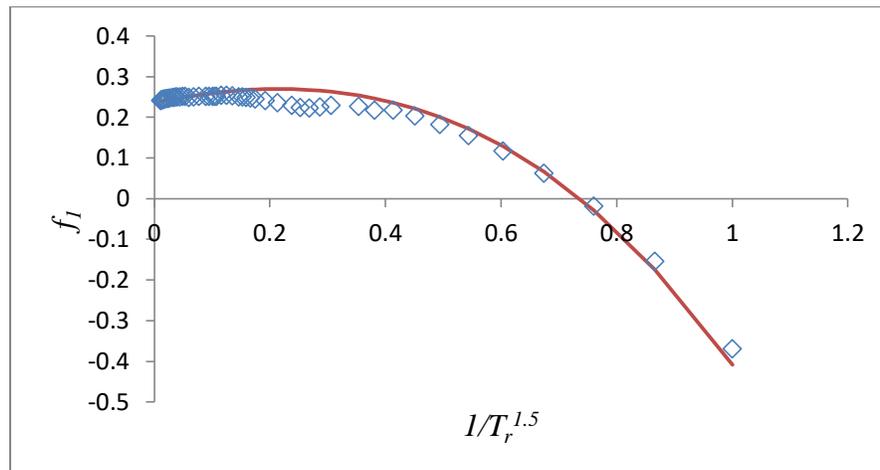
Own source

Once the functions f_{01} and f_{11} are determined at each T_r, it is possible to calculate the variation of the Boyle temperature with the acentric factor, by making $B_{r1} = 0$ in Equation (4A) and clearing the value of ω. The results are tabulated in Table 15 and plotted in Figure 50, and an equation similar to the one proposed by Danon & Pitzer (1962) was obtained:

(62)
$$T_B = \frac{T_C}{0.1427\omega + 0.3836} = \frac{2.6068 T_C}{1 + 0.3720\omega}$$

TABLE 15.

Reduced Boyle temperature versus ω.

T_{BR}	ω
1.90	1,0388
2.00	0,7990
2.20	0,4655
2.30	0,3418
2.40	0,2227
2.50	0,1141
2.60	0,0118
2.80	-0,1546

Own source

Figure 50.

Reduced Boyle temperature versus ω.

$$y = 0.1427x + 0.3836$$
$$R^2 = 0.9964$$
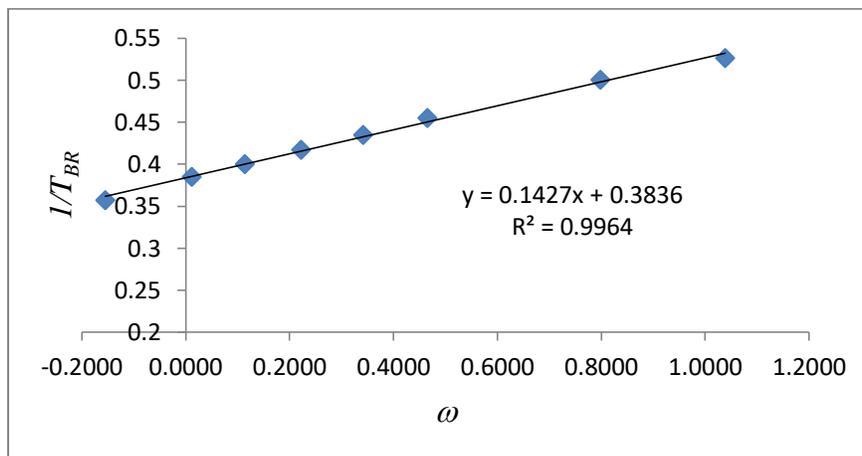
Own source

Using Equation (4A) and the tabulated values of f_{01} and f_{11}, $B_{r1}(T_r)$ for all substances can be calculated and a comparison can be made. The results are rated from good to excellent for most substances. Examples of excellent fit are the n-alkanes, cyclohexane, propene, ethyne, benzene, molybden hexafluoride, carbon disulfide and nitrogen trifluoride, among others. Some of these had to be taken out during the development of the correlation.

On the other side, the fit is less than good for some other substances, such as carbon tetrachloride, 1,3-butadiene, boron trichloride, silicon fluoride, silicon chloride and tetrafluoroethene, among others. Many of these were taken out during the development of the correlation; however, the calculated values are not far from the recommended ones. In general, the fit is better at middle and high temperatures, while at low temperature the calculated values are more negative; there are cases that show better and poorer fits. In the following figures, examples are given of both substances with excellent fit and substances with less-than-good fit. The filled squares are the recommended values, while the empty squares are the calculated values.

Figure 51.
Comparison of B_{r1} values for nitrogen.
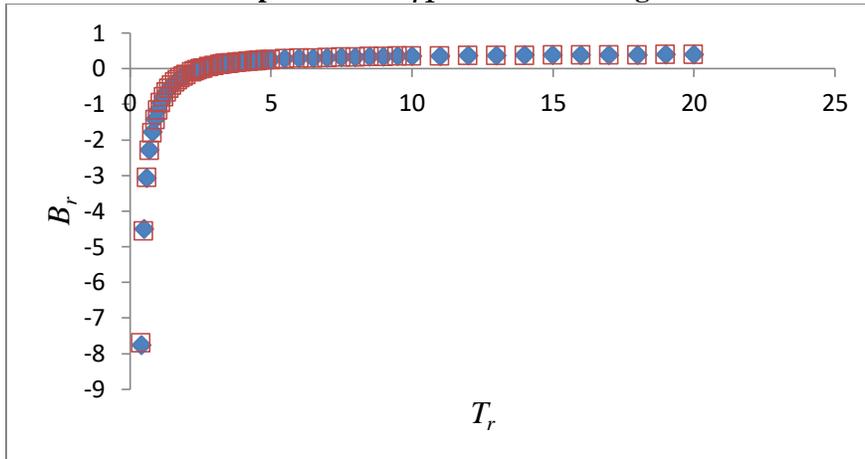
Own source

Figure 52.
Comparison of B_{r1} values for propene.
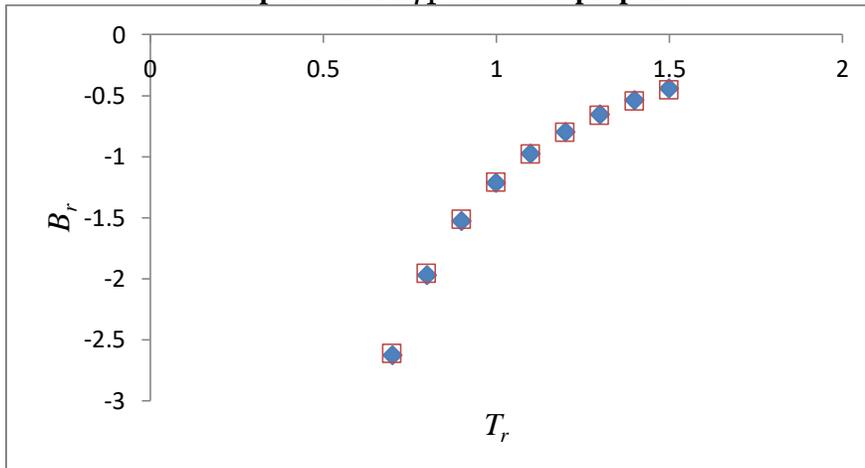
Own source

Figure 53.
Comparison of B_{r1} values for acetylene (ethyne).
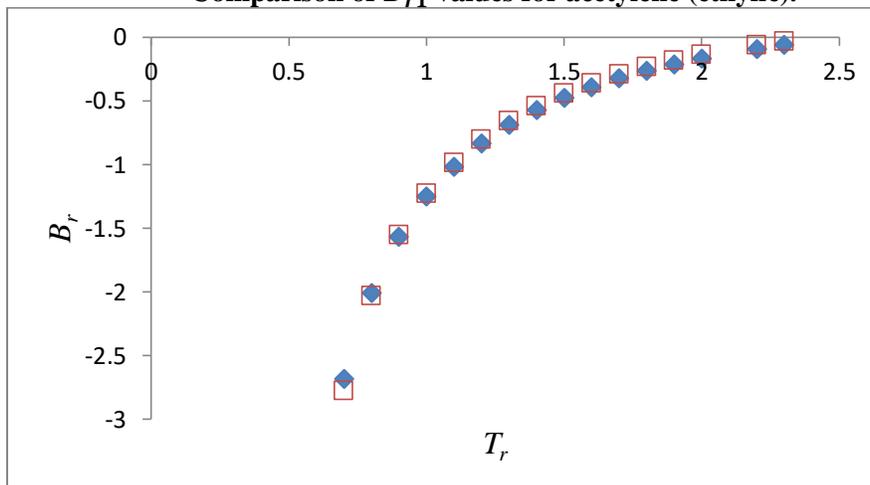
Own source

Figure 54.
Comparison of B_{r1} values for octane.
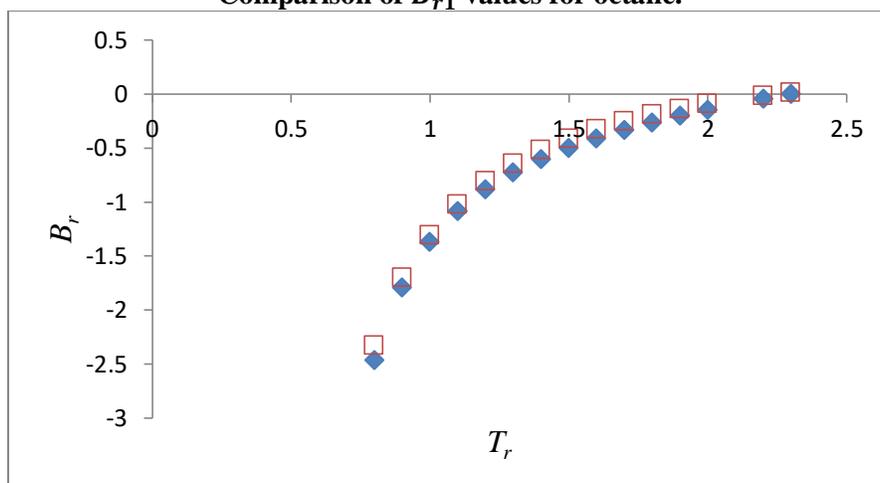
Own source

Figure 55.
Comparison of B_{r1} values for tetrachloromethane.
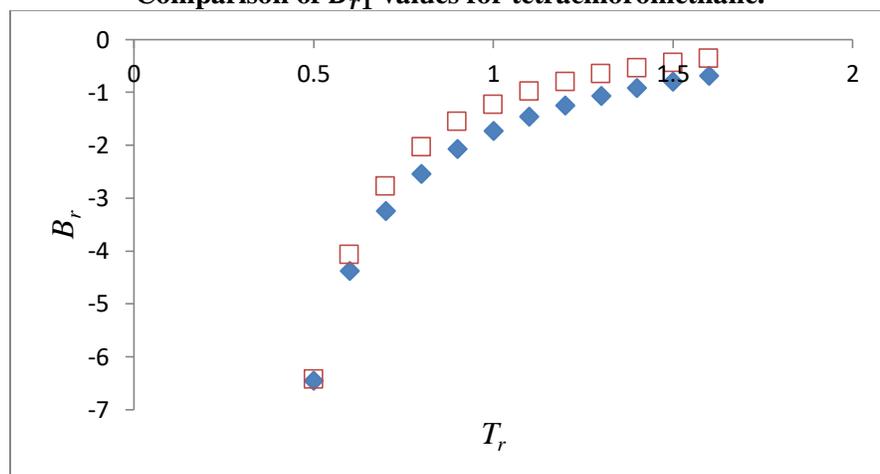
Own source

Figure 56.
Comparison of B_{r1} values for trimethyl gallium.
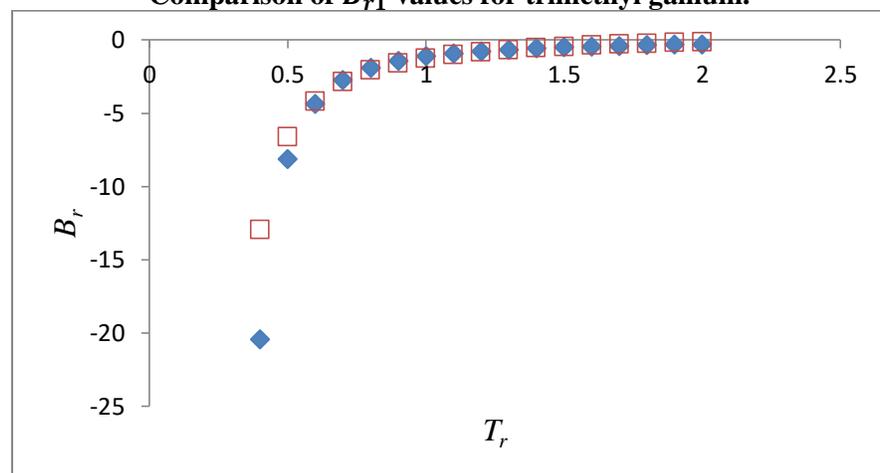
Own source

Figure 57.

Comparison of B_{r1} values for trans-2-butene.
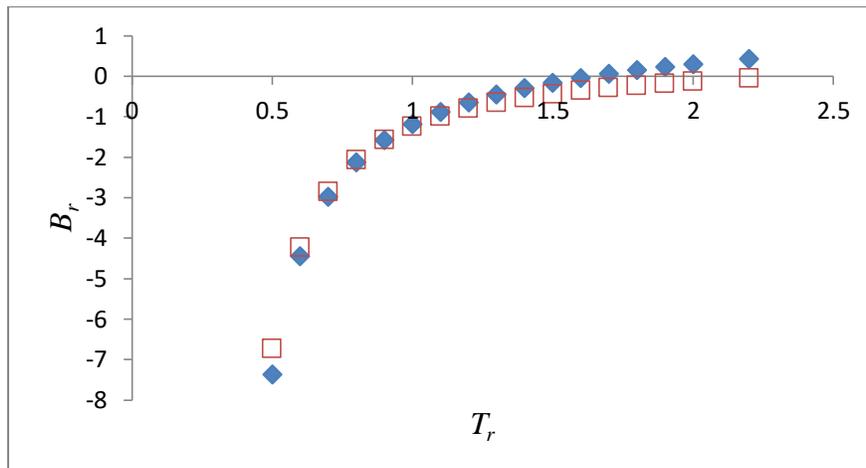
Own source

Figure 58.

Comparison of B_{r1} values for cycloperfluorohexane.
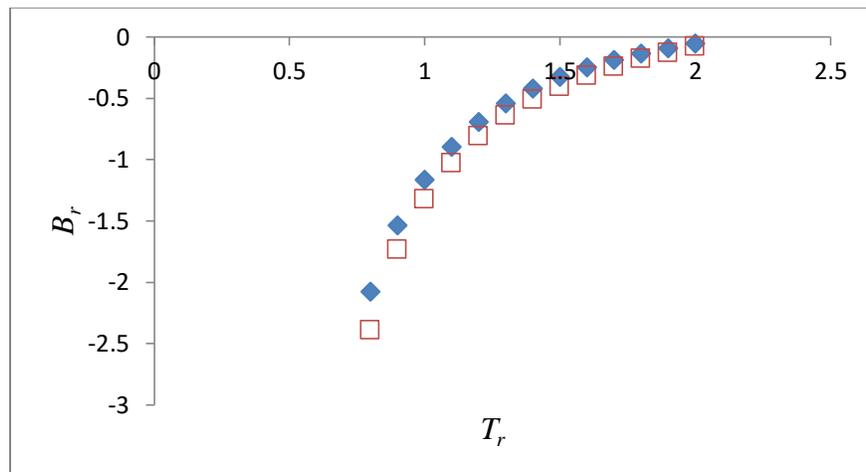
Own source

As the Corresponding States Principle must apply, the differences between the experimental or recommended values and the calculated ones have to be studied carefully because the data for some substances could be wrong. The possible sources of error will be discussed later in this chapter.

Comparison of the Correlation for B_{r1} with Others

It is now possible to make a comparison between the correlation for B_{r1} obtained in the previous section and several previous correlations. As most correlations are reduced in terms of

RT_c/P_c, the current correlation will be multiplied by 0.291, i.e. the critical compresibility of simple fluids, for comparison purposes. This would apply for both the comparisons of f_{01} and f_{11}.

As seen in Figures 59 and 60 below, f_{01} is one of the less negative functions at low temperatures, falling near the McGlashan & Potter f_{01} curve which is quadratic, the Zhixing et al. f_{02} curve which is cubic, and the Meng et al. f_{02} curve which is of grade 8. The new curve is only slightly less negative than the Pitzer & Curl f_{02} curve.

Figure 59.
Comparison of f_{01} from this work with other correlations.
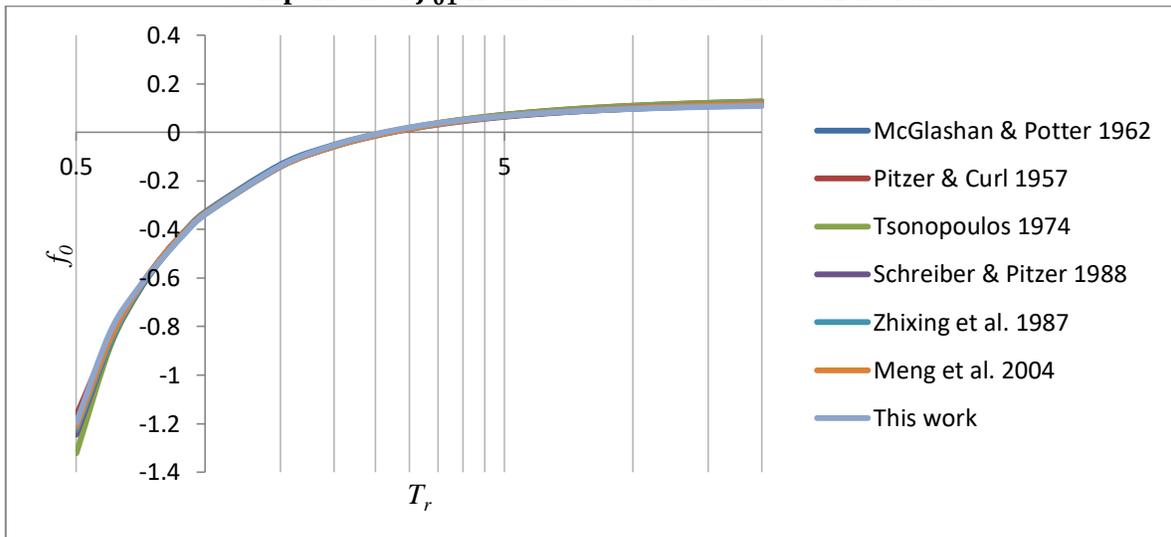
Own source

Figure 60.
Comparison of f_{01} from this work with other correlations.
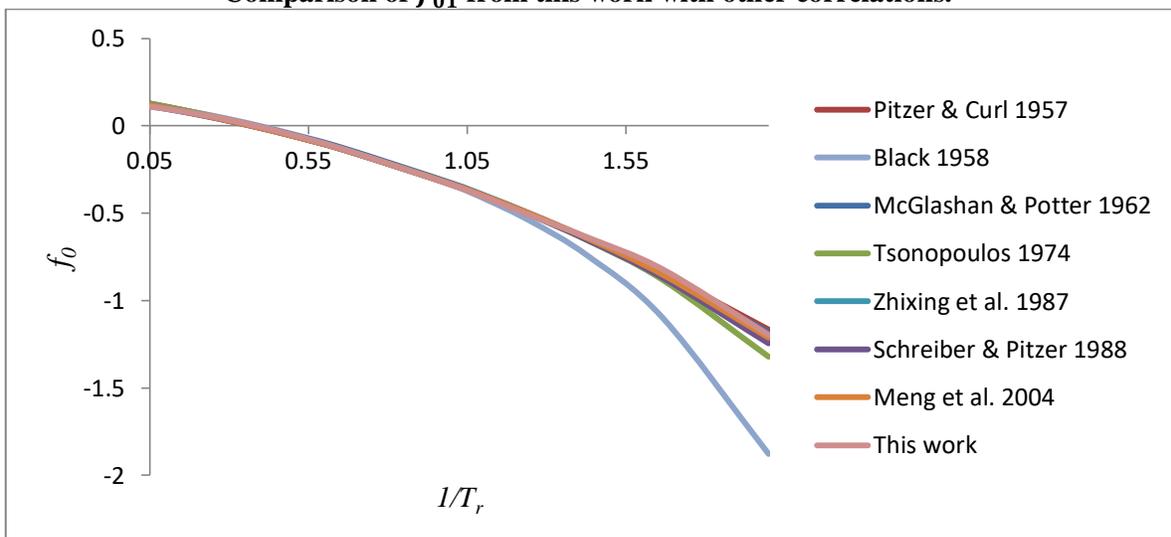
Own source

Figure 61 below is a comparison between the function f_{11} obtained here with other correlations, the result is a function that is different to any previous model. It is less negative at $T_r = 0.5$ than the Tsonopoulos curve, falling near the Pitzer and Curl, Zhixing et al. and Meng et al. curves; it becomes more negative than these equations between $T_r = 0.5$ and $T_r = 1$, being similar to the Schreiber and Pitzer curve; for values higher than $T_r = 1$, it tends to fall near the curves with lowest values such as the Pitzer & Curl, Tsonopoulos and Weber ones. At high temperature, this function *descends* towards a constant value: this behavior is related to the positive coefficient of the T_r^{-1} term, a characteristic shared only with both models developed by K. S. Pitzer (Pitzer & Curl 1957; Schreiber & Pitzer 1988).

Figure 61.

Comparison of f_1 from this work with other correlations.
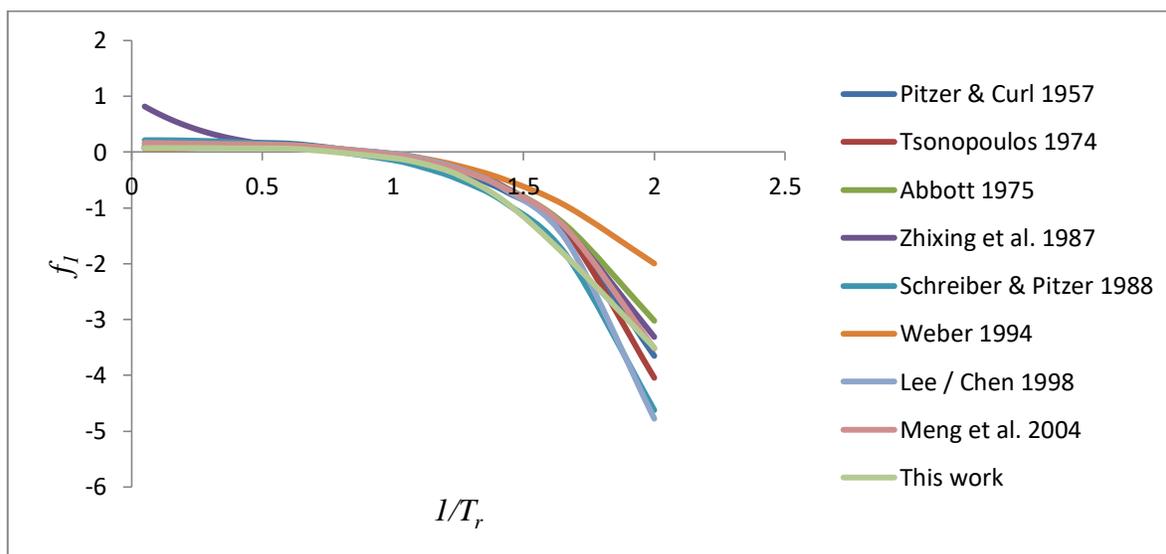
Own source

5.2. Correlation in RT_c/P_c

This correlation is based on the application of Equation (4B), as explained above:

(4B) $$B_{r2} = BP_c/RT_c = f_{02}(T_r) + \omega \cdot f_{12}(T_r)$$

It is not equal to the correlation in V_c for the reasons discussed in Chapter 4. There is a factor equal to Z_c between both correlations, which is different for each individual substance, breaking any similitude between them.

As with the previous correlation, a plot of the 62 reduced constants a_0 versus the acentric factor can be made, with similar results, as shown in Figure 62. Only one point (uranium hexafluoride) had to be removed because it was very large, an "outlier". A linear trend is obtained

but the slope is very large, as shown in the figure below: the black line is the obtained trend, while the blue line is the trend predicted by using the reference substances only, and by the generalized correlation.

Figure 62.

**Plot of a_0 reduced on RT_c/P_c versus ω, all substances.**
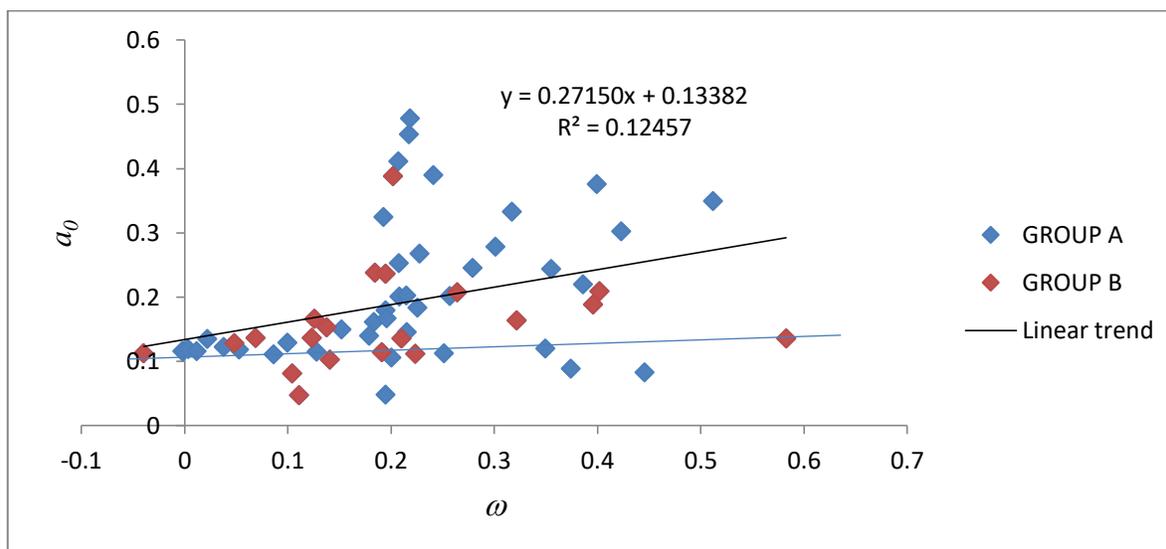
Own source

A linear trend with a much lower slope was obtained using the reference substances only; this trend was later found to be the correct one, it is represented in Figure 63 and by the equation:

(63) $$a_0 = 0.0336\omega + 0.1193$$

Figure 63.

Plot of a_0 reduced on RT_c/P_c versus ω, reference substances.
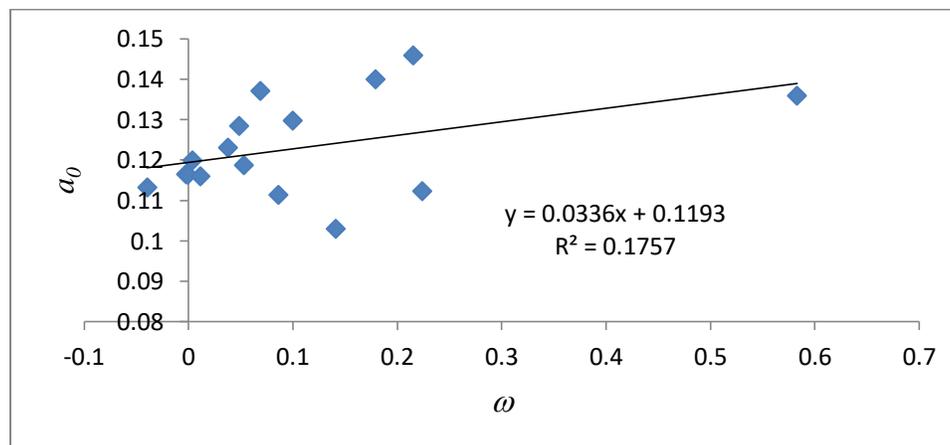
Own source

Equation (63) could be useful to adjust the constants of the individual equations, in case a further refinement of the generalized correlation is desired; also for estimating the constants of the f_{02} and f_{12} functions, if the tabular data is fitted to equations.

A table of B_{r2} for the 62 values of ω and 60 values of T_r was generated. A plot of B_{r2} versus the acentric factor at each constant T_r were made, and a linear fit of the data was calculated. In all cases a linear trend could be identified, although there were some data dispersion; this could be seen in the following figures, covering selected T_r values from the range 0.2 to 20.

Figure 64.

B_{r2} **versus acentric factor at** $T_r = 0.2$**.**
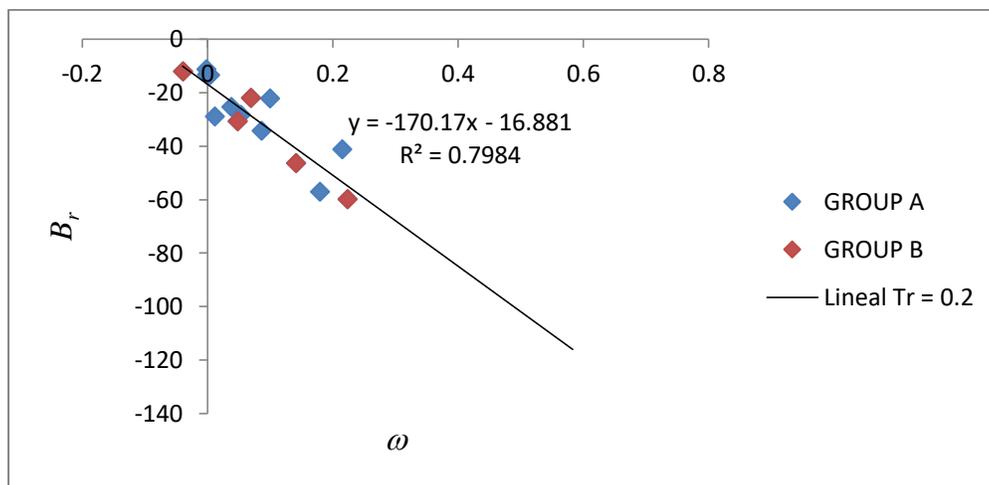
Own source

Figure 65. B_{r2} versus acentric factor at $T_r = 1$.

Own source

129
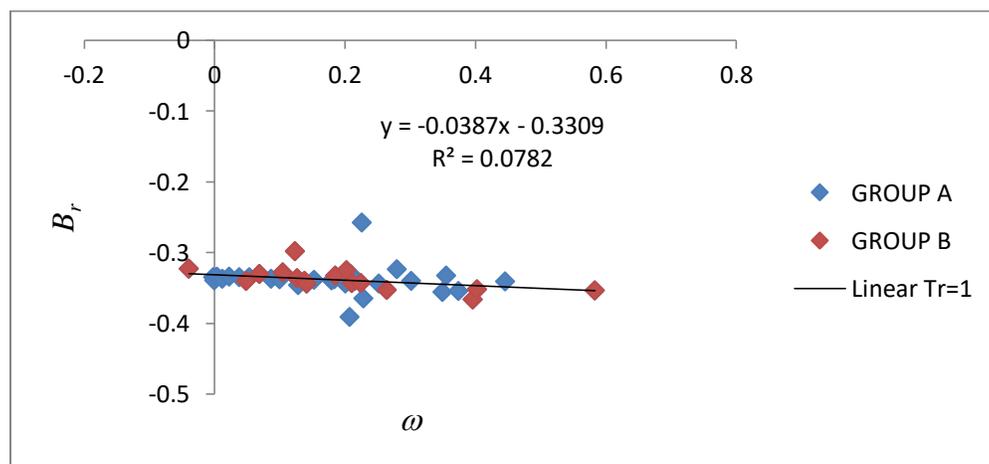
Figure 66.

B_{r2} versus acentric factor at $T_r = 2$.
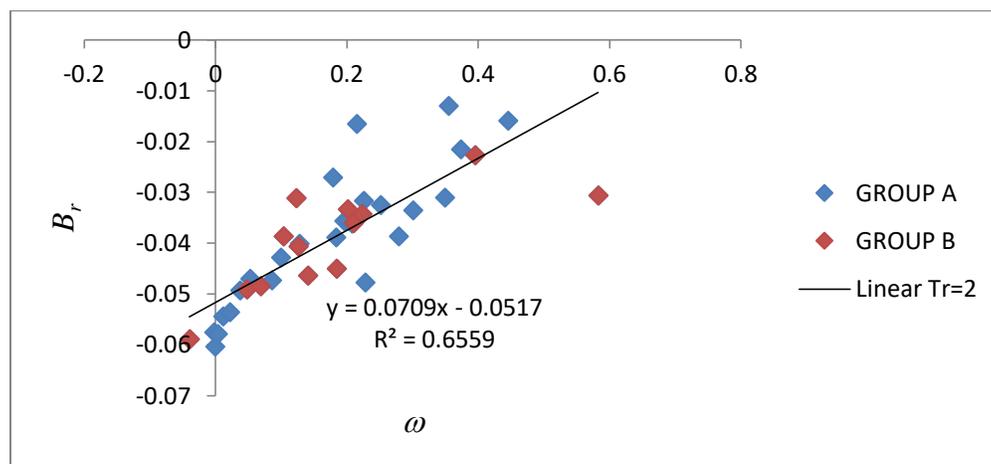
Own source

Figure 67.

B_{r2} versus acentric factor at $T_r = 20$.
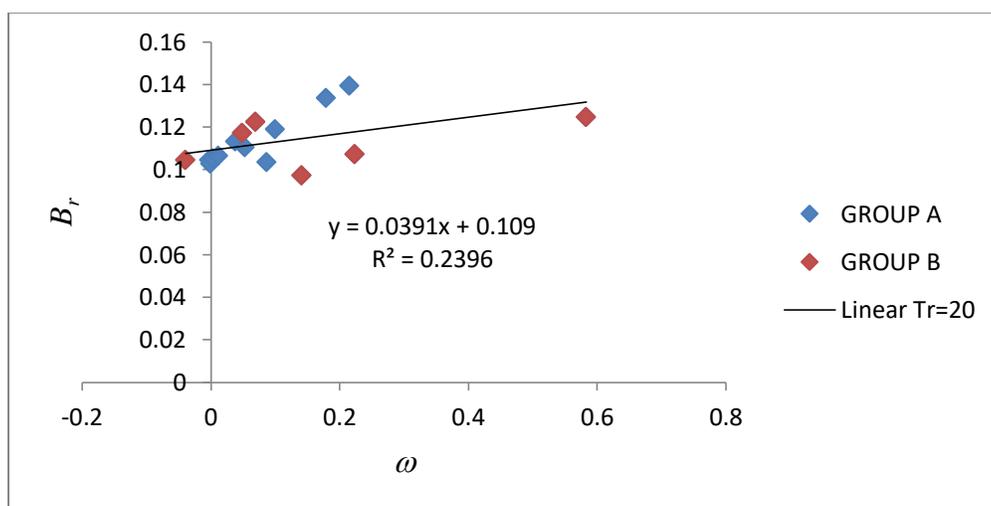
Own source

As with the other correlation, there are more points at intermediate temperatures, and fewer points at the highest and lowest temperatures: basically the later are the values from the reference equations, which were very relevant at these temperature ranges.

The same eighteen compounds taken out during the first study were not considered for this one because their temperature trends were different than the general trend, as it was previously explained.

During the fitting procedure and analysis of the B_{r2} plots, the same two basic requirements to identify and discard outliers were applied:

d) The line intercepts ($\omega = 0$) must fall near the points that represent the noble gases, ideally between argon ($\omega = -0.00219$) and xenon ($\omega = +0.00363$);

e) The line slopes must fall over the points of the reference substances, such as N_2, CO, F_2, C_2H_6, Cl_2, among others. These compounds have low acentric factor, so they follow the Corresponding States Principle closely, and their data are also known with high accuracy for a wide temperature range.

The following table contains the numerical values of the f_{02} and f_{12} functions for 60 values of T_r, covering a range from $T_r = 0.2$ to $T_r = 20$. Taking argon as an example, it represents a temperature range from 75 to 3000 K approximately. The f_{02} and f_{12} functions are also represented in several ways in Figures 68 to 73.

<div align="center">

TABLE 16.

Values of f_{02} and f_{12} for correlation in RT_c/P_c.

</div>

T_r	f_{02}	f_{12}	T_r	f_{02}	f_{12}
0.2	-16.881	-170.17	3.6	0.0415	0.0578
0.3	-4.0203	-29.427	3.8	0.0469	0.0570
0.4	-1.8980	-8.1793	4.0	0.0516	0.0555
0.5	-1.1963	-2.9488	4.2	0.0558	0.0562
0.6	-0.8209	-1.4890	4.4	0.0588	0.0538
0.7	-0.6338	-0.6537	4.5	0.0605	0.0534
0.8	-0.5027	-0.2986	4.6	0.0621	0.0531
0.9	-0.4050	-0.1149	4.8	0.0651	0.0524
1.0	-0.3309	-0.0387	5.0	0.0678	0.0518
1.1	-0.2731	0.0089	5.5	0.0736	0.0503
1.2	-0.2278	0.0360	6.0	0.0783	0.0491
1.3	-0.1910	0.0514	6.5	0.0822	0.0479
1.4	-0.1606	0.0606	7.0	0.0852	0.0476
1.5	-0.1350	0.0661	7.5	0.0879	0.0468
1.6	-0.1133	0.0695	8.0	0.0902	0.0461
1.7	-0.0948	0.0717	8.5	0.0922	0.0455
1.8	-0.0786	0.0704	9.0	0.0940	0.0449
1.9	-0.0642	0.0709	9.5	0.0955	0.0444
2.0	-0.0517	0.0677	10	0.0969	0.0439
2.2	-0.0304	0.0655	11	0.0992	0.0431
2.3	-0.0220	0.0617	12	0.1011	0.0424
2.4	-0.0142	0.0617	13	0.1027	0.0417
2.5	-0.0073	0.0605	14	0.1040	0.0412
2.6	-0.0007	0.0730	15	0.1052	0.0407
2.8	0.0107	0.0632	16	0.1061	0.0403
3.0	0.0206	0.0610	17	0.1070	0.0400
3.2	0.0284	0.0594	18	0.1077	0.0396
3.3	0.0321	0.0590	19	0.1084	0.0393
3.4	0.0354	0.0586	20	0.1090	0.0391
3.5	0.0386	0.0582			

Own source

Figure 68.

Function f_{02} versus T_r for correlation in RT_c/P_c.
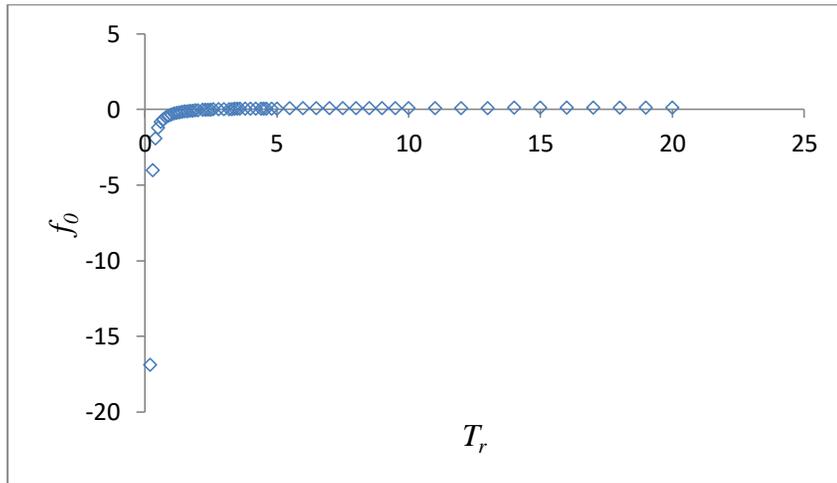
Own source

Figure 69.

Function f_{12} versus T_r for correlation in RT_c/P_c.
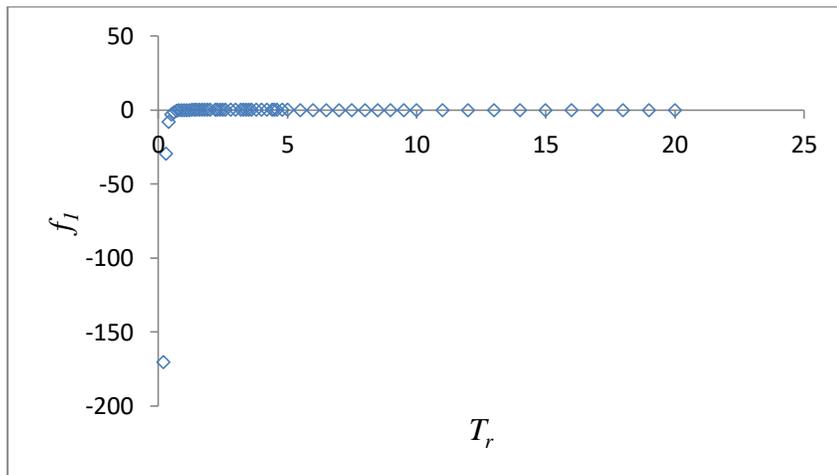
Own source

Figure 70.

Function f_{02} versus $1/T_r$ for correlation in RT_c/P_c.
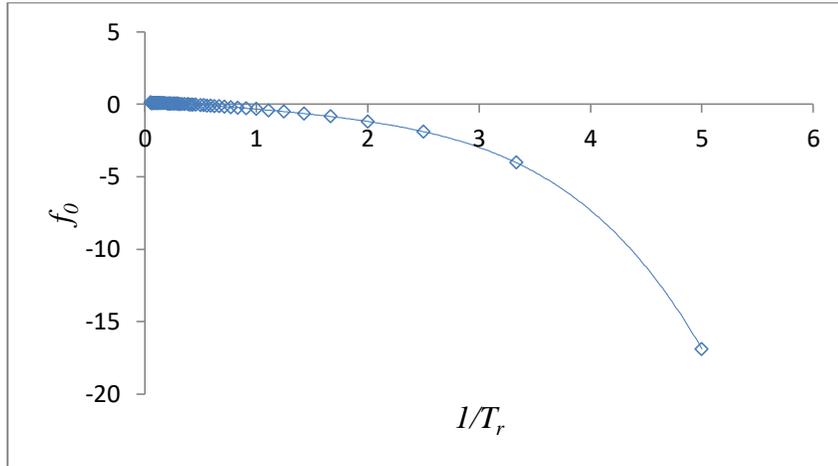

Own source

Figure 71.

Function f_{12} versus $1/T_r$ for correlation in RT_c/P_c.
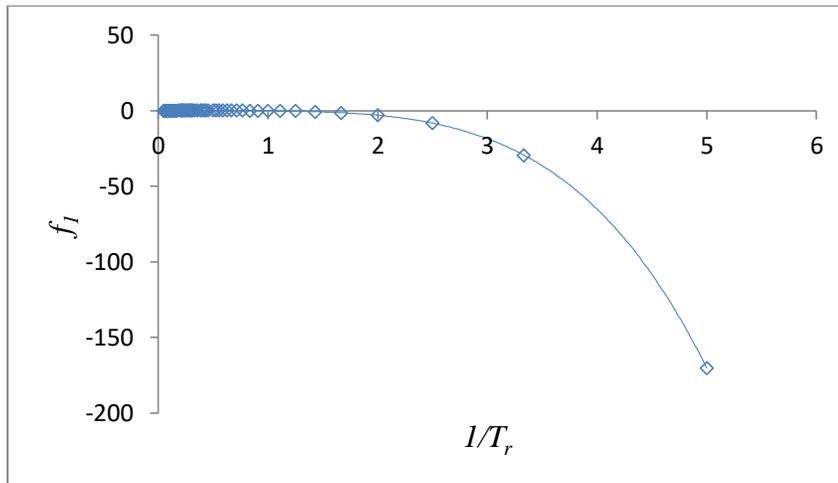
Own source

Figure 72.

Close-up of Figure 66.
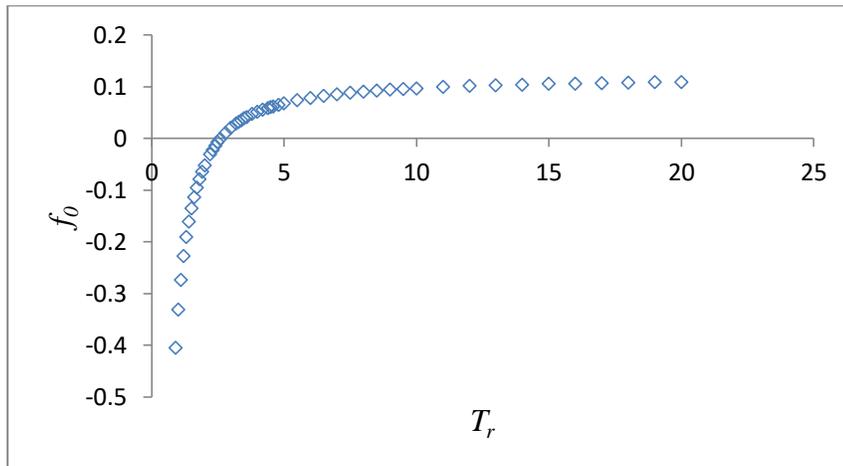
Own source

Figure 73.

Close-up of Figure 69.
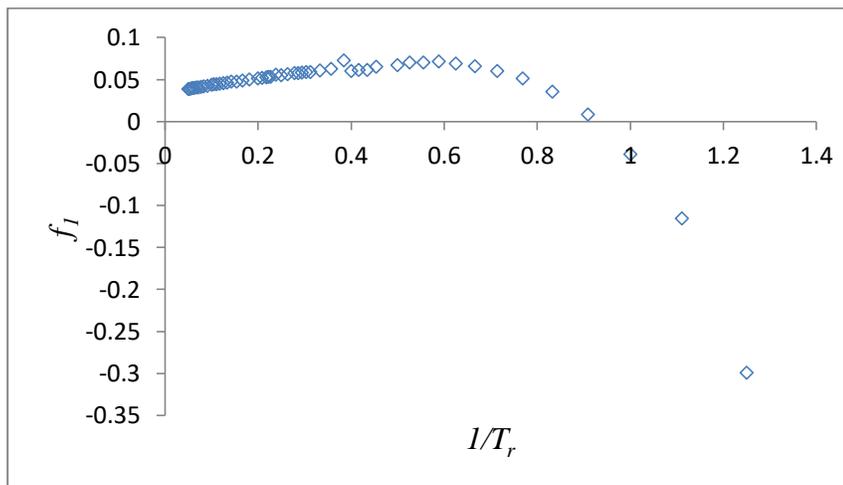
Own source

As seen from the figures above, f_{02} is also a well behaved, i.e. continuous monotonic function, very similar to the curve of argon and other noble gases. The function f_{02} is easily adjusted to a 4th-order polynomial in $1/T_r$:

(64) $f_{02} = 0.11655 - 0.16394T_r^{-1} - 0.41599T_r^{-2} + 0.17537T_r^{-3} - 0.044319T_r^{-4}$

As Equations (60) and (64) both represent the simple fluids, their coefficients should be proportional, being $Z_c = 0.291$ the quotient. As they were independently obtained, some variation is expected in the quotients: their values range from 0.2741 to 0.2957, with an average value of 0.2889. This represents about $\pm 5\%$ variation and 0.3% bias, which are very good results.

The function f_{12} is smoother that the similar one obtained in the previous correlation; however, it is difficult to fit due to its particular form, descending at high temperature. It could be represented by a 4th-order model, but the values of the coefficients depend on the range of data used. The f_{12} value at the lowest temperature cannot be reproduced without affecting the fit at higher temperatures. As with the other correlation, the following equation provides an acceptable fit of the data, and its highest power of T_r is equal to -4.5, similar to the Abbott (1975) and McGlashan & Potter (1962) correlations:

(65) $f_{12} = 0.0395438 + 0.1347783 T_r^{-1.5} - 0.0969967 T_r^{-3} - 0.1151858 T_r^{-4.5}$

Figure 74 is a comparison between the values of f_{12} calculated with Equation (65) and the original values. The recommended procedure, until best-fit equations are developed, is to use directly the tabulated values in calculations, or to interpolate for values of T_r not in Table 16.

Figure 74.

Function f_{12}, Equation (65) versus original values.
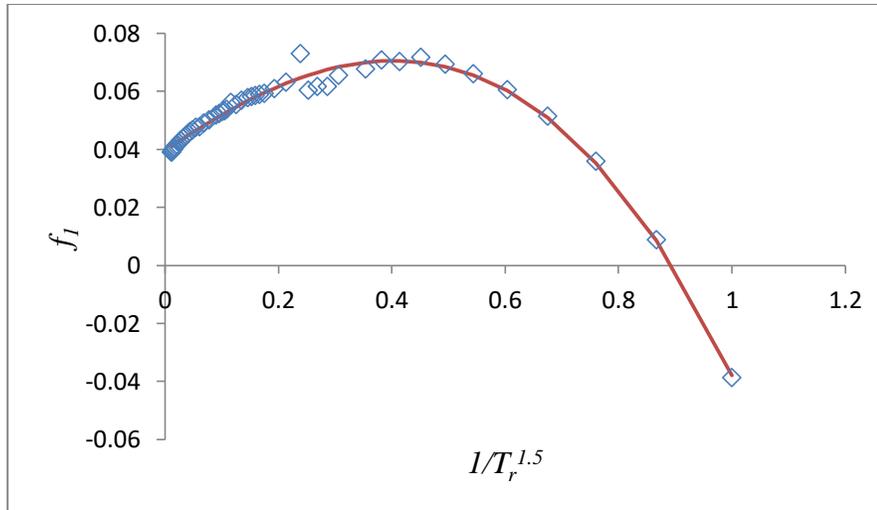
Own source

It is now possible to calculate the variation of the Boyle temperature with the acentric factor, by making $B_{r2} = 0$ in Equation (4A) and clearing the value of ω. Results are included in Table 17 and Figure 75, and an equation similar to the one proposed by Danon & Pitzer (1962) was obtained:

(66) $$T_B = \frac{T_c}{0.1564\omega + 0.3818} = \frac{2.6192 T_c}{1 + 0.4096\omega}$$

TABLE 17.

Reduced Boyle temperature versus ω.

T_{BR}	ω
1.90	0.9055
2.00	0.7637
2.20	0.4641
2.30	0.3566
2.40	0.2301
2.50	0.1207
2.60	0.0096
2.80	-0.1693

Own source

Figure 75.

Reduced Boyle temperature versus ω.
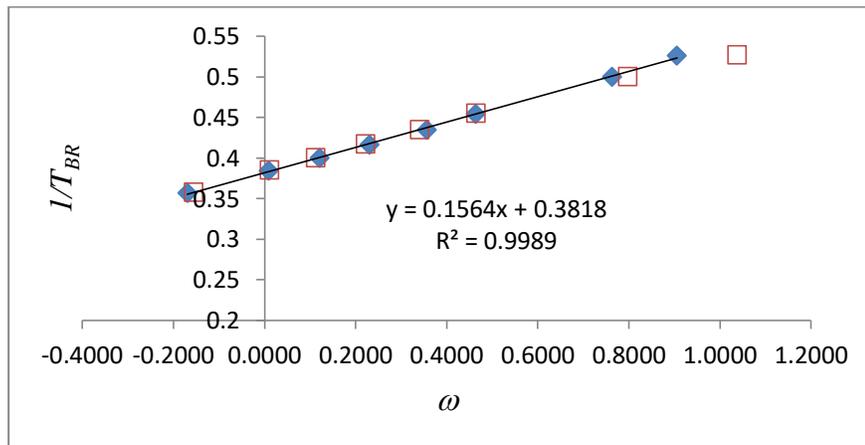
Own source

The red squares in Figure 75 represent the data used to obtain Equation (62): the two sets of data fall very close one from the other, as it should because they represent the relationship between the same variables; however, the data in Table 17 are more linear as indicated by the coefficient of determination of Equation (66), $R^2 = 0.9989$. In comparison, Equation (62) has a coefficient of determination $R^2 = 0.9964$; this represents a reduction in the variability by a factor of:

$$\frac{(1 - 0.9964)}{(1 - 0.9989)} = 3.27$$

Using Equation (4B) and the tabulated values of f_{02} and f_{12}, $B_{r2}(T_r)$ for all substances can be calculated and a comparison can be made. The results are rated from good to excellent for most substances; there is an improvement with respect to the previous correlation to be discussed later. Examples of excellent fit are the n-alkanes, cyclohexane, propene, ethyne, benzene, molybden hexafluoride, carbon disulfide, nitrogen trifluoride and silicon chloride, among others; the last example was not well fitted by the other correlation.

On the other side, the fit is less than good for some other substances, such as carbon tetrachloride, 1,3-butadiene, boron trichloride, silicon fluoride and tetrafluoroethene, among others; however, the calculated values are not far from the recommended values. In general, the fit is better at middle and high temperature, while at low temperature the calculated values are more negative; there are cases that show better and poorer fits. In the following figures, the same examples are given as with the previous correlation. Filled squares are the recommended values, while the empty squares are the calculated values.

Figure 76.

Comparison of B_{r2} values for nitrogen.
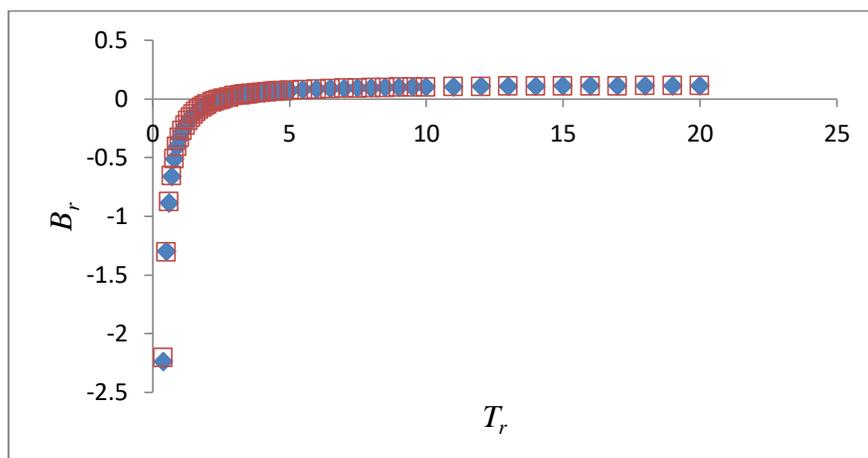
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Figure 77.

Comparison of B_{r2} values for propene.
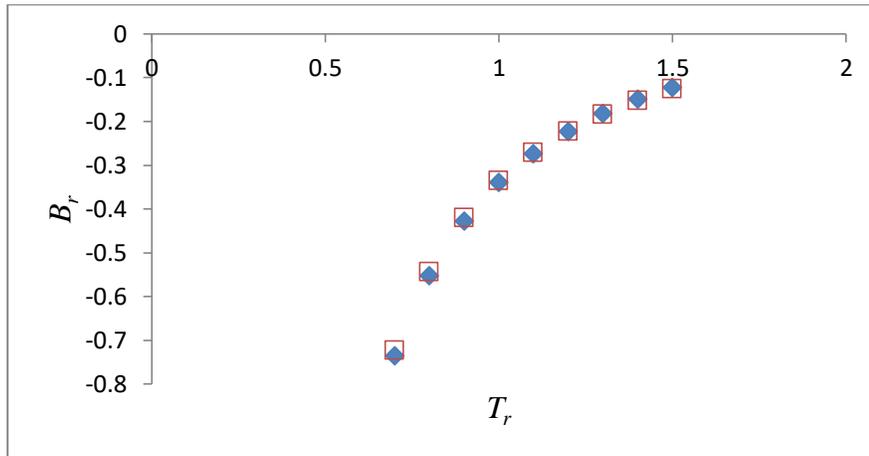
Own source

Figure 78.

Comparison of B_{r2} values for acetylene (ethyne).
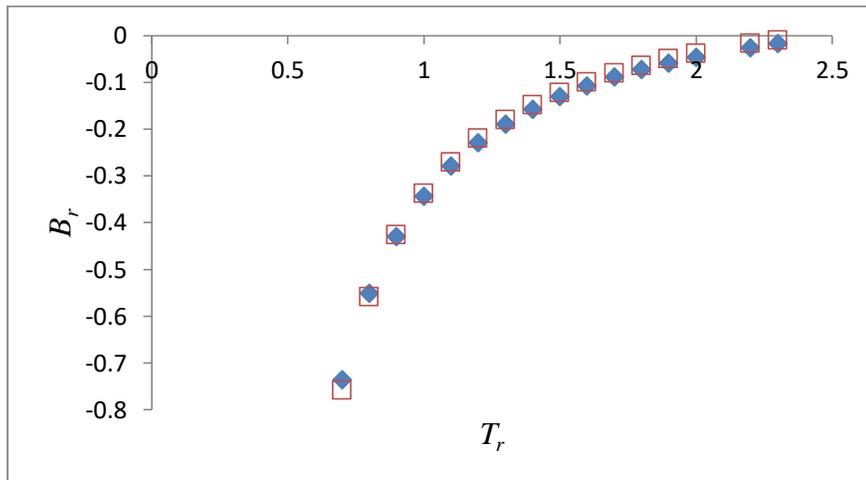
Own source

Figure 79.

Comparison of B_{r2} values for octane.
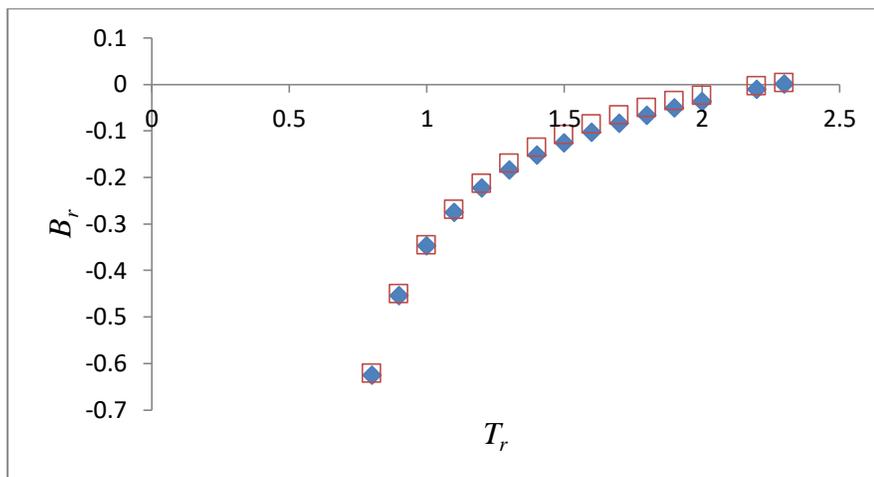
Own source

Figure 80.

Comparison of B_{r2} values for tetrachloromethane.
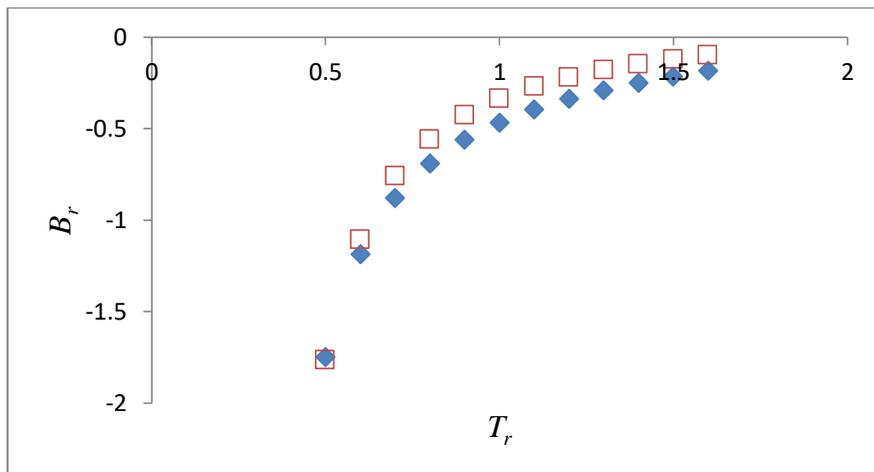
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Figure 81.

Comparison of B_{r2} values for trimethyl gallium.
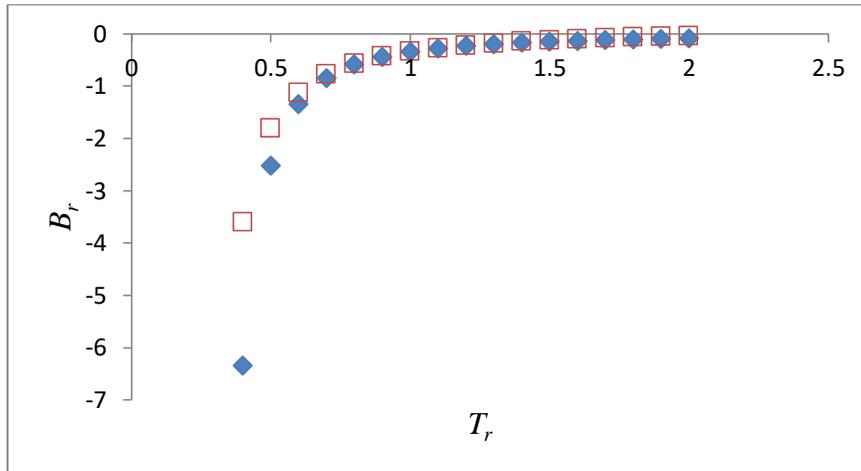
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Figure 82.

Comparison of B_{r2} values for trans-2-butene.
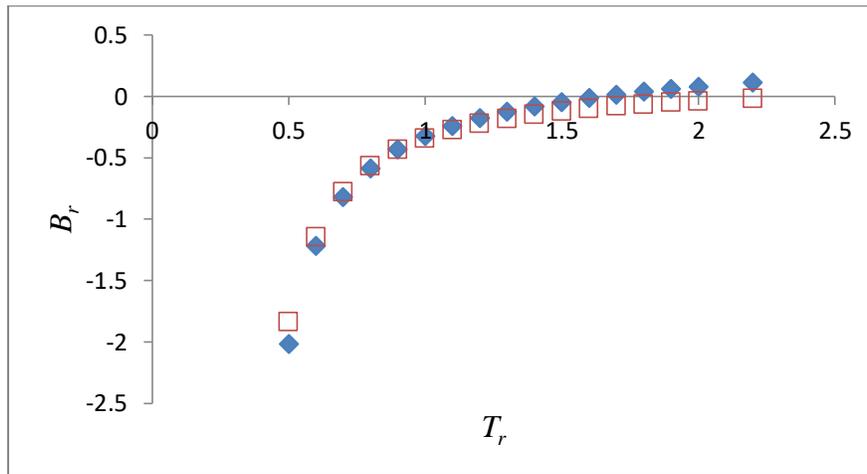

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Figure 83.

Comparison of B_{r2} values for cycloperfluorohexane.
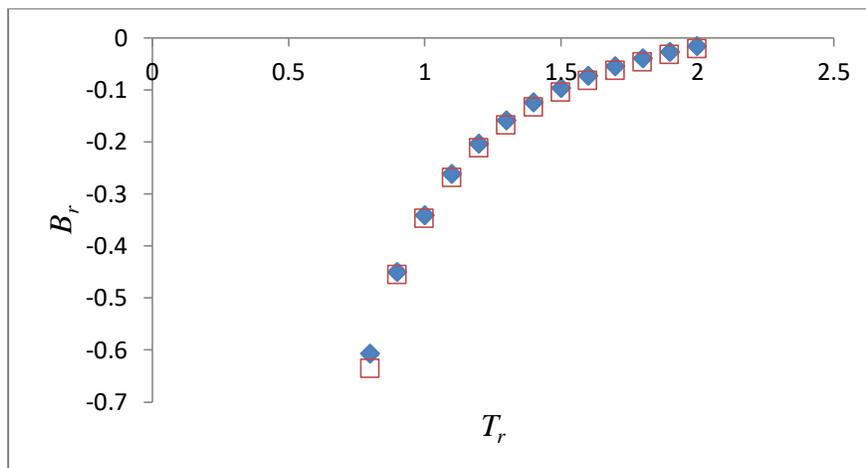
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Comparison of the Correlation for B_{r2} with Others

It is now possible to make a direct comparison between the correlation for B_{r2} obtained in the previous section, and several previous correlations. As seen in Figures 84 and 85 below, f_{02} is one of the less negative functions at low temperatures, falling near the McGlashan & Potter f_{01} (quadratic), the Zhixing et al. f_{02} (cubic), and the Meng et al. f_{02} (grade 8) curves; it is only slightly less negative than the Pitzer & Curl f_{02} curve.

Figure 84.

**Comparison of f_{02} from this work with other correlations.**
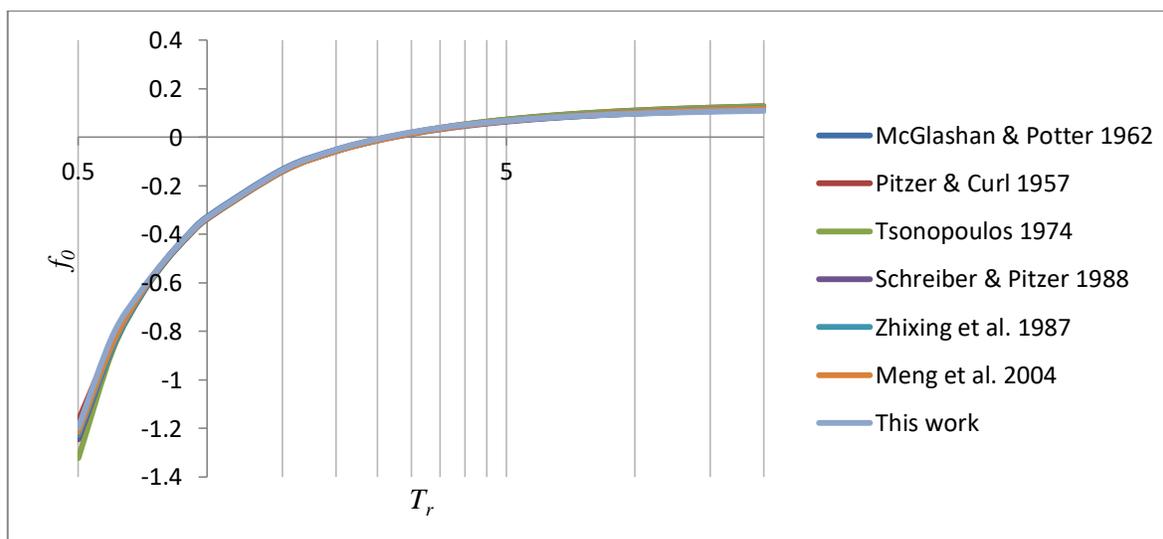
Own source

Figure 85.

Comparison of f_{02} from this work with other correlations.
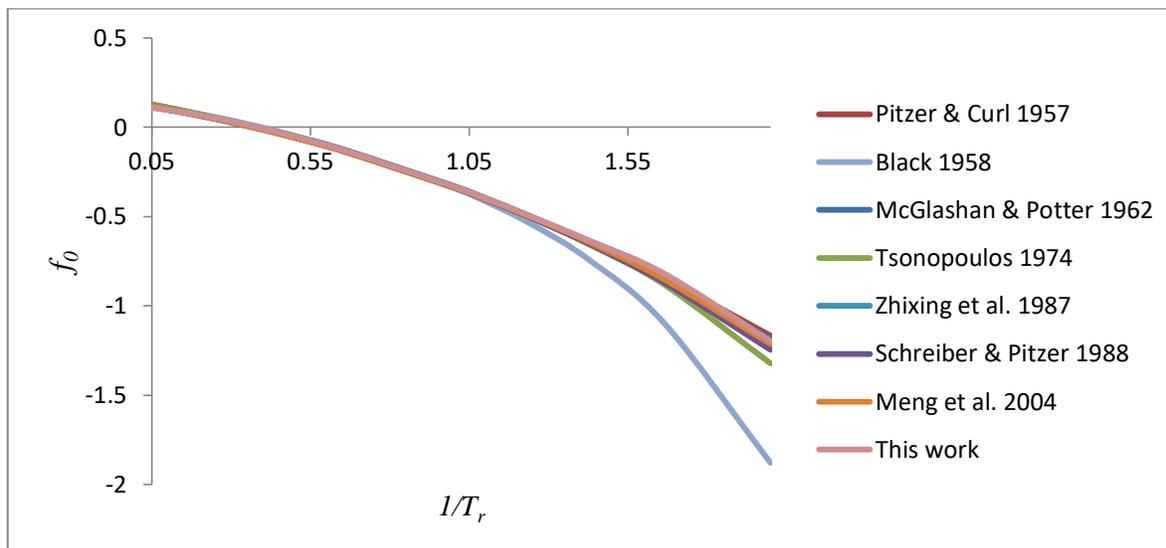
Own source

Figure 86 below is a comparison between the function f_{12} obtained here with other correlations, the result is a function less negative than most previous models. At $T_r = 0.5$, the function falls over the Abbott curve, and the only curve more positive that this is the Weber one. Between $T_r = 0.5$ and $T_r = 1$, the function follows a similar path than the other curves, except for the Schreiber and Pitzer one which is more negative. For values higher than $T_r = 1$, it is the curve with the lowest values. According to these results, the models with more negative values of B_r at low temperatures are not justified.

At high temperature, this function *descends* towards a constant value: this behavior is related to the positive coefficient of the T_r^{-1} term, a characteristic shared only with both models developed by K. S. Pitzer (Pitzer & Curl 1957; Schreiber & Pitzer 1988).

Figure 86.

Comparison of f_{12} from this work with other correlations.
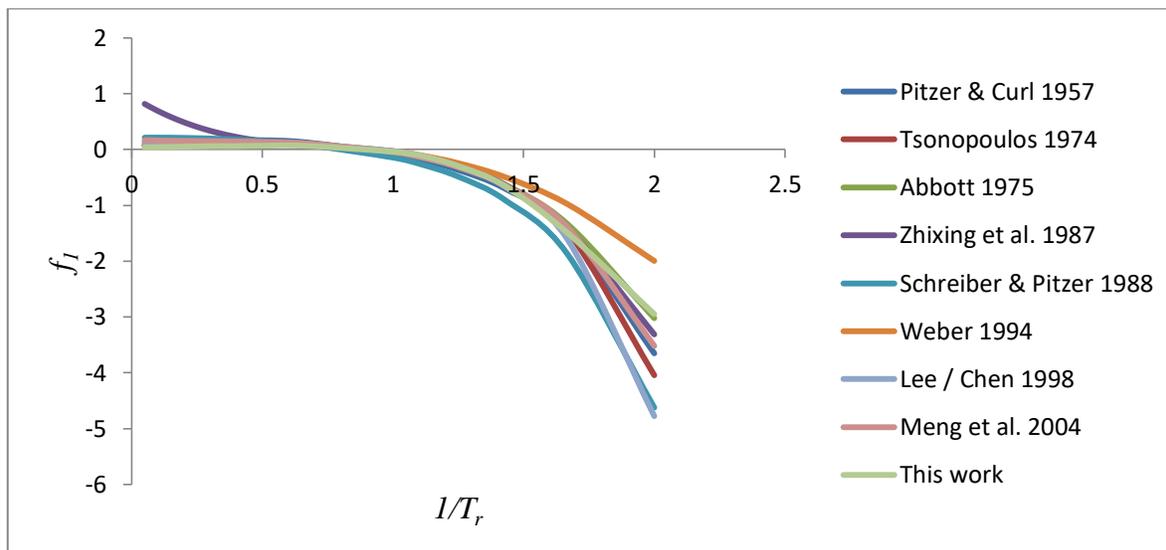
Own source

5.3. Discussion

Many details have already been discussed during the development of this research. This section will focus on discussing if the objectives have been fulfilled, the possible sources of error, and whether there are ways to improve the accuracy of the obtained correlations or not.

In general, the results presented here confirm the validity and power of the Corresponding States Principle for the development of generalized correlations. Several statistical tools, especially those related to multiple linear regression, were required to analyze big amounts of data and extract model information. The visualization of data was also a very useful tool to identify inconsistent data or models. Graphical and statistical tools available in MS Excel software made much easier and faster the intensive work of analyzing 62 substances and obtaining from them not one, but two generalized correlations for *B(T)*.

The model-free approach proposed here allowed to obtain a new type of f_{11} curve, not reported previously, as seen in Figure 61. Both f_1 curves are different than most of the previous models, descending at high temperature: the only models with that trend in f_1 are the Abbott and the two Pitzer ones (Abbott 1975; Pitzer & Curl 1957; Schreiber & Pitzer 1988). It is concluded that the objectives of this study were fulfilled satisfactorily.

It was possible to fit the f_0 data to a quartic model, a similar order to the model proposed by Eslami (2000). In Chapter 2, it was indicated as a desirable requirement that f_0 could follow a quadratic model, and this is already true over a narrow range of temperature; however, the quadratic

model is not accurate enough for the complete range of temperatures covered in this study ($T_r = 0.2$ to $T_r = 20$, a ratio of 100:1 between both values), so a fourth-order model was required. The specification of Chapter 2 is right in another sense: that a higher-order power, such as 6 or 8, is not required to model f_0, as it has been proposed for some of the models reviewed in that chapter (for example Tsonopoulos 1974; Schreiber & Pitzer 1988; Meng et al. 2004).

Unlike its partner, the function f_1 proved difficult to be modeled. Data could be fitted to a model of order "4.5" in T_r^{-1} for both correlations, but it seems that a higher order model would be required to fine-tune the coefficients. A sixth-order additional term could be adequate, to make f_1 similar to the Schreiber & Pitzer model (1988); an eighth-order term could be used instead as an option, making f_1 similar to other proposed equations (such as Tsonopolos 1974; Meng et al. 2004).

The specifications, criteria and tools developed in previous chapters were all fully validated during both research and the final results. First, the critical constants and acentric factors were validated in Chapter 2, looking for trends among families of compounds. The specifications developed in Chapter 2 helped to develop reference equations, which were useful at the temperature extremes during the development of the correlations. In Chapter 4, the experimental, calculated (from reference equations) or estimated Boyle temperatures were useful to extend the temperature range of the individual equations.

Although the results were remarkable, they were not "perfect": there were cases of noticeable deviations between the experimental (or recommended) data and the calculated ones. There are at least three potential sources of error:

a) The first source of error is in the several constants required, such as the critical constants (T_c, P_c, V_c), the acentric factor ω and the Boyle temperatures. Most of these constants were determined experimentally and they have uncertainty associated; for example, there are differences between the acentric factors reported in the literature. Data such as the critical volume can have an uncertainty of up to 10%, and when this information was validated for some families of compounds in Chapter 2, some substances did not follow any trend (the hexafluorides), and in two cases a correction was necessary (c-C_6F_{12}, n-C_6F_{14}). Another example of uncertainty is the failure to find a trend in the critical compressibility Z_c data for compounds different of the normal alkanes, although trends were found for each of the critical constants. Moreover, other data such as some of the Boyle temperatures were estimated so the estimation process adds more uncertainty to the correlations. Finally, there was little information about some of the substances: for example the acentric factor of uranium hexafluoride is reported in one source only

(Anderson et al. 1994) and they report two very different values, $\omega = 0.2842$ and $\omega = 0.09215$; because of this, it was decided to obtain ω directly by fitting vapor pressure data from Perry et al. (2008).

b) The second source of error is the second virial coefficient data. Not all the data in the Dymond et al. compilation are of the same quality, as in some cases there were a few points available, perhaps from one source only. Examples are cyclopentane (three points, one source from 1949), tetrafluoroethene (five points; one source from 1980), dodecafluorocyclohexane (six points; one source from 1970) and decafluorobutane (five points; two sources from 1962 and 1969). Also for some substances the experimental data are quite old: examples are acetylene (two sources from 1937 and 1958) and propadiene (two sources from 1940 and 1953). Several cases of more positive or more negative data points were found during the study: examples discussed in Chapter 4 include 2-methyl pentane, carbon disulfide, acetylene and toluene. This last substance is a significant case because the Dymond et al. data do not follow the Corresponding States Principle (when compared to benzene) and could not be used; the p-xylene and hexafluorobenzene data were analyzed too and they could have the same problem. One conclusion is that the recommended values of *B(T)* in the Dymond et al. compilation, and even the experimental values, must be taken with care and verified in some way. Other possible conclusion is that the correlations developed here can be used to identify sets of data that are inconsistent or contain systematic errors, due to adsorption, measurement, human judgment or other causes.

c) The third source of error corresponds to the values of both functions f_1 obtained in this study, as they have some uncertainty at the higher temperatures. This is reflected in the fact that the f_1 curves were not smooth in some temperature regions. This uncertainty is added to the estimated second virial coefficient when the f_1 values are used with Equation (4A) or (4B). The f_{12} curve obtained from the correlation in RT_c/P_c shows less uncertain data and more smoothness, so these data could be the basis to "fix" or improve the f_{11} curve obtained from the correlation in V_c. It must be concluded that both sets of f_1 could be subject to verification and improvement.

It was explained in Chapter 2 that the correlations for second virial coefficients based on V_c and the ones based on RT_c/P_c are different, not related simply by a proportionality constant. This was verified in this study, and slightly better results were obtained with the correlation in RT_c/P_c.

Two supporting results are the smoothness of the associated f_{12} curve, and the fact that silicon chloride was fitted well by the correlation in RT_c/P_c and less than well with the correlation in V_c. One of the possible reasons for these results is the uncertainty associated with the critical volumes.

One difference between the correlations developed here and the rest of other correlations is the fact that they predict lower values of the second virial coefficient at the highest temperatures. The main reason for this fact is that accurate theoretical *B(T)* values for sixteen substances were used to fit the correlations in the high temperature region; the data was taken from the studies of Kestin et al. (1984) and Boushehri et al. (1987). Data from higher temperatures are near the maximum that the *B(T)* curve has for real gases, so the slope of the curve and the actual values of *B(T)* must be lower that the values estimated from lower temperature data, or from correlations based on experimental and/or older values.

It was shown in Chapter 2 that the constant a_0 for the normal alkanes followed a definite trend; if the data were perfect, the resulting equations from this study would show a definite trend among same coefficients a_0, a_1, a_2, etc.; with real data this trend can be identified only for the first one or two coefficients. This was shown in Figure 20 and Table 7 for the n-alkanes, a family of compounds for which a large amount of reliable data exists.

An unexpected result was that all of the Zarkova equations had to be discarded: the curves obtained with these equations were steeper than the general trend, indicated by the experimental data. This was associated to the presence of very large constants in these equations: this is one of the reasons they predict more positive values at high temperature, and very low Boyle temperatures.

The fluoroalkanes and fluorocompounds in general are in need to be studied more critically, because they seem to follow another temperature trend. It could be that they follow another Corresponding States Principle, but this is not possible, so the cause must be a different one. Their critical constants also followed a different trend than the normal alkanes during the validation in Chapter 2. It must be concluded that some of the information is wrong for these substances (the critical constants and/or the second virial coefficient data).

The presence of a slight polar moment or a quadrupole moment did not seem to affect the fit of the substances of Group B. For example, acetylene and benzene both show a very good fit with the present correlations, having both substances a big quadrupolar moment. Other examples of a good fit are propene and toluene, both slightly polar. In those cases where the fit was less than good (boron trichloride), it cannot be assured that the cause is the presence of a dipole of a quadrupole.

Although it is usual in this kind of studies to make a determination of error and bias between calculated points and the recommended values by Dymond et al. compilation, this was not attempted in this study because there are reasons to believe that these recommended values are not

always the best ones, except for the most reliable substances (simple fluids and normal alkanes). For the same reason, a quantitative comparison between the correlations developed in this study and other models is considered not useful, as most of the previous models are based on older, uncertain data. In this sense, a comparison of the correlations developed here against wrong data would be unfair; for a comparison to be effective, it must be done on a set of data of the highest quality. Another possibility (sensitivity analysis) will be discussed later.

The trend found for the Boyle temperature T_B is similar to the one proposed by Danon & Pitzer in 1962, but the coefficients are different, as seen when comparing Equations (56), (62) and (66). In case one equation has to be recommended for use, it would be Equation (66) due to its higher coefficient of determination between the data and the equation. This T_B formula and the Iglesias-Silva et al. one, Equation (58), share the fact that they are never negative. Equations (62) and (66) represent a new tool for the estimation of Boyle temperatures.

Chapter 6.

CONCLUSIONS AND RECOMMENDATIONS

The objectives established at the beginning of this study were achieved, and the following conclusions can be made:

a) A validation was made of the critical constants and the acentric factors for several families of compounds (normal alkanes, cyloalkanes, α-alkenes, n-fluoroalkanes, cycloperfluoro-alkanes). This validation was not possible for the critical compressibility.

b) It was demostrated that the second virial coefficient for normal fluids follows Equations (4A) and (4B). In this sense, the hypotheses established in Chapter 1 about the behavior of $B(T)$, based on the Corresponding States Principle, were verified.

c) A set of three mandatory requirements was established for a model of the second virial coefficient $B(T)$ to have the correct behavior at low and high temperatures; twelve non-mandatory (desirable) requirements were also proposed.

d) A critical analysis was made of the recommended second virial coefficients in the Dymond et al. (2002) compilation; it was shown that several sets of data had inconsistent points and that several of the fitting equations predicted inconsistent behavior.

e) It was demonstrated that the use of the Boyle temperature, real or estimated, is a reliable tool to expand the range of temperature of the *B(T)* equations.

f) As part of the study, reference equations for the second virial coefficient of sixteen substances were developed; these equations allowed the accurate estimation of *B(T)* for a wide range of temperatures.

g) Not one, but two correlations for *B(T)* were developed: one reduced by the critical volume, and the other one reduced by the combination RT_c/P_c. Both correlations allow the estimation of second virial coefficient for reduced temperatures up to $T_r = 20$; this represents a temperature up to 3000 K for some substances.

h) For each of the above correlations, a table of values of f_0 and f_1 for 60 values of T_r was developed; these tables could be used directly and values can be interpolated.

i) Equations were fitted to the obtained values of f_0 and f_1 for both correlations; they are represented by Equations (60), (61), (64) and (65). These equations can be used for calculations in simulation software and programmable calculators, among the possible uses.

j) It was demonstrated that a model-free approach can be applied to determine the true form of the functions f_0 and f_1, to be used in Equations (4A) and (4B).

k) The function f_{11} of the correlation based on V_c is very different from the ones proposed by other authors; this was an unexpected result only possible because of the model-free approach.

l) The function f_1 of both correlations has lower values than other models at high temperatures; this is the correct behavior, and it is a consequence of the use of the reference equations at this temperature range.

m) For each of the above correlations, an equation for the dependence of the constant a_0 with the acentric factor was developed. These are represented by the Equations (59) and (63).

n) For each of the above correlations, an equation for the dependence of the Boyle temperature with the acentric factor was developed; these equations are similar to the one proposed by Danon & Pitzer (1962), but with different constants. These are represented by the Equations (62) and (66).

o) An approximate relationship between the constant a_0 of the *B(T)* equations and the Lennard-Jones constant b_0 was found; this is useful for estimation purposes.

p) The visual methods used were very relevant for model testing and validation since they allowed identification of inconsistent sets of data and models.

q) It was determined that the correlation based on RT_c/P_c is slightly better than the one based on V_c. This could be useful to refine the values of f_{11} from the later correlation.

r) It was determined that a slight dipole or quadrupole moment do not have an effect on the normal fluid behavior of Group B compounds.

s) All the equations developed by the Zarkova group, introduced in Chapter 5, had to be discarded because they have the wrong temperature dependence and predict high *B(T)* values at high temperatures, and low Boyle temperature values. This was an unexpected result.

In future research, it would be possible to improve both correlations developed in this study, fine-tuning the values of f_0 and f_1. In order to determine the feasibility if this objective, a critical analysis of each step must be done, as follows:

a. A sensitivity analysis of the specific constants should be done for each substance, changing parameters such as the critical constants or the acentric factor in order to see if the fit is improved;

b. All the available *B(T)* data in the Dymond compilation could be used instead of the recommended data only. This would allow the identification of inconsistent sets of data, but also sets following the trend found in this study (assuming it is the correct trend).

c.   In addition to the Dymond et al. compilation, other sources for $B(T)$ data should be used. For example, data not included in Dymond et al. were found in the Infotherm database for toluene and hexachlorobenzene.

d.   Currently there are highly accurate reference equations for many substances, and this is a potential source for second virial coefficient values and for verification of their temperature trend. Reference equations were used in this study to obtain accurate $B(T)$ data for xenon (Sifner & Klomfar 1994), fluorine (Prydz & Straty 1970), ethane (Bücker & Wagner 2006) and toluene (Goodwin 1989). The reference equation development usually includes the second virial coefficients as a data input, and some studies include a comparison between experimental and calculated B values, which could be considered then reference values.

e.   More information about accurate theoretical calculations of second virial coefficients should be obtained. The accurate calculations from of Kestin et al. (1984) and Bousheri et al. (1987) were used to extend the range of the individual equations for noble gases and simple fluids; this can be done also for other substances. These calculations are currently at a high level, and the resulting data are comparable or even better than the experimental values; therefore, they can be considered reference values.

f.   Now the same model can be used to fit all the substances; for example, a fourth-plus-sixth-order model. Initially in this study, this was not desirable in order to avoid influencing the result, but now the form of the functions is known and becomes an almost necessary recommendation, in order to get consistency in the coefficients.

g.   Depending of which correlation is used, the constant a_0 of each individual substance could be now fitted to Equation (59) or Equation (63), in order to adjust these coefficient to the linear trend represented by these equations. This step, as well as the previous one, should help to reduce the variability of the $B(T)$ data.

h.   As the developed equations for the individual substances comply with the specifications developed in Chapter 2, they can be extrapolated both at low and high temperatures, in order to obtain more data for the fitting of the f_0 and f_1 functions; however, this must be

made with care, and an analysis of this option must be made for each substance in order to determine how much can the individual equations be extrapolated with accuracy.

i. After all these previous steps have been done, the results from the substances of Group B should be analyzed with more detail in order to separate possible effects of dipole and/or quadrupole moments. The concept of homomorph (a non-polar compound with similar shape than a polar or quadrupolar compound, see Tsonopoulos 1974, Hayden & O'Connell 1975) could be useful here for comparison purposes.

j. Another strategy, different from the one followed here and by most previous researchers, would be trying models based on other parameters instead of the acentric factor and the critical properties. For example, Eslami (2000) based its correlation on the normal boiling point temperature and density without a third parameter. Another option would be to use the Boyle temperature as a parameter instead of the critical temperature, such as Iglesias-Silva et al. (2001) did. In both cases, the use of a third parameter different from the acentric factor should be analyzed.

Other subjects that could be covered in future research are the following:

a) To study the derivatives of $B(T)$, trying to make the correlations able to reproduce them.

b) To use the model for argon developed in Chapter 2, Equation (54), which is able to reproduce the first and second derivatives of argon, as the basis of a correlation for $B(T)$. This model could be used as an alternative to function f_0.

c) To determine which the correct relationship between the constant a_0 of the $B(T)$ equations and the Lennard-Jones constant b_0 is. The former because a value of $0.25\, b_0$ was found for the a_0 of normal alkanes in Chapter 2, while a value of $0.50\, b_0$ was found for the a_0 of normal fluids in Chapter 3 by a different method.

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El segundo coeficiente virial es una propiedad importante para determinar el efecto de la no idealidad en los gases reales, la cual es aplicable a la gran mayoría de los procesos de la industria química. Esta obra presenta un análisis de las correlaciones más importantes del segundo coeficiente virial de fluidos normales, así como el desarrollo de dos nuevas correlaciones basadas en un enfoque novedoso. El libro está dirigido a estudiantes, investigadores y profesionales interesados, no solo en los aspectos fundamentales de este tema, sino en otros más avanzados, así como en la aplicación a los cálculos de procesos químicos.

The second virial coefficient is a relevant property for determining the effect of the non-ideality of real gases, applicable to the vast majority of existing chemical and industrial processes. An analysis of the most relevant correlations for the second virial coefficient of normal fluids is introduced, as well as the development of two new correlations, based on a new approach. This book can be used by students, researchers and professionals interested in both the fundamentals and the most advanced aspects of the subject, as well as in the application to chemical process calculations.