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Correction Factors of Interacting Gaseous Systems: A Molecular Approach

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The formulation of equation of state for a classical chemically interacting gaseous system by incorporating correction factors to ideal volume and pressure is reported. The probabilistic consideration of the average inter-molecular separation has provided a helpful method of evaluating the correction factor to the volume of an imperfect gas. A physical interpretation of the van der Waals constant, 'a' has been made possible through a completely theoretical basis arriving from the results of F. London's dispersion forces.

Key Words: Imperfect gases, Volume and pressure corrections.

INTRODUCTION

The formulation of equation of state pertaining to real gases is a fascinating topic of research for the past several decades[1]. In spite of the large number of established equations of state in literature, this still is a topic of considerable interest for a number of branches in physics and chemistry in view of the fact that every equation of state presents its own qualitative picture of the gaseous state and a better perspective of the chemical interactions. In the present communication, we report an equation of state for spherical interacting gaseous systems derived from a molecular basis.

While various types of equations of state have been reported till now, the classical van der Waals equation of state has itself been subjected to critical analysis, with regard to the physical interpretation of the two constants 'a' and 'b', which respectively represent the intermolecular attractions and the volume correction. In spite of giving a good qualitative picture of the gaseous state, the van der Waals equation is only valuable as an empirical formula, since not many convincing theoretical derivations have been attributed to the general arguments of van der Waals. Hence, a theoretical derivation for the pressure correction term of real gases arriving from London's expression for dispersive attraction potential is discussed. Further, a novel correction factor to the ideal volume is also being incorporated through the probabilistic considerations of the average intermolecular separation.

Methodology

Volume correction term: The basic premise, on which the correction term for imperfect gases is based, consists in evaluating the probabilistic distribution of gaseous species in accordance to their average intermolecular separation. As shown in Fig. 1, when two sample molecules are separated by their average intermolecular distance, 'x_a' (a constant at constant temperature and pressure), they exclude the cylindrical volume (shown in dotted space) for the movement of other molecules. Denoting 'V_1' as the volume excluded by two such molecules, we obtain

$$V_1 = \{\pi\sigma^2 x_a P(x_a)\}/4 \quad (1)$$

where, 'σ' is the collision diameter of the colliding species and '$P(x_a)$' denotes the probability that two such molecules might be separated by the distance 'x_a'. It is however important to note that when two molecules are not separated by the distance 'x_a', their intermolecular separation can range from '$x_a + dx_a$' or '$x_a - dx_a$' where 'dx_a' is a small deviation from the average value of inter-molecular separation, which leads to the fact that the two molecules separated by these distances exclude the following volumes for the movement of other molecules in the system:

$$V_2 = \{\pi\sigma^2(x_a + dx_a) P(x_a + dx_a)\}/4 \quad (2)$$

$$V_3 = \{\pi\sigma^2(x_a - dx_a) P(x_a + dx_a)\}/4 \quad (3)$$

This directly suggests that one molecule in such a real gaseous system must exclude a volume that is half the sum of the volumes V_1, V_2 and V_3.

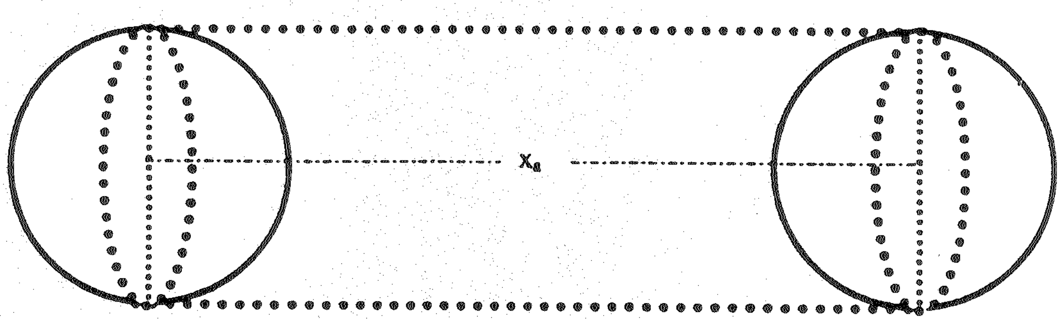

Fig. 1. Excluded volume phenomena

Denoting 'b_n' as the net volume excluded by one mole of an imperfect gas, we obtain

$$b_n = N_a\pi\sigma^2[x_a P(x_a) + (x_a - dx_a) P(x_a - dx_a) + (x_a + dx_a) P(x_a + dx_a)]/8 \quad (4)$$

A more useful expression could be derived on considering that 'x', the intermolecular distance, behaves as a random variable that follows continuous normal probability distribution function with mean, 'x_a', accepting any value from 'x_{max}' to 'σ', where 'x_{max}' is the maximum possible distance of separation between two gaseous species at a given temperature and pressure. It is therefore of utmost importance to point out that by the symmetry law of normal distribution function, $P(x_a + dx_a) = P(x_a - dx_a)$ and $P(x_a) + P(x_a + dx_a) + P(x_a - dx_a) = 1$. Hence the expression for 'b_n' reduces to,

$$b_n = N_a \pi \sigma^2 x_a/8 \tag{5}$$

where N_a is the Avogadro number.

A perusal of Table-1 clearly indicates the range of values of 'b_n' derived on this basis, when $x_a = 3 \times 10^{-9}$m at a temperature of 15°C and 1 atmosphere pressure[2]. Fig. 2 shows a graphical comparison of 'b_n' and 'b_{vdw}', the volume correction term of van der Waals equation of state for a variety of gases.

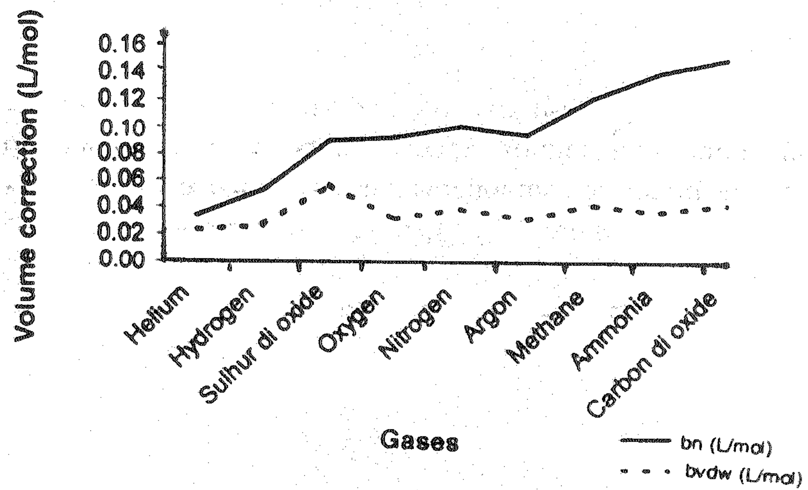

Fig. 2. Graphical Comparisonof 'b_n' and 'b_{vdw}'

TABLE-1
COMPARISON OF 'b_n' AND 'b_{vdw}' VALUES

Gas	b_n (L/mol) [eqn. (5)]	b_{vdw} (L/mol)	b_n/b_{vdw}
Helium	0.0337	0.0237	1.421941
Hydrogen	0.0533	0.0266	2.003759
Sulphur dioxide	0.0894	0.0564	1.585106
Oxygen	0.0919	0.0318	2.889937
Nitrogen	0.1003	0.0391	2.565217
Argon	0.0941	0.0322	2.922360
Methane	0.1217	0.0428	2.843458
Ammonia	0.1399	0.0371	3.770889
Carbon dioxide	0.1501	0.0427	3.515222

Pressure Correction Term of van der Waals Equation

As suggested by F. London, the expression for potential energy of inter-molecular dispersion attractions *via* quantum mechanical approach is given by[3]

$$U_A = (-3\alpha^2 h\nu)/\{4x^6(4\pi\varepsilon_0)^2\} \tag{6}$$

where 'α' is the polarizability of the gaseous species, 'ν' their characteristic frequency, 'h' is the Planck's constant and 'x' denotes the intermolecular separation at a particular temperature and pressure.

The origin and nature of these dispersion forces suggest very clearly that the dispersion effect is alone capable of producing considerable amount of molecular attractions, excepting for systems with very high permanent dipole moments, where orientation effects become appreciable[4].

On differentiating the above expression partially with respect to 'x', the intermolecular distance, the expression for intermolecular dispersion forces is obtained as

$$F_A = \delta U_A/\delta x = (9\alpha^2 h\nu)/\{2x^7(4\pi\varepsilon_0)^2\} \tag{7}$$

It is of significance to note at this juncture that the pressure of an ideal gaseous system is equivalent to the sum of expected value of pressure of an imperfect gas and that due to the attractive components present exclusively in real gases. Hence, $P_{Ideal} = P_{Real} + P_{Attractions}$, where $P_{Attractions}$ is given as the pressure contribution by the attractive component to the net pressure of the system (as given in eqn. (7)) per unit surface area of the walls of the container.

Hence, what follows is an expression for the ideal pressure, which can be given as

$$P_{Ideal} = P_{Real} + [(9\alpha^2 h\nu)/\{2Ax^7(4\pi\varepsilon_0)^2\}] \tag{8}$$

where 'A' denotes the area of the walls of the container in which the gaseous system is being observed and the expression of '$F_{attractions}$' is obtained from eqn. (7). If the gaseous system under consideration is being observed in a cubical container of side 'L' units, the area of the six walls of the container is given as $A = 6\ V_{Co}/L$, where V_{Co} is the volume of the container (L^3).

Since $V_{Co} = V_{Ideal} = V$, on substituting for 'A' in eqn. (8), we obtain

$$P_I = P_R + (3\alpha^2 h\nu L)/\{4Vx^7(4\pi\varepsilon_0)^2\} \tag{9}$$

On multiplying and dividing the second term in the above equation by 'V' and substituting for 'V' as 'L^3' in the numerator, we obtain the expression for ideal pressure as

$$P_I = P_R + (3\alpha^2 h\nu L^4)/[\{4x^7(4\pi\varepsilon_0)^2\}V^2] \tag{10}$$

The above expression is of the same form as that of the pressure correction term of van der Waals equation, which predicts the term to be (a/V^2). At very low temperature and pressure though, the second term in the equation (10) vanishes and the equation reduces to $PV = RT$, the ideal gas law. It is quite important to state that though the present derivation assumes the cubical shape of the container, this result holds good for any geometry of the vessel. This is effected by considering the given vessel of any geometry to be made up of a large number of infinitesimally small cubes, for which the result holds good.

Hence, the pressure correction term for real gases is being derived in a theoretical manner, making it possible to theoretically compute the values of van der Waals constant 'a' from the expression,

$$a_{vdw} = (3\alpha^3 h\nu L^4)/\{4x^7(4\pi\varepsilon_0)^2 n^2\} \quad (11)$$

where 'n' denotes the number of moles of the system. The values of 'ν' per molecule of the real gaseous systems are evaluated by employing the values of 'U_A' and 'α', when the molecules are separated by their mean distance of separation[5], which is about 3×10^{-9} m at 15°C and 1 atmosphere pressure[2] from the expression derived from eqn. (6),

$$\nu = (4U_A x^6 (4\pi\varepsilon_0)^2)/(3\alpha^2 h N_A) \quad (12)$$

where 'N_A' is the Avogadro number. To check and confirm the accuracy of this method, the value of 'a_{vdw}' per mol^2 of the gaseous system in a vessel of unit length is calculated from eqn. (11), when the particles are at their closest possible distance of separation[3], which is about 0.2×10^{-9} m. Table-2 reveals the representative data of the comparison between the theoretical and the calculated values of 'a_{vdw}' by the above methodology.

The reasonable agreement of values presented in Table-2 proves beyond doubt that the values of the van der Waals constant 'a' reported in the literature as a result semi-theoretical attempts, correspond to a higher temperature and pressure of the system since the intermolecular separation value of 3×10^{-9} m has been computed for the conditions of 15°C and 1 atmosphere pressure.

TABLE-2

COMPARISON OF THEORETICAL AND CALCULATED VALUES OF 'a_{vdw}'

Gas	a_{vdw} Theoretical (10^{-1} Nm^4 mol^{-2})	a_{vdw} Calculated (10^{-3} Nm^4 mol^{-2}) [eqn. (11)]
Hydrogen	0.2470	0.4539
Nitrogen	1.4080	2.2130
Argon	1.3610	2.4110
Carbon monoxide	1.5020	2.4680
Methane	2.2260	3.2060
Chlorine	6.5430	8.7660
Hydrogen bromide	4.4860	6.2310
Ammonia	4.2040	4.1700
Water	5.5050	2.2550

Hence the availability of data for the average intermolecular separation for gaseous systems at various temperatures and pressures, which according to the best of our knowledge doesn't exist till date in the literature, will yield a better agreement between the calculated and the theoretical values of 'a_{vdw}'.

RESULTS AND DISCUSSION

A novel volume correction term is being proposed by the probabilistic consideration of the average intermolecular separation of imperfect gases. The pressure correction term of the phenomenological van der Waals equation of state has been derived on a theoretical basis arriving from London's dispersion energy expression. The presence of the term 'x', the intermolecular distance in both the correction terms, makes these terms sensitive to the changes in pressure or temperature of the system and hence are functions of 'P' and 'T'. The proposed approach to the correction factors of the classical chemically interacting gaseous systems discards the consideration of simplifying assumptions, like the gaseous molecules behaving as hard impenetrable spheres during collisions, and hence presents a qualitatively better physicochemical picture of the gaseous state than most of the equations of state in the literature.

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