H. Rhodes

Report No. 106

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

INTERNAL REPORT

MODIFIED REDLICH-KWONG EQUATIONS FOR
HYDROGEN AND FOR NEON

BY

Philip C. Tully

and

Jonnie M. Estes

BRANCH Fundamental Research

PROJECT NO. 5571

DATE April, 1967

AMARILLO, TEXAS

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by

Philip C. Tully [1/] and Jonnie M. Estes [2/]

ABSTRACT

As part of an over-all program to develop a single equation of state for helium and its mixtures to be used in equilibrium thermodynamic consistency calculations, coefficients of the B term of the Redlich-Kwong equation for pure hydrogen and neon are presented. For normal hydrogen, the original Redlich-Kwong (R-K) value of B, which is $\frac{.0867T_c}{P_cT_c}$, is changed to $\frac{.08063T_c}{P_cT_c}$. For temperatures from 98° to 423° K and pressures up to 2,950 atmospheres, this gives an average deviation of 0.63 percent from experimental data. For neon, B is changed to $\frac{.1025T_c}{P_cT_c}$. For temperatures from 120° to 973° K and pressures up to 2,900 atmospheres, this gives an average deviation of 0.48 percent from experimental data. No changes were made in the value of A for either gas.

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INTRODUCTION

The PVT properties of gaseous hydrogen and neon have been represented by various types of equations. It is well known that these two gases do not obey the law of corresponding states and so cannot be well represented by generalized equations of state.

Virial-form equations have been given for hydrogen by Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9).[3/] Equations of this type have been used for neon by Michels, Wassenaar, and Louwerse (10); Holborn and Otto (6); Nicholson and Schneider (11); and Sullivan and Sonntag (14). For both of these gases Gunn, Chueh, and Prausnitz (5) have published "effective critical constants" to be used in conjunction with Pitzer's (12) generalized tables.

Goodwin (4) has published a six-constant "approximate wide-range equation" for hydrogen. Ziegler, McWilliams, and Keller (16) have redetermined these constants for temperatures to 300° K and pressures to 100 atmospheres.

McCarty and Stewart (8) have developed an 18-constant modified Benedict-Webb-Rubin equation for neon for temperatures from 25° to 300° K and pressures from 0.1 to 200 atmospheres.

This paper presents a modification of the R-K (13) equation of state which is specific for hydrogen. A similar specific modification is made for neon.

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

The R-K equation is

$$P = RT/\ (V-b) - a/T^{1/2}V(V+b) \tag{1}$$

or

$$Z = 1/(1-h) - (A^2/B)h/(1+h) \quad , \tag{2}$$

where

$$Z = PV/RT \quad , \tag{3}$$

$$A^2 = a/R^2T^{2.5} = 0.4278\ T_c^{2.5}/P_cT^{2.5} \quad , \tag{4}$$

$$B = b/RT = 0.0867\ T_c/P_cT \quad , \tag{5}$$

and

$$h = b/V = BP/Z \quad . \tag{6}$$

Equation 2 can be solved by successive approximations in Z. The work discussed in this paper was done on an IBM 1620 computer.[4/]

4/ Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

A list of the nomenclature used in this report is appended.

SELECTION OF COEFFICIENTS

Previous papers (2,3) have presented a method for modifying the R-K equation for helium. This modification consists of developing a new coefficient for the B term, and is based on the limiting volume of helium. Similar individualized coefficients are given here for hydrogen and for neon. However, the technique used to determine the new coefficient for helium could not be used for hydrogen and neon because there is no extremely high pressure data for these gases. Although Bridgman's (1) data for hydrogen extend to 13,000 kg/cm^2,

this pressure is not high enough to warrant extrapolation to the limiting volume. We were unable to find any PVT data above 3000 atm for neon.

The selection of the coefficient for hydrogen was based on the data of Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9). The highest (423° K) and lowest (273° K) isotherms at their highest pressure (2,900 atm) were chosen for optimizing the coefficient because we wanted to fit the high pressure data to less than one percent. (The original R-K equation does quite well at low pressures.) Values of Z were calculated at all points along these two isotherms by using numerous B coefficient values near the original (.0867) value. The value of 0.08063 was selected to yield a maximum deviation of < 1 percent at high and low pressures. The optimum value is obviously a function of pressure, but this single value was selected to maintain the simplicity of the equation.

A similar procedure was employed for neon by using the data of Michels, Wassenaar, and Louwerse (10), also at 273° and 423° K. A value of 0.1025 was selected.

The experimental criticals used were P_c = 12.80 atm and T_c = 33.25° K for hydrogen and P_c = 26.86 atm and T_c = 44.45° K for neon. This gives

$$B = \frac{.2094}{T} \quad \text{for hydrogen}$$

$$B = \frac{.1696}{T} \quad \text{for neon.}$$

RESULTS

Compressibility factors calculated by using these two coefficients are compared with experimental data over the ranges shown in table 1.

TABLE 1. - Ranges of experimental conditions over which calculated Z's were compared with experimental Z's

Investigator	Temperature range, °K	Approximate pressure range, atm	
		Min	Max
	HYDROGEN		
Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)	273-423	20	1/ 2425-2950
Do	98-248	5	1/ 325-1000
Johnston and White (7) .	35-300	1	200
Woolley, Scott and Brickwedde (15) . .	273-600	20	1/ 800-1700
	NEON		
Michels, Wassenaar, and Louwerse (10) . . .	273-423	25	1/ 2600-2900
Holborn and Otto (6) . .	90-673	1	100
Nicholson and Schneider (11)	273-973	10	80
Sullivan and Sonntag (14)	70-120	10	300

1/ Maximum pressure differs with each isotherm.

Over wide pressure ranges, such as are shown in table 1, plots of P vs Z data for helium, hydrogen, and neon show that dZ/dP goes through a maximum before reaching very high reduced-pressure values (see figure 1). Neither the original R-K equation nor the modifications

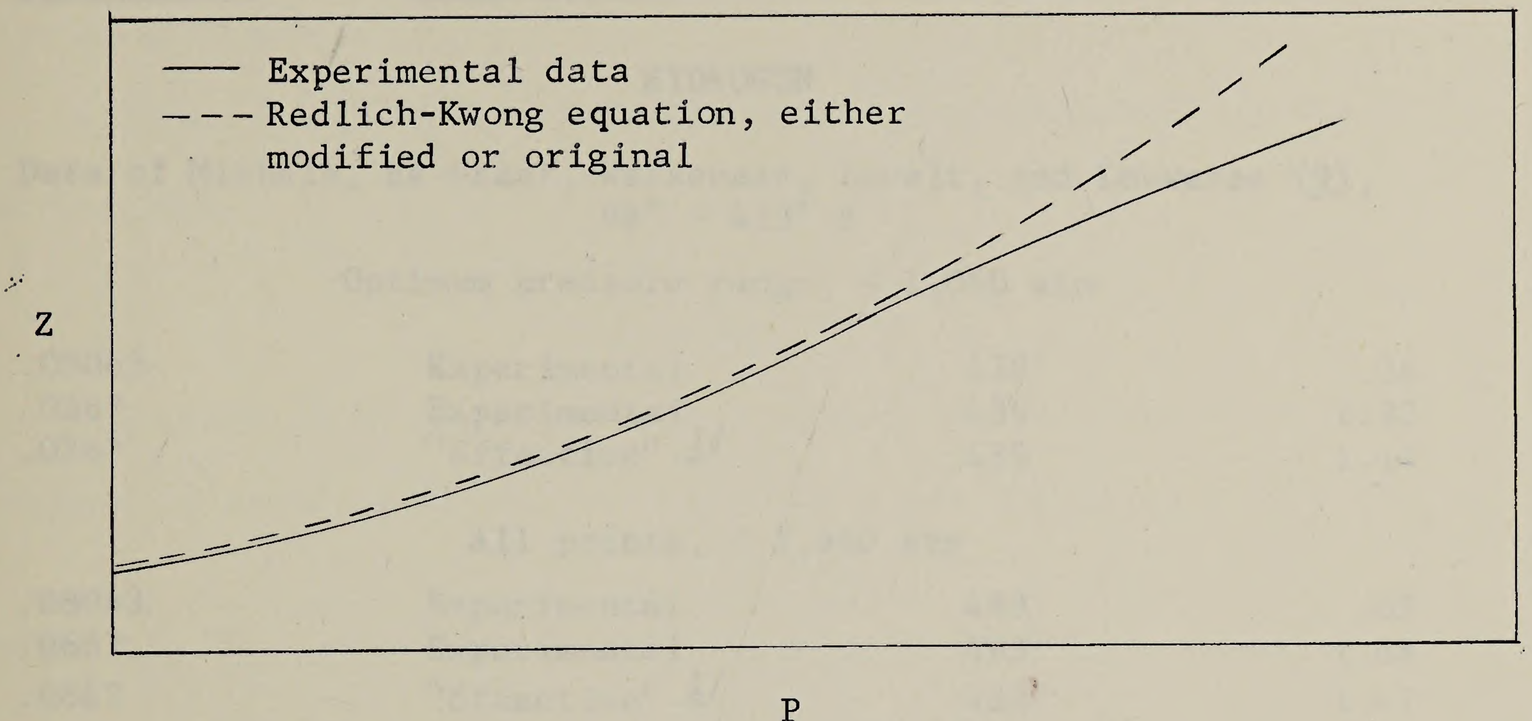

Figure 1. P vs Z for Experimental Data and for Z's Calculated by the Redlich-Kwong Equation

suggested here reproduce this change in slope. Therefore, there is increasing divergence between experimental and calculated values at very high pressures.

The maximum deviation is < 1 percent up to 1,050 atm for hydrogen, (with the exception of a few low temperature points) and up to about 1,500 atm for neon. The average percentage absolute differences over these ranges are given in table 2. For the higher pressure points (up to 2,950 atm), the maximum deviations are considerably greater (< 8.8) than 1 percent. However, the "all-points" averages, also given in table 2, are still < 1 percent. In addition, the table

TABLE 2. - Average percentage absolute difference between Z_{exp} and Z_{calc} for various forms of the R-K equation

Coefficient, B term	Critical constants used	Number of points	Average percentage absolute difference
	HYDROGEN		
Data of Michels, de Graaf, Wassenaar, Levelt, and Louwerse (9), 98° - 423° K			
	Optimum pressure range, < 1,050 atm		
.08063	Experimental	439	.36
.0867	Experimental	439	1.32
.0867	"Effective" 1/	439	1.44
	All points, < 2,950 atm		
.08063	Experimental	483	.63
.0867	Experimental	483	1.88
.0867	"Effective" 1/	483	1.47
	NEON		
Data of Michels, Wassenaar, and Louwerse (10); Nicholson and Schneider (11); and Holborn and Otto (6); 120° - 973° K			
	Optimum pressure range, < 1,500 atm		
.1025	Experimental	444	.34
.0867	Experimental	444	1.82
.0867	"Effective" 1/	444	1.67
	All points, < 2,900 atm.		
.1025	Experimental	479	.48
.0867	Experimental	479	2.12
.0867	"Effective" 1/	479	1.91

1/ Developed by Gunn, Chueh, and Prausnitz (5).

shows the performance of the original R-K equation when two different sets of critical constants are used: (1) the experimental critical constants; and (2) the "effective critical constants" proposed by Gunn, Chueh, and Prausnitz (5), which will be discussed later.

A future paper will discuss the use of these modified equations for mixtures.

Hydrogen

The range of greatest usefulness of the modified equation for hydrogen is shown in figure 2. A similar graph showing how well the

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FIGURE 2. - Percentage Absolute Difference Between Experimental Z's for Hydrogen and Those Calculated by the Modified Redlich-Kwong Equation.

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unmodified R-K equation fits these same data is shown in figure 3.

FIGURE 3. - Percentage Absolute Difference Between Experimental Z's for Hydrogen and Those Calculated by the Original Redlich-Kwong Equation.

Down to about 40° K, the low temperature, experimental data of Johnston and White (7) are better represented by the modified equation than by the original. However, since the modified equation gives deviations as large as 2.6 percent at 90°, it is not recommended for use below 98°. Woolley, Scott, and Brickwedde (15) state that the available PVT data

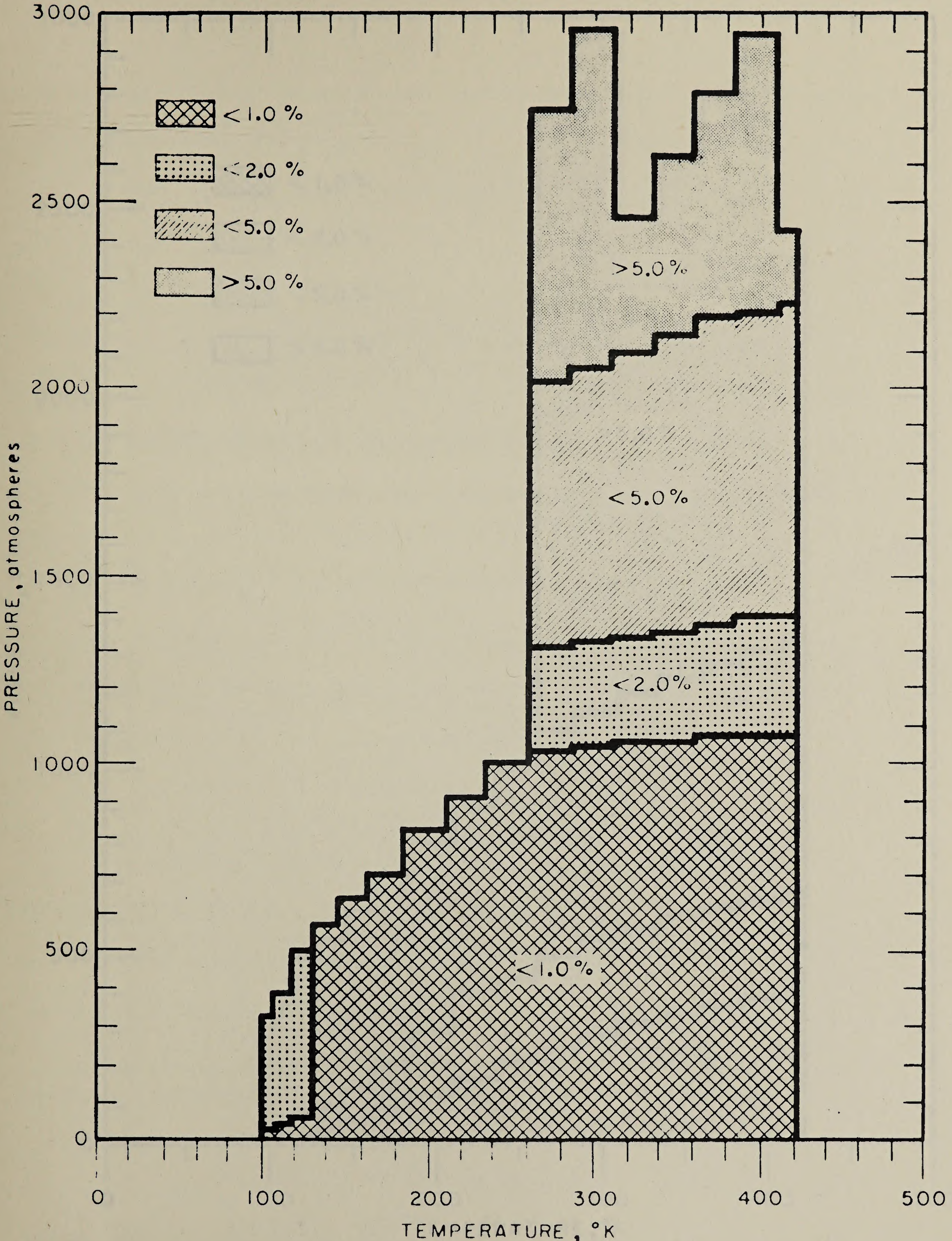

FIGURE 2.— Percentage Absolute Difference Between Experimental Z's For Hydrogen And Those Calculated By The Modified Redlich—Kwong Equation.

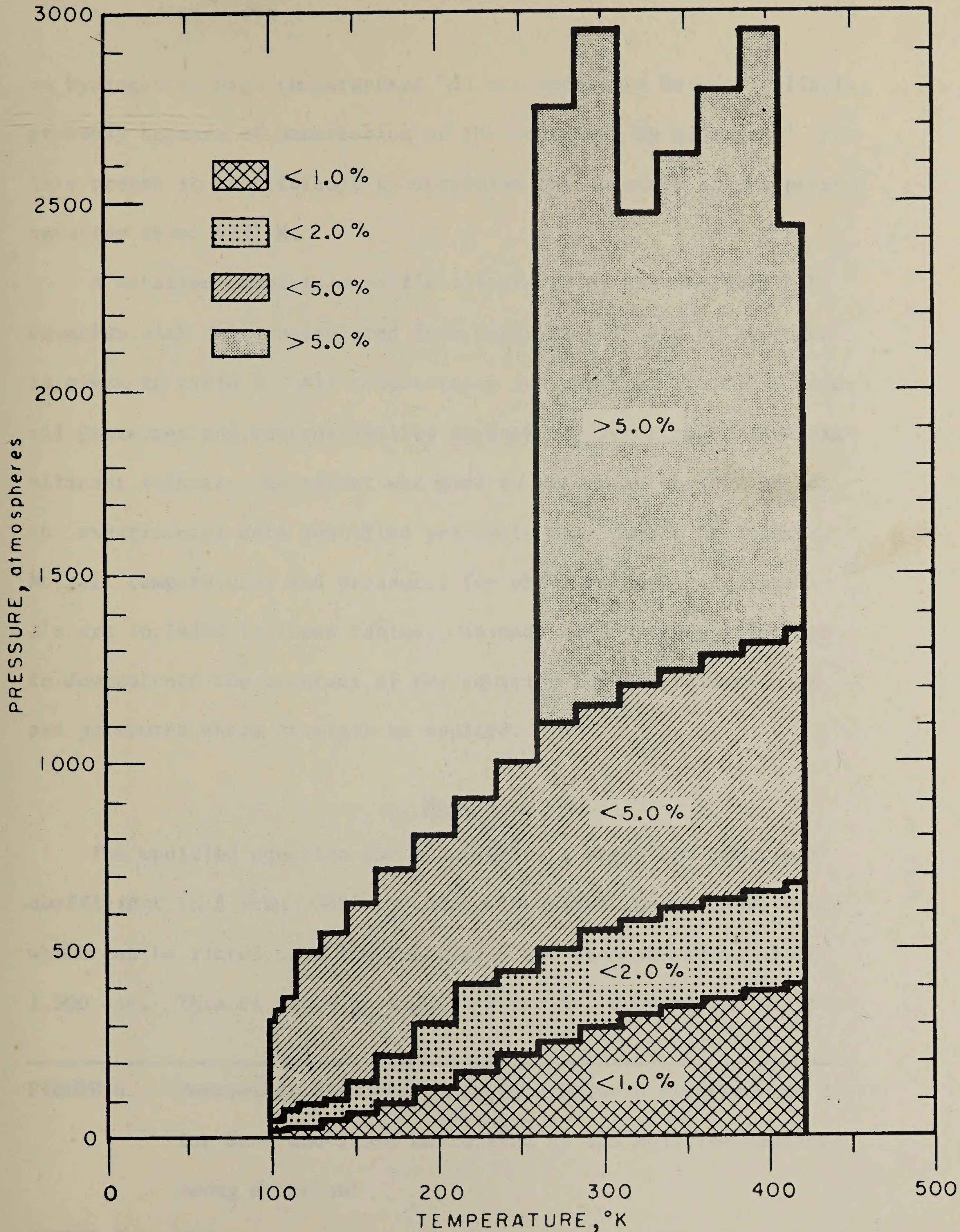

FIGURE 3.–Percentage Absolute Difference Between Experimental Z's For Hydrogen And Those Calculated By The Original Redlich–Kwong Equation.

on hydrogen at high temperatures "do not appear to be very reliable, probably because of penetration of the container by hydrogen." For this reason it is difficult to determine the accuracy of the present equation above 423° K.

A detailed comparison of Z's calculated by the modified R-K equation with those calculated from experimental data on hydrogen is given in table 3. All temperatures are reported to .01° K, and all pressures and compressibility factors are reported to five significant figures. No effort was made to determine whether or not the experimental data justified precisely this number of figures. Not all temperatures and pressures for which we have calculated Z's are included in these tables. We made an arbitrary selection to demonstrate the accuracy of the equation for the temperatures and pressures where it might be applied.

Neon

The modified equation for neon, which changes the numerical coefficient in B from .0867 to .1025, increases the pressure range which can be fitted to < 1 percent from 100 atmospheres to about 1,500 atm. This is shown in figures 4 and 5. Down to 120° K this

FIGURE 4. - Percentage Absolute Difference Between Experimental Z's for Neon and Those Calculated by the Modified Redlich-Kwong Equation.

FIGURE 5. - Percentage Absolute Difference Between Experimental Z's for Neon and Those Calculated by the Original Redlich-Kwong Equation.

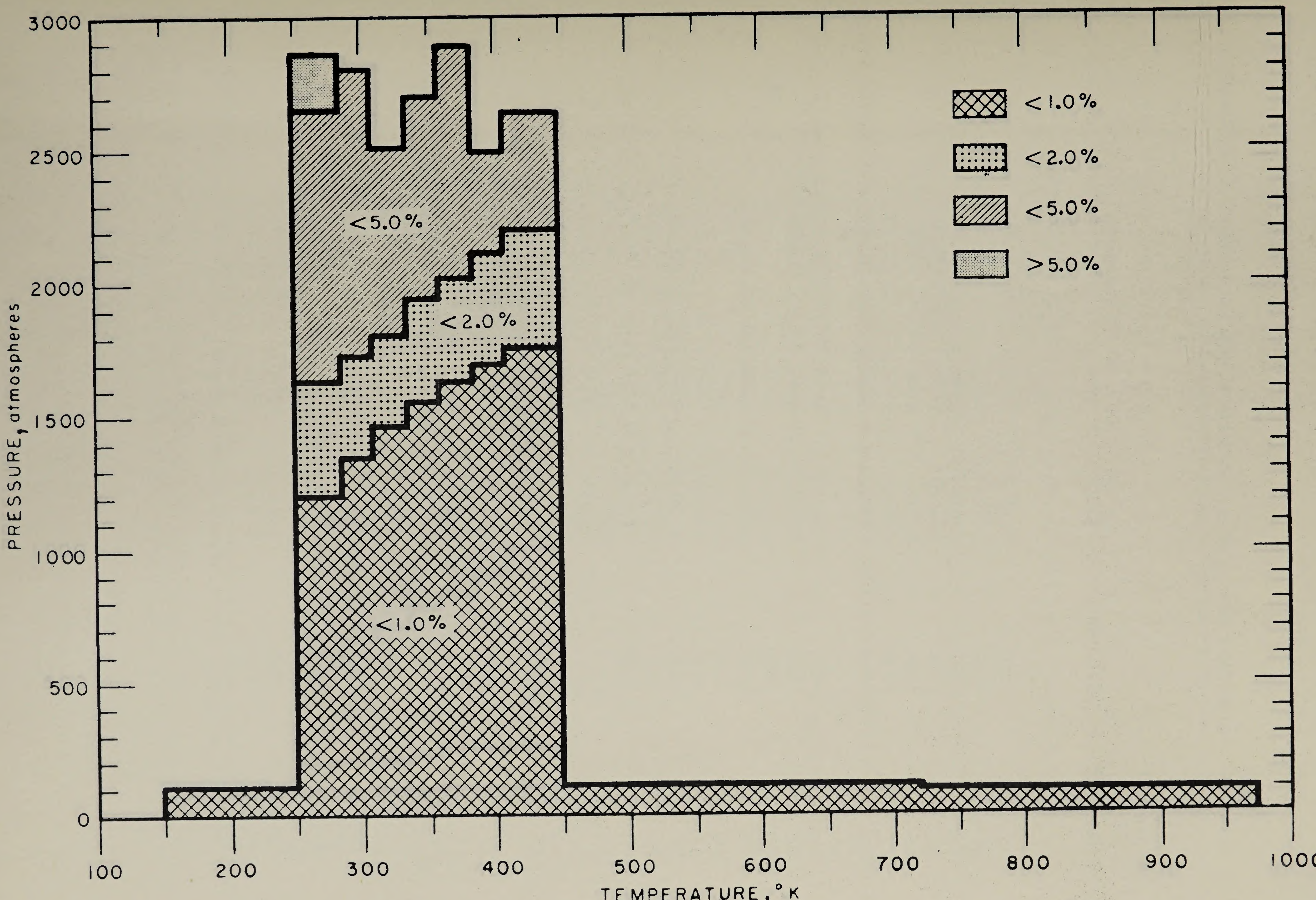

FIGURE 4.- Percentage Absolute Difference Between Experimental Z's For Neon And Those Calculated By The Modified Redlich-Kwong Equation.

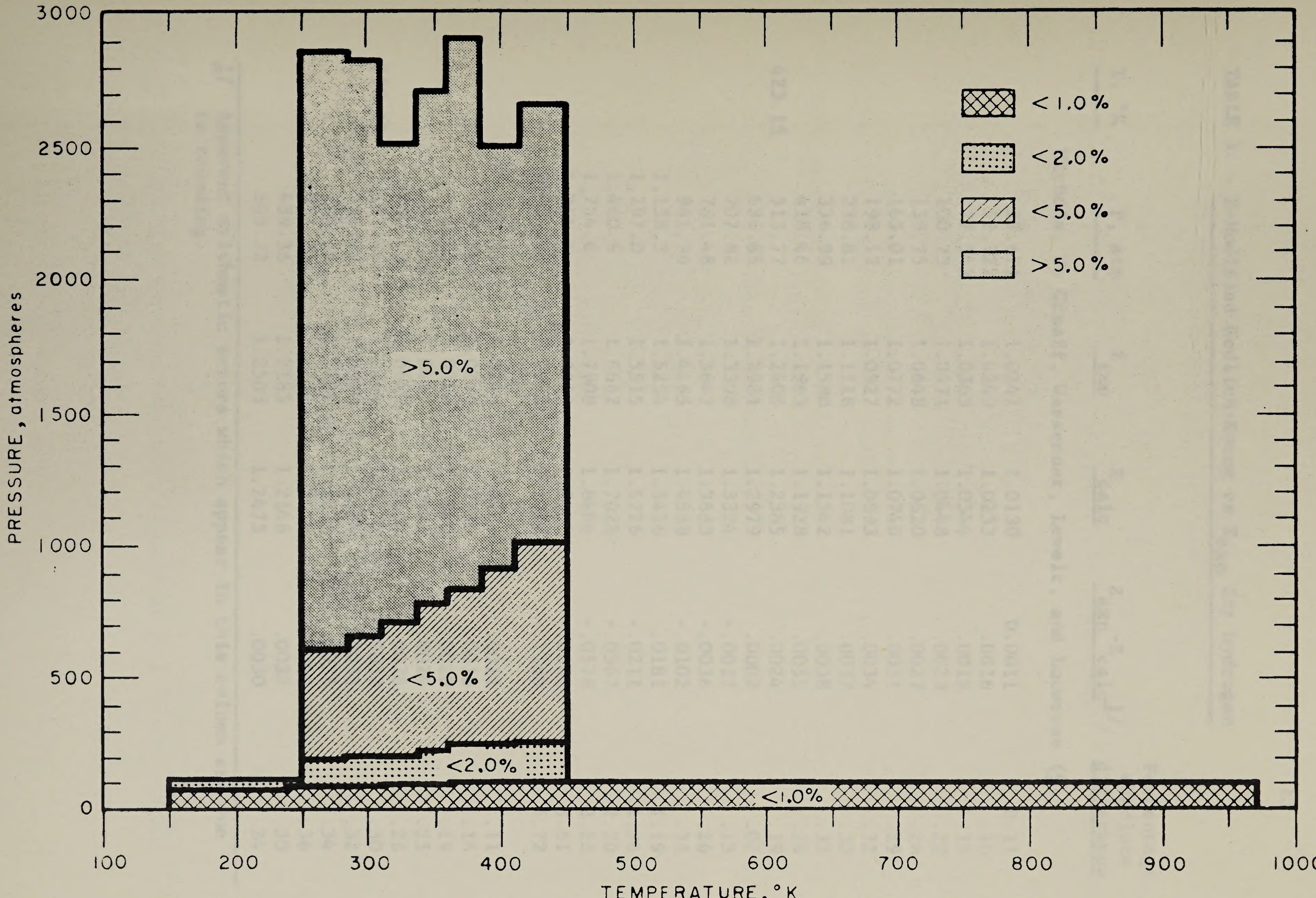

FIGURE 5.—Percentage Absolute Difference Between Experimental Z's For Neon And Those Calculated By The Original Redlich-Kwong Equation.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)					
	29.671	1.0141	1.0130	0.0011	0.11
	52.722	1.0249	1.0233	.0016	.16
	77.542	1.0363	1.0344	.0019	.19
	100.73	1.0471	1.0448	.0023	.22
	138.75	1.0648	1.0620	.0027	.26
	165.01	1.0772	1.0740	.0031	.29
	198.12	1.0927	1.0893	.0034	.32
	238.81	1.1118	1.1081	.0037	.33
	336.99	1.1580	1.1542	.0038	.33
	418.46	1.1963	1.1928	.0035	.29
423.15	513.77	1.2408	1.2385	.0024	.19
	636.85	1.2981	1.2979	.0002	.01
	707.82	1.3308	1.3324	-.0017	.13
	781.48	1.3647	1.3683	-.0036	.26
	961.96	1.4465	1.4568	-.0102	.71
	1,138.3	1.5254	1.5436	.0181	1.19
	1,197.0	1.5515	1.5726	-.0211	1.36
	1,460.6	1.6662	1.7028	-.0367	2.20
	1,754.6	1.7908	1.8486	-.0578	3.23
	1,854.4	1.8322	1.8983	-.0661	3.61
	2,424.1	2.0632	2.1812	-.1180	5.72
	27.915	1.0140	1.0129	.0011	.11
	49.594	1.0246	1.0230	.0016	.16
	72.937	1.0360	1.0340	.0020	.19
	94.739	1.0467	1.0443	.0024	.23
	130.48	1.0642	1.0614	.0028	.26
398.15	155.16	1.0764	1.0732	.0032	.30
	186.27	1.0919	1.0884	.0035	.32
	224.51	1.1109	1.1071	.0038	.34
	316.81	1.1570	1.1528	.0042	.36
	439.36	1.2183	1.2146	.0037	.30
	503.72	1.2503	1.2473	.0030	.24

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)					
	598.95	1.2975	1.2961	0.0014	0.11
	665.82	1.3304	1.3306	-.0002	.02
	735.25	1.3646	1.3665	-.0019	.14
	838.16	1.4147	1.4200	-.0053	.37
	905.56	1.4472	1.4551	-.0079	.54
398.15	1,072.2	1.5271	1.5423	-.0152	.99
	1,363.7	1.6636	1.6954	-.0318	1.91
	1,656.8	1.7972	1.8499	-.0528	2.94
	1,751.6	1.8393	1.8999	-.0606	3.29
	2,295.0	2.0760	2.1868	-.1108	5.34
	2,952.5	2.3489	2.5342	-.1853	7.89
	26.157	1.0138	1.0127	.0011	.11
	46.463	1.0242	1.0226	.0016	.15
	68.324	1.0355	1.0335	.0020	.19
	88.743	1.0461	1.0437	.0024	.23
	122.21	1.0635	1.0606	.0029	.28
	164.29	1.0856	1.0821	.0036	.33
	210.22	1.1098	1.1058	.0040	.36
	296.57	1.1557	1.1512	.0044	.38
373.15	411.27	1.2168	1.2126	.0042	.34
	560.78	1.2962	1.2939	.0023	.18
	688.65	1.3638	1.3642	-.0004	.03
	785.35	1.4144	1.4177	-.0034	.24
	1,005.6	1.5282	1.5405	-.0123	.81
	1,280.7	1.6670	1.6946	-.0276	1.66
	1,647.7	1.8460	1.9012	-.0551	2.99
	2,163.6	2.0883	2.1920	-.1037	4.97
	2,791.8	2.3699	2.5464	-.1765	7.45
	24.397	1.0135	1.0125	.0010	.10
348.15	43.332	1.0238	1.0223	.0015	.15
	63.713	1.0349	1.0329	.0020	.19
	82.738	1.0454	1.0430	.0024	.23

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen
(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)					
348.15	113.93	1.0626	1.0596	0.0030	0.28
	153.12	1.0844	1.0809	.0036	.33
	195.87	1.1084	1.1044	.0040	.36
	276.25	1.1538	1.1493	.0045	.39
	383.07	1.2147	1.2102	.0046	.38
	522.47	1.2944	1.2911	.0032	.25
	641.82	1.3623	1.3614	.0009	.07
	732.21	1.4134	1.4149	-.0015	.11
	938.46	1.5285	1.5379	-.0094	.62
	1,196.8	1.6696	1.6932	-.0236	1.41
	1,457.7	1.8083	1.8505	-.0422	2.33
	1,542.7	1.8526	1.9017	-.0491	2.65
	2,031 1	2.1011	2.1971	-.0960	4.57
	2,628.7	2.3917	2.5585	-.1668	6.98
323.15	22.638	1.0132	1.0122	.0010	.09
	46.479	1.0268	1.0253	.0015	.15
	65.669	1.0379	1.0359	.0020	.19
	90.195	1.0522	1.0497	.0024	.23
	123.70	1.0719	1.0689	.0030	.28
	160.10	1.0936	1.0900	.0036	.33
	269.41	1.1597	1.1551	.0046	.40
	374.59	1.2242	1.2195	.0047	.39
	520.67	1.3142	1.3108	.0034	.26
	642.27	1.3890	1.3880	.0010	.07
	796.12	1.4827	1.4866	-.0039	.26
	870.54	1.5276	1.5345	-.0069	.45
	999.77	1.6049	1.6179	-.0130	.81
	1,111.8	1.6711	1.6906	-.0195	1.17
	1,232.2	1.7411	1.7688	-.0278	1.59
	1,496.4	1.8918	1.9407	-.0489	2.58
	1,896.6	2.1138	2.2016	-.0878	4.15
	2,462.7	2.4140	2.5708	-.1568	6.50

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen (Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
	Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)				
	20.877	1.0127	1.0119	0.0008	0.08
	42.849	1.0260	1.0246	.0014	.13
	70.697	1.0431	1.0411	.0020	.19
	97.295	1.0597	1.0571	.0025	.24
	121.26	1.0747	1.0718	.0029	.27
	175.51	1.1094	1.1057	.0037	.33
	295.25	1.1878	1.1831	.0047	.39
	395.70	1.2547	1.2500	.0047	.37
298.15	495.16	1.3213	1.3175	.0038	.28
	591.06	1.3855	1.3833	.0022	.16
	733.15	1.4799	1.4818	-.0020	.13
	921.87	1.6040	1.6137	-.0097	.61
	1,138.5	1.7435	1.7661	-.0226	1.29
	1,385.2	1.8982	1.9402	-.0421	2.22
	1,760.3	2.1264	2.2054	-.0790	3.72
	2,294.4	2.4375	2.5833	-.1457	5.98
	2,946.3	2.7976	3.0441	-.2466	8.81
	19.116	1.0122	1.0115	.0007	.07
	39.217	1.0250	1.0238	.0011	.11
	64.675	1.0415	1.0398	.0017	.17
	88.967	1.0576	1.0554	.0022	.21
	110.85	1.0724	1.0697	.0026	.24
	160.34	1.1062	1.1029	.0034	.31
	226.31	1.1525	1.1484	.0041	.35
	314.46	1.2158	1.2112	.0047	.38
273.15	437.10	1.3053	1.3009	.0043	.33
	539.56	1.3805	1.3773	.0032	.23
	669.79	1.4757	1.4756	.0001	.01
	843.30	1.6016	1.6080	-.0064	.40
	1,043.3	1.7439	1.7615	-.0176	1.01
	1,272.6	1.9034	1.9384	-.0350	1.84
	1,622.3	2.1390	2.2085	-.0695	3.25
	2,123.1	2.4621	2.5956	-.1335	5.42
	2,736.1	2.8358	3.0690	-.2332	8.22

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)					
248.15	7.1755	1.0050	1.0045	0.0005	0.05
	28.480	1.0189	1.0182	.0007	.07
	48.181	1.0323	1.0312	.0011	.11
	88.667	1.0608	1.0589	.0019	.18
	123.46	1.0859	1.0836	.0023	.21
	186.62	1.1332	1.1301	.0031	.28
	235.16	1.1708	1.1671	.0037	.32
	335.48	1.2503	1.2459	.0044	.35
	425.92	1.3233	1.3190	.0043	.33
	609.50	1.4723	1.4706	.0017	.11
	845.19	1.6619	1.6688	-.0069	.41
	1,005.6	1.7885	1.8048	-.0163	.91
223.15	6.5000	1.0046	1.0043	.0004	.04
	25.779	1.0177	1.0173	.0004	.04
	60.785	1.0430	1.0421	.0009	.09
	80.087	1.0574	1.0563	.0011	.10
	111.43	1.0818	1.0803	.0015	.14
	168.24	1.1277	1.1256	.0021	.18
	211.87	1.1645	1.1619	.0026	.23
	302.08	1.2431	1.2397	.0034	.28
	461.19	1.3866	1.3829	.0036	.26
	549.73	1.4672	1.4645	.0027	.18
	642.12	1.5512	1.5505	.0007	.04
	764.49	1.6616	1.6652	-.0036	.22
	911.69	1.7928	1.8040	-.0112	.63
198.15	5.8140	1.0042	1.0039	.0003	.03
	28.994	1.0205	1.0203	.0001	.01
	54.203	1.0394	1.0393	.0001	.01
	99.146	1.0757	1.0756	.0001	.01
	149.44	1.1196	1.1192	.0003	.03
	224.48	1.1897	1.1887	.0010	.08
	340.09	1.3047	1.3024	.0023	.18
	488.11	1.4570	1.4543	.0028	.19
	570.93	1.5429	1.5411	.0018	.12

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen (Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)					
198.15	681.22	1.6568	1.6576	-0.0008	0.05
	814.64	1.7931	1.7995	-.0064	.36
	6.6416	1.0046	1.0045	.0001	.01
	25.460	1.0175	1.0181	-.0005	.05
	47.491	1.0342	1.0353	-.0011	.11
	86.595	1.0668	1.0688	-.0020	.18
173.15	130.20	1.1076	1.1099	-.0023	.21
	195.12	1.1742	1.1764	-.0021	.18
	295.28	1.2865	1.2871	-.0006	.04
	424.46	1.4394	1.4379	.0015	.10
	594.89	1.6443	1.6432	.0011	.07
	713.93	1.7864	1.7885	-.0021	.12
	5.9055	1.0036	1.0038	-.0002	.02
	30.241	1.0194	1.0213	-.0019	.18
	55.176	1.0387	1.0418	-.0031	.30
	94.388	1.0738	1.0786	-.0048	.44
153.15	143.55	1.1249	1.1307	-.0058	.51
	203.71	1.1954	1.2010	-.0055	.46
	311.07	1.3344	1.3371	-.0026	.20
	436.39	1.5056	1.5048	.0008	.05
	523.40	1.6258	1.6239	.0019	.12
	630.30	1.7728	1.7718	.0010	.05
	6.3094	1.0034	1.0037	-.0003	.03
	27.293	1.0151	1.0179	-.0028	.27
	49.651	1.0312	1.0359	-.0047	.46
	102.44	1.0799	1.0882	-.0083	.77
138.15	181.54	1.1750	1.1846	-.0095	.81
	276.98	1.3106	1.3167	-.0062	.47
	389.35	1.4818	1.4830	-.0012	.08
	468.11	1.6042	1.6026	.0016	.10
	565.62	1.7553	1.7524	.0029	.16
123.15	5.6428	.99918	1.0026	-.0034	.34

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
	Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)				
	11.257	1.0038	1.0055	-0.0017	0.17
	24.314	1.0068	1.0133	-.0066	.65
	44.056	1.0186	1.0280	-.0094	.93
	74.689	1.0434	1.0568	-.0134	1.28
123.15	133.81	1.1104	1.1278	-.0174	1.57
	201.15	1.2083	1.2250	-.0167	1.38
	289.84	1.3553	1.3668	-.0115	.85
	341.05	1.4443	1.4525	-.0082	.57
	411.23	1.5682	1.5721	-.0039	.25
	498.98	1.7234	1.7240	-.0006	.03
	7.9670	1.0013	1.0027	-.0014	.14
	22.316	1.0052	1.0094	-.0043	.43
	55.345	1.0232	1.0338	-.0106	1.03
	102.33	1.0690	1.0858	-.0168	1.57
113.15	143.52	1.1249	1.1433	-.0184	1.64
	216.35	1.2464	1.2615	-.0151	1.21
	261.76	1.3301	1.3412	-.0111	.84
	308.66	1.4199	1.4264	-.0065	.46
	383.66	1.5663	1.5660	.0003	.02
	7.2712	.99934	1.0008	-.0015	.15
	31.162	1.0016	1.0096	.0079	.79
	61.248	1.0172	1.0326	-.0154	1.51
	91.635	1.0464	1.0670	-.0206	1.97
103.15	127.96	1.0962	1.1194	-.0232	2.12
	192.36	1.2110	1.2309	-.0199	1.64
	232.84	1.2929	1.3082	-.0153	1.18
	274.92	1.3819	1.3918	-.0098	.71
	342.84	1.5294	1.5306	-.0012	.08
	6.9217	.99821	.99976	-.00155	.16
	11.566	.99715	1.0001	-.0030	.30
	29.547	.99649	1.0052	-.0087	.87
98.15	47.235	1.0017	1.0157	-.0140	1.40
	69.428	1.0162	1.0360	-.0197	1.94
	101.60	1.0521	1.0768	-.0247	2.35
	120.09	1.0791	1.1050	-.0259	2.40

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 3. - Z-Modified Redlich-Kwong vs Z_{exp} for hydrogen

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
	Michels, de Graaff, Wassenaar, Levelt, and Louwerse (9)				
	151.31	1.1332	1.1584	-0.0252	2.22
98.15	218.10	1.2702	1.2881	-.0179	1.41
	257.73	1.3588	1.3706	-.0118	.87
	322.04	1.5068	1.5089	-.0022	.14
		Johnston and White (7)			
	1.0000	1.0001	.99956	.0006	.06
	10.000	.99416	.99672	-.0026	.26
	20.000	.98942	.99583	-.0064	.65
	30.000	.98726	.99732	-.0101	1.02
90.00	40.000	.98793	1.0012	-.0132	1.34
	60.000	.99673	1.0154	-.0187	1.87
	80.000	1.0142	1.0374	-.0232	2.29
	100.00	1.0388	1.0658	-.0270	2.60
	150.00	1.1315	1.1562	-.0247	2.19
	200.00	1.2430	1.2629	-.0198	1.60

1/ Apparent arithmetic errors which appear in this column are due to rounding.

modification gives a better fit to experimental data than the original equation. Below this temperature, however, the original equation should be used. All indications are that this modified equation can be used at temperatures much higher than 423° K and pressures higher than the 100 atm shown in figure 4.

A detailed comparison of experimental Z's with those calculated by this modification is shown in table 4, which was compiled on the same basis as table 3.

TABLE 4. - Z-Modified Redlich-Kwong vs Z_{exp} for neon

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
		Nicholson and Schneider (11)			
973.15	20.000	1.0030	1.0033	-0.0004	0.04
	40.000	1.0065	1.0067	-.0002	.02
	60.000	1.0100	1.0100	-.0001	.01
	80.000	1.0135	1.0134	.0001	.01
873.15	20.000	1.0034	1.0037	-.0004	.03
	40.000	1.0072	1.0074	-.0002	.02
	60.000	1.0111	1.0111	-.0000	.00
	80.000	1.0150	1.0148	.0001	.01
773.15	20.000	1.0038	1.0041	-.0003	.03
	40.000	1.0081	1.0083	-.0001	.01
	60.000	1.0125	1.0124	.0000	.00
	80.000	1.0168	1.0166	.0002	.02
		Holborn and Otto (6)			
673.09	1.3157	1.0001	1.0003	-.0002	.02
	26.316	1.0063	1.0062	.0001	.01
	52.632	1.0128	1.0124	.0004	.05
	78.947	1.0194	1.0186	.0008	.08
	105.26	1.0259	1.0248	.0011	.11
573.10	1.3157	1.0001	1.0004	-.0002	.02
	26.316	1.0075	1.0071	.0004	.04
	52.632	1.0152	1.0142	.0009	.09
	78.947	1.0229	1.0214	.0015	.14
	105.26	1.0306	1.0286	.0020	.20
473.12	1.3157	1.0002	1.0004	-.0002	.02
	26.316	1.0086	1.0083	.0003	.03
	52.632	1.0178	1.0167	.0011	.10
	78.947	1.0270	1.0252	.0018	.17
	105.26	1.0364	1.0337	.0027	.26

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 4. - Z-Modified Redlich-Kwong vs Z_{exp} for neon

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
	Michels, Wassenaar, and Louwerse (10)				
423.15	37.568	1.0146	1.0130	0.0016	0.16
	61.434	1.0236	1.0214	.0022	.22
	86.687	1.0332	1.0303	.0030	.29
	114.21	1.0436	1.0400	.0036	.34
	132.69	1.0508	1.0467	.0041	.39
	155.22	1.0594	1.0548	.0046	.44
	192.63	1.0738	1.0683	.0054	.50
	229.82	1.0880	1.0819	.0060	.56
	268.87	1.1030	1.0963	.0067	.61
	304.07	1.1167	1.1094	.0074	.66
	353.51	1.1356	1.1278	.0078	.68
	415.64	1.1597	1.1513	.0084	.72
	503.86	1.1938	1.1848	.0090	.75
	599.41	1.2306	1.2215	.0090	.74
	688.32	1.2648	1.2560	.0088	.70
	772.51	1.2971	1.2887	.0083	.64
	825.92	1.3172	1.3097	.0075	.57
	950.25	1.3643	1.3585	.0057	.42
	1,154.0	1.4412	1.4391	.0020	.14
	1,479.7	1.5620	1.5689	-.0068	.44
	1,762.9	1.6651	1.6824	-.0172	1.04
	2,039.7	1.7642	1.7934	-.0291	1.65
	2,210.0	1.8245	1.8619	-.0374	2.05
	2,635.5	1.9733	2.0332	-.0598	3.03
398.15	35.339	1.0144	1.0128	.0016	.15
	57.781	1.0232	1.0210	.0021	.21
	81.523	1.0327	1.0298	.0029	.28
	112.90	1.0452	1.0415	.0037	.35
	140.17	1.0561	1.0518	.0043	.40
	161.54	1.0647	1.0599	.0047	.44
	181.06	1.0726	1.0674	.0052	.49
	215.99	1.0867	1.0808	.0059	.54
	252.67	1.1017	1.0951	.0066	.60
	309.79	1.1249	1.1175	.0074	.66
	390.46	1.1578	1.1495	.0083	.72

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 4. - Z-Modified Redlich-Kwong vs Z_{exp} for neon (Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
	Michels, Wassenaar, and Louwerse (10)				
	473.26	1.1917	1.1828	0.0089	0.75
	562.97	1.2283	1.2193	.0090	.74
	683.43	1.2773	1.2688	.0086	.67
	775.69	1.3147	1.3070	.0077	.59
	892.58	1.3620	1.3558	.0062	.46
398.15	1,122.6	1.4542	1.4524	.0017	.12
	1,468.2	1.5905	1.5988	-.0084	.53
	1,657.6	1.6640	1.6795	-.0155	.93
	1,927.4	1.7672	1.7947	-.0275	1.56
	2,079.9	1.8249	1.8598	-.0349	1.91
	2,482.4	1.9754	2.0320	-.0566	2.87
	33.109	1.0140	1.0126	.0014	.14
	54.126	1.0227	1.0207	.0020	.20
	76.345	1.0319	1.0293	.0026	.25
	100.57	1.0422	1.0388	.0034	.32
	131.23	1.0550	1.0510	.0040	.38
	151.23	1.0635	1.0590	.0046	.43
	202.15	1.0852	1.0796	.0056	.52
	267.31	1.1132	1.1064	.0068	.62
	310.72	1.1319	1.1245	.0074	.65
	442.56	1.1891	1.1804	.0086	.72
373.15	526.34	1.2253	1.2166	.0087	.71
	639.01	1.2743	1.2658	.0085	.67
	725.20	1.3115	1.3038	.0077	.59
	834.58	1.3588	1.3523	.0064	.47
	1,049.8	1.4510	1.4487	.0023	.16
	1,300.9	1.5574	1.5621	-.0047	.30
	1,551.5	1.6618	1.6758	-.0140	.84
	1,805.1	1.7660	1.7913	-.0253	1.44
	1,948.7	1.8243	1.8569	-.0325	1.78
	2,327.5	1.9762	2.0298	-.0536	2.71
	2,894.5	2.1976	2.2891	-.0916	4.17
348.15	30.881	1.0137	1.0123	.0014	.14

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 4. - Z-Modified Redlich-Kwong vs Z_{exp} for neon

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
	Michels, Wassenaar, and Louwerse (10)				
	50.475	1.0222	1.0202	0.0019	0.19
	71.182	1.0312	1.0287	.0025	.25
	98.538	1.0432	1.0400	.0032	.31
	122.30	1.0538	1.0499	.0039	.37
	157.90	1.0698	1.0650	.0047	.44
	188.30	1.0835	1.0781	.0054	.50
	220.20	1.0980	1.0919	.0061	.55
	269.85	1.1206	1.1137	.0068	.61
	339.93	1.1527	1.1450	.0077	.67
	439.26	1.1986	1.1902	.0084	.70
348.15	562.26	1.2558	1.2472	.0086	.68
	667.82	1.3044	1.2968	.0077	.59
	776.24	1.3546	1.3482	.0064	.47
	943.06	1.4315	1.4280	.0035	.24
	1,210.8	1.5536	1.5575	-.0038	.25
	1,444.8	1.6586	1.6713	-.0127	.76
	1,682.0	1.7637	1.7871	-.0234	1.32
	1,816.4	1.8226	1.8528	-.0303	1.66
	2,171.5	1.9762	2.0267	-.0505	2.56
	2,704.8	2.2010	2.2883	-.0873	3.97
	28.652	1.0133	1.0120	.0013	.13
	53.146	1.0244	1.0224	.0020	.20
	73.369	1.0337	1.0311	.0026	.25
	91.354	1.0420	1.0390	.0030	.29
	118.00	1.0546	1.0508	.0038	.36
	146.30	1.0679	1.0635	.0044	.41
323.15	174.43	1.0813	1.0763	.0050	.46
	203.93	1.0955	1.0899	.0056	.52
	254.90	1.1202	1.1137	.0065	.58
	314.61	1.1494	1.1421	.0073	.63
	452.95	1.2176	1.2097	.0080	.65
	583.32	1.2825	1.2749	.0076	.59
	717.71	1.3493	1.3432	.0061	.46
	903.14	1.4414	1.4386	.0027	.19

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 4. - Z-Modified Redlich-Kwong vs Z_{exp} for neon

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
		Michels, Wassenaar, and Louwerse (10)			
	1,120.0	1.5483	1.5515	-0.0032	0.21
	1,337.2	1.6538	1.6654	-.0115	.70
323.15	1,557.7	1.7597	1.7814	-.0217	1.24
	1,682.7	1.8191	1.8474	-.0283	1.56
	2,013.2	1.9739	2.0219	-.0480	2.43
	2,512.7	2.2028	2.2861	-.0833	3.78
	26.424	1.0129	1.0116	.0013	.13
	48.997	1.0237	1.0217	.0020	.19
	67.617	1.0325	1.0301	.0024	.23
	92.974	1.0450	1.0419	.0031	.30
	114.82	1.0557	1.0522	.0036	.34
	134.68	1.0655	1.0616	.0039	.37
	160.52	1.0785	1.0741	.0044	.41
	187.61	1.0923	1.0874	.0050	.45
	211.96	1.1048	1.0994	.0053	.48
	289.18	1.1451	1.1386	.0065	.57
298.15	373.29	1.1894	1.1824	.0071	.59
	477.39	1.2450	1.2378	.0071	.57
	572.54	1.2959	1.2895	.0064	.49
	828.89	1.4338	1.4316	.0022	.15
	1,028.4	1.5408	1.5441	-.0033	.22
	1,228.4	1.6467	1.6576	-.0109	.66
	1,425.7	1.7501	1.7702	-.0201	1.15
	1,547.6	1.8132	1.8400	-.0267	1.47
	1,853.9	1.9701	2.0155	-.0454	2.30
	2,317.4	2.2020	2.2813	-.0793	3.60
	2,824.1	2.4487	2.5721	-.1234	5.04
	24.194	1.0123	1.0111	.0012	.12
	50.228	1.0250	1.0233	.0017	.17
273.15	76.959	1.0385	1.0363	.0022	.21
	99.321	1.0502	1.0473	.0028	.27
	123.06	1.0626	1.0593	.0033	.31
	146.61	1.0752	1.0714	.0038	.36

1/ Apparent arithmetic errors which appear in this column are due to rounding

TABLE 4. - Z-Modified Redlich-Kwong vs Z_{exp} for neon

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
		Michels, Wassenaar, and Louwerse (10)			
	171.27	1.0885	1.0843	0.0042	0.39
	209.65	1.1096	1.1047	.0049	.44
	263.68	1.1397	1.1342	.0055	.48
	318.99	1.1708	1.1650	.0058	.49
	434.66	1.2373	1.2315	.0059	.47
	599.38	1.3331	1.3291	.0040	.30
	728.12	1.4087	1.4069	.0018	.13
273.15	935.85	1.5305	1.5344	-.0039	.26
	1,118.5	1.6366	1.6476	-.0109	.67
	1,299.1	1.7407	1.7601	-.0195	1.12
	1,410.9	1.8044	1.8299	-.0255	1.41
	1,691.7	1.9623	2.0058	-.0435	2.22
	2,118.2	2.1970	2.2731	-.0761	3.46
	2,586.7	2.4482	2.5670	-.1189	4.86
	2,865.7	2.5945	2.7416	-.1471	5.67
		Holborn and Otto (6)			
	1.3157	1.0004	1.0006	-.0002	.02
	26.316	1.0131	1.0130	.0002	.02
223.16	52.632	1.0272	1.0266	.0006	.06
	78.947	1.0418	1.0409	.0008	.08
	105.26	1.0570	1.0558	.0011	.11
	1.3157	1.0003	1.0006	-.0003	.03
	26.316	1.0123	1.0126	-.0004	.04
173.17	52.632	1.0258	1.0269	-.0011	.10
	78.947	1.0405	1.0426	-.0021	.20
	105.26	1.0562	1.0596	-.0035	.33
		Sullivan and Sonntag (14)			
	10.114	1.0014	1.0012	.0001	.01
120.0	29.444	1.0054	1.0058	-.0004	.04
	50.451	1.0117	1.0138	-.0021	.21

1/ Apparent arithmetic errors which appear in this column are due to rounding.

TABLE 4. - Z-Modified Redlich-Kwong vs Z_{exp} for neon

(Con.)

T, °K	P, atm	Z_{exp}	Z_{calc}	$Z_{exp}-Z_{calc}$ 1/	Percentage absolute difference
		Sullivan and Sonntag (14)			
	72.576	1.0206	1.0256	-0.0049	0.48
	105.30	1.0385	1.0485	-.0100	.96
120.0	155.56	1.0760	1.0941	-.0181	1.68
	239.07	1.1599	1.1889	-.0290	2.50
	304.79	1.2386	1.2735	-.0349	2.82

1/ Apparent arithmetic errors which appear in this column are due to rounding.

OTHER REPRESENTATIONS OF THE PVT PROPERTIES OF THESE GASES

Virials

The virial-form equations mentioned in the Introduction naturally give a far better fit to the discrete isotherms they represent than do the two modified equations. No two-constant equation developed for a wide temperature range can be expected to achieve the same degree of accuracy as a six-constant equation designed to fit a single isotherm. The usefulness of these modified R-K equations lies in their ability to predict data over large ranges of pressure and temperature. Within certain limitations, they are also useful for mixtures.

Various Other Equations

The six-constant equations of Goodwin (4) and of Ziegler, McWilliams, and Keller (16) for hydrogen have been used to calculate volumes which were compared with experimental volumes taken from Michels, de Graaff,

Wassenaar, Levelt, and Louwerse (9) and from Johnston and White (7). Because the work of Ziegler, McWilliams, and Keller consisted of a redetermination of Goodwin's constants, their equation gave a lower average percentage absolute deviation, as might have been expected. For temperatures of 100° K and below, their equation fits experimental data better than our modified R-K; above 100° the modified R-K fits better.

McCarty and Stewart's (8) equation for neon gives a better fit to experimental data than the modified R-K does in the temperature and pressure ranges for which their 18-constant equation was developed. At pressures and/or temperatures above this range the modified R-K fits experimental data better.

Effective Critical Constants

Gunn, Chueh, and Prausnitz (5) say "...Effective critical constants for helium and normal hydrogen have been determined by fitting experimental volumetric data for these gases to the generalized tables of Pitzer (12). The effective critical temperature and pressure are found to depend on the temperature and on the molecular mass in a simple manner ..." .

For hydrogen they give

$$T_c = \frac{43.6}{1 + \dfrac{21.8}{(1.008)(T)}} \quad \text{and} \quad P_c = \frac{20.2}{1 + \dfrac{44.2}{(1.008)(T)}} .$$

Similar equations are indicated for neon.

Of the various methods (other than virials) for representing

the low-temperature (35° - 150° K) PVT properties of hydrogen which we investigated, the Gunn, Chueh, and Prausnitz method fits the experimental data best. When this method is used on neon in the temperature range from 70° - 120° K, it gives about as good a fit to experimental data as McCarty and Stewart's equation does. Both of these methods for predicting volumetric data fit the values of Holborn and Otto (6) (which were available when the two methods were developed) better than the data of Sullivan (14) (which were not available, and which deviate slightly from those of Holborn and Otto). In the present report, no work was done on neon below 70° K.

Although Gunn, Chueh, and Prausnitz (5) said nothing about the use of their effective critical constants at temperatures and pressures higher than the range of Pitzer's tables, we investigated the use of these constants in conjunction with the original R-K equation at higher T's and P's. In general, this procedure gave a better fit to experimental data than did the original R-K, but a poorer fit than the modified equations (See table 2).

SUMMARY

Specific modifications of the R-K equation are developed for hydrogen and for neon. The numerical coefficient in B is changed to .08063 for hydrogen and to .1025 for neon. The equation for hydrogen is recommended for temperatures from 98° to 423 ° K with pressures to 1,050 atm. The neon modification is recommended for

temperatures from 120° to 973° K with pressures up to about 1,500 atm. Good performance is indicated above 973° K.

For temperatures lower than these, the use of the "effective critical constants" of Gunn, Chueh, and Prausnitz, in conjunction with Pitzer's tables, is suggested.

NOMENCLATURE

A = parameter of Redlich-Kwong equation

a = parameter of Redlich-Kwong equation

B = parameter of Redlich-Kwong equation

b = parameter of Redlich-Kwong equation

h = $\frac{BP}{Z}$

K = Kelvin temperature

P = pressure, atm

P_c = critical pressure

R = universal gas constant

R-K = Redlich-Kwong

T = temperature, degrees Kelvin

T_c = critical temperature

V = molal volume, cm^3/g mole

Z = compressibility factor, PV/RT

ACKNOWLEDGEMENTS

The authors wish to acknowledge the valuable assistance of Miss Jo Battle, Librarian of the Helium Research Center and her staff, who ordered many of the reprints needed for this report.

We also wish to acknowledge the untiring efforts of Mr. Billy Joe King who was Digital Computer Systems Operator for the Branch of Automatic Data Processing, Helium Activity, when this work was done.

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