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Measurement of the second virial coefficient of carbon (IV) oxide, CO_2 used in limca bottling company, Onitsha, Anambra State

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ABSTRACT

The second virial coefficient, B_2 was measured using the gas filling and handling apparatus made up of the gas sample and evacuation cylinders. After the experiment the compressibility factor of CO_2 was evaluated to be 0.268. The deviation from unity is an indication that CO_2 at 373k and 19.6 atm behaves non-ideally. From literature however, the compressibility factor of CO_2 at this temperature is 0.274, showing an error of 2.1%. This error is within allowable limit. Subsequently the second virial coefficient was deduced to be -73.2 as compared with the value of -72.2 contained in literature. In all, the results obtained are plausible, precise and reasonably accurate.

Key words: compressibility factor, carbon dioxide, non-ideally, second virial coefficient.

INTRODUCTION

That the ideal gas law, is an abstraction is evident when one considers the underlying assumptions made: that molecules are point masses, and they undergo

$$PV = nRT, \qquad (1)$$

only elastic collisions. Since we know these to be inherently false, it may be surprising how well the ideal gas law seems to work. At higher pressures and/or lower temperature, however, finite molecular volumes and intermolecular forces are considerable, and the expected deviations from (1) become too large to be ignored.

One logical and systematic way in which deviations from ideal gas behaviour can be expressed mathematically is to measure the state properties, *P*, *V*, and *T*, of *n* moles of a gas at equilibrium, and to determine the extent to which the *PV/nRT* quotient deviates from unity. The dimensionless expression *PV/nRT* is called the *compressibility factor,* and is denoted as *Z.* Since the extent to which *Z* differs from unity depends on the pressure [or alternatively, at a given temperature, the reciprocal molar volume, 1/*(V/n]*, Z can be expressed as a power series in either of these state variables. Thus,

$$Z = \frac{PV}{nRT} = 1 + B_2\left(\frac{n}{V}\right) + B_3\left(\frac{n}{V}\right)^2 + B_3\left(\frac{n}{V}\right)^3 + \cdots, \qquad (2)$$

where B_2, B_3, are called the second, third, … *virial coefficients.* (The term virial here indicates a power series). They are functions of temperature and actually relate to the *simultaneous interactions* of two, three, four… molecules, respectively. It can be understood, therefore, that the higher-order virial coefficients become significant only at smaller molar volumes (i.e., higher pressure).

The virial coefficients can be calculated from theoretical concepts involving statistical mechanics and knowledge of the intermolecular potential energy function appropriate to the particular molecular system. This is a case in which thermodynamics, which deals empirically with macroscopic systems, can be linked with microscopic entities, molecules [1].

Z can also be expressed as a power series in the pressure (it often being a more convenient state variable):

$$Z = 1 + A_2P + A_3P^2 + A_4P^3 + \cdots, \qquad (3)$$

where the temperature-dependent A_2, A_3, A_4, … are also virial coefficients. If equation (2) is solved for P and this expression is substituted in equation (3), the coefficients of (n/V) of equal powers in the two expressions can be equated. Thus,

$$B_2 = A_2RT \qquad B_3 = (A_2^2 + A_3)R^2T^2 \qquad (4)$$

and

$$B_4 = (A_2^3 + 3A_2A_3 + A_4)R^2T^2$$

For most gases at moderate pressures (below ca. 50 to 100 atm), the squared and higher terms can be neglected, and equation (3) reads

$$Z = \frac{PV}{nRT} = 1 + A_2P \qquad (5)$$

This is a one-parameter equation of state (considering R as a constant). If the van der Waals equation of state (1873)

$$P = \frac{RT}{V/n - b} - \frac{a}{(V/n)^{2,}} \qquad (6)$$

is cast into a virial form in either (V/n) or P [1, 2] and the results are compared with equation (2) or (3) respectively, it becomes evident that

$$B_2 = b - \frac{a}{RT'} \qquad (7)$$

and

$$A_2 = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$$

The temperature dependence of B_2 and A_2 here is explicit. Expressions for the higher virial coefficients can also be obtained in terms of a and b. Thus the virial coefficients can be estimated from the van der Waals a and b constants. Alternatively, a and b can be determined from the temperature dependence of B_2 (or A_2).

The Beattie-Bridgeman (BB) equation (1927), is a five-parameter equation of state:

$$P = \frac{RT(1-E)(V/n + B)}{(V/n)^2} - \frac{A}{(V/n)^{2,}} \qquad (8)$$

where $A = A_o[1 - a/(V/n)], B = B_o[1 - b(V/n)]$, and $E = c/[(V/n)T^3]$. Thus the five parameters are A_o, B_o, a, b and c. This equation, which, because of the five parameters, works well over a wider pressure range, can be cast into a virial form (i.e. power series) in which the second coefficient is

$$B_2 = B_o - \frac{A_o}{RT} - \frac{c}{T^3} \qquad (9)$$

Here, only three of the BB parameters appear. [2]
Once A_2 (or B_2) is determined, the equation of state

$$PV_m = RT + B_2P, \qquad (10)$$

where V_m is the molar volume (see equation 5) can be used to obtain certain real gas properties such as the fugacity coefficient (γ), internal energy *(U)*, $C_p - C_v$, and the Joule-Thomson coefficient. As an example of how the simple equation of state [10] can be used, we will consider the calculation of the fugacity coefficient. The molar Gibbs free energy (chemical potential). μ, for a gas under ideal conditions ($P \rightarrow 0 or\ V \rightarrow \propto$) is expressed as

$$\mu^{id} = \mu^{o}(T) + RT\ \ln\left(\frac{P}{P^{o}}\right) \qquad (11)$$

where *P* is the pressure in atmosphere (P^o = 1 atm) and μ^o is the standard state chemical potential of the gas at 1 atm pressure and under "ideal gas conditions."

At higher pressures where gas imperfection cannot be ignored, equation (11) is modified to express the chemical potential as

$$\mu = \mu^{o}(T) + \ RT\ \ln\left(\frac{f}{f^{o}}\right) \qquad (12)$$

where *f* is called the *fugacity* of the gas. In other words, the fugacity of a gas is a quantity whose logarithm in equation (12) represents the actual chemical potential of the gas. Thus as $P \rightarrow 0,\ f \rightarrow P$, and if we take the standard state pressure to be 1 atm, the dimensions of fugacity must also be in atmospheres in order to make the equation quantitatively correct.

We wish to find out how the fugacity depends on pressure (so we can use a particular equation of state to determine *f*). At constant temperature, the pressure dependence of the chemical potential is simply $d\mu = V_m dP$. Using this expression along with (12) we get

$$d\mu = RT\ d(\ln f) = V_m dP \qquad (13)$$

In principle, this result could be intergrated to get ln *f* as a function of *P*. The problem is with the lower boundary condition: for *P = 0* (ideal gas), *f = P*, and thus ln *f* is not finite. We can get around this problem by expressing the fugacity as a factor, γ, times the pressure:

$$f = \gamma P, \qquad (14)$$

where γ is called the *fugacity coefficient*, There is an analogy here between the fugacity coefficient (for gases) and the activity coefficient (usually used for solutions). We recognize that, in the limit of zero pressure, γ → 1. Substituting equation (14) into (13), we get [$after\ using\ d(\ln P) = dP/P$]

$$RT\ d(\ln\gamma) = \left(V_m - \frac{RT}{P}\right)dP \qquad (15)$$

This equation is used for calculating fugacity coefficients. After integration (using the dummy variable *P*´) between *P*´ = 0 (where $\ln\gamma = 0$) and *P*´= *P*. (15) yields

$$\ln\gamma = \frac{1}{\mathrm{RT}}\int_0^{\mathrm{P}}\left(\mathrm{V_m} - \frac{\mathrm{RT}}{\mathrm{P'}}\right)\mathrm{dP'} \qquad (16)$$

The integrand in equation (16) is obtained from an equation of state. Notice that the *RT/P*´term in (16) would appear to be troublesome as P′ → 0: however, in this limit $V_m = RT/P'$ and the integrand vanishes.

From the simple equation of state presented in equation (10), $V_m = RT/P = B_2$, and using this result in equation (16) and integrating between 0 and P gives finally

$$\ln\gamma = \frac{B_2 P}{RT} \qquad [3,4] \qquad (17)$$

MATERIALS AND METHODS

In determining the second virial coefficient (B_2) experimentally, the most straightforward procedure would be to measure *Z* as a function of pressure and, assuming a linear relation to hold (up to moderate pressures), to plot *Z* vs. *P* [as implied in equation (15), thereby obtaining B_2 as the slope. While *P*, *V*, and *T* can be easily measured, the determination of *n* – the number of moles of gas – is not straightforward. A gravimetric technique is inappropriate because the mass of vapor in the system is a very small fraction of the total mass of the container (which is constructed of heavy-gauge metal so that it is capable of withstanding high pressures). An indirect method is therefore needed to determine *n*, and an approach developed by Burnett in 1936 [3] and recently modified by Baskett and Matthews [4] is particularly straightforward. It involves filling a bomb (the *sample cylinder*) with the gas to be studied at a moderately high pressure (ca. 20 atm), reading the pressure, and then withdrawing a small amount of gas so that it fills another, somewhat larger, container (the *expansion cylinder*) at a known, low pressure (less than 1 atm). The ideal gas law can then be applied to the gas in the expansion vessel, and thus the number of moles of gas withdrawn can be determined. A schemetic diagram of the experimental arrangement is shown in Figure 1.

The mathematical treatment of the above experimental method that leads to an expression of $Z = f(P)$ follows. Let V^e and V^s be the volumes of the expansion and sample cylinders, respectively. P^e and P^s are the corresponding gas pressures in these containers. The experiment is carried out at a controlled temperature, *T*. Initially, the sample cylinder is filled (at high pressure) with n_o moles of the gas to be studied. A small amount of the gas is transferred to the expansion cylinder

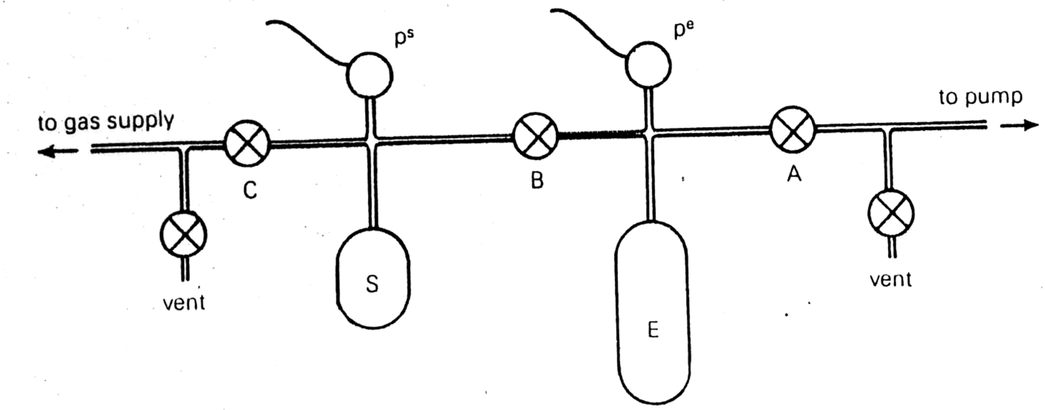

Figure 1: Schematic diagram of gas filling and handling apparatus. *S* and *E* are the sample and evacuation cylinders, and P^e and P^s are the respective pressure-sensing devices. The valves A, B, and C are indicated

which has been previously evacuated; the pressure then rises to $P^e{}_1$, which is not allowed to exceed ≈ 1 atm. In this way, the ideal gas law can be justifiably applied to the gas in the expansion cylinder. The pressure in the sample cylinder falls from $P^s{}_o$ to $P^s{}_1$. From the ideal gas law, the number of moles of gas *transferred* is

$$n_1 = P^e{}_1 v^e/RT$$

The expansion cylinder is then pumped out and refilled with another ≈ 1 atm amount of gas from the sample cylinder. The resulting pressures are now $P^e{}_2$ and $P^s{}_2$, and the number of moles transferred this time is $n_2 = P^s{}_o/RT$. The expansion cylinder is reevacuated and the cycle repeated until finally, in the *m*th transfer, the pressure in the sample cylinder drops to about 1 atm (or lower), i.e., $P^e{}_m = P^s{}_m$.

In order to proceed further, we must determine the number of moles of gas remaining in the sample cylinder after a given transfer. This is achieved as follows. The initial number of moles of gas in the sample cylinder, n_0, is equal to the number of moles of gas remaining after the *m*th expansion *plus* the total number of moles delivered via the individual transfers to the expansion cylinder; thus,

$$n_0 = \frac{1}{RT}(P_m^e V^s + P_1^e V^e + P_2^e V^s + \cdots + P_m^e V^e) \qquad (18)$$

or

$$n_0 = \frac{1}{RT}\left(P_m^e V^e + V^e \sum_{i=1}^{m} P_i^e\right)$$

where P_i^e is the pressure in the expansion cylinder after the *i*th expansion. Thus the number of moles of gas in the sample cylinder that remains after *r* expansions have been carried out is

]

$$n_r = n_0 - \sum_{i=1}^{r} n_i, \qquad (19)$$

where n_i is the number of moles of gas withdrawn in the *i*th expansion: $n_i = P_i^e V^e / RT$. Substituting n_i and n_o (equation 18) into (19) results in

$$n_r = \frac{1}{RT}\left(P_m^e V^s + V^e \sum_{i=1}^{r} P_i^m - V^e \sum_{i=1}^{r} P_i^e\right) \qquad (20)$$

or

$$n_r = \frac{1}{RT}\left(P_m^e V^s + V^e \sum_{i=r+1}^{m} P_i^e\right)$$

Using this result for n_r, we can now write the compressibility factor

$$Z_r = \frac{P_r^s V^s}{n_r RT} = \frac{P_r^s V^s}{P_m^e V^s + V^e \sum_{i=r+1}^{m} P_i^e} \qquad (21)$$

and this simplifies, after dividing by V_s, to

$$Z_r = \frac{P_r^s}{P_m^e + (V^e/V^e)\sum_{i=r+1}^{m} P_i^e} \qquad (22)$$

Equation (22) is the desired result and is the computational basis of this experiment. The measurables are $\{P_i^s\}$, the set of pressure readings in the sample cylinder, and $\{P_i^e\}$, the corresponding set of pressures in the expansion cylinder. The summation in equation (22) goes between (r + 1)th and the final *m*th, expansion, where *r* is a running index. The volume ratio, V^e/V^s, is separately measured by performing a gas expansion.

RESULTS AND DISCUSSION

The following readings were taken from the pressure sensing devices of the apparatus used:
Sample pressure, P^s = 19.6 atm
Pressure drop, P_m^e = 0.5 atm
Expansion pressure, P^e = 15, 10, 5 atm
Sample Volume, V^s = 418.5cm^3 at the 20 atm
Expansion volume, V^e = 1012.8cm^3 pressure
Temperature (operating) T = 373K

By using Equation (22), the compressibility factor, *Z* is calculated to be 0.268. For ideal behaviour, *Z* will be unity for all pressures and temperatures. For real gases, as the CO_2 studied, however, some deviation from unity will occur. So, the gas imperfection is apparent as the difference between the observed value of *Z* and unity. It is to be noted however, that at very low pressures almost all the gases have *Z* as unity and behave nearly perfectly. Deviations recorded at high pressures signify a higher molar volume than a perfect gas, because repulsive forces are now dominant.

Again, to obtain the second virial coefficient, B_2 the value of compressibility factor is substituted in Equation (5) and the result at the minimal pressure (0.01 atm) is -73.2. The values of virial coefficients of a gas are determined from measurements of its compressibility factor. An important point is that, although the equation of state of a real gas may coincide with the perfect gas law as $P \rightarrow 0$, not all its properties necessarily coincide with those of a perfect gas in that limit. Because several physical properties of gases depend on derivatives, the properties of real gases do not always coincide with the perfect gas values at low pressures. Again, since virial coefficients are temperature dependent, there are temperatures at which $Z \rightarrow 1$ with zero slope at low pressure or high molar volume. At this temperature, which is called the Boyle temperature, T_B, the properties of the real gas to coincide with those of a perfect gas as $P \rightarrow 0$.

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