

charcoal gave colorless crystals, melting at 154–156° C. This melting range corresponds with the range of values (154–160° C.) reported for 1,1'-binaphthyl and not with the 2,2' isomer (m.p. 187° C.) nor the 1,2' isomer (m.p. 79° C.). A mixture melting point with an authentic sample of 1,1'-binaphthyl was undepressed.

The 1,1'-bitetralyl should exist as the *meso* form and a *racemic* modification. The stereochemical composition of dimers of alkylbenzenes has been determined by gas chromatography (2). Using a similar column (1.5 meter column of Apiezon L on firebrick at 250° C.), the crystalline 1,1'-bitetralyl showed only a single well defined peak. The unrecrystallized distillate, however, showed two distinct peaks of approximately the same area. Adding a portion of the crystalline product to the liquid distillate reinforced the peak which emerged first. This indicated that during the recrystallization step one stereoisomer had been separated from the other. The mass spectrum of the liquid product was that characteristic of 1,1'-bitetralyl (very weak parent peak, major peak at  $m/e = 260$ , very intense fragment peak at  $m/e = 130$ ) which shows that the second peak on the chromatogram is not another bitetralyl isomer such as the 2,2'- or 5,5'-bitetralyl which have strong parent peaks. The NMR spectrum of the liquid distillate also

confirmed the 1,1'- linkage of the unrecrystallized distillate fraction. There were minor differences in the mass spectrum and the NMR spectrum between the crystalline product and the liquid distillate which were attributed to intrinsic differences between the stereoisomers. As expected, neither fraction was optically active. It is not known whether the crystalline product is *meso* or *racemic*.

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

- (1) Kharasch, M.S., McBay, H.C., Urry, W.H., *J. Org. Chem.* **10**, 401 (1945).
- (2) Morrison, Robert T., Unpublished results, New York University, New York.
- (3) Nenitzescu, C.D., Avram, M., *J. Am. Chem. Soc.* **72**, 3486 (1950).

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## Determination of Virial Coefficients by the Burnett Method

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Two methods of determining second and third virial coefficients with the Burnett apparatus are described. The first method is an improved way of determining the apparatus constant used in obtaining compressibility factors. The virials are then obtained from these compressibility factors in the conventional manner. The second method avoids the determination of the apparatus constant and furnishes the virial coefficients directly from the experimental data. This method is more accurate if the lowest pressures measured contain non random errors. Second and third virial coefficients for helium and nitrogen are compared by the two methods.

A METHOD for determining the volumetric behavior of gases which requires the measurement of only temperature and pressure on successive isothermal expansions was introduced by Burnett 1936 (1). Since its conception this expansion method has been applied by several investigators to measure compressibility over a wide range of temperature and pressure conditions (2, 10, 15, 16, 19, 21). Although its principal use has been for compressibility factors, the method has some attractive features for the evaluation of virial coefficients. It avoids not only the difficulties of precise measurement of volumes but also eliminates some of the uncertainties caused by adsorption encountered in the traditional low pressure volumetric methods. The virial coefficients can always be calculated from the compressibility factors, but the Burnett method as used earlier has required the evaluation of an apparatus constant which is a function of the cell volumes. This apparatus constant is evaluated from the measured pressure and temperature data

on a nearly ideal gas such as helium. These compressibility factors involve the apparatus constant raised to a power equal to the number of expansions. The evaluation of this constant requires a separate experimental investigation of great precision. The purpose of this paper is to show that virial coefficients and compressibility factors can be obtained directly from the pressure measurements on the unknown gas without requiring the evaluation of the apparatus constant and additional source of error which this entails. This procedure is limited to pressures at which the contribution of the fourth and higher virials is negligible. This means that the initial pressures at which the expansion begins must be slightly lower than when the apparatus constant method is used.

#### APPARATUS CONSTANT METHOD OF OBTAINING VIRIAL COEFFICIENTS

The Burnett apparatus consists of two vessels of unspecified volume connected to each other by means of an

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expansion valve and maintained at the same temperature by immersion in an isothermal bath. Initially, the first vessel is filled with the gas to be studied and its temperature and pressure are measured. The second vessel is evacuated. The expansion valve is then opened, and the pressures are allowed to equalize between the vessels. The second vessel is isolated and evacuated again and the expansions are continued until a pressure is reached which is low enough so that extrapolation to zero pressure is possible. The initial pressure is represented by  $P_0$ . Pressures after subsequent expansions are  $P_1, P_2, \dots, P_j$ . Before the  $j^{\text{th}}$  expansion, the following expression describes the gas in the first vessel:

$$P_{j-1}(V_1) = Z_{j-1} n_{j-1} RT_{j-1} \quad (1)$$

$V_1$  and  $V_2$  represent the total volumes of each of the two vessels. After equalization of the pressures, the equation of state becomes:

$$P_j (V_1 + V_2) = Z_j n_j RT_j \quad (2)$$

Since  $V_2$  is evacuated before each expansion, the number of moles remains unchanged so that  $n_{j-1} = n_j$ . In addition,  $T_{j-1} = T_j$  if the equilibrium temperature of the bath remains unchanged. Dividing Equation 2 by Equation 1 and rearranging yields:

$$\frac{P_j N_j}{Z_j} = \frac{P_{j-1}}{Z_{j-1}} \text{ where } N_j = \frac{(V_1 + V_2)}{(V_1)_{j-1}}, \text{ the apparatus constant.} \quad (3)$$

If the values of  $P_{j-1}/Z_{j-1}$  from Equation 3 for  $j \geq 2$  are successively substituted into Equation 3 for  $j=1$  the following relation is obtained:

$$\frac{P_j N_1 N_2 \dots N_j}{Z_j} = \frac{P_0}{Z_0} \quad (4)$$

From Equation 3, the value of the apparatus constant at zero pressure,  $N_{\infty}$ , is equal to the zero pressure limit of  $P_{j-1}/P_j$  since  $Z_j = Z_{j-1} = 1$  at zero pressure. Similarly the value of  $P_0/Z_0$  is obtained as the limit of the left hand side of Equation 4 as  $P_j$  approaches zero. Graphical or analytical methods can be employed to obtain each limit from the experimental data which consists of a series of decreasing pressures collected at a given temperature. Determination of an apparatus constant and the subsequent evaluation of virial coefficients has been discussed by Kramer and Miller (9) and by Silberberg, Kobe, and McKetta (21).

Canfield (4) has proposed a modified method of evaluating the apparatus constant at zero pressure which permits the use of higher pressure data. In terms of the virial expansion, a rigorous equation of the form,

$$Z = 1 + B/\bar{V} + C/\bar{V}^2 + D/\bar{V}^3 + \dots \quad (5)$$

can be written. Algebraic rearrangement gives,

$$(Z-1)\bar{V} = B + C/\bar{V} + D/\bar{V}^2 + \dots \quad (6)$$

where  $\bar{V}$  is the molal volume. Equation 6 requires that the variation of  $(Z-1)\bar{V}$  with  $1/\bar{V}$  be linear at sufficiently low density. Therefore, if the experimental values of  $(Z-1)\bar{V}$  plotted vs.  $1/\bar{V}$  can be shown to be linear within experimental error in a range of densities from a low density  $\rho_1$  to a higher density  $\rho_2$ , it is necessary according to Equation 6 that the plot be linear at all densities lower than  $\rho_1$ . This condition provides a powerful method for the accurate determination of  $N_{\infty}$ . Figure 1 shows that a value of  $N_{\infty}$  which is too small causes the value of  $\bar{V}(Z-1)$  to vary in a nonlinear manner at low density while at higher densities the variation becomes quite linear. Although the range of density in Figure 1 is not sufficient to show the behavior

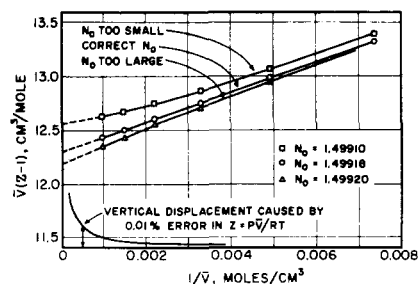


Figure 1. Determination of the second virial coefficient of helium at  $-90^{\circ}\text{C}$ . (Also shown is the effect of varying the value of  $N_0$ )

at the higher densities, the variation of  $\bar{V}(Z-1)$  with  $1/\bar{V}$  is essentially linear between 50 and 500 atm., the deviation from linearity occurring only at low density. Figure 1 also shows the behavior of  $(Z-1)\bar{V}$  for a value of  $N_{\infty}$  which is slightly too large. Canfield obtained a first approximation of  $N_{\infty}$  by the method of Equation 3 and then by trial and error adjusted this value slightly to meet the criterion of linearity of  $\bar{V}(Z-1)$  vs.  $1/\bar{V}$  at low pressure. With his experimental data, the values of  $N_{\infty}$  at a given temperature determined with different helium calibration runs agree within 1-2 parts in 100,000 while the agreement by the method of Equation 3 was usually 1 part in 10,000.

Once the value of  $N_{\infty}$  at a particular temperature was ascertained with helium calibration runs, Canfield used the following procedure in evaluating the second and third virial coefficients for the mixtures under study. Since the apparatus constant varied slightly with pressure because of distortion in the cell volumes and a shift in the null point of the differential pressure indicator, the values of  $N_j$  for Canfield's equipment were calculated by the equation

$$N_j = N_{\infty} \frac{1 + aP_j}{1 + bP_{j-1}} \quad (7)$$

where  $a = 2.06 \times 10^{-6} \text{ atm.}^{-1}$  and  $b = 2.08 \times 10^{-6} \text{ atm.}^{-1}$ . Using the corrected values of  $N_j$ , the value of  $P_0/Z_0$  was obtained by extrapolating the low pressure values of  $P_j N_1 N_2 \dots N_j$  to zero pressure. The extrapolation was carried out analytically by least-square fitting the last four to seven values of  $P_j N_1 N_2 \dots N_j$  to first- or second-degree polynomials in pressure. Equation 4 was then used to calculate the compressibility factors at the experimental pressures. The values of  $Z$  are used with Equation 6 to determine the second and third virial coefficients defined by:

$$B = \lim_{1/\bar{V} \rightarrow 0} [\bar{V}(Z-1)]_T \quad (8)$$

$$C = \lim_{1/\bar{V} \rightarrow 0} \left[ \frac{\bar{V}(Z-1)}{(1/\bar{V})} \right]_T \quad (9)$$

Canfield (3) has shown that the apparatus constant is also affected significantly by temperature changes and must be determined separately for each isotherm.

#### DIRECT METHOD OF OBTAINING VIRIAL COEFFICIENTS

The data required in order to determine the second virial coefficient by this method are the measured pressures and temperatures, an estimate of the random experimental errors in these, an estimate of the expected values of  $B$  and  $C$ , and an order of magnitude estimate of the errors in  $B$  and  $C$ .

The expansion in the cell prior to measuring the  $(j + 1)^{\text{th}}$  pressure is expressed by:

$$\frac{P_j}{Z_j} = \frac{P_{j+1}N_{j+1}}{Z_{j+1}} \quad (10)$$

Equation 7 shows that  $N$  does not change by more than 3 parts in  $10^5$  between adjacent expansions. Consequently, ( $N_{j+1} = N_j$ ) and Equations 3 and 10 lead to:

$$\left(\frac{P_j}{Z_j}\right)^2 - \left(\frac{P_{j-1}P_{j+1}}{Z_{j+1}Z_{j-1}}\right) = 0 \quad (11)$$

There are two infinite series expansions which are used for the compressibility factor  $Z = P\bar{V}/RT$ , the one given in Equation 5 and the series in Equation 12;

$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (12)$$

For historical reasons Equation 5 is known as the Leiden expansion and Equation 12 as the Berlin expansion. If the pressure is not too high, an isotherm can be represented by Equation 5 when it has been truncated after the third coefficient in the form:

$$Z = \left[1 + B \frac{1}{\bar{V}} + C \left(\frac{1}{\bar{V}}\right)^2\right] \quad (13)$$

At pressures for which Equation 13 is valid, isothermal plots of  $(Z - 1)\bar{V}$  vs.  $1/\bar{V}$  should be linear with  $B$  as the intercept and  $C$  as the slope. The direct method determines the virials from experimentally measured pressures at which Equation 13 represents an isotherm within the experimental error. Scott and Dunlap (20) and Canfield (3) have discussed the relative linearity of plots of this type for the Leiden and Berlin expansions. The pressure region over which Equation 13 is valid is often larger than the range over which a similar abbreviation in the form:

$$Z = [1 + B'P + C'P^2] \quad (14)$$

is adequate. The Berlin fourth virial  $D'$  in Equation 12 becomes an important contributor to the series at a pressure much lower than that at which it becomes necessary to add the Leiden virial  $D$  in Equation 5.

Since volumes are never measured in the Burnett method, one can express compressibility factor isotherms in terms of experimental data only with the Berlin expansion in powers of the pressure. However, in view of the much more rapid convergence of the Leiden expansion in terms of reciprocal volumes, it is necessary to predict the Leiden coefficients  $B$  and  $C$ . This can be done by developing a new type of Berlin expansion in the form:

$$Z = 1 + a_1P + a_2P^2 + a_3P^3 + \dots + a_nP^n + \dots \quad (15)$$

The coefficients  $a_n$  are not necessarily the true virials of the Berlin expansion but are the proper coefficients to make Equation 15 equal to the truncated Leiden series in Equation 13. The general relationship between all the virial coefficients in the Leiden and Berlin expansions has been presented by Putnam and Kilpatrick (17) and the coefficients in Equation 15 may be found by applying this relationship when the Leiden expansion contains only the  $B$  and  $C$  virials. The result relates the coefficients  $a_n$  to the Leiden  $B$  and  $C$  terms as follows:

$$a_n = \sum_{k=0}^{\frac{n}{2}} \left[ \frac{(-1)^{n-k-1} (2n-k-2)!}{(RT)^n (n-1)!} \frac{B^{n-2k} C^k}{(n-2k)! k!} \right] \quad (16)$$

The upper limit of the summation in Equation 16 means that the index,  $k$ , terminates at the integral value nearest to, but less than,  $(n/2)$ . Thus, the first coefficient  $a_1$  has only one term in the sum for which  $n = 1, k = 0$ :

$$a_1 = \frac{B}{RT} \quad (17)$$

For  $n = 2, k = 0, 1$ :

$$a_2 = \frac{C - B^2}{(RT)^2} \quad (18)$$

and similarly for all higher coefficients. In using Equation 15 the expansion was continued until two values of  $Z$  for consecutive values of  $n$  differed by less than one part in  $10^6$ .

The first step in applying the direct method is to select from among the experimentally determined pressures on successive expansions, the maximum pressure for which Equation 13 is valid within experimental error. This pressure is first selected by trial and must be checked later. The virial calculation is then possible by an iteration process which proceeds as follows: An initial value of  $B$  alone is used to begin the iteration. This first trial  $B$  value may be obtained from a corresponding states plot of  $B/Vc$  vs.  $T/Tc$  such as that presented by Danon and Pitzer (5) or by McGlashan and Potter (11). This first value of  $B$  is then used to obtain a first trial value of  $C$  and an improved  $B$  value. These  $B$  and  $C$  values then furnish improved values of both  $B$  and  $C$  and so on until convergence.

The initial  $B$  value is applied at pressures below some value intermediate between the maximum pressure at which Equation 13 is valid and the lowest measured pressure. In this pressure range Equation 13 is assumed replaceable by:

$$Z = 1 + \frac{B}{\bar{V}} \quad (19)$$

The coefficients  $a_n$  which made Equation 15 equivalent to Equation 19 are designated as  $a'_n$  values and are obtained from Equation 16:

$$a'_n = \sum_{k=0}^{\frac{n}{2}} \left[ \frac{(-1)^{n-k-1} (2n-k-2)!}{(RT)^n (n-1)!} \frac{B^{n-2k}}{(n-2k)!} \right] \quad (20)$$

Each three successive pressures in this range can now be used to furnish an apparent value of  $B$ . This is obtained by substituting Equation 15, with coefficients expressed by (20), into Equation 11 which becomes:

$$\frac{P_j^2}{P_{j+1}P_{j-1}} - \frac{\left(1 + \sum_{n=1}^{\infty} a_n P_j^n\right)^2}{\left(1 + \sum_{n=1}^{\infty} a_n P_{j+1}^n\right) \left(1 + \sum_{n=1}^{\infty} a_n P_{j-1}^n\right)} = 0 \quad (21)$$

The coefficients  $a_n$ , at this state, are the values  $a'_n$  which depend on  $B$  alone. Consequently, Equation 21 can be solved for  $B$  by trial and error using the initial value from the corresponding states plot as first trial. Because of the approximate nature of Equation 19, the result is not the correct  $B$  value but is designated as an apparent value of  $B'_j$  associated with the pressure  $P_j$ . Each three successive pressures in the range where Equation 19 is reasonable then furnish an apparent  $B'_j$  value in this manner. Now

the approximation for  $1/\bar{V}_j$  at each of these pressures  $P_j$  is:

$$\frac{1}{\bar{V}_j} = \frac{P_j}{RT \left[ 1 + \sum_{n=1}^{\infty} a_n P_j^n \right]} \quad (22)$$

where the  $a_n$  values are evaluated with the apparent  $B_j'$  values by Equation 20. Using these  $a_n$  values, a plot of:

$$RT \left( \sum a_n P_j^{n-1} \right) (1 + \sum a_n P_j^n) \text{ vs. } \frac{P_j}{RT (1 + \sum a_n P_j^n)}$$

should be linear in this range. The intercept at  $P_j = 0$  is a better value of  $B$  and the slope of the line gives the initial value for  $C$ . This is the equivalent of a plot of  $(Z-1)\bar{V}$  vs.  $1/\bar{V}$  in the determination of virial coefficients from  $P$ - $V$ - $T$  data.

These values of  $B$  and  $C$  are now improved by extending the groups of three successive pressures up to the maximum pressure at which Equation 13 is valid. Instead of using  $a_n$  values as the coefficients in Equation 21, the  $a_n$  values obtained from Equation 16 involving both  $B$  and  $C$  are now used. The first trial  $C$  value is now assigned to the  $C$  term in the  $a_n$  coefficient and Equation 21 is once more solved by trial and error for an apparent value of  $B_j'$  at each pressure  $P_j$ . This time the improved  $B$  value from the previously obtained intercept is used as first trial solution. These apparent  $B_j'$  values are then used to plot  $RT \left( \sum a_n P_j^{n-1} \right) (1 + \sum a_n P_j^n)$  once more against  $P_j/RT (1 + \sum a_n P_j^n)$  but the  $a_n$  terms now involve both a  $B$  and  $C$  term. The intercept of the best straight line fit gives a better value for  $B$  and the slope of this line yields a better value of  $C$ . This process is then continued until the  $B$  and  $C$  values do not change.

During this iteration process it is important to establish a criterion for fitting the best straight lines to the plots of  $RT \left( \sum a_n P_j^{n-1} \right) (1 + \sum a_n P_j^n)$  vs.  $P_j/RT (1 + \sum a_n P_j^n)$ . Since the Burnett method must measure pressure changes at constant volume, the apparatus must have a differential pressure indicator to indicate pressure equivalence between the gas in the apparatus cell and an external pressure transmission fluid. Low pressure measurements become more inaccurate because this indicator must operate with a negligible displacement to preserve constant volume conditions. Other slight errors in pressure also become more important at low pressures. This sets a limit on how low a pressure can be measured. If low enough pressures are measured there will inevitably be an important relative error in the data at low pressures in any Burnett apparatus. Furthermore, in the direct virial determination, if pressures are high enough so that Equation 13 is no longer valid, there will be deviation from linearity at the high pressure end. Consequently, a weighting procedure must be used in fitting the best straight line.

A study of the general problem of fitting best straight lines when both ordinate and abscissa are subject to experimental error has been made by Madansky (12). He has shown that when the expected errors  $\delta y$  in an ordinate  $y$  and  $\delta x$  in an abscissa  $x$  are zero and are uncorrelated with  $n$  observed quantities then the best straight line,  $y = mx + b$ , will produce a minimum in:

$$\sum_{j=1}^n \left( \frac{k}{(\delta y_j)^2 + m^2 (\delta x_j)^2} \right) (y_j - b - mx_j)^2 \quad (23)$$

where  $k$  is a proportionality constant which appears in a weighting factor coefficient of the square of the deviation of  $y_j$  from its prediction by  $(mx_j + b)$ . In the application here,  $k$  is taken as unity, the slope  $m$  is the third virial coefficient  $C$ , and the intercept  $b$  is the second virial  $B$ .

The ordinate  $y_j$  is the equivalent of  $(Z-1)\bar{V}$ :

$$y_j = RT \left( \sum a_n P_j^{n-1} \right) (1 + \sum a_n P_j^n) \quad (24)$$

and  $x_j$ , the equivalent of  $1/\bar{V}$ , is:

$$x_j = \frac{P_j}{RT (1 + \sum a_n P_j^n)} \quad (25)$$

In the particular experimental data analyzed here, errors due to temperature proved to be negligible. The only error induced was thus assumed to be that due to errors in the measured pressures. The error in  $y_j$  caused by a small error  $\delta P_j$  in pressure is (25):

$$(\delta y_j)^2 = \left( \frac{\partial y_j}{\partial P_j} \right)^2 (\delta P_j)^2 + \sum_n \left( \frac{\partial y_j}{\partial a_n} \right)^2 (\delta a_n)^2 \quad (26)$$

Since all the straight line fitting is carried out with a constant  $C$ , the error in the  $a_n$  coefficients is caused by pressure errors which alter the value of  $B'$  obtained from Equation 21. The error in any coefficient  $a_n$  is then obtained from Equation 16 as:

$$(\delta a_n) = \sum_{k=0}^{n-2} \frac{(-1)^{n-k-1} (n-2k) (2n-k-2)! C^n (B')^{n-2k-1} (\delta B')}{(RT)^n (n-1)! (n-2k)! k!} \quad (27)$$

And the error in  $B'$  due to pressure errors is

$$(\delta B')^2 = \left( \frac{\partial B'}{\partial P_j} \right)^2 (\delta P_j)^2 + \left( \frac{\partial B'}{\partial P_{j+1}} \right)^2 (\delta P_{j+1})^2 + \left( \frac{\partial B'}{\partial P_{j-1}} \right)^2 (\delta P_{j-1})^2 \quad (28)$$

The coefficients in Equation 28 could be determined numerically by substituting the errors in  $P_j$ ,  $P_{j+1}$ , and  $P_{j-1}$  into Equation 21 and calculating the effect on the  $B'$  value which solves the equation. This error  $(\delta B')$  could then be substituted into Equation 27 and the resulting  $(\delta a_n)$  substituted into Equation 26. Fortunately however, small errors in pressure do not usually have an effect on the  $B'$  values obtained from Equation 21. In fact, if the error in pressure is proportional to the magnitude of the pressure so that:

$$\left| \frac{\delta P_j}{P_j} \right| = \left| \frac{\delta P_{j-1}}{P_{j-1}} \right| = \left| \frac{\delta P_{j+1}}{P_{j+1}} \right| \quad (29)$$

then the error in the calculated  $B'$  value is zero when all the pressure errors are in the same direction or when the errors in  $P_{j-1}$  and  $P_{j+1}$  are in the same direction and opposite to the error in  $P_j$ . The work of Canfield (3) showed that Equation 29 is approximately true except at very low pressures. This means that the  $(\delta a_n)$  errors in Equation 26 are zero and Equation 26 involves only errors in  $P_j$ . When  $y_j$  is defined by Equation 24, Equation 26 then becomes:

$$(\delta y_j)^2 = [RT \left( \sum a_n n P_j^{n-1} \right) (1 + 2 \sum a_n P_j^n)]^2 (\delta P_j)^2 \quad (30)$$

In a similar manner:

$$(\delta x_j)^2 = \left[ \frac{1}{RT} \left( \frac{1}{1 + \sum a_n P_j^n} \right) \left( 1 - \frac{\sum a_n n P_j^n}{1 + \sum a_n P_j^n} \right) \right]^2 (\delta P_j)^2 \quad (31)$$

Equations 30 and 31 are then used in Equation 23 and the straight lines are fitted to produce minimum values of:

$$\sum_{j=1}^n \left[ \frac{(y_j - B - Cx_j)^2}{(\delta y_j)^2 + C^2 (\delta x_j)^2} \right] \quad (32)$$

The only remaining difficulty is the fact that the highest pressure chosen must be tested to make sure that fourth virials are negligible over the range. This test is carried out by repeating the determination starting with the next lowest pressure. The final virials must be independent of the starting pressure. If this is not the case the series beginning with the highest pressure must be discarded and the starting pressure lowered until this independence is achieved. The choice of too high a starting pressure can also cause nonconvergence of Equation 15.

### COMPARISON OF THE TWO METHODS

In Table I the virial coefficients of helium and nitrogen calculated by the direct method and by the apparatus constant method are listed with values reported by other investigators. Calculations for the direct method were carried out with a Control Data Corp. 1604-A digital computer. The two methods compared in this study both used the experimental data of Canfield (3). The results in Table I are obtained from the combination of two separate series of expansions at each temperature.

In the direct method the lowest three or four experimental points were essentially excluded by the weighting factor. However, these points did not scatter from the best linear fit in a random manner but usually followed a trend. This is shown in Figures 2 and 3. These low pressure points generally lie above the line and become farther from it as the pressure is lowered. The error analysis does not apply

to systematic errors and although these points are given a low weight by the function in Equation 32 they do have a noticeable influence due to their nonrandom character.

Consequently these points were neglected entirely. They are shown as solid points in Figures 2 and 3. This deviation is probably caused by the fact that the low pressures measured at the end of the expansion are likely to be relatively less accurate due to frictional resistance in the dead weight gage piston and low pressure insensitivity of the differential pressure indicator. Although the apparatus has been considerably improved since taking the data used here, there is always some low pressure limit in any Burnett determination at which pressures will tend to deviate in this manner.

The advantage of the direct method lies in the fact that the more accurate higher pressure points can define the linear relation. Low pressure points should be deleted successively beginning with the lowest observed pressure as long as the summation in Equation 32 decreases with the deletions. When this sum stops decreasing and begins to fluctuate, no further deletions should be made.

The accuracy of the pressure measurements using a dead weight gage is limited by the accuracy to which the effective piston area is known. The first term in Equation 21 is independent of this area and the second term becomes so at low pressures. The zero pressure limit of both terms is equal to 1. Calculations by the direct method for one isotherm show that a shift of all  $P_i$  by one part in  $10^4$  in one direction (equivalent to an error in the piston area of 0.01% in the opposite direction) causes only a 0.013% change in  $B$  and a

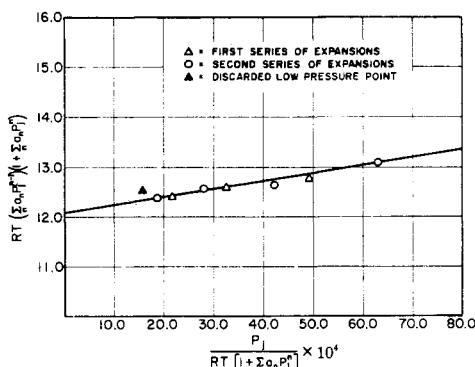


Figure 2. Determination of  $N_2$  virial coefficients by the direct method.  $T = 183.15^\circ \text{K}$ .

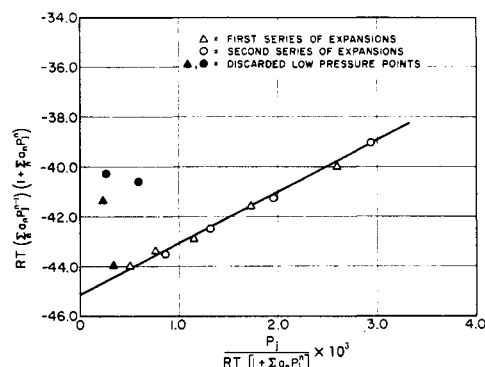


Figure 3. Determination of He virial coefficients by the direct method.  $T = 183.15^\circ \text{K}$ .

Table I. Comparison of Virial Coefficients Obtained

Temp., ° K.	Direct Method		Apparatus Method (3, 4)		Other Investigations $B$ (Cc./Mole)
	$B$ (cc./mole)	$C$ (cc./mole) <sup>2</sup>	$B$ (cc./mole)	$C$ (cc./mole) <sup>2</sup>	
	$N_2$				
273.15	-10.56	1573	-9.70	1416	-9.50(23) -10.34(8) -11.11(22) -10.27(14)
223.13	-26.05	1850	-25.17	1636	-26.37(8)
183.15	-45.15	2119	-45.35	2132	
158.15	-64.14	2530	-63.50	2414	
143.14	-79.59	2914	-79.56	2920	-79.76(8)
133.15	-91.99	3119	-91.95	3100	
	$He$				
273.15	11.96	117.5	12.09	116	12.08(24) 11.86(13) 11.97(18) 11.48(9) 11.85(7)
223.13	12.23	121.8	12.46	108	11.93(7) 11.59(9)
183.15	12.09	149	12.30	150	
158.15	11.98	163.8	12.25	156	
143.14	11.84	175	12.20	159	
133.15	11.97	172	12.10	182	

0.04% change in  $C$ . A shift of 1:1000 of the  $P_1$  caused only a 0.05% change in  $B$  and a 0.13% change in  $C$ . Thus, a small systematic error in the piston area does not make an important change in the virial coefficients when the direct method is used.

In the apparatus constant method the value of the constant at zero pressure must be determined very precisely. Errors in this constant introduce an error in the compressibility factor which increases as the number of expansions increase. The method of determining the constant using helium in a pressure range where fourth virials are negligible is shown in Figure 1. The proper selection of the zero pressure constant is indicated by a linear relationship resulting. Unfortunately, the deviations from linearity are shown most sensitively by the low pressure points and these points are most influential in determining the constants as shown in Figure 1. As has been discussed above these points are the least accurate and may have a systematic error. The scatter in these points is considerably dampened in the apparatus constant method since the compressibility factors at which they are determined are calculated from higher pressures in the expansion. However, even a small systematic error in these points will cause a significantly erroneous choice of the apparatus constant necessary to linearize them. Since the lower pressures are generally too high, this causes the second virial coefficient, as given by the intercept in Figure 1, to be too large. In almost every case the second virials of the apparatus constant method are larger than those predicted by the direct method.

Because many of the difficulties in the apparatus constant method are avoided, the direct method proposed here is the more accurate procedure for the determination of virial coefficients from Burnett data. The data obtained by Canfield are very accurate over a wide pressure range and the pressure at which the systematic errors begin is quite low. Consequently the results of the two methods for these data are very close. If all pressures could be determined with equal relative accuracy with no nonrandom deviations at low pressures, then the results of the two methods should be identical.

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#### LITERATURE CITED

- (1) Burnett, E.S., *J. Appl. Mech., Trans. ASME* **58**, A136 (1936).
- (2) Cook, D., *Can. J. Chem.* **35**, 268 (1957).
- (3) Canfield, F.B., Ph.D. Thesis, Rice University, Houston, Texas, 1962.
- (4) Canfield, F.B., Leland, T.W., Kobayashi R., *Advan. Cryog. Eng.* **8**, p. 146, Plenum Press, New York, 1963.
- (5) Danon, F., Pitzer, K.S., *J. Chem. Phys.* **36**, 425 (1962).
- (6) Hill, T.L., "An Introduction to Statistical Thermodynamics," p. 261, Addison-Wesley, Reading, Mass., 1960.
- (7) Holborn, L., Otto, J., *Z. Phys.* **23**, 77 (1924).
- (8) *Ibid.* **33**, 1 (1925).
- (9) Keesom, W.H., "Helium", Elsevier, Amsterdam, (1942).
- (10) Kramer, G.M., Miller, J.G., *J. Phys. Chem.* **61**, 785 (1957).
- (11) McGlashan, M.L., Potter, D.J.B., *Proc. Roy. Soc. (London)* **A267**, 478 (1962).
- (12) Madansky, A., *J. Am. Stat. Assn.* **54**, 173 (1959).
- (13) Michels, A., Wouters, H., *Physica* **8**, 923 (1941).
- (14) Michels, A., Wouters, H., DeBoer, J., *Ibid.* **1**, 587 (1934).
- (15) Mueller, W.H., Leland, T.W., Jr., Kobayashi, R., *A.I.Ch.E.J.* **7**, 267 (1961).
- (16) Pfefferle, W.C., Goff, J.A., Miller, J.G., *J. Chem. Phys.* **23**, 509 (1955).
- (17) Putnam, W.E., Kilpatrick, J.E., *J. Chem. Phys.* **21**, 951 (1953).
- (18) Schneider, W.G., *Can. J. Res.* **27B**, 339 (1949).
- (19) Schneider, W.G., Duffie, J.A.H., *J. Chem. Phys.* **17**, 751 (1949).
- (20) Scott, R.L., Dunlap, R.D., *J. Phys. Chem.* **66**, 639 (1962).
- (21) Silberberg, I.H., McKetta, J.J., Kobe, K.A., *J. CHEM. ENG. DATA* **4**, 314, 323 (1959).
- (22) Verschoyle, T.T.H., *Proc. Roy. Soc. (London)* **A111**, 522 (1926).
- (23) White, D., Ohio State University, *Eng. Exp. Sta. News* **24**, No. 3, 12 (1952).
- (24) White, D., Rubin, T., Camky, P., Johnson, H.L., *J. Phys. Chem.* **64**, 1607 (1960).
- (25) Young, H.D., "Statistical Treatment of Experimental Data," McGraw-Hill, New York, 1962.

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## Thermoanalytical Study of Lithium Chlorate

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**E**LUCIDATION of the trends in thermal stability and of those chemical and physical processes occurring during the pyrolysis of the alkali metal (M) perchlorates has been facilitated through application of differential thermal analysis (DTA) and of thermogravimetric analysis (TGA) (39). In contrast, the alkali metal chlorates appear not to have been studied systematically by the use of these techniques. Accordingly, the present investigation of the thermal decomposition of  $\text{LiClO}_3$  was undertaken with the views in mind of gauging the applicability of DTA and of TGA in this area, of defining the order of thermal

stability of the lithium compounds of chlorine-containing oxyanions ( $\text{ClO}_x^-$ ,  $x = 1, 2, 3, 4$ ), and ultimately, of determining the pyrolysis relationships among the alkali metal chlorates in general.

#### EXPERIMENTAL

**Thermoanalytical Techniques.** DTA experiments to about 700° were performed in a closed muffle furnace with equipment previously described (35, 39, 44) in conjunction with calibrated chromel-alumel thermocouples (24 B. and S. gage) and quartz sample tubes (3 inches  $\times$  1/2 inch o.d.