

Report No. _____

UNITED STATES DEPARTMENT OF THE INTERIOR BUREAU OF MINES HELIUM ACTIVITY HELIUM RESEARCH CENTER

INTERNAL REPORT

TESTS ON THE STATISTICAL METHOD OF TREATING THE 0° C HELIUM

DATA OBTAINED FROM A BURNETT COMPRESSIBILITY APPARATUS





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HELIUM RESEARCH CENTER

INTERNAL REPORT

TESTS ON THE STATISTICAL METHOD OF TREATING THE 0° C HELIUM DATA OBTAINED FROM A BURNETT COMPRESSIBILITY APPARATUS

Ву

B. J. Dalton

Branch of Fundamental Research

Project 4335

May 1966

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TESIS ON THE STATISTICAL METHOD OF TREATING THE 0° C HELIUM DATA OBTAINED FROM A BURNETT COMPRESSIBILITY APPARATUS

by

B. J. Dalton^{1/}

ABSTRACT

This report describes tests on the statistical method of treating the 0° C helium data obtained from the Helium Research Center's Burnett compressibility apparatus. Tests have been carried out to show: 1. the effect an error in the determination of the pressure distortion corrections of the high-pressure bombs produces in the compressibility factor, Z, which is a function of virial coefficients, and in the value of the volume ratio at zero pressure, N; 2. the effect an error in the fractional change in the effective area of the piston (at 25° C, P=0) with pressure induces in Z and N; and 3. the effect an error of ignoring the change in volume of the containers with pressure produces in Z and N. The statistical tests are given for the compressibility factor isotherm expressed in terms of the Berlin expansion in powers of the pressure, assuming the contribution of fourth and higher virials to be negligible.

1/ Research chemist, Helium Research Center, Bureau of Mines, Amarillo, Texas.

Work on manuscript completed May 1966.

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INTRODUCTION

Compressibility data obtained by the Burnett method involve: 1. calculating pressures from a series of experimental observations of gage temperatures, gage pressures, barometer readings, barometer temperatures, and relative humidity values; 2. determining corrections for the pressure distortion of the high-pressure containers; and 3. evaluating the parameters appearing in the expression for the compressibility of the gas and also to evaluate, simultaneously, the volume ratio at zero pressure, N.

The general expression for the Burnett experiment is of the form

$$Z_{r} = (Z_{o}/P_{o}) f_{r} N^{r} P_{r}$$
(1)

where Z_r is the compressibility factor of the gas at pressure P_r and Z_o is the corresponding value at pressure P_o ; N is the ratio of the volumes of both containers at zero pressure to that of the first container at zero pressure; r is the expansion number; P_r is the equilibrium pressure after the $r\frac{th}{r}$ expansion; P_o is the initial pressure;

$$r = \frac{(1+\alpha P_1) (1+\alpha P_2) \dots (1+\alpha P_r)}{(1+\beta P_0) (1+\beta P_1) \dots (1+\beta P_{r-1})}$$

 α is the pressure coefficient of the volume of both containers; and β is the pressure coefficient of the volume of the first container. The pressures are expressed in either psia or standard atmosphere units and are calculated by the method previously outlined $(\underline{7}), \underline{2}/2$

2/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.



which is based on a general program developed for this particular purpose (5).

In this report, we assume Z_r is a function of the second and third virial coefficients and is expressible in terms of a Berlin expansion in powers of P_r ,

$$Z_r = 1 + BP_r + CP_r^2$$
 (2)

For the interested reader, a more detailed discussion of the case where Z_r is of some other functional form than that given by equation (2) or where Z_r is an explicit function of the molal density, ρ_r , in which case Z_r is to be considered an implicit function of P_r , is given in (2).

 f_r of equation (1) is a function of all of the observed pressures but is completely independent of the pressure distortion coefficients of the bombs which have been previously determined. The principles connected with the evaluation of α and β have been given by Briggs (5) 6) and, therefore, will not be repeated in this report.

Statistical tests were carried out on the experimental compressibility data on helium at 0° C for run number 3 obtained by Briggs ($\underline{5}$) in order to illustrate: 1. the effect an error in the determination of the distortion coefficients of the high-pressure containers with pressure produces in the compressibility factor, Z, which is a function of B and C, and in the volume ratio at zero pressure, N; 2. the effect an error in the fractional change in the effective area of the piston (at 25° C, P=0) with pressure introduces in Z and N; and 3. the effect an error of ignoring the pressure distortion of the bombs induces in Z

and N.

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For the interisted reader, a more intelled discussion of the case where Σ_{μ} is of some other functional form that the share by equation (2) or where Σ_{μ} is of some other function of the main density, Σ_{μ} . In which case Σ_{μ} is to be considered an implicit function of ψ_{μ} is given in (2) is case Σ_{μ} is to be considered an implicit size function of ψ_{μ} is given in (2) is to be the considered an implicit of all of the ubserved proparates for the boombe which there are an providered of all of the proparates function of ψ_{μ} is given in (2) is the boombe which there are an providered of all of the ubserved proparates for the boombe which there are an providered of the proparate distantion for the providered of the boombe which there are are provided by the boombe which there are are provided by the boombe which the restance of a and by here have been by determined. The principles (3) and, the boombe which the restance of a and by here there are a former of a and the second of the second state of a and the second state of the second state of the second state of a and the boombe which the restance of a and by here there are a former of a and the second state of a state of the second state of the second

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The parameters of equation (1), assuming Z_r to be expressible by equation (2), were evaluated by the method outlined in (2), which is based on the general non-linear least squares problem developed for this particular problem (1, 3, 4, 8). The calculations and results of the statistical tests on the experimental PVT data for helium at 0° C for run number 3 reported in (5) are given in the following sections.

THE EFFECT AN ERROR IN THE DETERMINATION OF α And β PRODUCES IN Z, B, C, AND N

The experimental results of Briggs (5) compressibility measurements on helium at 0° C for run number 3 are given in table 1 of this report. The values of column 1 are expansion numbers corresponding to the observed pressures of column 2. The pressures are in standard atmosphere units and the number after the letter E merely indicates the power of 10 by which each pressure is multiplied.

Equation (1),

$$Z_{r} = (Z_{o}/P_{o}) f_{r} N^{r} P_{r} , \qquad (1)$$

was applied to the data of table 1 assuming Z_r to be of the form as given by equation (2),

$$Z_r = 1 + BP_r + CP_r^2$$
 (2)

The values of the pressure distortion coefficients of the highpressure bombs were taken to be (5, 6):

$$\alpha$$
 (0° C) = 1.6678 x 10⁻⁶ atm⁻¹, (3)

$$\beta$$
 (0° C) = 1.6671 x 10⁻⁶ atm⁻¹. (4)

TABLE	1Original	expe	rimental	obse	ervation	is on	helium	at	0°	С	for	run
	number	3 as	reported	1 by	Briggs	(<u>5</u>)						

Z _r =	$(Z_0/P_0) f_r N^r P_r, P_r \text{ in atm}$
Z _r =	$1 + BP_r + CP_r^2$
Q =	$1.6678 \times 10^{-6} \text{ atm}^{-1}$
β =	$1.6671 \times 10^{-6} \text{ atm}^{-1}$
<u>1/</u> =	$-3.50 \times 10^{-8} \text{ in}^2/\text{in}^2 \text{ psi}$

r	Pr(obs)
0	7.0128236E02
1	3.0170799E02
2	1.4061376E02
3	6.8033559E01
4	3.3517320E01
5	1.6660572E01
6	8.3186011E00
7	4.1639855E00

1/ b is the fractional change in the effective area of the piston (at 25° C, P=0) with pressure. This value was supplied by the Ruska Instrument Corporation; see (5) and (7) for a more detailed discussion of this constant. TANLE 1 - Original asperimental operations on helice at 0° 5 for run number 3 as reported by Brians (3)



5- = -3.50 × 10 17 /10 gal

103A90100A.	

b is the transional change in the affective area of the platon (at 25"C, E=O) with pressure this value was supplied by the Rusks instrument Corporation; see (5) and (2) for a more detailed discussion of this constant The three parameters of equation (1), B, C, and N, were evaluated by an iteration technique (2) to give the results reported in table 2 of this report, assuming α and β to be defined by equations (3) and (4), respectively. The values of column 1 of this table are expansion numbers corresponding to the observed pressures of column 2. The pressures of column 3 are those pressures which exactly satisfy equation (1). Column 4 is the residual of $P_{r(obs)}$ and is just the difference of columns 2 and 3. The relative error of the observed pressure, column 5, is just column 4 divided by column 2.

The best estimates of the unknown parameters of equation (1) are also included in table 2 along with the best estimate of the uncertainty of each of these quantities. The best values for B, C, and N were taken to be the least squares values, where the observed pressures were taken to be of equal reliability. The quantities S_N , S_B , and S_C are the calculated standard errors of N, B, and C evaluated by the method outlined in (8). The quantities given under the heading VARI-ANCES AND COVARIANCES are just variances and covariances of the parameters calculated by the method outlined in (8) (i.e., S2N is the variance of N; S2BC is the covariance of BC; etc.).

From the data of table 2 and equation (2), the compressibility factors of table 3 were calculated, together with the standard deviation of each Z. The values of column 1 of this table are nominal pressures in standard atmosphere units. Column 2 gives values of Z corresponding to the pressures of column 1, while the standard deviations of these compressibility factors, SZ, are given in column 3.

9

ine three periodices of equation (2), a C, and M, seee conjusted by at location michange (2) in give the results separted in reble 2 of this report, assuming 2 and 7 to a defined by equations (2) and (3), respectively. The varues of course 1 of this this takin are expenditor muchan corresponding to the observed pressures of column 3. The area succes of column 1 is the take three preserves distributes and the forest fill, column 1 is the matter of the observes distributes and the filter columns 2 and 3. The relative second of the operator of the take of the the matter of the observes distributes and to the difference of the take of the the matter of the second of the second preserves of the second of the the matter of the operators of the take the difference of the take of the the matter of the operators of the operators of the second of the the matter of the operators of the the second preserves of the take column 5 and 1 is the matter of the operators of the difference of the take column 5 and 1 is the matter of the operators of the difference of the take column 5 and 1 is the matter of the operators of the difference of the take column 5 and 1 is the matter of the operators of the difference of the take column 5 and 1 is the matter of the operators of the difference of the take column 5 and 1 is the matter of the operators of the difference of the take column 5 and 1 is the matter of the operators of the take operators of the difference of the take column 5 and 1 is the matter of the operators of the difference of the take operators of the difference of the take operators of take operators of take o

The verified to colore 2 along with the braines estimate of equation (1) are relaty of each of these quantities. The base values to the waterware taken to be the iteest equated values where the deserved pressures were taken to be the iteest equated values where the deserved pressures are the calculated standard errors of 3, b, and C evaluated by the are the calculated to [3]. The quantities sizen water the heading WMLdestrictions is in the nethod calculated in (2) (i.e., 50% is the are taken of its inclusion of the constitutes in (3) (i.e., 50% is the are the calculated by the method calculated in (3) (i.e., 50% is the area the size of the teep of the constitutes of 50, is the section of the area is a size of the teep of the constitutes and constitutes the area is a size of the teep of the constitutes are and constitutes the area is a size of the teep of the constitutes are and constitutes the area is a size of the teep of the constitution of (2) (i.e., 50% is the area is a size of the teep of the constitutes of 50, i.e., 50% is the

From the date of table 2 and equilited (2), the construction deviation fractors it table 2 units calculated togetoer with the structure deviation of apple 5. The values of column 1 of the structure method presentes in standard attraphene with . Column 2 gives values of 2 dorrespondies to the presentes of robust 1, shifts the attracted deviations of these courses thiller income (6), are given in column 1.

Ø.

TABLE 2.-Results of the analysis of the data of table 1 for α and β defined by equations (3) and (4)

				P,OBSP,CAL.
r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBSP,CAL.	P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4-99133E-04	-1.65435E-06
2	1.4061376E&02	1.4061112E&02	2.64039E-03	1.87776E-05
3	6.8033559E&01	6.8037124E&01	-3.56490E-03	-5.23991E-05
4	3.3517320E&01	3.3518813E&01	-1.49289E-03	-4.45411E-05
5	1.6660572E&01	1.6659332E&01	1.23916E-03	7.43771E-05
6	8.3186011E-00	8.3161327E-00	2.46844E-03	2.96737E-04
7	4.1639855E-00	4.1603444E-00	3.64111E-03	8.74430E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30445E-05

1

CONSTANTS AND STANDARD ERRORS

N 1.994559047E-00	SN	1.29990E-04
B 5.277062588E-04	SB	8.84365E-07
C -4.739061450E-08	SC	5.96411E-10

VARIANCES AND COVARIANCES

S2N	1.68975E-08
S2B	7.82102E-13
S2C	3.55707E-19
S2BC	-5.22569E-16
S2BN	-1.10699E-10
S2CN	7.13077E-14

TABLE 2. - Maguing of the analysis of the days of table 1 for 2 and 5 defined

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		PrOBS. ATH.	
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SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.304436-0

CONSTANTS AND STANDARD ERRORS

VARIANCES AND COVARIANCES

-

1	ABLE 5Comp	ressibilit	y factors :	for nelli	um at U G	Jasai	unct	.10n
	of	pressure,	evaluated	from equ	uation (2) and th	еB	and
	C	values of	table 2					
1	PRESSURE, A	ATM.	Z			SZ		
	1.000E-00)	1.0005276	6588E-0	0 1.	05758E	-06	
	2.000E-00	0	1.0010552	2229E-0	0 2.	04752E	-06	
	5.000E-00	D	1.0026373	3465E-0	0 4.	89493E	-06	
	1.000E&01	L	1.0052723	3235E-0	0 9.	44892E	-06	
	2.500E&01	La contra con	1.0131630	0373E-0	0 2.	24701E	-05	
	5.000E&01		1.0262668	3364E-0	0 4.	30866E	-05	
	7.500E&01		1.0393113	3972E-0	0 6.	28415E	-05	
	1.000E802	2	1.052296	7197E-0	0 8.	19129E	-05	
	1.250E&02	2	1.0652228	3039E-0	0 1.	00365E	-04	
	1.500E&02	2	1.0780890	5499E-0	0 1.	18224E	-04	
	2.000E&02	2	1.1036450	5271E-0	0 1.	52167E	-04	
	2.500E&02	2	1.1289640	6512E-0	0 1.	83675E	-04	
	3.000EE02	2	1.154046	7223E-0	0 2.	12614E	-04	
	3.500E&02	2	1,1788918	3403E-0	0 2.	38822E	-04	
	4-000F802	2	1.2035000	0052E-0	0 2	62127F	-04	
	4.500F&02	-	1.2278712	2170F-0	0 2.	82357F	-04	
	5-000E802	2	1.2520054	4757E-0	0 2.	99346E	-04	
	6-000EE02	-	1.2995631	1340E-0	0 3.	22985F	-04	
	7.000FE02	2	1.3461729	9800F-0	0 3.	31965F	-04	
	8-000EE03		1.3918350	137E-0	0 3	25547F	-04	
	9-000EE02	2	1.436549	2351F-0	0 3.	03584F	-04	
	1.0005503		1 480315	5442E-0	0 2	67134F	-04	
	Leourau.	,	TO TOOTIO	JTTLL U	V 60	UTI JIL	UT	

resilts grown to cable 4, the compressibility Inctors of table 5 save

itility footons for holium at 0° C a TADTO O

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		PRESSURE, AIM.
		/
		3.5006802

Now suppose the determinations of the pressure distortion coefficients of the high-pressure containers are in error - this is not to imply or be construed to mean that α and β are incorrect! However, to illustrate the first statistical test carried out on the 0° C helium data for run number 3, we assume these quantities to be in error by some amount. Then on solving equation (1), we would get new values for B, C, and N as well as new values of Z. The problem, therefore, is to reevaluate these parameters and compressibility factors and to decide whether the effect an error in α and β produces a statistically significant difference in the values of B, C, N, and Z.

Let us assume errors in α and β of $\pm 10\%$ and $\pm 20\%$:

0.8 0	¥ =		1.33424	x	10 ⁻⁶	atm ⁻¹ ,	0.8 β	=	1.33368	x	10 ⁻⁶	atm ⁻¹ ;
0.9 0	2 =	:	1.50102	x	10 ⁻⁶	atm ⁻¹ ,	0.9 β	=	1.50039	x	10 ⁻⁶	atm ⁻¹ ;
1.1 0	· =		1.83458	x	10 ⁻⁶	atm ⁻¹ ,	1.1 β	=	1.83381	x	10 ⁻⁶	atm ⁻¹ ;
1.2 0	¥ =	:	2.00136	x	10 ⁻⁶	atm ⁻¹ ,	1.2 β	=	2.00052	x	10 ⁻⁶	atm ⁻¹ .

Table 4 of this report gives the results of the new values of the parameters assuming errors in α and in β of ±10% and ±20%. The values given in table 4 have the same meaning as those of table 2. From the results given in table 4, the compressibility factors of table 5 were calculated, together with the uncertainty of each Z factor.

From the data given in tables 1, 2, 3, 4, and 5 of this report, the following significant results indicate that:

1. Even if the determination of the pressure distortion coefficients of the bombs is in error by as much as $\pm 20\%$, the least squares Now suppose the determinations of the pressure distortion coefficients of the high-pressure containers are in error - this is not to imply or be construed to seem that a and b are incorract! Somewar, to filterfrate the first statistical test carried out on the 0° C bellum date for run number 1, we assure these quantities to be 19 error by areas smouth. Then on solving equation (1), we would get new values for 2, C, and 8 as well as now values of 2. The problem, therefore, is to resolute the effect an erfor in 0, and f produces a statistically decide whether the effect an erfor in 0, and f produces a statistically algolificant difference in the values of 3, C, M, and k.

Lat us seature errors in a nul 8 of 1101 and 1707;

0.8 a = 1.32224 x 10⁻⁰ ara⁻¹, 0.8 b = 1.33368 x 10⁻⁰ arm⁻¹; 0.9 a = 1.50102 x 10⁻⁰ arm⁻¹, 0.9 b = 1.50039 x 10⁻⁰ arm⁻¹; 1.1 a = 1.53458 x 10⁻⁰ arm⁻¹, 1.1 B = 1.53331 x 10⁻⁰ arm⁻¹; 1.2 a = 2.00136 x 10⁻⁰ arm⁻¹, 1.2 b = 2.00038 x 10⁻⁰ arm⁻¹. Table 4 of this report gives the results of the max values of the parameters assumpting errors in a and in 5 of 102 and 1203. The values given in table 4 have the same resoling as those of facle 2. From the results given in table 4, the compressibility factors of table 5 wave

From the data given in tables 1, 2, 3, 4, and 5 of this report, the following significant results indicate that:

 Even if the determination of the pressure distortion coefficelents of the bombs is intervar by as much as 10%, the least squares

12

TADLC	4 Results of the analysis of the da	ita of table i assuming errors in	
	$lpha$ and eta of $\pm 10\%$ and $\pm 20\%$		
	Statement of the state story states (Cons.)		
	$0.8\alpha = 1.33424 \times 10$ atm	$0.8\beta = 1.33368 \times 10^{\circ}$ atm	
		ACTOR - LABORY - IN ACTOR	
		P,OBSP,CAL	
r	P,OBS., ATM. P,CAL., ATM.	P,OBSP,CAL. P,OBS.	
0	7.0128236E&02 7.0128236E&02	0.00000E-99 0.00000E-99	9
1	3.0170799E&02 3.0170849E&02	-4.99511E-04 -1.65561E-00	5
2	1-4061376E802 1-4061112E802	2-64261E-03 1-87934E-09	5
2	6.8033559EE01 6.8037128EE01	-3.56832E-03 -5.24494E-05	5
1	3 35173205501 3 35199145501	-1 40367E-03 -4 45641E-01	5
T .	1 (((DE72ECO1 1 ((E022)ECO1		
2	1.0000572E601 1.0059531E601		3
6	8.3180011E-00 8.3161305E-00	2.41058E-03 2.96995E-04	t
7	4.1639855E-00 4.1603425E-00	3.64300E-03 8.74884E-04	ŧ

1

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.31114E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559505E-00	SN	1.30086E-04
B	5.273648758E-04	SB	8.84952E-07
C -	-4.754640934E-08	SC	5.96924E-10

VARIANCES AND COVARIANCES

S2N	1.69224E-08
S2B	7.83141E-13
S2C	3.56319E-19
S2BC	-5.23370E-16
S2BN	-1.10854E-10
S2CN	7.14232E-14

	1542.1 = 0814	
	PEBSSEERTH.	

SUN OF MELENTED SOUARES OF THE RESIDUALS 4.311140-05

CONSTANTS AND STANDARD ERRORS

1

VANLANCES AND COVARIANA

TABLE	4Results of the	analysis of the da	ata of table l assur	ning errors in
	α and β of ± 1	0% and ±20% (Con.)	
	$0.9\alpha = 1.50102$	$\times 10^{-6} \text{ atm}^{-1}$	$0.9\beta = 1.50039$	$\times 10^{-6}$ atm ⁻¹
				P, OBSP, CAL.
r	P,OBS.,ATM.	P, CAL., ATM.	P,OBSP,CAL.	P,OBS.
0	7.0128236E&02	7.0128236E&02	0.0000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4.99322E-04	-1.65498E-06
2	1.4061376E&02	1.4061112E&02	2.64150E-03	1.87855E-05
3	6.8033559E&01	6.8037126E&01	-3.56661E-03	-5.24243E-05
4	3.3517320E&01	3.3518813E&01	-1.49328E-03	-4.45526E-05
5	1.6660572E&01	1.6659332E&01	1.23992E-03	7.44224E-05
6	8.3186011E-00	8.3161316E-00	2.46951E-03	2.96866E-04
7	4-1639855E-00	4.1603434E-00	3.64206E-03	8.74657E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30780E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559276E-00	SN	1.30038E-04
B	5.275355672E-04	SB	8.84659E-07
C -	4.746851200E-08	SC	5.96668E-10

VARIANCES AND COVARIANCES

S2N	1.69100E-08
S2B	7.82621E-13
S2C	3.56013E-19
S2BC	-5.22969E-16
S2BN	-1.10777E-10
S2CN	7.13654E-14

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CONSTANTS AND STRAMBAND EQACT

8 5.279905125A726-00 79905125A726-00 7990512006-00

VARIANCES AND COVARIANCES:

TADLE	4 Results of the analysis of the da	ala UI LADIE I ASSU	ming errors in
	α and β of $\pm 10\%$ and $\pm 20\%$ (Con.)	
	1 1 1 00/50 10-61	1 10 1 00001	10-6 -1
	$1.1\alpha = 1.83458 \times 10$ atm	$1.1\beta = 1.83381$	x 10 atm
			P.OBSP.CAL
r	PORSSATMA POCAL ATMA	P.OBSP.CAL.	P.OBS.
-	. ionosiutto i totta interio		
0	7.0128236E&02 7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02 3.0170849E&02	-4.98944E-04	-1.65373E-06
2	1.4061376E&02 1.4061112E&02	2.63928E-03	1.87697E-05
3	6.8033559EE01 6.8037123EE01	-3.56319E-03	-5.23740E-05
4	3.3517320E&01 3.3518812E&01	-1.49251E-03	-4.45296E-05
5	1.6660572E&01 1.6659333E&01	1.23841E-03	7.43318E-05
6	8.3186011E-00 8.3161337E-00	2.46737E-03	2.96608E-04
7	4-1639855E-00 4-1603453E-00	3.64016E-03	8.74202E-04
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SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30111E-05

CONSTANTS AND STANDARD ERRORS

N	1.994558817E-00	SN	1.29942E-04
B	5.278769505E-04	SB	8.84071E-07
C	-4.731271686E-08	SC	5.96155E-10

VARIANCES AND COVARIANCES

S2N	1.68850E-08
S2B	7.81583E-13
S2C	3.55401E-19
S2BC	-5.22169E-16
S2BN	-1.10622E-10
S2CN	7.12500E-14

2.0832 2.20.0		1	r Az. 280, 4
		5934	

SUM OF WELCHIER, SQUARES OF THE RESIDUALS +. SOLLIE-O

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VARIANCES AND LAVARIANCES

4. 30	

TABLE 4.-Results of the analysis of the data of table 1 assuming errors in α and β of ±10% and ±20% (Con.)

$$1.2\alpha = 2.00136 \times 10^{-6} \text{ atm}^{-1}$$
 $1.2\beta = 2.00052 \times 10^{-6} \text{ atm}^{-1}$

				POURS - POLAL
r	P:OBS.:ATM.	P & CAL . & ATM.	P,OBSP,CAL.	P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4.98754E-04	-1.65310E-06
2	1.4061376E&02	1.4061112E&02	2.63817E-03	1.87618E-05
3 -	6.8033559E&01	6.8037121E&01	-3.56148E-03	-5.23489E-05
4	3.3517320E&01	3.3518812E&01	-1.49212E-03	-4.45181E-05
5	1.6660572E&01	1.6659334E&01	1.23765E-03	7.42865E-05
6	8.3186011E-00	8.3161348E-00	2.46629E-03	2.96479E-04
7	4.1639855E-00	4.1603463E-00	3.63922E-03	8.73975E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.29777E-05

CONSTANTS AND STANDARD ERRORS

N	1.994558588E-00	SN	1.29894E-04
B	5.280476424E-04	SB	8.83778E-07
C	-4.723481905E-08	SC	5.95898E-10

VARIANCES AND COVARIANCES

S2N	1.68726E-08
S2B	7.81063E-13
S2C	3.55095E-19
S2BC	-5.21769E-16
S2BN	-1.10544E-10
S2CN	7.11924E-14

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SUM OF WEIGHTED SUDARES OF THE RESIDUALS ARRETOR.

CONSTANTS AND STANDARD ENLINES

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VARIANALS AND COVARIANES

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TRIDLE J. 00	mpreuu	TNTTT	cy rucci	510	LOL III	CILUM		U CVUI	uaccu	II UII
	the B	and C	values	of	table	4 and	equat	ion (2	<u>)</u>	
		-6	5 -1					-6	-1	
$0.8\alpha = 1.$	33424	x 10 ⁻⁰	atm		0.8β	= 1.3	3368 x	10-0	atm	
PRESSURE,	ATM.			Ζ				SZ		
1.000E-0	00		1.0005	273	173E	-00	1.	05818	8E-06	
2.000E-	00		1.0010	545	395E	-00	2.	04872	2E-06	
5.000E-	00		1.0026	356	357E	-00	40	89791	E-06	
1.000E&	01		1.0052	688	941E	-00	9.	45481	E-06	
2.500E&	01		1.0131	544	053E	-00	2.	24846	E-05	
5.000E&	01		1.0262	493	777E	-00	4.	31147	'E-05	
7.500E&	01		1.0392	849	171E	-00	6.	28827	E-05	
1.000E&	02		1.0522	610	234E	-00	8.	19665	E-05	
1.250E&	02		1.0651	776	968E	-00	1.	00431	E-04	
1.500E&	02		1.0780	349	371E	-00	1.	18301	E-04	
2.000E&	02		1.1035	5711	187E	-00	1.	52264	E-04	
2.500E&	02		1.1288	695	683E	-00	1.	83790)E-04	
3.000E&	02		1.1539	302	859E	-00	2.	12744	E-04	
3.500E&	02		1.1787	'532	713E	-00	2.	38965	5E-04	
4.000E&	02		1.2033	385	248E	-00	2.	62280)E-04	
4.500E&	02		1.2276	860	462E	-00	2.	82518	3E-04	
5.000E&	02		1.2517	958	355E	-00	2.	99512	2E-04	
6.000E&	02		1.2993	022	181E	-00	3.	23153	3E-04	
7.000E&	02		1.3458	1576	724E	-00	3.	32126	5E-04	
8.000E&	02		1.3914	621	986E	-00	3.	25693	8E-04	
9.000E&	02		1.4361	157	966E	-00	3.	03709)E-04	
1.000E&	03		1.4798	184	664E	-00	2.	67233	BE-04	

TABLE 5. -Compressibility factors for helium at 0° C evaluated from

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	and the second second	
TUDIT DCOMPLESSIDITI	Ly Idectors for heritum a	L O C EVALUALEU IIOM
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the B and C	values of table 4 and e	equation (2) (Con.)
	-6 -1	-6 -1
$0.9\alpha = 1.50102 \times 10$	$a tm = 0.9\beta = 1.500$	039 x 10 atm
DOCCCUDE ATM	7	C 7
FRESSURES ATMO	2	JL
1.000E-00	1.0005274880F-00	1.05788E-06
2.000E-00	1,0010548812E-00	2.04812E-06
5-000E-00	1.0026364911E-00	4-89642E-06
1.000E801	1,0052706088F-00	9-45187E-06
2.500F&01	1.0131587213E-00	2-24774E-05
5.000E&01	1.0262581070E-00	4.31006E-05
7-500E601	1.0392981571E-00	6.28621E-05
1.000E802	1.0522788716E-00	8.19397E-05
1.250E&02	1.0652002504E-00	1.00398E-04
1.500E&02	1.0780622935E-00	1.18262E-04
2.000E&02	1.1036083729E-00	1.52215E-04
2.500E&02	1.1289171098E-00	1.83732E-04
3.000E&02	1.1539885040E-00	2.12679E-04
3.500E&02	1.1788225558E-00	2.38894E-04
4.000E&02	1.2034192649E-00	2.62204E-04
4.500E&02	1.2277786315E-00	2.82437E-04
5.000E&02	1.2519006556E-00	2.99429E-04
6.000E&02	1.2994326760E-00	3.23069E-04
7.000E&02	1.3460153261E-00	3.32045E-04
8.000E&02	1.3916486060E-00	3.25620E-04
9.000E&02	1.4363325157E-00	3.03647E-04
1.000E&03	1.4800670552E-00	2.67183E-04

TABLE 5. - Compressibility factors for helium at 0° C evaluated from

		D. 96 - 1. 50102
		5033003-0

and the second s	And some the second sec	
the B and C	values of table 4 and equ	ation (2) (Con.)
	-6 -1	-6 -1
$1.1\alpha = 1.83458 \times 10$	$a tm = 1.1\beta = 1.83381$	x 10 atm
PRESSURE, ATM	7	57
TRESSOREY ATTIC	-	52
1.000E-00	1.0005278296E-00	1.05728E-06
2.000E-00	1.0010555646E-00	2.04692E-06
5.000E-00	1.0026382019E-00	4.89345E-06
1.000EE01	1.0052740382E-00	9.44598E-06
2.500E&01	1.0131673533E-00	2.24629E-05
5.000E&01	1.0262755657E-00	4.30725E-05
7.500E&01	1.0393246372E-00	6.28209E-05
1.000E&02	1.0523145678E-00	8.18861E-05
1.250E&02	1.0652453576E-00	1.00333E-04
1.500E&02	1.0781170064E-00	1.18186E-04
2.000E&02	1.1036828814E-00	1.52118E-04
2.500E&02	1.1290121928E-00	1.83618E-04
3.000E&02	1.1541049406E-00	2.12549E-04
3.500E&02	1.1789611248E-00	2.38751E-04
4.000E&02	1.2035807455E-00	2.62051E-04
4.500E&02	1.2279638025E-00	2.82277E-04
5.000E&02	1.2521102960E-00	2.99264E-04
6.000E&02	1.2996935922E-00	3.22901E-04
7.000E&02	1.3463306341E-00	3.31884E-04
8.000E&02	1.3920214216E-00	3.25474E-04
9.000E&02	1.4367659548E-00	3.03522E-04
1.000E&03	1.4805642336E-00	2.67084E-04

TABLE 5. -Compressibility factors for helium at 0° C evaluated from the B and C values of table 4 and equation (2) (Con.)



TABLE 5 Compressibil	ity factors for helium at	0° C evaluated from
the B and	C values of table 4 and eq	uation (2) (Con.)
	-6 -1	-6 -1
$1.2\alpha = 2.00136 \times 10^{-1}$) $a tm^{-1}$ $1.2\beta = 2.0005$	52 x 10 atm
DRESSIDE, ATM	7	\$7
TRESSOREY ATTO	The Paracetopic Care Care Section	JL
1-000E-00	1,0005280004E-00	1.05698F-06
2.000E-00	1.0010559063E-00	2.04632E-06
5.000E-00	1.0026390573E-00	4.89196E-06
1.000E&01	1.0052757529E-00	9.44303E-06
2.500E&01	1.0131716692E-00	2.24557E-05
5.000E&01	1.0262842950E-00	4.30584E-05
7.500E&01	1.0393378773E-00	6.28003E-05
1.000E&02	1.0523324160E-00	8.18593E-05
1.250E&02	1.0652679112E-00	1.00300E-04
1.500E&02	1.0781443629E-00	1.18148E-04
2.000E&02	1.1037201357E-00	1.52070E-04
2.500EG02	1.1290597344E-00	1.83560E-04
3.000E&02	1.1541631590E-00	2.12484E-04
3.500E&02	1.1790304095E-00	2.38679E-04
4.000E&02	1.2036614859E-00	2.61974E-04
4.500E&02	1.2280563882E-00	2.82197E-04
5.000E&02	1.2522151164E-00	2.99181E-04
6.000E&02	1.2998240506E-00	3.22817E-04
7.000E&02	1.3464882883E-00	3.31804E-04
8.000E&02	1.3922078297E-00	3°22401E-04
9.000E&02	1.4369826747E-00	3.03459E-04
1.000E£03	1.4808128234E-00	2.67034E-04

I had not appreciated balons, is that the independencing determined veloce of the pressure distortion coefficients of the house apprently have little influence on the provision of the PVI data obtained trob a Burnett compressibility apparatus. This weak, descents, that any error in the determination of a and 5 abould not significantly influence the internal precision of compressibility measurements on

	i i i i i i i i i i i i i i i i i i i
	PRESSURE, ATH.
1.00032800092-00 1.00003290638-00 1.000539905736-00 1.005339905736-00 1.03933787336-00 1.03933787336-00 1.03933787336-00 1.035233241805-00 1.035233241805-00 1.035233241805-00 1.03523327600	1.0001-00 2.0006-00 5.0006-00 1.0006201 5.0006201 1.0006203 1.25002603 1.25002603 1.25002603 1.25002603
1.129059739412-00 1.129059734412-00 1.17903061480312-00 1.22330561480312-00 1.222275111042-00 1.22227511042-00 1.26946028814-00 1.39220782812-00 1.49081782342-00 1.49081782342-00	

Link 3. -Compare a la 1 21 2 1 2 201 10 1 201 moltom and 0" C ovelasted from

solution for the volume ratio at zero pressure, N, is not significantly affected. We conclude, therefore, that errors of as much as $\pm 20\%$ in the determination of α and β produce insignificant differences in the least squares solution of N.

2. The least squares solutions for the second and third virial coefficients, B and C, assuming errors of as much as $\pm 20\%$ in the pressure distortion coefficients, differ from those evaluated for $1.0 \alpha = 1.6678 \times 10^{-6} \text{ atm}^{-1}$ and $1.0 \beta = 1.6671 \times 10^{-6} \text{ atm}^{-1}$ by less than the uncertainty with which we know these quantities. This is interpreted to mean that a $\pm 20\%$ error in the determination of the pressure distortion coefficients of the bombs produces differences in the least squares solutions of B and of C which are statistically insignificant.

3. The values of the compressibility factor differ by no more than the stated deviations of these Z's for the five solutions: 0.8 α ; 0.9 α ; 1.0 α ; 1.1 α ; 1.2 α . We conclude, therefore, that errors of this magnitude in α and β produce differences in Z which are no greater than the calculated uncertainties with which we know these quantities.

One of the important points to come out of this analysis, which I had not appreciated before, is that the independently determined values of the pressure distortion coefficients of the bombs apparently have little influence on the precision of the PVT data obtained from a Burnett compressibility apparatus. This means, therefore, that <u>any</u> error in the determination of α and β should not significantly influence the <u>internal</u> precision of compressibility measurements on solution for the volume ratio of zero pressure, N. (s not significantly affected. We annotate, therefore, that errors of se much as 1200 th the determination of a dud & produce insignificant differences in the

2. The beach equates constitute for the second and third virial conflictionic. A and C, are shift, errors of an origin as "25% is the pressure of a total contain coefficients, differ from these evaluated inclines a labor of a labor and the 30 ° and 100° and 100

One of the important parate to none out of this analysis, which I had not appreciated before, is that the independently autoraland values of the provisions distortion coefficients of the bombs appareatly have [fools influence on the provision of the BVT date outsined, from a Burnett compressionility apparents. This means, therefore, that any error in the decervination of a and p should not significantly influence the internal oracision of a and p should not significantly

the gas. This has been found to be true in the analysis of the 0° C helium isotherm data of Briggs (5) for run number 3.

THE EFFECT AN ERROR IN THE FRACTIONAL CHANGE IN THE EFFECTIVE AREA OF THE PISTON (AT 25° C, P=O) WITH PRESSURE PRODUCES IN Z, B, C, AND N

To illustrate better the second statistical test applied to the experimental results reported in (5), the expression from which pressures are calculated (7) is introduced:

$$P_{g} = \frac{M_{a} (1 - \rho_{a}/\rho_{b}) g_{L}/g_{S}}{A_{o} (1 + bP_{g})[1 + c(t-25)]}, \qquad (5)$$

where

- P_{σ} = calculated gage pressure (<u>5</u>, <u>7</u>), psig,
- M = apparent mass, as determined by comparison with brass standards, in air, 1b,

$$p_{L} = density of brass, g/cc$$

g_T = local acceleration due to gravity, gal,

g_S = standard acceleration due to gravity, gal,

- b = fractional change in A with pressure, in^2/in^2 psi,
- c = temperature coefficient of linear expansion of the piston-cylinder combination, in/in °C, and

t = temperature of the piston-cylinder, °C.

the gas. This has been found to be true in the milvets of the G C hallow includes date of Crisse (2) for our compare i.

To tilinstrice briter the second stillstreat rest applied to the spectamental results reported in (21. the expression from which pres-

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enderstant of the plane of the

Suppose the value of b is in error by some amount. Then the pressures as calculated from equation (5) would be different and, hence, we would get new values for B, C, and N as well as new values for the compressibility factor. The problem is to determine the effect an error in b produces in the volume ratio at zero pressure, the virial coefficients, and the compressibility factor and to decide whether this error is statisticallly significant.

Let us assume the fractional change in the effective area of the piston (at 25° C, P=0) with pressure to be in error $\pm 10\%$ and $\pm 20\%$:

0.8 b = $-2.80 \times 10^{-8} \text{ psi}^{-1}$; 0.9 b = $-3.15 \times 10^{-8} \text{ psi}^{-1}$; 1.1 b = $-3.85 \times 10^{-8} \text{ psi}^{-1}$; 1.2 b = $-4.20 \times 10^{-8} \text{ psi}^{-1}$.

Table 6 of this report gives the new values for the pressures as determined from the solution of equation (5) using the method outlined in (5) and (7). All pressures are expressed in standard atmosphere units. The values of column 1 of this table are expansion numbers corresponding to the observed pressures of columns 2, 3, 4, and 5.

Equation (1) was applied to the data of table 6, assuming Z_r to be expressible by equation (2). Table 7 of this report gives the results of the analysis of the data of table 6 for α and β defined by equations (3) and (4), where the quantities given in this table have the same meaning as those of table 2. From the values of B and C of table 7, the compressibility factors of table 8 were calculated. Suppose the value of b is in error by some server, Then the pressures as calculated from equation (5) would be Mifferent and, hence, we would get new values for 3, C, and 3 as well as our values for the compressibility factor. The problem is to decerains the effect an error in b produces in the volume ratio at zero pressure, the virial coefficients, and the compressibility factors and to decide whether this error

Let us assume the fractional change in the affective area of the

0.8 6 - -2.80 x 10⁻⁰ gal⁻¹; 0.9 0 - -3.15 - 10⁻⁸ gal⁻¹; 1.1 0 - -3.85 x 10⁻⁸ pal⁻¹;

Table 5 of this report gives the new values for the pressures as determined from the solution of equation (5) using the method autilius in (5) and (2). All pressures are expressed in standard stancphere units. The values of column 1 of this table are expansion numbers corresponding to the observed pressures of columns 2, 3, 4, and 5.

be expressible by equation (2). Sails 7 of this report gives the results of the analysis of the dote of table 6 for a and 3 defined by equations (3) and (4), where the quantities given in this table have the same meaning as those of table 2. From the values of 8 and 6 of table 7, the tempressibility factors of table 8 wars calculated.

r	$P_{r(obs)}$	$P_{r(obs)}^{2/}$	$P_{r(obs)}$	$P_{r(obs)}$
0	7.0123187E02	7.0125711E02	7.0130761E02	7.0133287E02
1	3.0169868E02	3.0170334E02	3.0171265E02	3.0171731E02
2	1.4061175E02	1.4061276E02	1.4061477E02	1.4061577E02
3	6.8033095E01	6.8033327E01	6.8033791E01	6.8034023E01
4	3.3517210E01	3.3517265E01	3.3517375E01	3.3517429E01
5	1.6660546E01	1.6660559E01	1.6660584E01	1.6660597E01
6	8.3185954E00	8.3185983E00	8.3186040E00	8.3186068E00
7	4.1639844E00	4.1639849E00	4.1639860E00	4.1639866E00

1/ Pressures as calculated by the method outlined in (5) and (7),

- assuming b to be in error by -20%.
- $\frac{2}{2}$ Pressures as calculated by the method outlined in (5) and (7), assuming b to be in error by -10%.
- <u>3</u>/ Pressures as calculated by the method outlined in (5) and (7), assuming b to be in error by +10%.
- 4/ Pressures as calculated by the method outlined in (5) and (7), assuming b to be in error by +20%.

	12 (ado) 7	14 (200) 7 3
	7.0125711802 3.017033030202 1.4061276802 0.8033127801 1.5850333801 8.3185983200 6.1675660200	

be in error by +20%.

TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4)

 $0.8b = -2.80 \times 10^{-8} \text{ psi}^{-1}$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBSP,CAL.	P,OBSP,CAL. P,OBS.
0	7.0123187E&02	7.0123187E&02	0.00000E-99	0.00000E-99
1 :	3.0169868E&02	3.0169918E&02	-4.99031E-04	-1.65407E-06
2	1.4061175E&02	1.4060911E&02	2.63970E-03	1.87729E-05
3	6.8033095E&01	6.8036659E&01	-3.56376E-03	-5.23828E-05
4	3.3517210E&01	3.3518703E&01	-1.49266E-03	-4.45341E-05
5	1.6660546E&01	1.6659307E&01	1.23865E-03	7.43466E-05
6	8.3185954E-00	8.3161277E-00	2.46771E-03	2.96651E-04
7	4.1639844E-00	4.1603439E-00	3.64045E-03	8.74273E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30223E-05

CONSTANTS AND STANDARD ERRORS

N	1.994558905E-00	SN	1.29960E-04
B	5.276058057E-04	SB	8.84184E-07
С	-4.739691916E-08	SC	5.96346E-10

VARIANCES AND COVARIANCES

S2N	1.68896E-08
S2B	7.81781E-13
S2C	3.55628E-19
S2BC	-5.22405E-16
S2BN	-1.10651E-10
S2CN	7.12832E-14

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		4.116398441-00

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TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4) (Con.)

$$0.9b = -3.15 \times 10^{-8} \text{ psi}^{-1}$$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBSP,CAL.	P,OBSP,CAL. P,OBS.
0	7.0125711E&02	7.0125711E&02	0.00000E-99	0.00000E-99
1	3.0170334E&02	3.0170383E&02	-4.99082E-04	-1.65421E-06
2	1.4061276E&02	1.4061012E&02	2.64005E-03	1.87753E-05
3	6.8033327E&01	6.8036892E&01	-3.56433E-03	-5.23910E-05
4	3.3517265E&01	3.3518758E&01	-1.49277E-03	-4.45376E-05
5	1.6660559E&01	1.6659320E&01	1.23891E-03	7.43619E-05
6	8.3185983E-00	8.3161302E-00	2.46808E-03	2.96694E-04
7	4.1639849E-00	4.1603441E-00	3.64078E-03	8.74351E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30334E-05

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CONSTANTS AND STANDARD ERRORS

N 1.994558976E-00	SN	1.29975E-04
B 5.276560323E-04	SB	8.84274E-07
C -4.739376953E-08	SC	5.96378E-10

VARIANCES AND COVARIANCES

S2N	1.68936E-08
S2B	7.81942E-13
S2C	3.55667E-19
S2BC	-5.22487E-16
S2BN	-1.10675E-10
S2CN	7.12955E-14

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SUM OF MELCATED SULARES OF THE RESIDUALS 4.303346-03

CONSTANTS AND STANDARD ERRORS

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VARIANCES AND COVARIANCES

TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4) (Con.)

 $1.1b = -3.85 \times 10^{-8} \text{ psi}^{-1}$

				P, OBS P, CAL.
r	P,OBS.,ATM.	P,CAL.,ATM.	P, OBSP, CAL.	P,OBS.
0	7.0130761E&02	7.0130761E&02	0.00000E-99	0.00000E-99
1	3.0171265E&02	3.0171315E&02	-4.99183E-04	-1.65450E-06
2	1.4061477E&02	1.4061213E&02	2.64074E-03	1.87799E-05
3	6.8033791E&01	6.8037357E&01	-3.56547E-03	-5.24073E-05
4	3.3517375E&01	3.3518868E&01	-1.49301E-03	-4.45446E-05
5	1.6660584E&01	1.6659345E&01	1.23942E-03	7.43923E-05
6	8.3186040E-00	8.3161352E-00	2.46880E-03	2.96781E-04
7	4.1639860E-00	4.1603446E-00	3.64144E-03	8.74508E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30556E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559117E-00	SN	1.30005E-04
B	5.277564850E-04	SB	8.84456E-07
С	-4.738745396E-08	SC	5.96444E-10

VARIANCES AND COVARIANCES

S2N	1.69015E-08
S2B	7.82262E-13
S2C	3.55746E-19
S2BC	-5.22652E-16
S2BN	-1.10724E-10
S2CN	7.13200E-14

	by equations (1) and (4) (Cour)
	1.1b. = -3.25 x 10 ⁻² net-1
-280-4	

TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4) (Con.)

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 $1.2b = -4.20 \times 10^{-8} \text{ psi}^{-1}$

				P, OBS P, CAL.
r	P,OBS.,ATM.	P+CAL.,ATM.	P,OBSP,CAL.	P;OBS.
0	7.0133287E&02	7.0133287E&02	0.00000E-99	0.00000E-99
1	3.0171731E&02	3.0171780E&02	-4.99234E-04	-1.65464E-06
2	1.4061577E&02	1.4061313E&02	2.64109E-03	1.87823E-05
3 .	6.8034023E&01	6.8037589E&01	-3.56604E-03	-5.24155E-05
4	3.3517429E&01	3.3518923E&01	-1.49313E-03	-4-45481E-05
5	1.6660597E&01	1.6659357E&01	1.23967E-03	7.44075E-05
6	8.3186068E-00	8.3161377E-00	2.46916E-03	2.96824E-04
7	4.1639866E-00	4.1603448E-00	3.64176E-03	8.74586E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30667E-05

CONSTANTS AND STANDARD ERRORS

N 1.994559188E-00	SN 1.30021E-04
B 5.278067112E-04	SB 8.84546E-07
C -4.738428794E-08	SC 5.96477E-10

VARIANCES AND COVARIANCES

S2N	1.69054E-08
S2B	7.82423E-13
S2C	3.55785E-19
S2BC	-5.22734E-16
S2BN	-1.10748E-10
S2CN	7.13323E-14

EABLE 7. -Results of the analysis of the days of table 5 for a dad 2 defined by squattings (3) and (2) (Con.)

1.2b = -4.20 × 10-0 per-t

		" .MTA 280.9
	7.01332876502 3.01717806502 1.40613136502 6.80379096501 3.35189236501 1.66593576601 8.31613776-00	

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.3055YE-D

CONSTANTS AND STANDARD ERRORS

VARIANCES AND COVARIANCES

TABLE 8.-Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2)

 $0.8b = -2.80 \times 10^{-8} \text{ psi}^{-1}$

PRESSURE, ATM.

Z

1.000E-00	1.0005275584E-00	1.05732E-06
2.000E-00	1.0010550220E-00	2.04704E-06
5.000E-00	1.0026368441E-00	4.89381E-06
1.000E&01	1.0052713183E-00	9.44682E-06
2.500E&01	1.0131605220E-00	2.24653E-05
5.000E&01	1.0262617979E-00	4.30775E-05
7.500E&01	1.0393038277E-00	6.28283E-05
1.000E&02	1.0522866113E-00	8.18957E-05
1.250E&02	1.0652101488E-00	1.00344E-04
1.500E&02	1.0780744401E-00	1.18199E-04
2.000E&02	1.1036252843E-00	1.52134E-04
2.500E&02	1.1289391439E-00	1.83634E-04
3.000E&02	1.1540160190E-00	2.12566E-04
3.500E&02	1.1788559094E-00	2.38766E-04
4.000E&02	1.2034588152E-00	2.62064E-04
4.500E&02	1.2278247364E-00	2.82287E-04
5.000E&02	1.2519536730E-00	2.99270E-04
6.000E&02	1.2995005925E-00	3.22897E-04
7.000E&02	1.3460995736E-00	3.31867E-04
8-000E&02	1.3917506163E-00	3.25443E-04
9.000E&02	1.4364537206E-00	3.03477E-04
1.000E&03	1.4802088865E-00	2.67028E-04

SZ

	.0,
2.125866-04	

TABLE 8.-Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2) (Con.)

 $0.9b = -3.15 \times 10^{-8} \text{ psi}^{-1}$

PRESSURE, ATM.

Z

SZ

1.000E-00	1.0005276086E-00	1.05745E-06
2.000E-00	1.0010551224E-00	2.04728E-06
5.000E-00	1.0026370953E-00	4.89437E-06
1.000E&01	1.0052718209E-00	9.44787E-06
2.500E&01	1.0131617797E-00	2.24677E-05
5.000E&01	1.0262643171E-00	4.30820E-05
7.500E&01	1.0393076124E-00	6.28349E-05
1.000E&02	1.0522916655E-00	8.19043E-05
1.250E&02	1.0652164763E-00	1.00355E-04
1.500E&02	1.0780820450E-00	1.18211E-04
2.000E&02	1.1036354556E-00	1.52150E-04
2.500E&02	1.1289518974E-00	1.83655E-04
3.000E&02	1.1540313704E-00	2.12590E-04
3.500E&02	1.1788738745E-00	2.38794E-04
4.000E&02	1.2034794098E-00	2.62096E-04
4.500E&02	1.2278479762E-00	2.82322E-04
5.000E&02	1.2519795737E-00	2.99308E-04
6.000E&02	1.2995318623E-00	3.22941E-04
7.000E&02	1.3461362755E-00	3.31916E-04
8.000E&02	1.3917928133E-00	3.25495E-04
9.000E&02	1.4365014757E-00	3.03530E-04
1.000E&03	1.4802622627E-00	2.67081E-04

TARGE 8 - Compressibility factors for Helicon at 0° 6 avaluated from

10,96 = -3,15 x 10 pat

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TABLE 8. -Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2) (Con.)

 $1.1b = -3.85 \times 10^{-8} \text{ psi}^{-1}$

PRESSURE, ATM.

1.000E-00 1.00052770 1.00105532 2.000E-00 5.000E-00 1.00263759 1.000E&01 1.00527282 2.500E&01 1.01316429 1.02626935 5.000E&01 7.500E&01 1.03931518 1.000E&02 1.05230177 1.250E&02 1.06522913 1.500E&02 1.07809725 2.000E&02 1.10365579 2.500E&02 1.12897740 3.000E&02 1.15406207 3.500E&02 1.178909800 4.000E&02 1.20352060 1.22789445 4.500E&02 5.000E&02 1.25203137 6.000E&02 1.29959440 1.34620968 7.000E&02 8.000E&02 1.39187721 9.000E&02 1.43659699

1.000E&03

Z

SZ

1.0005277090E-00	1.05771E-06
1.0010553234E-00	2.04777E-06
1.0026375977E-00	4.89549E-06
1.0052728261E-00	9.44997E-06
1.0131642949E-00	2.24726E-05
1.0262693556E-00	4.30911E-05
1.0393151819E-00	6.28481E-05
1.0523017739E-00	8.19215E-05
1.0652291316E-00	1.00376E-04
1.0780972550E-00	1.18237E-04
1.1036557988E-00	1.52183E-04
1.1289774054E-00	1.83695E-04
1.1540620746E-00	2.12639E-04
1.1789098066E-00	2.38850E-04
1.2035206014E-00	2.62159E-04
1.2278944588E-00	2.82392E-04
1.2520313790E-00	2.99385E-04
1.2995944076E-00	3.23030E-04
1.3462096871E-00	3.32014E-04
1.3918772175E-00	3.25599E-04
1.4365969988E-00	3.03638E-04
1.4803690311E-00	2.67187E-04

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TABLE 8. -Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2) (Con.)

 $1.2b = -4.20 \times 10^{-8} \text{ psi}^{-1}$

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PRESSURE, ATM.

1.000E-00		1.0005277593E-00	
2.000E-00)	1.0010554238E-00	
5.000E-00)	1.0026378489E-00	
1.000E&01		1.0052733286E-00	
2.500E&01		1.0131655526E-00	
5.000E&01	C. NGHEKKE	1.0262718748E-00	
7.500E&01	L	1.0393189667E-00	
1.000E&02	2	1.0523068282E-00	
1.250E&02	2	1.0652354594E-00	
1.500E&02	2	1.0781048602E-00	
2.000E&02	2	1.1036659707E-00	
2.500E&02	2	1.1289901598E-00	
3.000E&02	2	1.1540774274E-00	
3.500E&02	2	1.1789277736E-00	
4.000E&02	2	1.2035411984E-00	
4.500E&02	2 All Cherry	1.2279177017E-00	
5.000E&02	2	1.2520572836E-00	
6.000E&02		1.2996256830E-00	
7.000E&02	2	1.3462463967E-00	
8.000E&02		1.3919194247E-00	
9.000E&02	2	1.4366447668E-00	
1.000E&03	5	1.4804224232E-00	

assuming around of 0.8 b and 1.2 b, differ from 0 avaluated for 1.0 b by about 1/100 the calculated uncertainty of the chird wiright conflirient. The corresponding differences, samuning wrote al 0.0 b and 1.1 b, are (1/200 S_C). This is interpreted to mean that errors in the value of b of as much as 1.001 produce insignificant differences in the least squares solution of C, the third wiright conflictent of the

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1.05784E-06 2.04801E-06 4.89605E-06 9.45102E-06 2.24750E-05 4.30957E-05 6.28547E-05 8.19301E-05 1.00387E-04 1.18249E-04 1.52200E-04 1.83716E-04 2.12663E-04 2.38878E-04 2.62190E-04 2.82427E-04 2.99423E-04 3.23074E-04 3.32063E-04 3.25652E-04 3.03692E-04 2.67240E-04

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From the results given in tables 1, 2, 3, 6, 7, and 8, the following significant results indicate that:

1. The least squares solution for the volume ratio at zero pressure, N, is not affected by errors of $\pm 10\%$ or $\pm 20\%$ in the fractional change of the effective area of the piston (at 25° C, P=0) with pressure. This was taken to mean that errors in b of as much as $\pm 20\%$ do not significantly influence the least squares value of the volume ratio at zero pressure.

2. The least squares solutions for B, assuming $\pm 10\%$ errors in b, differ from the second virial coefficient evaluated for b = -3.5 x 10^{-8} in^2/in^2 psi by about 1/17 the calculated uncertainty of this parameter; the corresponding differences for $\pm 20\%$ errors in b are about 9 times smaller than the uncertainty of B. This means, therefore, that errors of as much as $\pm 20\%$ in the value of the fractional change in the effective area of the piston (at 25° C, P=0) with pressure influences the least squares value of the second virial coefficient of the gas an insignificant amount.

3. The least squares solutions for the third virial coefficient, assuming errors of 0.8 b and 1.2 b, differ from C evaluated for 1.0 b by about 1/100 the calculated uncertainty of the third virial coefficient! The corresponding differences, assuming errors of 0.9 b and 1.1 b, are (1/200 S_C). This is interpreted to mean that errors in the value of b of as much as ±20% produce insignificant differences in the least squares solution of C, the third virial coefficient of the gas.

From the results given in tables 1, 2, 3, 6, 7, and 8, the follow-

1. The laset equares solution for the volume ratio at tero preseure. N. is not effected by errors of s10% or 120% to the tractional charge of the effective area of the piston (at 25° C. P+0) with pressure This was taken to dean that arcors in b of as much as 120% do not s(gmifficantly influence the least equares value of the volume ratio at zero

2. The least squares solutions for 5, assuming 1105 errors to 5, differ from the second virial confficient evaluated for $b + -3.5 \times 10^{-6}$ in $^{2}/10^{-2}$ per by about 1/17 the calculated uncertainty of this permater; the corresponding differences for -205 errors in b are shout 9 thems enabled to a corresponding differences for -205 errors in b are shout 9 thems of as much as -205 in the value of the fractional change in the effective area of the platon (at 25° C, 7°0) with pressure influences the insignificant equares value of the second virial coefficient of the gap an

3. The least squares solutions for the third virial coefficient, essuming errors of 0.8 b and 1.2 b, differ from C evaluated for 1.0 b by about 1/100 the calculated uncertainty of the third virial coefficient! The corresponding differences, assuming errors of 0.9 b and 1.1 b, are $(1/200 \ S_{\rm C})$. This is interpreted to mean that errors in the value of b of as much as $\pm 20\%$ produce insignificant differences in the least squares solution of C, the third virial coefficient of the

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4. The values of Z, assuming 0.8 b and 1.2 b, differ from Z evaluated for 1.0 b by about $(1/5 S_Z)$ over the pressure range 1 to 700 atmospheres; the corresponding differences, assuming 0.9 b and 1.1 b, are almost an order of magnitude smaller than the uncertainty of the compressibility factor over this same pressure range. We conclude, therefore, that errors as great as 0.8 b and 1.2 b produce differences in Z which are no greater than 1/5 the uncertainty with which we know these compressibility factors over the pressure range of this experiment.

We also note that the independently determined value of the fractional change in the effective area of the piston (at 25° C, P=O) with pressure, b, has no significant influence on the precision of the PVT data or on N. This means, therefore, that <u>any</u> error in the determination of b should not affect the internal precision of compressibility measurements on the gas or the value of the zero pressure volume ratio of the Burnett apparatus. We found this to be true in the analysis of these data.

THE EFFECT AN ERROR OF IGNORING THE CHANGE IN THE VOLUME RATIO WITH PRESSURE PRODUCES IN Z, B, C, AND N

The final test applied to the experimental compressibility measurements of table 1 was to determine the effect an error of ignoring the pressure distortion of the bombs produces in the compressibility factor, the virial coefficients, and the zero pressure volume ratio and then to decide whether this assumption of $\alpha = \beta = 0$ differs significantly from the results previously calculated using the present values for these

We the values of 2, assuming 0.6 b and 1.2 b, allier from E evaluseed for 1.0 b by shuft $(2/5 \frac{1}{2})$ over the pressure range 1 to 700 stoom pheres; the corresponding differences, assuming 0.9 b and 1.1 b, are almost an order of magnitude saulter that the uncertainty of the compressibility factor over this same pressure range. We conclude, instefore, that errors as great at 0.8 b and 1.2 b produce differences in 2 which are no greater the uncertainty with the store that the compressibility factor over the uncertainty of the second compressibility factor over the pressure range. We conclude, inste-

We also note that the independently derivated value of the fractional change in the effective area of the platon far 25° 0, P=0) with presents, b, has no significant influence on the procletes of the FVI deta or on M. fore means therefore, that any error in the determination of b should not affect the forereal preclation of cospressibility measurements on the gas of the value of the recordering of the analysis of these data.

THE SECT AN SERVE OF ICREATED OF CHANGE

The final rest applied to the experimental cospirationity measurements of twile I was to determine the offer r an error of ignoring the pressure distortion of the bomes produces in the compress (bility factor the virial coefficients, and the zero pressure volume varies and then in decide whether this assumption of 0 = 2 = 0 differs significantly from pressure distortion coefficients (i.e., $\alpha = 1.6678 \times 10^{-6} \text{ atm}^{-1}$, $\beta = 1.6671 \times 10^{-6} \text{ atm}^{-1}$).

Equation (1) was applied to the data of table 1, where Z_r is expressible by equation (2), to give the results of table 9 for $\alpha = \beta = 0$. The values given in table 9 have the same meaning as those of table 2. From the results of table 9 and equation (2), the compressibility factors of table 10 were calculated. The deviations, S_Z , given in this table are standard deviations as determined by the method previously given in (8).

The results of tables 1, 2, 3, 9, and 10 indicate the following:

1. The least squares solution for N, assuming $\alpha = \beta = 0$, differs from that evaluated for $\alpha = 1.6678 \times 10^{-6} \text{ atm}^{-1}$ and $\beta = 1.6671 \times 10^{-6}$ atm⁻¹ by (1/100 S_N). This was interpreted to mean that ignoring the pressure distortion coefficients of the bombs does not produce a statistically significant difference in the least squares solution for the zero pressure volume ratio.

2. The solution for B, assuming $\alpha = \beta = 0$, differs from that previously calculated using the present values for these pressure distortion coefficients by more than one would expect from the calculated uncertainties. This suggests, therefore, that ignoring the change in the volume ratio with pressure could be significant insofar as the second virial coefficient of the gas is concerned.

3. The solution for C, assuming $\alpha = \beta = 0$, differs from that evaluated using the present values for these pressure distortion coefficients by no more than one would expect; that is, the difference is less pressure distortion cosfficients (t.e., o ~ 1.0578 x 10 " atm " 5 1.5571 x 10 " arm ").

Equation (1) was applied to the data of table 1, where 2, it aspressible by equation (2), to give the rebains of table 9 for 2 = 3 = 0. The values given in table 9 have the same medular as those of table 2. From the results of table 3 and equation (3), the compress bility factors of table 10 were taiculated. The deviations, 52, given in this table are similard deviations as determined by the method previously given in (8).

The results of tables 1, 2, 3: 9, and 10 fodicate the following: 1. The less: aquares solution for 3, securize o = 4 = 0, differs from thet evaluated for a = 1.8678 × 10⁻⁰ and 8 = 1.6671 × 10⁻⁰ arm⁻¹ by (1/100 S₀). This was interpreted to asso thes ignoring the pressure distortion coefficients of the bodys does not produce a statistically significant difference in the least squares solution for the data pressure volume cario.

2. The solution for 2, assuming $\alpha = \beta = 0$, differo from that proviously calculated units one present values for these presence diatorijon racificients by more than one would avoid from the calculated uncertainties. This suggerts, therefore, that ignoring the divinge in the volume ratio with pressure could be significant incofer as the accord virial cuefficient of the gas is concerned.

3. The solution for C. assigning Q = B = 0, differs from that evaluated using the present values for these pressure distortion meefficients by no more than one would expect; that is, the difference is less

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TABLE	9Re	sults	of	the	anal	ysis	of	tab.	le	1,	ass	uming	the	volume	ratio	to	be
		indep	ende	ent	of th	e pr	essi	ure	(α	=	0 =	β)					

				P,OBSP,CAL.
r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBSP,CAL.	P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-5.01023E-04	-1.66062E-06
2	1.4061376E&02	1.4061111E&02	2.65149E-03	1.88565E-05
3	6.8033559E&01	6.8037141E&01	-3.58199E-03	-5.26504E-05
4	3.3517320E&01	3.3518817E&01	-1.49675E-03	-4.46560E-05
5	1.6660572E&01	1.6659325E&01	1.24671E-03	7.48301E-05
6	8.3186011E-00	8.3161219E-00	2.47917E-03	2.98027E-04
7	4.1639855E-00	4.1603349E-00	3.65058E-03	8.76703E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.33797E-05

CONSTANTS AND STANDARD ERRORS

N	1.994561338E-00	SN	1.30470E-04
B	5.259993502E-04	SB	8.87300E-07
С	-4.816958247E-08	SC	5.98977E-10

VARIANCES AND COVARIANCES

S2N	1.70224E-08
S2B	7.87302E-13
S2C	3.58774E-19
S2BC	-5.26578E-16
S2BN	-1.11476E-10
S2CN	7.18860E-14

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2-6524 18-03		
CO-SITOPS-I		

TABLE 10.-Compressibility factors for helium at 0° C evaluated from the data of table 9 and equation (2)

Ζ SZ PRESSURE, ATM. 1.0005259511E-00 1.06059E-06 1.000E-00 2.000E-00 1.0010518060E-00 2.05352E-06 1.0026287925E-00 5.000E-00 4.90978E-06 1.0052551765E-00 9.47836E-06 1.000E&01 2.25423E-05 2.500E&01 1.0131198777E-00 1.0261795435E-00 4.32272E-05 5.000E&01 1.0391789973E-00 6.30473E-05 7.500E&01 1.000E&02 1.0521182391E-00 8.21807E-05 1.250E&02 1.0649972690E-00 1.00692E-04 1.0778160869E-00 1.18607E-04 1.500E&02 2.000E&02 1.1032730867E-00 1.52651E-04 2.500E&02 1.1284892386E-00 1.84249E-04 3.000E&02 1.1534645426E-00 2.13264E-04 1.1781989987E-00 2.39535E-04 3.500E&02 4.000E&02 1.2026926068E-00 2.62891E-04 4.500E&02 1.2269453671E-00 2.83158E-04 5.000E&02 1.2509572794E-00 3.00172E-04 3.23823E-04 6.000E&02 1.2982585604E-00 7.000E&02 1.3445964497E-00 3.32769E-04 8.000E&02 1.3899709474E-00 3.26277E-04 3.04207E-04 9.000E&02 1.4343820534E-00 1.4778297677E-00 2.67628E-04 1.000E&03

TARKS ID .-Compressivity Causing the seliment of C mentioned from

	1+5002102

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than the uncertainty with which we know this difference. We conclude, therefore, that ignoring the pressure distortion of N has an insignificant effect on the least squares value of C.

4. The compressibility factors of the gas calculated for zero distortion of the volume ratio with pressure differ from those evaluated using $\alpha = 1.6678 \times 10^{-6} \text{ atm}^{-1}$, $\beta = 1.6671 \times 10^{-6} \text{ atm}^{-1}$ by more than is to be expected from the calculated uncertainties. This means, therefore, that the effect of ignoring the pressure distortion coefficients of the bombs has a statistically significant effect on the values of Z which amounts to more than three times the expected difference at 700 atmospheres; about twice the expected difference at 300 atmospheres, and about 1.4 times the expected difference at 50 atmospheres.

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then the uncertainty with which we know this difference. We complute, therefore, then ignoring the presence distortion of N has an insignificant effect on the least squares value of C.

¹. The compressibility factors of the gas calculated for zero discortion of the volume ratio with pressure differ from those avaluated using $c = 1.6673 \times 10^{-6}$ arm⁻¹, $5 = 1.6671 \times 10^{-6}$ arm⁻¹ by more than is to be expected from the calculated uncertisinfies. This means, therefore, that the effect of ignoring the pressure distortion coefficience of the bombs has a scatterizably eignificant effect or the values of 2 which amounts to more than three these the expected differences at 300 stress pheres; about twice the expected differences at 300 stress about 1.4 times the expected difference at 30 stress and

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