Volumetric Data and Virial Coefficients for Helium, Krypton, and Helium–Krypton Mixtures

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Volumetric data for helium, krypton, and three mixtures of helium and krypton (24.8, 49.7, and 74.6 mol % helium) were obtained by the Burnett technique. Measurements were made at temperatures of −50, 0, and 50 °C at pressures between 7 and 150 bar. Compressibility factors and virial coefficients are presented for the pure substances and mixtures, as are the interaction second virial coefficients, B_{12}.

I. Introduction

As part of a long-range study of the properties of simple mixtures (*10*, *11*, *13*, *14*), a Burnett apparatus was constructed to facilitate measurements of gas-phase volumetric properties. The apparatus was used to obtain *PVT* data on helium, krypton, and helium–krypton mixtures. These data were acquired primarily to provide information on the interaction second virial coefficient, B_{12}, of helium–krypton. The B_{12} values, in turn, supply information on the nature of unlike-molecule interactions (*14*) which sensitively govern the excess thermodynamic properties of mixtures.

The Burnett method, itself, is an experimentally simplified *PVT* method in which neither the quantity of gas nor a volume is measured. Instead accurate isothermal pressure measurements are made before and after stepwise expansions between two volumes. The measured pressures are converted into a finite series representation of the isothermal compressibility factors. This is accomplished through data reduction involving the least-squares evaluation of the series coefficients in Burnett nonlinear equations.

II. Experimental Section

The experimental apparatus and procedures used in this work have been described in detail by Dillard (*7*) and are briefly summarized below. The general arrangement of the apparatus is illustrated in Figure 1.

In these experiments the pressure measurements were made with a combination of an oil piston gauge, L (see Figure 1), and either a quartz gauge or a mercury barometer. For convenience the quartz gauge, which agreed with the barometer to within 0.01%, was mainly used to measure the barometric pressure. The sample gas being studied was separated from the pressure measuring instrumentation by a differential pressure transducer, D, closely coupled to the Burnett chambers. This allowed for all of the sample gas contained within the Burnett volumes to be thermostated at the isotherm temperature. A counterbalancing gas used to produce the null of the transducer was itself separated from the oil piston gauge by a similar transducer, J. The pressure actually measured was that of the counterbalancing gas required to produce the null conditions for both transducers.

Table I. Analyses of Helium and Krypton

component	gas analyses, molar ppm: pure helium: helium measurements	pure helium: mixture measurements	krypton
nitrogen	0.9	5.0	29.0
hydrogen	0.0		2.0
oxygen & argon	0.3	0.5	20.0
neon	0.9		
xenon			25.0
water	2.5	0.2	0.2
hydrocarbon	0.0	1.0	2.8
carbon dioxide	0.1		

Table II. Composition Analyses of Helium-Krypton Mixtures

composition, mol% He in Kr: nominal compn	gas chromatograph[a]	mass spectrometer[b]
25	24.8	24.4
50	49.7	48.9
75	74.6	74.6

[a] By Air Products, Inc. [b] By Helium Research Center.

The Burnett cell, E, was fabricated from a 28-cm length of 7.5-cm diameter 303 stainless-steel cylinder. A 1.5-cm diameter cavity was bored axially into each end of the cylinder and capped to form a primary Burnett chamber with a volume of 20 cm^3. Prior to the capping, one of the cavities was filled with a stainless-steel rod to give a volume ratio of 1.5 between the combined volumes of the chambers and the volume of the unfilled chamber. The chambers, the cryogenic differential pressure transducer, and the filling-vacuum facilities of the Burnett apparatus were connected by high-pressure stainless-steel tubing and nonrotating stem valves with Teflon packing as shown in Figure 1.

The Burnett apparatus was thermostated in a stirred liquid bath F where ethanol or ethylene glycol, depending on the temperature range, was used as the bath fluid. Temperature variations of the bath were typically less than 0.002 °C during an experimental run. The bath temperature as defined by the International Temperature Scale of 1968 was measured with two NBS-calibrated platinum resistance thermometers, which were periodically checked during these experiments at the triple point of water. No shift in the reference resistance of either thermometer was detected within the precision of the L&N Mueller bridge and detector used for the four-terminal resistance measurements, the equivalent of 0.001 °C. A three-mode

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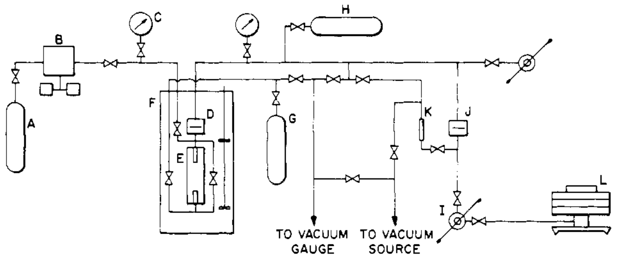
Table III. Experimental Results of Burnett Experiments

−50 °C			0 °C			50 °C		
P, bar	($\Delta P/P$) × 10^6[a]	*Z*	*P*, bar	($\Delta P/P$) × 10^6[a]	*Z*	*P*, bar	($\Delta P/P$) × 10^6[a]	*Z*
Krypton								
78.2729	0	0.3662	139.0187^b			108.4511	−71	0.8498
67.4137	23	0.5008	98.1119	6	0.7232	71.8612	47	0.8942
54.5519	26	0.6436	68.7235	−1	0.8046	47.0276^b		
40.5091	−8	0.7591	46.7140	12	0.8686	30.3733	102	0.9535
28.2905	1	0.8419	30.9496	18	0.9139	19.4493	−80	0.9700
18.9997	−14	0.8980	20.1389	10	0.9445	12.3822	30	0.9809
12.4540	−16	0.9348	12.9488	−40	0.9645	7.8501	−29	0.9878
8.0415	10	0.9586	8.2616^b			139.5479	50	0.8212
75.7457^b			119.1059^b			92.8148	80	0.8676
65.0218	−35	0.5314	84.3762	−7	0.7600	61.2166	30	0.9088
51.6352	−10	0.6701	58.3494	−18	0.8347	39.8419	41	0.9394
37.7811	7	0.7787	39.1877	5	0.8903	25.6486	31	0.9606
26.1328	8	0.8554	25.7384	−5	0.9287	16.3832	−13	0.9747
17.4458	−7	0.9069	16.6521	30	0.9542	10.4105	−58	0.9839
11.3933	11	0.9406	10.6668	−25	0.9708			
7.3394	4	0.9623	6.7903	17	0.9815			
24.8% Helium-75.2% Krypton								
			139.5301	−13	0.8909	140.5492^b		
			90.1415^b			89.0615	1	0.9647
			58.3662	−76	0.9394	56.6247	−31	0.9743
			37.5058	−4	0.9592	35.9477	−10	0.9824
			23.9630	22	0.9733	22.7690	7	0.9884
			15.2359	69	0.9828	14.3939	30	0.9924
			9.6541^b			9.0860	2	0.9952
			116.2579	29	0.8993	114.8441^b		
			75.3012	3	0.9251	72.9624	12	0.9689
			48.6093	22	0.9483	46.3698	13	0.9781
			31.1686	33	0.9657	29.3944^b		
			19.8665^b			18.6088	12	0.9904
			12.6117	−42	0.9857	11.7554	−7	0.9938
			7.9826	−43	0.9909	7.4170	30	0.9960
49.7% Helium-50.3% Krypton								
140.6660	−10	0.9726	138.3258	23	1.0167	139.3626	25	1.0350
88.2517	−33	0.9690	85.9894	−95	1.0039	86.2884	−17	1.0178
55.9310	−21	0.9753	53.9302	5	0.9998	53.8877	24	1.0095
35.4667^b			33.9264	58	0.9988	33.7846	8	1.0053
22.4698	24	0.9882	21.3616	30	0.9988	21.2216	−6	1.0031
14.2077	76	0.9922	13.4537	18	0.9991	13.3428	−42	1.0018
8.9700	−35	0.9950	8.4728	−38	0.9994	8.3942	8	1.0011
113.9646	30	0.9687	112.2940	3	1.0094	112.6440	−34	1.0258
71.9641	19	0.9714	70.1530	18	1.0015	70.0697	−6	1.0134
45.6499	5	0.9786	44.0717	41	0.9992	43.8507	20	1.0074
28.9386	−5	0.9852	27.7378	−5	0.9988	27.5197	8	1.0042
18.3133	−26	0.9902	17.4673	−58	0.9889	17.2955	19	1.0025
11.5715	−24	0.9936	10.9983^b			10.8774	−6	1.0015
7.3009^b								
74.6% Helium-25.4% Krypton								
85.8361	−93	1.0439	138.1628	5	1.0722	139.7764	2	1.0673
53.1233	58	1.0256	84.6083	−3	1.0427	85.7964	11	1.0405
33.1148	39	1.0155	52.4125	16	1.0258	53.2002	16	1.0248
20.7272	21	1.0095	32.6799	−1	1.0158	33.1837	14	1.0153
8.1701	−23	1.0036	20.4550	14	1.0098	20.7718	7	1.0095
113.4806	42	1.0602	12.8317	−32	1.0061	13.0301	−22	1.0060
69.7472	−66	1.0348	8.0594^b			8.1848	−29	1.0037
43.3203	−93	1.0207	111.7223	−8	1.0574	69.6543	−34	1.0327
27.0598	−76	1.0126	68.8122	3	1.0343	43.3194	−10	1.0201
16.9568	−42	1.0077	42.7642	−20	1.0209	27.1075		1.0078
10.6466	−23	1.0048	26.7154	−2	1.0129	16.9625	25	1.0049
6.6919	−16	1.0030	16.7408	27	1.0080	10.6478	20	
			10.5102^b					
Helium								
151.9290	8	1.0972	146.7326	−2	1.0758	146.2489	14	1.0626
92.3743	−20	1.0595	89.8994	−8	1.0468	90.0165	−20	1.0388
56.9181	−7	1.0368	55.6486	−4	1.0291	55.8789	9	1.0242
35.3592	12	1.0229	34.6678	9	1.0181	34.8690	−3	1.0151
22.0772	15	1.0143	21.6834	36	1.0114	21.8302	−12	1.0095
13.8277	16	1.0090	13.5946	−30	1.0071	13.6957	12	1.0059
8.6774	−24	1.0056	139.4303	32	1.0721	117.6858	19	1.0506
121.3254	34	1.0779	85.5319	−13	1.0445	72.7396	2	1.0314
74.2715	−7	1.0479	52.9871	−7	1.0277	45.2686	5	1.0196

Table III (*Continued*)

−50 °C			0 °C			50 °C		
P, bar	$(\Delta P/P) \times 10^{6\,a}$	Z	P, bar	$(\Delta P/P) \times 10^{6\,a}$	Z	P, bar	$(\Delta P/P) \times 10^{6\,a}$	Z
45.9566	−11	1.0297	33.0258	8	1.0173	28.2918	−28	1.0123
28.6240	−22	1.0185	20.6612	−29	1.0108	17.7293	−35	1.0077
17.9012	−39	1.0116	12.9564	−74	1.0068	11.1293	−2	1.0048
11.2246	−11	1.0073	8.1385	82	1.0043	6.9936	37	1.0030
7.0492	34	1.0046	36.0708	0	1.0189	131.6192	−19	1.0565
149.3155	−10	1.0955	22.5547	−6	1.0118	81.1891	−9	1.0350
90.8423	−13	1.0585	14.1401	12	1.0074	50.4653	13	1.0218
55.9962	10	1.0362	8.8787	−6	1.0047	31.5172	26	1.0137
34.7951	27	1.0225	139.4432	−20	1.0721	19.7416	16	1.0086
21.7280	5	1.0141	85.5454	−14	1.0445	12.3886	2	1.0054
13.6104	−3	1.0088	52.9977	16	1.0277	7.7833	−29	1.0034
8.5420	−16	1.0055	33.0334	43	1.0173	104.4518	−11	1.0449
136.8473	−11	1.0877	20.6664	−9	1.0108	64.6966	4	1.0280
83.4888	1	1.0538	12.9601	−16	1.0068	40.3170	15	1.0175
51.5509	13	1.0333	8.1397	−17	1.0043	25.2193	−3	1.0109
32.0662	9	1.0208	110.6369	−1	1.0574	15.8131	2	1.0069
20.0376	−3	1.0130	68.2285	3	1.0356	9.9299	−7	1.0043
12.5569	−9	1.0081	42.4056	−1	1.0222			
			26.4845	1	1.0139			
			16.5910	−9	1.0087			
			10.4133	6	1.0055			

[a] $\Delta P = P_{\mathrm{calcd}} - P_{\mathrm{exptl}}$. [b] Deleted points in regressions.



A - SAMPLE GAS
B - DIAPHRAGM COMPRESSOR
C - PRESSURE GAUGE
D - DIFFERENTIAL PRESSURE INDICATOR
E - BURNETT CELL
F - CONSTANT TEMPERATURE BATH
G - SAMPLE RECOVERY
H - HIGH PRESSURE HELIUM
I - SCREW PUMP
J - DIFFERENTIAL PRESSURE INDICATOR
K - OIL MANOMETER
L - DEAD WEIGHT PISTON GAUGE

Figure 1. Schematic representation of Burnett apparatus.

temperature controller, consisting of proportional, integral, and differential response to the temperature variation from the isotherm temperature, was used to control a resistance heater for bath temperatures greater than ambient. For lower temperatures, the resistance heater was used in combination with continuous cooling, supplied either from mechanical refrigeration or from liquid nitrogen.

The krypton and helium-krypton mixture sample gases were purchased from Air Products, Inc. Helium was donated by the U.S. Bureau of Mines, Helium Research Center, Amarillo, Texas. Composition analyses performed by both groups are given in Tables I and II.

III. Data Reduction

The experimental data from this work have been used to determine compressibility factors and virial coefficients by the analytical method described by Waxman, Davis, and Hastings (*22*). In the language of that method, and Burnett experimental method may be described analytically by the equation

$$P_r = \frac{\rho_0}{N_1 N_2 \ldots N_r} RT \left[1 + \sum_{j=1}^{J} B_j \left(\frac{\rho_0}{N_1 N_2 \ldots N_r} \right) \right] \qquad (1)$$

where the true pressure P_r is related to the initial gas density ρ_0, the volume ratio N_r of the sum of the initial and expansion gas volumes to that of the initial volume alone, the virial coefficients B_j's of a finite density series representation of the compressibility factor Z, the gas constant R, and the sample gas temperature T. The volume ratio N_r is defined further in terms of the pressure distortion of the Burnett volumes $F(P_r,P_{r-1})$ and the zero-pressure value of the volume ratio N_0 as

$$N_r = N_0[1 + F(P_r,P_{r-1})] \qquad (2)$$

where the subscripts $r - 1$ and r denote the condition of the sample gas before and after an expansion for a sequence of expansions extending from $r = 1$ to $r = R$. Since the measured variables are always assumed to contain only random errors independent of any variable range, the least-squares constraint with uniform weighting is introduced into the parameter evaluation to relate each measured variable to its true value. Generally more than one sequence of expansions (run) is necessary to determine adequately the *PVT* properties of a gas over an isotherm. Then, eq 1 and 2 combined with the least-squares constraint are applied to such Burnett data to form an overdetermined set of equations from which the unknown parameters, that is, the virial coefficients, the initial density for each sequence of expansions, and the cell constants, can be evaluated.

In this work the function $F(P_r,P_{r-1})$ was principally estimated from elasticity equations for thick-wall cylinders and the mechanical properties of the stainless steel used to fabricate the Burnett cell. For any isotherm, the data consisted of the measurements from multiple sequences of expansions with the initial density of each sequence experimentally adjusted to intersperse the data. The number of runs for any isotherm was sufficiently large to allow for the accurate least-squares evaluation of the $2 + j$ unknown parameters in eq 1 and 2. The only unknown parameter characterizing the Burnett volumes, N_0, was determined from the helium runs and used as an input parameter in the regressions for the krypton and the helium-krypton runs, for reasons detailed elsewhere (*22*).

The number of virial coefficients retained for a given run was decided from an analysis of the value of the sum of the squares of the residual errors and the standard deviations of the virial coefficients. In some of the runs, the highest pressure points were deleted in preference to increasing the number of virial coefficients; this was justified by our primary interest in evaluating accurate second virial coefficients (rather than high-pressure compressibilities).

Table IV. Virial Coefficients for Helium-Krypton Mixtures[a]

% compn % He	j	−50 °C		0 °C		50 °C	
		B_j	$\sigma(B_j)$	B_j	$\sigma(B_j)$	B_j	$\sigma(B_j)$
0	2	−93.04816	0.026	−61.52562	0.010	−41.72257	0.032
	3	3075.096	12.	2543.566	1.8	2126.274	5.3
	4	65866.22	1683.				
	5	−4013177.	150583.				
24.8	2			−26.15478	0.084	−14.67762	0.025
	3			1425.342	31.	1284.040	7.5
	4			10686.12	3034.		
49.7	2	−10.72073	0.056	−1.980098	0.036	3.371407	0.019
	3	855.8534	17.	796.8511	5.7	719.5617	3.8
	4	8800.246	1381.				
74.6	2	8.19084	0.034	10.65991	0.018	12.18499	0.021
	3	395.0242	5.7	363.2843	2.8	331.9954	4.1
100	2	12.03921	0.032	11.93013	0.063	11.68673	0.046
	3	133.5033	2.4	115.4398	5.8	105.5495	5.4

[a] Units on B_j are $(\mathrm{cm}^3/\mathrm{mol})^j$.

In the course of the data analysis, several data points were discovered which had unexpectedly large pressure deviations from the values obtained from the least-squares fit. These seemed to be due to the pressure measurements themselves rather than to incomplete evacuation, leaks, incomplete equilibration, etc., since subsequent points in the series of expansions for a given run were unaffected. Although the cause of these anomalies was unclear, such data points were deleted in the final regressions.

In addition, the two runs made for the 24.8% helium mixture at −50 °C yielded substantially different results and neither run appeared consistent with other runs from the present work. Although some contamination of these samples appeared likely, no definite conclusion was reached as to the cause of the anomalous data; therefore, these data are not presented here.

The interaction second virial coefficient for each mixture at an isotherm temperature was calculated from the equation

$$B_l = Y_{1l}^2 B_{11} + 2Y_{1l}(1 - Y_{1l})B_{12} + (1 - Y_{1l})^2 B_{22} \tag{3}$$

where Y_{1l} represents the mole fraction of component "1" and the subscript l refers to a particular composition. These results were then combined on a least-squares basis with and without weighting factors. The least-squares-combined value was essentially independent of the use of weighting factors. The regressions were performed using the two separate mixture composition analyses of Table II. The least-squares value of the interaction second virial obtained from the chromatographic analyses had a standard deviation about a factor of 3 lower than that obtained from the mass spectrometric analyses. For this reason the compositions based on the former analyses were selected for use in final calculations.

IV. Results

Thirty-six Burnett experiments are reported on the two pure substances and three mixtures at each of the three temperatures. Table III presents the results of these experiments, including the measured pressures, the relative pressure residuals, and the calculated compressibility factors. The standard deviations of the relative precision of the pressure data in the regressions for the different isotherms vary from 2 to 7 × 10^{-5}; several isotherms with standard deviations near 2 × 10^{-5} indicate that 0.002% is the limit of the precision for the present work.

Table IV presents the virial coefficients evaluated from the data and their standard deviations. The virial coefficients are presented to seven digits to retain the consistency of our data analysis; the significant number of digits for the virial coefficients is indicated by their standard deviations. Table V gives the values of N_0 evaluated from the pure helium isothermal data and their standard deviations. The average values of N_0 shown in the table were used as fixed input to regressions for other mixture compositions. At 0 and 50 °C, the N_0 value was essentially independent of the data set composed from varied combinations of runs. The minute variations in these N_0 values, less than 12 ppm, affected only the compressibility factor by 0.0001 or less. However, at −50 °C the variation was 50 ppm and consequently had a larger effect, i.e., 0.0003, on the compressibility factor.

Table V. Helium Cell Constants

Run	N_0 (σ × 10^5) −50 °C	0 °C	50 °C
1	1.588 19 (3)	1.588 23 (4)	1.588 45 (3)
2	1.588 08 (2)	1.588 25 (4)	1.588 59 (2)
3	1.588 14 (3)	1.588 19 (4)	1.588 50 (3)
4	1.588 10 (3)	1.588 22 (4)	1.588 46 (3)
5		1.588 17 (4)	
Av	1.588 13	1.588 21	1.588 50

The compressibility factors evaluated for pure helium and krypton from this work are compared to previous literature data in Tables VI and VII. For helium, agreement among investigators is generally good. The data of Blancett (*2*) and the present work agree at 0 °C to within 1 × 10^{-4} at all pressures to 152 bar; for all isotherms the maximum deviation is 7 × 10^{-4}. At 0 and 50 °C, the data from the Bureau of Mines Helium Research Center (*4*, *5*) differ from the present work by no more than 4 × 10^{-4} at pressures to 152 bar.

For krypton, Table VII shows larger compressibility factor differences among investigators than are found for helium. However, the present data and those of Trappeniers (*20*) are in excellent agreement at 0 and 50 °C, the maximum deviation being 5 × 10^{-4}. At −50 °C, the only available data for comparison are those of Bearman (*19*). His isochoric measurements, interpolated to −50 °C, covered the pressure range from 66 and 78 bar. These data were consistently 15 × 10^{-4} lower than the data of the present work.

Second virial coefficients from this work are compared with selected literature sources in Tables VIII and IX. For helium, Table VIII shows that at 0 °C the values of this work, Blancett (*2*), Canfield (*9*), and Vogel (*21*) all agree within their standard deviations, about 0.06 cm^3/mol. At 50 °C, there is similar agreement among this work, Blancett, the Bureau of Mines (*5*), and Holborn (*8*). At −50 °C, the results show more scatter, a range of 0.2 cm^3/mol, with no definitive agreement among investigators.

For krypton, Table IX shows that at 0 and 50 °C, the works of Beattie (*1*) and Schneider (*16*) differ by no more than 0.3 cm^3/mol. The more recent values of this work and Trappeniers (*20*) show similar agreement; however, the two sets of investigations differ by more than 1.0 cm^3/mol. At −50 °C,

Table VI. Comparison of Selected Helium Compressibility Factors

		Z ($\Delta Z \times 10^4$)^a		
P, bar	Ref	−50 °C	0 °C	50 °C
25.331	this work	1.0164	1.0133	1.0110
	Blancett (*2*)	1.0166 (2)	1.0133 (0)	1.0111 (1)
	Canfield (*6*)	1.0169 (5)	1.0135 (2)	
	White (*25*)		1.0138 (5)	
	Holborn (*8*)	1.0164 (0)	1.0131 (−2)	
	Schneider (*16*)		1.0131 (−2)	
	Bureau of Mines (*4, 5*)		1.0133 (0)	1.0111 (1)
	Michels (*15*)		1.0132 (−1)	1.0108 (−2)
	Vogl (*21*)		1.0133 (0)	
50.663	this work	1.0328	1.0265	1.0219
	Blancett	1.0331 (3)	1.0264 (−1)	1.0221 (2)
	Canfield	1.0336 (8)	1.0268 (3)	
	Holburn	1.0329 (1)	1.0262 (−3)	
	Schneider		1.0263 (−2)	
	Bureau of Mines		1.0266 (1)	1.0221 (2)
	Michels		1.0262 (−3)	1.0216 (−3)
101.325	this work	1.0652	1.0526	1.0436
	Blancett	1.0657 (5)	1.0526 (0)	1.0440 (4)
	Canfield	1.0666 (14)	1.0533 (7)	
	Holborn	1.0633 (−19)	1.0525 (−1)	
	Bureau of Mines		1.0529 (3)	1.0439 (3)
	Michels		1.0520 (−6)	1.0430 (−6)
151.988	this work	1.0973	1.0785	1.0650
	Blancett	1.0980 (7)	1.0785 (0)	1.0657 (7)
	Canfield	1.0991 (18)	1.0795 (10)	
	Bureau of Mines		1.0788 (3)	1.0654 (4)
	Michels		1.0773 (−12)	1.06404 (−10)

[a] $\Delta Z = Z_{\text{lit.}} - Z_{\text{this work}}$.

Table VII. Comparison of Selected Krypton Compressibility Factors

		Z ($\Delta Z \times 10^4$)^a		
P, bar	Ref	−50 °C	0 °C	50 °C
25.311	this work	0.8603	0.9299	0.9611
	Beattie (*1*)		0.9281 (−18)	0.9597 (−14)
	Schneider (*24*)		0.9295 (−4)	0.9603 (−8)
	Trappeniers (*20*)		0.9304 (5)	0.9614 (3)
50.663	this work	0.6786	0.8571	0.9237
	Beattie		0.8546 (−25)	0.9222 (−15)
	Schneider			0.9234 (−3)
	Trappeniers		0.8576 (5)	0.9239 (2)
75.994	this work	0.3881	0.7837	0.8888
	Beattie		0.7809 (−28)	0.8869 (−19)
	Trappeniers		0.7841 (4)	0.8890 (2)
	Bearman (*19*)	0.3865 (−14)		
101.325	this work		0.7152	0.8577
	Beattie		0.7113 (−39)	0.8553 (−24)
	Trappeniers		0.7154 (2)	0.8577 (0)
151.988	this work		0.6340	0.8126
	Beattie			0.8103 (−23)

[a] $\Delta Z = Z_{\text{lit.}} - Z_{\text{this work}}$.

agreement among investigators is less satisfactory, about 4 cm^3/mol.

Interaction second virial coefficients, B_{12}, calculated from the experimental data are given in Table X. Included in the table are values of B_{12} calculated from each measured mixture virial coefficient by solving eq 3 for B_{12} and also the least-squares value of B_{12} for each isotherm. The excellent precision of the experimental data is illustrated by the maximum deviation of only 0.12 cm^3/mol in the individual values of B_{12} from the least-squares values and the average absolute deviation of 0.05 cm^3/mol.

Exclusive of this work, the only other study of the He–Kr system is that of Brewer (*3*), who determined the excess virial coefficient, E, where

$$E = B_{12} - \tfrac{1}{2}(B_{11} + B_{22}) \qquad (4)$$

by a technique employing measurement of the pressure change on mixing the pure gases at low pressures. Table XI compares the results of Brewer's work with values calculated from the present data using eq 4. The excess virial coefficient comparison is quite good at −50 and 50 °C, 0.0 and 0.6 cm^3/mol. At 0 °C, agreement is much less satisfactory, 2.1 cm^3/mol; however, a plot of Brewer's complete data (−125 to 50 °C) indicates that his datum at 0 °C is inconsistent with his other data. A value of E = 45.4 cm^3/mol at 0 °C was interpolated from his other data points. This value is in much better agreement with results of the present work, 0.6 cm^3/mol. The consistent values of E from these two works employing totally different experimental methods indicate that, by using the average values from the two works, the excess virial coefficients can be defined with a probable accuracy of ±0.3 cm^3/mol.

V. Conclusion

Volumetric data and virial coefficients have been determined for helium–krypton mixtures. The compressibility factors for pure

Table VIII. Comparison of Selected Second Virial Coefficients for Pure Helium

ref	temp, °C	B_2, cm³/mol
this work	-50.00	12.04
Blancett (*2*)	-50.00	12.16
Holborn (*8*)	-49.99	11.93
Keesom (*12*)	-49.99	11.59
Canfield (*6*)	-50.02	12.46 (12.23[a])
Sengers (*18*)	-50.00	12.2[b]
this work	0.00	11.93
Blancett	0.00	11.94
Bureau of Mines (*4*)	0.00	12.00
Holborn	0.01	11.85
Keesom	0.01	11.48
Canfield	0.00	12.09 (11.96[a])
White (*25*)	0.01	12.08
Wiebe (*26*)	0.01	11.76
Michels (*15*)	0.01	11.87
Schneider (*16*)	0.01	11.77
Vogl (*21*)	0.00	11.94
Sengers	0.00	12.0[b]
this work	50.00	11.69
Blancett	50.00	11.76
Bureau of Mines (*5*)	49.99	11.76
Holborn	50.01	11.74
Keesom	50.01	11.30
Wiebe	50.01	11.45
Michels	50.01	11.52
Sengers	50.00	11.7[b]

[a] Data recalculated in ref 9. [b] Correlation value.

Table IX. Comparison of Second Virial Coefficients for Pure Krypton

ref	temp, °C	B_2, cm³/mol
this work	-50.00	-93.05
Schramm (*17*)	-50.00	-97.6
Rowlinson (*23*)	-48.96	-95.46
Sengers (*18*)	-50.00	-95.3[a]
this work	0.00	-61.53
Beattie (*1*)	0.01	-62.97
Schneider (*16*)	0.01	-62.70
Schramm	0.00	-64.4
Trappeniers (*20*)	0.01	-61.24
Sengers	0.00	-62.9[a]
this work	50.00	-41.72
Beattie	50.00	-42.78
Schneider	50.01	-42.78
Schramm	50.00	-42.8
Trappeniers	50.01	-41.44
Sengers	50.00	-42.7[a]

[a] Correlation value.

Table X. Interaction Second Virial Coefficients

y_{He}	B_{12}, cm³/mol		
	-50 °C	0 °C	50 °C
0.248		21.21	21.97
0.497	19.70	21.28	22.08
0.746	19.77	21.09	22.08
least-squares value	19.74	21.21	22.05

Table XI. Comparison of Excess Second Virial Coefficients

Temp, °C	excess second virial coefficient, *E* (cm³/mol)		
	this work	Brewer (*3*)	difference
-50	60.2	60.2	0.0
0	46.0	43.9 (45.4)[a]	2.1 (0.6)[a]
50	37.1	36.5	0.6

[a] Interpolated from Brewer's data at other temperatures.

helium and krypton are in good agreement with recent literature data. The volumetric data for krypton at -50 °C cover a range not previously investigated in detail.

Interaction second virial coefficients from this work show imprecisions of less than ±0.1 cm³/mol; these data and those of Brewer are believed to establish B_{12} values accurate to ±0.3 cm³/mol.

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