# An Analytical Method of Determining Second Virial Coefficients from Intermediate Pressure Compressibility Data

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A LARGE NUMBER of modifications of the perfect gas law have been put forward to describe the behavior of nonideal gases. These equations of state are largely empirical, and involve constants which must be determined experimentally.

Kamerlingh-Onnes (*5*) was the first to suggest that for any gas, the expression of the compressibility factor, $Z$, in terms of an infinite series in $1/V$ is a valid representation for the isothermal $P$-$V$-$T$ characteristics. Thus,

$$Z = PV/RT = 1 + B'/V + C'/V^2 + D'/V^3 + \dots \tag{1}$$

or

$$Z = PV/RT = 1 + BP + CP^2 + DP^3 + \dots \tag{2}$$

where

$P$ = pressure
$V$ = molal volume
$T$ = absolute temperature
$R$ = gas constant
and $B = B'/RT$; $C = (C' - B'^2)/(RT)^2$; etc.

The coefficients $B'$, $C'$, and $D'$ are termed the second, third, and fourth virial coefficients, which for any particular gas are functions of the temperature only. Furthermore, $B'$, $C'$, and $D'$ give a measure of the deviations from ideality due to binary, ternary, and quaternary molecular interactions.

The virial coefficients of a gas can be predicted from theoretical considerations, provided the potential energy of attraction of the molecules is known in terms of the fundamental molecular characteristics.

At present, the agreement between theory and experiment is satisfactory for the second virial coefficient for only a few gases, because the functions which express the potential energy of a system in terms of the physical variables are not accurately known except for simple atoms and molecules.

## EXPERIMENTAL EVALUATION OF SECOND VIRIAL COEFFICIENTS

The most common method of determining the second virial coefficients from experimental compressibility data is a graphical one. In this method, the virial equation is rearranged to give a function which, when plotted *vs.* $1/V$ or $P$ gives as its intercept $-B'$ or $-B$. The required rearrangements are:

$$(1 - Z)V = -B' - C'/V - \dots \qquad (1 - Z)/P = -B - CP - \dots$$

$$\lim_{1/V \to 0} (1 - Z)V = -B' \qquad \lim_{P \to 0} (1 - Z)/P = -B$$

In the limits described above, $Z$ approaches unity as $P$ approaches zero, and consequently, small errors in $Z$ become large errors in $1 - Z$. It therefore follows that the graphical methods require extremely accurate compressibility data at very low pressures. For $P$-$V$-$T$ data taken at relatively high pressures, the location of the intercepts in a plot of $(1 - Z)V$ *vs.* $1/V$ or $(1 - Z)/P$ *vs.* $P$ involves considerable subjectivity.

It is also possible to determine the second virial coefficients analytically. On fitting Equation 2 to the experimental $P$-$V$-$T$ measurements by means of a least squares procedure, unique values of the coefficients $B$, $C$, ... are obtained. Furthermore, if the errors in the experimental measurements are normally distributed, the values obtained for $B$, $C$, ... will also be the most probable estimates of these coefficients.

In the face of the practical impossibility of calculating an infinite series, some workers (*8*) have adopted as an approximation a finite series of the form

$$Z = 1 + A_1P + A_2P^2 + A_3P^j \tag{3}$$

where $j$ is usually assigned a value of 4. It is assumed in this equation that deviations from ideality due to molecular interactions higher than ternary will be included in the single term $A_3P^j$.

A similar approach (*4*) is to adopt a finite polynomial

$$Z = \sum_{i=0}^{i=k} A_iP^i \tag{4}$$

where the value of $k$ is assigned arbitrarily.

In each of these methods, $A_1RT$ is taken to be the second virial coefficient.

In this article, a method is outlined for determining the number of terms of a finite polynomial appropriate to each particular set of isothermal compressibility data.

For a compressibility-pressure isotherm, the coefficients $A_i$ in Equation 4 can be evaluated uniquely by a least squares procedure. As the value of $k$ increases, a closer reproduction of the experimental data points is achieved, so that for $n$ data points, a polynomial order $n - 1$ will reproduce the experimental data points identically. However, if the polynomial is to be acceptable for purposes of interpolation and estimation of virial coefficients, it must satisfy the restrictions imposed by the shape of the isotherm as indicated by the trend of the experimental data.

## RESTRICTIONS ON ANALYTICAL SOLUTION

The restrictions which are to be satisfied by the least squares solutions of Equation 4 will be examined in relation to the compressibility data of 2-methylbutane (*9*).

The data were obtained on a Burnett apparatus which did not permit measurements to be made within the pressure range of 0 to 1 atm. In calculating the coefficients $A_i$, all the data points which conform with the trend of the isotherms at low pressures were employed. These include the compressibilities at pressures up to saturation for isotherms below the critical temperature, and compressi-

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bilities at pressures below the critical region for isotherms above the critical temperature. Table I gives the temperatures at which isotherms were determined, the pressure range for each isotherm, the saturation pressure, and the number of experimental points available for each isotherm.

For each isotherm, the coefficients $A_i$ in Equation 4 were calculated by a least squares routine for $k = 1, 2, 3, \ldots, n - 1$. The plots of $Z$ *vs.* $P$ for 2-methylbutane (*9*) indicate clearly that the slope and the curvature of each isotherm are negative over the entire range of pressures examined. As a result, any polynomial in which both the coefficients $A_1$ and $A_2$ are not negative is not acceptable, because these coefficients are related to the slope and the curvature of the isotherms as $P$ approaches zero as follows:

$$A_1 = (\partial Z/\partial P)_{P=0} \qquad 2A_2 = (\partial^2 Z/\partial P^2)_{P=0}$$

For the polynomials in which both $A_1$ and $A_2$ are negative, if their curvature is negative over the entire range of pressures, then their slopes are also negative over the same range. This follows from the fact that a polynomial is a single valued, continuous function.

Table I. Temperature and Pressure Ranges of Compressibility Isotherms

| Temp., °C. | Pressure Range, Atm. | Saturation Pressure, Atm. | No. of Points[a] |
|---|---|---|---|
| 50 | 0– 2.0 | 2.025 | 8 |
| 75 | 0– 3.9 | 3.983 | 14 |
| 100 | 0– 7.0 | 7.106 | 21 |
| 125 | 0–11.6 | 11.787 | 25 |
| 150 | 0–18.1 | 18.449 | 29 |
| 175 | 0–27.4 | 27.556 | 34 |
| 188.5 | 0–31.7 | [b] | 21 |
| 200 | 0–37.7 | [b] | 30 |

[a] Includes $P = 0.0000$, $Z = 1.0000$.

[b] Critical temperature of 2-methylbutane is 187.8° C.

## SECOND VIRIAL COEFFICIENTS OF 2-METHYLBUTANE

The order of the acceptable polynomials of $Z$ in terms of $P$—i.e., those which describe the isotherm correctly as to slope and curvature—and their coefficients $A_i$ are given in Table II. The negativity of the curvature of each polynomial was ascertained by examining its second derivative at regular intervals of 0.05 atm. from $P = 0$ up to the maximum pressure.

For each isotherm, the value of the coefficient $A_1$ which occurs in the highest order acceptable polynomial was chosen to estimate the value of $B'$, ($B' = A_1RT$), the second virial coefficient. The values of $A_1RT$ are given in Table III.

In Table IV, a comparison is given between the percentage residuals, $(Z_{\text{obsd.}} - Z_{\text{calcd.}})\,100/Z_{\text{obsd.}}$, and the estimated maximum experimental errors (*9*) in determining the values

Table II. Coefficients $A_i$ of All Acceptable Polynomials $Z = \sum_{i=0}^{i=k} A_i P^i$

| Temp., °C. | $k$ | $A_0$ | $A_1 \times 10^2$ | $A_2 \times 10^4$ | $A_3 \times 10^5$ | $A_4 \times 10^6$ |
|---|---|---|---|---|---|---|
| 50 | 1 | 0.99960816 | −3.6584917 | | | |
| 75 | 1 | 1.0028402 | −2.9576883 | | | |
| | 2 | 0.99952888 | −2.5324205 | −10.284228 | | |
| | 4 | 1.0000048 | −2.5832263 | −17.162174 | 63.049460 | −113.65423 |
| | 5 | 1.0000053 | −2.5936475 | −15.253042 | 50.754788 | −80.423967 |
| 100 | 1 | 1.0047020 | −2.4345525 | | | |
| | 2 | 0.99881099 | −1.9525196 | −6.7251232 | | |
| | 3 | 0.99988468 | −2.1187441 | −0.81268160 | −5.5814615 | |
| 125 | 1 | 1.0072075 | −2.0550094 | | | |
| | 2 | 0.99771404 | −1.5245690 | −4.6710511 | | |
| | 4 | 0.99991109 | −1.7231826 | −1.1662607 | −0.53093630 | −1.1250019 |
| | 6 | 0.99997981 | −1.6854939 | −7.2994107 | 28.261556 | −57.612598 |
| | 8 | 1.0000090 | −1.7178162 | −4.4384247 | 25.456424 | −96.395228 |
| 150 | 1 | 1.0115168 | −1.7781456 | | | |
| | 2 | 0.99598463 | −1.1523503 | −3.6683986 | | |
| | 4 | 0.99933014 | −1.3474609 | −2.1188107 | 0.89982920 | −0.72638324 |
| 175 | 1 | 1.0231045 | −1.6579654 | | | |
| | 2 | 0.98970414 | −0.73059102 | −3.4903931 | | |
| | 4 | 0.99736594 | −0.93372900 | −5.4546598 | 3.4277563 | −0.93467584 |
| | 6 | 0.99949764 | −1.1004047 | −3.7364872 | 6.5442843 | −6.3572541 |
| | 8 | 0.99986789 | −1.1602931 | −2.2314362 | 8.9339980 | −18.140016 |
| 188.5 | 1 | 1.0296749 | −1.5133786 | | | |
| | 2 | 0.98926459 | −0.67228118 | −2.6236214 | | |
| | 4 | 0.99808439 | −0.87629795 | −3.8069234 | 2.0012275 | −0.47588374 |
| | 6 | 0.99987374 | −1.0405172 | −1.5722063 | 2.4066044 | −2.2654993 |
| 200 | 1 | 1.0298854 | −1.4190488 | | | |
| | 2 | 0.98801397 | −0.56945833 | −2.3164221 | | |
| | 4 | 0.99716683 | −0.75532377 | −3.6593548 | 1.6565327 | −0.32596987 |
| | 6 | 0.99966208 | −0.91793592 | −1.9165886 | 2.2316467 | −1.6306168 |
| | 8 | 0.99999735 | −0.96914958 | −0.34964810 | 0.97312090 | −2.1265863 |
| | 9 | 0.99998596 | −0.96204394 | −0.86846651 | 2.4121913 | −4.1217699 |
| | | $A_5 \times 10^7$ | $A_6 \times 10^8$ | $A_7 \times 10^9$ | $A_8 \times 10^{11}$ | $A_9 \times 10^{14}$ |
| 75 | 5 | −32.081006 | | | | |
| 125 | 6 | 48.946756 | −15.472657 | | | |
| | 8 | 197.36119 | −236.05385 | 149.84088 | −386.36487 | |
| 175 | 6 | 2.6224139 | −0.40708731 | | | |
| | 8 | 17.580103 | −9.1037407 | 2.4096214 | −2.5767082 | |
| 188.5 | 6 | 0.84133494 | −0.11748380 | | | |
| 200 | 6 | 0.50098160 | −0.058531700 | | | |
| | 8 | 1.6646745 | −0.66552083 | 0.13397502 | −0.10940662 | |
| | 9 | 3.2172451 | −1.3746704 | 0.32260754 | −0.37977136 | 1.6133517 |

Table III. Second Virial Coefficients of 2-Methylbutane

| Temp., ° C. | $-A_1RT$, Liter/Gram Mole<br>Unweighted polynomials | $-A_1RT$, Liter/Gram Mole<br>Weighted polynomials |
|---|---|---|
| 50 | 0.97011126 | 0.97651470 |
| 75 | 0.74095477 | [a] |
| 100 | 0.64874715 | 0.65079210 |
| 125 | 0.56122395 | [a] |
| 150 | 0.46786726 | 0.48310445 |
| 175 | 0.42668038 | 0.41927100 |
| 188.5 | 0.39416076 | 0.39625464 |
| 200 | 0.37351221 | [a] |

[a] Weighting not necessary.

Table IV. Comparison of Residuals and Experimental Errors

| Temp., ° C. | Residuals, %<br>Unweighted Polynomials<br>Av. | <br>Unweighted Polynomials<br>Max. | <br>Weighted Polynomials<br>Av. | <br>Weighted Polynomials<br>Max. | Estd. Max. Exptl. Error, % |
|---|---|---|---|---|---|
| 50 | 0.04 | 0.08 | 0.04 | 0.10 | 0.15 |
| 75 | 0.05 | 0.13 | | | 0.15 |
| 100 | 0.03 | 0.09 | 0.03 | 0.09 | 0.25 |
| 125 | 0.03 | 0.06 | | | 0.25 |
| 150 | 0.05 | 0.12 | 0.05 | 0.13 | 0.30 |
| 175 | 0.02 | 0.08 | 0.04 | 0.27 | 0.30[a]<br>0.60 |
| 188.5 | 0.02<br>0.09 | 0.08<br>0.22 | 0.02<br>0.09 | 0.08<br>0.22 | 0.30[b]<br>3.0 [c] |
| 200 | 0.01<br>0.04 | 0.04<br>0.10 | | | 0.30[b]<br>0.65[c] |

[a] At saturation. [b] Below 27 atm. [c] 27–37 atm.

of $Z_{\text{obsd.}}$ All the residuals are well within the limits of experimental error.

## POLYNOMIALS CALCULATED FROM WEIGHTED DATA

In calculating the least squares fits for each isotherm, a value of $Z = 1.0000$ at $P = 0.0000$ was added to the experimental results, and was given a weight equal to the weight of each experimental data point. In the polynomials adopted to represent the compressibility, $Z$, over the pressure ranges examined, the values of the first terms ($A_0$) represent the estimates of the first virial coefficients. The fact that for some isotherms these values are not equal to 1.0000 will now be considered.

Deviation of $A_0$ from 1.0000 arises from either random or systematic errors in the data. It is possible to force the polynomial to go through 1.0000 at zero pressure by weighting the point (0.0000, 1.0000) more than the experimental points, but it must be kept in mind that the second virial coefficient is represented by the slope of the polynomial at zero pressure. If the errors are random, then the data points fall on either side of the true isotherm, and forcing $A_0$ to be 1.0000 will result in a slope which is valid for estimating the second virial coefficient. However, if the errors are systematic, the data points fall mostly on one side of the isotherm, and forcing the polynomial to go through 1.0000 at zero pressure will give an incorrect slope. In fact, if the compressibility data are known to contain systematic errors, the slope of a polynomial calculated without the addition of the point (0.0000, 1.0000) would give the better estimate of the second virial coefficient.

Inasmuch as no systematic errors were known to exist in the data, each highest order acceptable polynomial was forced through 1.0000 at zero pressure. For the highest order polynomials at each temperature in which $A_0$ was not equal to 1.0000, increasing weighting factors were applied to the point $Z = 1.0000$ at $P = 0.0000$ and the least squares fits were recalculated. The resulting polynomials were then tested as to slope and curvature. In order not to reduce the influence of the experimental data points unduly, the smallest weighting factor which made $A_0 = 1.0000$ in the highest order acceptable polynomial was employed.

The coefficients of all the acceptable weighted polynomials are given in Table V, along with the order of the polynomials and the weighting factor employed in each case. In these polynomials, the coefficients $A_0$ are equal to 1.0000, and the coefficients $A_1$ are those employed in estimating the second virial coefficients. Values of $A_1RT$, the second virial coefficients estimated from the weighted polynomials, are given in Table III.

Table IV gives the residuals of the weighted polynomials and the estimated maximum experimental errors. Again, the residuals are all within the limits of the experimental error.

## SMOOTHED VALUES OF SECOND VIRIAL COEFFICIENT

The estimates of the second virial coefficients obtained from both the weighted and weighted polynomials of $Z$ *vs.* $P$ (Table III) were plotted against temperature. (Figure 1). The values reported by Scott and others (7) were also included to extend the temperature to 0° C.

A smooth curve of positive slope and negative curvature describes the results satisfactorily over the 0° to 200° C.

Table V. Coefficients $A_i$ of All Acceptable Weighted Polynomials $Z = \sum_{i=0}^{i=k} A_iP^i$

| Temp., ° C. | Weighting Factor | $k$ | $A_0$ | $A_1 \times 10^2$ | $A_2 \times 10^4$ | $A_3 \times 10^5$ | $A_4 \times 10^6$ | $A_5 \times 10^7$ | $A_6 \times 10^8$ |
|---|---|---|---|---|---|---|---|---|---|
| 50 | 3.30 | 1 | 0.99995176 | −3.6826404 | | | | | |
| 100 | 1.66 | 1 | 1.0036497 | −2.4100569 | | | | | |
| | | 2 | 0.99932702 | −1.9833749 | −6.3576637 | | | | |
| | | 3 | 0.99995098 | −2.1254227 | −0.62834810 | −5.7301874 | | | |
| 150 | 5.00 | 1 | 1.0036158 | −1.7041281 | | | | | |
| | | 2 | 0.99931067 | −1.2397828 | −3.2385870 | | | | |
| | | 4 | 0.99995720 | −1.3913444 | −1.2393085 | 0.23955280 | −0.56099880 | | |
| 175 | 3.95 | 1 | 1.0111186 | −1.5893103 | | | | | |
| | | 2 | 0.99679988 | −0.85158319 | −3.1093830 | | | | |
| | | 4 | 0.99965329 | −1.0450068 | −3.9574719 | 2.6828610 | −0.81171518 | | |
| | | 6 | 0.99995934 | −1.1401444 | −2.6318618 | 5.1786318 | −5.5256232 | 2.3781652 | −0.37945895 |
| 188.5 | 1.75 | 1 | 1.0219725 | −1.4792729 | | | | | |
| | | 2 | 0.99367784 | −0.72782355 | −2.4809787 | | | | |
| | | 4 | 0.99924043 | −0.92019810 | −3.3288370 | 1.8041599 | −0.44852591 | | |
| | | 6 | 0.99995721 | −1.0460447 | −1.4515823 | 2.2867144 | −2.2057859 | 0.82681610 | −0.11611221 |

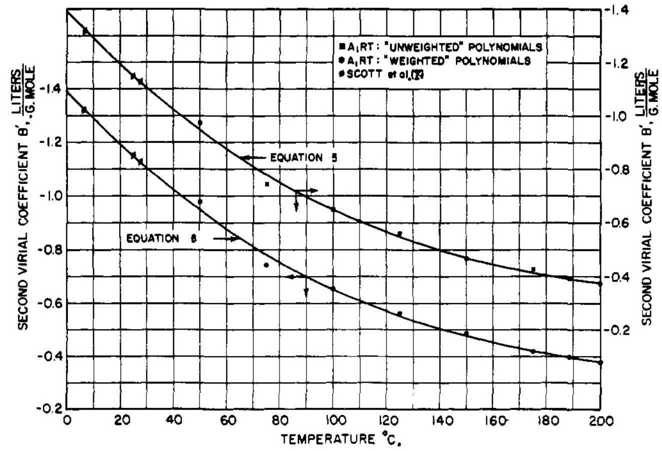

Figure 1. Second virial coefficient of 2-methylbutane

range. The expression $B' = \sum_{i=0}^{i=k} b_i t^i$, $k = 1, 2, \ldots, n-1$, where $n$ is the number of data points at different values of $t$, was fitted to each set of data. The highest order polynomial which described the results correctly as to slope and curvature was found in each case to be ternary. The third-order polynomials representing the smoothed estimates of the second virial coefficients are:

$$B' = -1.3900977 + 1.0733631 \times 10^{-2}t - 3.8092474 \times 10^{-5}t^2 + 4.8604950 \times 10^{-8}t^3 \qquad (5)$$

$$B' = -1.3902695 + 1.0728781 \times 10^{-2}t - 3.8748487 \times 10^{-5}t^2 + 5.2181227 \times 10^{-8}t^3 \qquad (6)$$

where 0° C. $\leqq t \leqq$ 200° C.

Equation 5 represents the smoothed estimates obtained from the unweighted polynomials, and Equation 6 those from the weighted polynomials of $Z$ vs. $P$.

The average and maximum residuals ($A_1RT - b_0 - b_1t - b_2t^2 - b_3t^3$) are given below for each case.

| | Residuals, Liters/Gram Mole | | | |
|---|---|---|---|---|
| | Equation 5 | | Equation 6 | |
| Temperature Range | Av. | Max. | Av. | Max. |
| Below critical | 0.013 | 0.038 | 0.012 | 0.041 |
| Above critical | 0.003 | 0.005 | 0.002 | 0.003 |

Guggenheim (*3*) points out that for numerically small second virial coefficients, it is possible to obtain an accuracy as good as 0.001 or 0.002 liter per gram mole. However, when the second virial coefficient is numerically large, as is generally the case below the critical temperature, the accuracy is rarely as good as 0.020 liter per gram mole, and usually no better than 0.050 liter per gram mole.

Table VI gives the smoothed values of $B'$ calculated from Equations 5 and 6.

Table VI. Smoothed Values of Second Virial Coefficients B′

| Temp., ° C. | Smoothed $B'$, L./Gram Mole Eq. 5 | Smoothed $B'$, L./Gram Mole Eq. 6 | Temp., ° C. | Smoothed $B'$, L./Gram Mole Eq. 5 | Smoothed $B'$, L./Gram Mole Eq. 6 |
|---|---|---|---|---|---|
| 0 | -1.390 | -1.390 | 100 | -0.649 | -0.653 |
| 10 | -1.286 | -1.287 | 110 | -0.606 | -0.610 |
| 20 | -1.190 | -1.191 | 120 | -0.567 | -0.571 |
| 30 | -1.101 | -1.102 | 130 | -0.532 | -0.536 |
| 40 | -1.018 | -1.020 | 140 | -0.501 | -0.504 |
| 50 | -0.942 | -0.944 | 150 | -0.473 | -0.477 |
| 60 | -0.873 | -0.875 | 160 | -0.449 | -0.452 |
| 70 | -0.809 | -0.811 | 170 | -0.427 | -0.430 |
| 80 | -0.750 | -0.753 | 180 | -0.409 | -0.410 |
| 90 | -0.697 | -0.700 | 190 | -0.392 | -0.393 |
| | | | 200 | -0.387 | -0.377 |

## REDUCED CORRELATION OF SECOND VIRIAL COEFFICIENTS

The reduced second virial coefficients $B'_r = B'/V_c$ for 2-methylbutane calculated from Equation 6 over the temperature range 50° to 200° C. at intervals of 25° C. were plotted *vs.* the reduced temperature $T_r = T/T_c$. The data of Scott and others (*7*) on 2-methylbutane, of Beattie, Levine, and Douslin (*2*) on *n*-pentane, and of Beattie, Douslin, and Levine (*1*) on 2,2-dimethylpropane were also plotted on the same graph (Figure 2). A single curve of positive slope and negative curvature correlates all the data satifactorily.

The critical volume, $V_c$, and the critical temperature, $T_c$, used for the three pentanes are those reported by Rossini and others (*6*). Table VII gives $B'$, $B'_r$, and $T_r$ at the different temperatures.

As a smoothing procedure, polynomials of the form

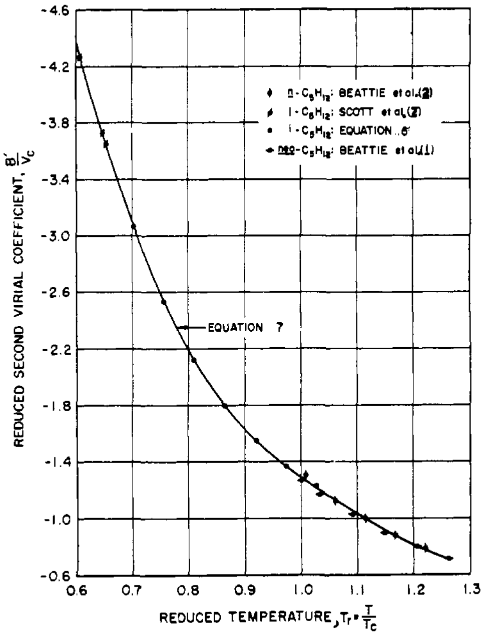

Figure 2. Reduced second virial coefficient of pentanes

Table VII. Reduced Second Virial Coefficients

| | Temp., ° C. | $-B'$, L./G. Mole | $T_r$ | $-B'_r$ |
|---|---|---|---|---|
| *n*-Pentane (*1, 2*) | 200 | 0.405 | 1.007 | 1.302 |
| | 225 | 0.350 | 1.060 | 1.125 |
| | 250 | 0.311 | 1.114 | 1.000 |
| | 275 | 0.274 | 1.167 | 0.881 |
| | 300 | 0.244 | 1.220 | 0.784 |
| Isopentane (*7*) | 6.32 | 1.313 | 0.606 | 4.263 |
| | 25.00 | 1.149 | 0.647 | 3.730 |
| | 37.85 | 1.126 | 0.653 | 3.656 |
| Isopentane, Eq. 6 | 50 | 0.944 | 0.701 | 3.065 |
| | 75 | 0.781 | 0.755 | 2.536 |
| | 100 | 0.653 | 0.809 | 2.120 |
| | 125 | 0.553 | 0.864 | 1.795 |
| | 150 | 0.477 | 0.918 | 1.549 |
| | 175 | 0.420 | 0.972 | 1.364 |
| | 200 | 0.377 | 1.026 | 1.224 |
| Neopentane (*1, 2*) | 160.60 | 0.383 | 1.000 | 1.264 |
| | 175 | 0.354 | 1.033 | 1.168 |
| | 200 | 0.312 | 1.091 | 1.030 |
| | 225 | 0.273 | 1.148 | 0.901 |
| | 250 | 0.243 | 1.206 | 0.802 |
| | 275 | 0.216 | 1.264 | 0.713 |

$B_r' = \sum_{i=0}^{i=k} A_i(T_r)^i$ where $k = 1, 2, \ldots, n - 1$ were fitted to the data by a least squares procedure. The fifth-order polynomial

$$B_r' = 12.091380 - 159.95107\ T_r + 457.84870\ T_r^2 - 562.84123\ T_r^3 + 322.28864\ T_r^4 - 70.717253\ T_r^5 \qquad (7)$$

where $0.60 \leqq T_r \leqq 1.27$
satisfied the characteristics of the curve over the reduced temperature range $T_r = 0.60$ up to $T_r = 1.27$. The average and maximum residuals, $(B'_{r\ \text{obsd.}} - B'_{r\ \text{calcd.}})$ are given below, and are probably well within the experimental accuracy of the data.

| | |
|---|---|
| Average residual | 0.011 |
| Maximum residual | 0.041 |

Table VIII gives the smoothed values of $B_r'$ calculated from Equation 7.

Table VIII. Smoothed Reduced Second Virial Coefficients

| $T_r$ | $-B_r'$ | $T_r$ | $-B_r'$ | $T_r$ | $-B_r'$ |
|---|---|---|---|---|---|
| 0.60 | 4.36 | 0.85 | 1.87 | 1.10 | 1.03 |
| 0.65 | 3.68 | 0.90 | 1.62 | 1.15 | 0.91 |
| 0.70 | 3.09 | 0.95 | 1.43 | 1.20 | 0.81 |
| 0.75 | 2.59 | 1.00 | 1.28 | 1.25 | 0.73 |
| 0.80 | 2.18 | 1.05 | 1.15 | 1.27 | 0.72 |

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# Kinetics of Reaction of Certain Diisocyanates

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THE MOLECULAR structure of condensation polymers prepared from diisocyanates is substantially affected by the reactivity of the isocyanate groups and in particular by the difference in reactivity between the two isocyanate groups in an unsymmetrical diisocyanate.

In unsymmetrical diisocyanates the isocyanate groups react more independently the larger the difference in reactivity between the two groups; thus the reaction of each group can be controlled by an appropriate choice of conditions. The statistical randomness of the product which arises when symmetrical diisocyanates are used can thus be avoided.

As part of an experimental program on polyurethanes the reactivity of certain unsymmetrical diisocyanates with alcohol was determined.

## EXPERIMENTAL

**Rate Measurements.** The method used to determine the reactivities of the isocyanate groups was very similar to the one described previously by Bailey and coworkers (*1*). Chlorobenzene was used as the solvent, however, and a 10-fold excess of isoamyl alcohol was used to react with the diisocyanate. In this method the rate of disappearance of the NCO-band at 4.5 microns in the infrared spectrum of the reaction mixture is measured. The infrared spectra were run in an air-conditioned room, which was maintained at about 21-3° C., but the reaction mixture itself in the absorption cell was not thermostated. Many spectral determinations were made, and the smooth curve drawn through the data was used in determining the pseudo first-order rate constants after the reaction had proceeded to the extent of about 10 to 20% and after approximately 70 to 80% reaction had occurred. Because the diisocyanates frequently were used as distilled from the reaction mixture without further purification, and because of the other inaccuracies of the procedure used, the rate constants were determined to only one significant figure.

The third column of Table I lists the half lives of the reaction estimated from data after 10 to 20% reaction had taken place. In the fourth column the half lives of the reaction estimated from data after 70 to 80% of the reaction had been completed are given. The last column lists the ratio of the two half lives. This ratio may be taken as a measure of the difference in reactivity of the two isocyanate groups of the unsymmetrical diisocyanate. Although the half lives are reported to only one significant figure,