

4i. Pressure-Volume-Temperature Relationships of Gases; Virial Coefficients¹

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4i-1. Definition. Virial coefficients are the coefficients in the expansion of the compressibility factor PV of a gas in powers of the density $1/V$,

$$PV = RT \left(1 + \frac{B_V}{V} + \frac{C_V}{V^2} + \dots \right) \quad (4i-1)$$

or in powers of the pressure P ,

$$PV = RT(1 + B_P P + C_P P^2 + \dots) \quad (4i-2)$$

The density expansion is the more fundamental of the two. It can be proved that such an expansion exists for gases at moderate densities, and its consecutive coefficients can be related to interactions between pairs, triplets, etc., of molecules [1]. The pressure expansion is often more practical, the pressure being more readily mea-

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sured than the volume, but it usually converges more slowly, and its coefficients are not as simply related to molecular interaction. In what follows, the emphasis will be on the expansion (4i-1).

4i-2. Units. The units of the virials depend on the units of volume (4i-1) or pressure (4i-2) chosen. We will express the volume in cm³/mol and give the virials in the corresponding units. However, a practical unit of volume frequently used is the amagat unit; the volume in amagat units is the ratio of the actual volume of a gas over the normal volume, i.e., that which it would occupy at 0°C and 1 atm (1.013250 bars). The normal volume for a mole of a real gas differs slightly from the normal volume $V_0 = 22,413.6$ cm³/mol of a perfect gas, owing to deviations from ideality at 0°C and 1 atm. The virial expansion used in conjunction with amagat units of volume is

$$PV_A = A_A + \frac{B_A}{V_A} + \frac{C_A}{V_A^2} + \dots \quad (4i-3)$$

In Table 4i-1, the virials $B_P, C_P; A_A, B_A, C_A$ are expressed in terms of B_V, C_V .

TABLE 4i-1. RELATIONS BETWEEN VOLUME AND PRESSURE VIRIAL COEFFICIENTS

<i>Gas constant</i>	<i>Ideal-gas normal volume per mole</i>
$R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ (= 82.056 cm ³ at K ⁻¹ mol ⁻¹)	$V_0 = 22,413.6 \text{ cm}^3 \text{ mol}^{-1}$
(Both on unified scale)	
<i>Pressure virials (4i-2)</i>	<i>Amagat virials (4i-3)</i>
$B_P = B_V/RT$	$V_n = V_0/A_0$
$C_P = (C_V - B_V^2)/(RT)^2$	$A_0 = 1 - B_A(0^\circ\text{C}) - C_A(0^\circ\text{C}) \dots$
	$A_A = A_0 T/273.15$
	$B_A = B_V A_A/V_n$
	$C_A = C_V A_A/V_n^2$

4i-3. Theoretical Interest. Of great interest is the fundamental relationship of B_V, C_V, \dots to the molecular interaction. If the molecular field is represented by a function $\phi(r)$ where r specifies the relative coordinates of two molecules, then

$$B_V(T) = \frac{N}{2} \int_0^\infty (1 - e^{-\phi(r)/kT}) dr \quad (4i-4)$$

The virial $B_V(T)$ is uniquely determined through Eq. (4i-4) if the molecular interaction $\phi(r)$ is known but the reverse is not true. Higher virials can be likewise related to interactions between triplets, etc., of interacting molecules. These expressions for the higher virials are less useful in practice, not only because the higher virials are poorly known experimentally, but also because the influence of potential function nonadditivity [1] on these virials is poorly known theoretically. We have used the relationship (4i-4) between second virial and potential function for smoothing the experimental $B(T)$ values; for obtaining derivatives $dB/dT, d^2B/dT^2$; and where reasonable, for extrapolating the $B(T)$ tables beyond the temperature range where experimental data are available.

4i-4. Practical Importance. The virials B_V and C_V represent the initial deviations of the equation of state from ideality as a gas is compressed [Eqs. (4i-1 and 4i-2)]. Functions of these virials serve to estimate the initial density dependence of thermodynamic properties. Thus, the internal energy $U_i = U(V, T) - U(\infty, T)$ is given by

$$U_i = -RT \left(\frac{T}{V} \frac{dB_V}{dT} + \frac{T}{2V^2} \frac{dC_V}{dT} + \dots \right)$$

Similar expressions are valid for other thermodynamic functions [2].

TABLE 4i-2. THE SECOND VIRIAL COEFFICIENT OF HELIUM

T , K	B , cm ³ /mol	T , K	B , cm ³ /mol
9.00	-26.0	35.00	5.4
10.00	-21.7	40.00	6.6
11.00	-18.1	45.00	7.5
12.00	-15.2	50.00	8.2
13.00	-12.7	60.00	9.2
14.00	-10.5	80.00	10.6
15.00	-8.7	100.00	11.4
16.00	-7.1	120.00	11.8
17.00	-5.6	160.00	12.3
18.00	-4.3	200.00	12.3
19.00	-3.2	273.15	12.0
20.00	-2.2	373.15	11.3
22.00	-0.5	400.00	11.1
22.64	0.0	600.00	10.4
24.00	0.9	800.00	9.8
26.00	2.0	1000.00	9.3
28.00	3.0	1200.00	8.8
30.00	3.8	1400.00	8.4

TABLE 4i-3. THE SECOND VIRIAL COEFFICIENT OF NEON AND ITS TEMPERATURE DERIVATIVES

T , K	B , cm ³ /mol	$T \frac{dB}{dT}$, cm ³ /mol	$T^2 \frac{d^2B}{dT^2}$, cm ³ /mol
80.00	-11.8	37	-87
90.00	-7.8	31	-73
100.00	-4.8	27	-63
110.00	-2.3	24	-55
120.00	-0.4	21	-49
122.11	0.0	21	-48
130.00	1.2	19	-44
140.00	2.6	18	-40
160.00	4.8	15	-34
200.00	7.6	11	-26
240.00	9.4	9	-20
273.15	10.4	7	-17
280.00	10.6	7	-17
320.00	11.5	6	-14
360.00	12.1	5	-12
373.15	12.3	5	-12
400.00	12.6	4	-11
500.00	13.3	3	-8
600.00	13.8	2	-6
700.00	14.0	1	-5
800.00	14.2	1	-4
900.00	14.3	1	-3
1000.00	14.3	0	-3

4i-5. Determination; Errors. Virial coefficients, in the majority of cases, are not directly measured but are obtained by analysis of PVT data of gases. The most common practice is a least-squares fit of the PV values along isotherms with either density or pressure as an independent variable. Using this procedure, the precision of the virials can then be obtained from linear least-squares estimates of their standard deviations. For a single experimental set in the very best cases, it may be better

TABLE 4i-4. THE SECOND VIRIAL COEFFICIENT OF ARGON AND ITS TEMPERATURE DERIVATIVES

T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol	T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol
80.00	-288.0	577	-1,954	172.00	-66.9	135	-345
82.00	-274.2	544	-1,820	176.00	-63.8	130	-331
84.00	-261.4	514	-1,700	180.00	-60.9	126	-318
86.00	-249.7	488	-1,592	190.00	-54.4	116	-290
88.00	-238.7	463	-1,495	200.00	-48.7	107	-266
90.00	-228.6	441	-1,408	210.00	-43.7	100	-245
92.00	-219.1	420	-1,328	220.00	-39.2	93	-228
94.00	-210.3	401	-1,256	230.00	-35.2	88	-212
96.00	-202.0	384	-1,190	240.00	-31.5	83	-198
98.00	-194.3	367	-1,129	250.00	-28.2	78	-186
100.00	-187.0	352	-1,074	260.00	-25.3	74	-176
102.00	-180.2	338	-1,023	273.15	-21.7	69	-163
104.00	-173.8	325	-976	280.00	-20.1	67	-157
106.00	-167.7	313	-932	300.00	-15.7	61	-142
108.00	-161.9	302	-892	320.00	-11.9	56	-130
110.00	-156.5	292	-855	340.00	-8.7	51	-119
112.00	-151.3	282	-820	360.00	-5.8	48	-110
114.00	-146.4	272	-788	373.15	-4.2	46	-105
116.00	-141.7	264	-757	380.00	-3.4	44	-102
118.00	-137.3	255	-729	400.00	-1.1	42	-96
120.00	-133.1	247	-702	411.52	0.0	40	-92
124.00	-125.2	233	-654	450.00	3.4	36	-82
128.00	-118.0	220	-612	500.00	6.0	31	-71
132.00	-111.4	209	-573	550.00	9.7	28	-63
136.00	-105.4	198	-539	600.00	11.9	25	-57
140.00	-99.8	188	-509	700.00	15.4	20	-47
144.00	-94.6	180	-481	800.00	17.8	17	-40
148.00	-89.8	172	-456	900.00	19.7	14	-34
152.00	-85.3	164	-433	1000.00	21.1	12	-30
156.00	-81.1	157	-413	1100.00	22.2	11	-27
160.00	-77.2	151	-394	1300.00*	23.8	8	-21
164.00	-73.5	145	-376	1500.00	24.8	7	-18
168.00	-70.1	140	-360				

* Data below the dashed line in this and succeeding tables are extrapolations.

than 0.1 cm³/mol for B and 50 cm⁶/mol² for C . However, virial data from different experiments usually differ by much more than their combined precision because of the presence of systematic errors. The main sources of systematic errors are:

1. *Experimental*: (a) errors in the value of RT because of temperature errors or the use of scales other than the thermodynamic scale, (b) systematic errors in the volume because of calibration problems, and (c) difficulties with extrapolation to zero density, especially with data obtained by the Burnett method [3].

2. *Cutoff problems:* A finite polynomial has to be used rather than the theoretically correct infinite series [Eqs. (4i-1) and (4i-2)], but errors arise if the powers omitted would have contributed in the density range studied.

To minimize systematic errors, if there is evidence that any existed, we have refitted the experimental data when available. The data refitted are indicated by asterisks in the literature reference for the tables. Wherever feasible, we reduced temperatures

TABLE 4i-5. THE SECOND VIRIAL COEFFICIENT OF KRYPTON AND ITS TEMPERATURE DERIVATIVES

T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol	T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol
106.00	-394.3	807	-2,813	215.00	-102.4	198	-521
108.00	-379.6	771	-2,659	220.00	-97.9	191	-499
110.00	-365.8	737	-2,518	230.00	-89.8	178	-459
112.00	-352.8	706	-2,389	240.00	-82.4	166	-425
114.00	-340.5	677	-2,270	250.00	-75.9	156	-396
116.00	-329.0	650	-2,160	260.00	-69.9	147	-369
118.00	-318.1	625	-2,059	270.00	-64.5	139	-346
120.00	-307.8	601	-1,965	273.15	-62.9	136	-340
122.00	-298.0	579	-1,878	280.00	-59.6	132	-323
124.00	-288.8	559	-1,797	290.00	-55.1	125	-308
126.00	-280.0	539	-1,722	300.00	-51.0	119	-291
128.00	-271.6	521	-1,651	310.00	-47.2	113	-276
130.00	-263.7	504	-1,586	320.00	-43.7	108	-263
132.00	-256.1	488	-1,524	340.00	-37.4	100	-239
134.00	-248.9	473	-1,467	360.00	-31.9	92	-219
136.00	-242.0	458	-1,413	373.15	-28.7	87	-207
138.00	-235.4	444	-1,362	380.00	-27.1	85	-202
140.00	-229.1	432	-1,314	400.00	-22.9	80	-187
144.00	-217.3	408	-1,226	420.00	-19.1	75	-175
148.00	-206.4	386	-1,148	440.00	-15.8	70	-163
152.00	-196.4	366	-1,078	460.00	-12.7	66	-153
156.00	-187.1	348	-1,015	500.00	-7.5	59	-137
160.00	-178.5	332	-959	550.00	-2.2	52	-120
164.00	-170.5	317	-907	575.00	0.0	49	-113
168.00	-163.1	303	-860	600.00	2.0	47	-107
172.00	-156.1	290	-817	650.00	5.6	42	-96
176.00	-149.5	279	-778	700.00	8.5	38	-88
180.00	-143.4	268	-742	800.00	13.2	32	-74
186.00	-134.9	253	-693	900.00	16.7	28	-64
192.00	-127.1	239	-650	1000.00	19.5	24	-56
198.00	-119.9	227	-611	1100.00	21.6	21	-50
205.00	-112.2	214	-570	1300.00	24.8	17	-40
210.00	-107.2	206	-545	1500.00	27.0	14	-34

to the thermodynamic scale, using the known relation between this scale and the IPTS [4]. If a laboratory maintained its own gas scale, this scale was used. In a few cases, notably He at low temperatures, where one of the purposes of the experiment was gas thermometry, we had to leave the intercept free. Regarding the cutoff criterion [5], we chose the maximum density range in which the $(k + 1)$ th virial does not contribute beyond experimental error, and fitted this range with a polynomial of degree $k - 1$. Depending on the amount of low-density data available, we took $k = 3$ or 4. In order to do this, an estimate of the size of the $(k + 1)$ th

virial was necessary. In cases where it could not be obtained from the data, we used the theoretical value as calculated for the Lennard-Jones six-twelve potential. This procedure was justified since only order-of-magnitude estimates were needed.

After second and third virials had been obtained from each set of experimental data for a given substance, and after obviously wrong results had been eliminated, a smoothing or averaging procedure was established. Use was made of the fundamental relation (4i-1) between the second virial coefficient and the intermolecular potential.

4i-6. Potential Functions—Determination, Use. Equation (4i-4) applies to substances for which quantum effects are negligible. For such substances, Eq. (4i-4) is

TABLE 4i-6. THE SECOND VIRIAL COEFFICIENT OF XENON
AND ITS TEMPERATURE DERIVATIVES

T , K	B , cm ³ /mol	dB/dT , cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol	T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol
220.00	-230.7	429	-1,225	380.00	-78.5	175	-433
225.00	-221.2	411	-1,166	390.00	-74.0	169	-415
230.00	-212.4	395	-1,111	400.00	-69.8	163	-398
235.00	-204.0	380	-1,001	420.00	-62.2	152	-368
240.00	-196.2	366	-1,015	440.00	-55.4	142	-342
245.00	-188.7	353	-972	460.00	-49.2	133	-319
250.00	-181.7	341	-933	480.00	-43.7	126	-299
255.00	-175.1	329	-896	500.00	-38.8	119	-282
260.00	-168.8	319	-861	525.00	-33.1	111	-262
265.00	-162.8	308	-829	550.00	-28.1	104	-245
270.00	-157.2	299	-799	575.00	-23.6	98	-230
273.15	-153.7	293	-781	600.00	-19.6	93	-216
280.00	-146.6	281	-745	650.00	-12.5	84	-193
290.00	-137.0	266	-607	700.00	-6.6	76	-175
300.00	-128.3	252	-654	768.03	0.0	67	-154
310.00	-120.2	239	-616	800.00	2.7	64	-146
320.00	-112.8	227	-582	900.00	9.6	55	-125
330.00	-106.0	217	-551	1000.00	15.0	48	-110
340.00	-99.7	207	-523	1100.00	19.3	42	-97
350.00	-93.8	198	-497	1200.00	22.8	38	-87
360.00	-88.4	190	-474				
370.00	-83.3	182	-452	1300.00	25.6	34	-79
373.15	-81.7	180	-446	1400.00	28.0	31	-72
				1500.00	30.1	28	-66

exact. Quantum effects become important for only the lightest gases [6], e.g., helium, hydrogen, etc. These latter are generally referred to as *quantum gases*. For such gases, Eq. (4i-4) can represent only a first approximation whose quality goes down with decreasing molecular weight. In either case, i.e., whether Eq. (4i-4) is exact or an approximation, the use of it requires a knowledge of the intermolecular potential function $\phi(r)$. In principle, such functions can be obtained by direct quantum-mechanical calculation. In practice, this procedure is not feasible even for the simplest system. This has required, in effect, the partial reversal of the process. Thus, instead of using Eq. (4i-4) with a known function $\phi(r)$ to predict $B(T)$, one uses (4i-4), in part, to produce information on $\phi(r)$ and, in part, to predict $B(T)$. This is done by assuming a form for $\phi(r)$ (often referred to as a *potential model*), based on whatever fundamental knowledge is available, inserting a number of parameters in this form [for example, ϵ and σ of (4i-5)], and varying the values of these

parameters to obtain the best agreement between the $B(T)$ values calculated from Eq. (4i-4) and those determined from the analysis of PVT data described above. The predictive power of (4i-4) remains essentially intact, provided the number of experimental points used is far in excess of the number of parameters sought. Frequently used in this way to describe the intermolecular potential of simple nonpolar substances is the Lennard Jones twelve-six potential, a member of the more general class of spherically symmetric $m - 6$ potentials:

$$\phi(r) = \frac{m\epsilon}{m-6} \left(\frac{m}{6}\right)^{6/(m-6)} \left[\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^6 \right] \quad (4i-5)$$

TABLE 4i-7. THE SECOND VIRIAL COEFFICIENT OF NITROGEN AND ITS TEMPERATURE DERIVATIVES

T , K	B , cm ³ /mol	$T \frac{dB}{dT}$, cm ³ /mol	$T^2 \frac{d^2B}{dT^2}$, cm ³ /mol	T , K	B , cm ³ /mol	$T \frac{dB}{dT}$, cm ³ /mol	$T^2 \frac{d^2B}{dT^2}$, cm ³ /mol
100.00	-160.0	304	-874	210.00	-31.1	94	-224
102.00	-154.1	293	-837	220.00	-26.9	88	-209
104.00	-148.5	283	-802	230.00	-23.2	82	-195
106.00	-143.2	273	-769	240.00	-19.7	78	-183
108.00	-138.2	264	-739	260.00	-13.8	70	-163
110.00	-133.4	256	-711	273.15	-10.5	65	-152
112.00	-128.7	248	-684	280.00	-8.9	63	-147
116.00	-120.4	233	-637	300.00	-4.7	58	-134
120.00	-112.7	220	-594	320.00	-1.2	53	-122
124.00	-105.7	208	-557	327.22	0.0	52	-119
128.00	-99.3	197	-524	340.00	1.9	49	-113
132.00	-93.4	188	-494	360.00	4.6	46	-105
136.00	-87.9	179	-467	373.15	6.2	44	-100
140.00	-82.8	171	-442	380.00	7.0	43	-97
144.00	-78.1	163	-420	400.00	9.1	40	-91
148.00	-73.7	156	-400	450.00	13.5	34	-78
152.00	-69.7	150	-381	500.00	16.8	30	-68
156.00	-65.8	144	-364	550.00	19.5	26	-61
160.00	-62.3	139	-349	600.00	21.7	24	-54
166.00	-57.3	131	-327	700.00	25.0	19	-45
172.00	-52.7	125	-308	800.00	27.3	16	-38
178.00	-48.6	118	-291	900.00	29.1	14	-33
184.00	-44.7	113	-276	1000.00	30.4	12	-29
190.00	-41.2	108	-262	1200.00	32.3	9	-23
200.00	-35.9	100	-242	1400.00	33.5	7	-19

where ϵ and σ are parameters to be determined for each substance. This expression, with proper choice of m , adequately describes the second virial coefficient of simple nonpolar substances.

It should be noted that once a "best" set of parameters has been decided upon, a potential function exists which can serve as a representation for the "actual" potential function appropriate to the gas of interest. The use of such potential functions need not be restricted to Eq. (4i-4). They can also be employed in various statistical mechanical theories for calculating macroscopic thermodynamic quantities from molecular properties. In short, these potential functions have their own importance.

Various methods, of which the use of Eq. (4i-4) is only one example, by means of which potential parameters are determined from experimental data have recently been subjected to close scrutiny [7]. In that study it was determined that all reasonable three-parameter potential models should produce essentially the same set of second virial coefficients. Because of this it was reasonable to fix on one particular model, and we chose Eq. (4i-5) for that purpose. A second result of the study of methods for determining potential parameters was the discovery of a reduced temperature range, for each property, over which that property cannot be used to distinguish between

TABLE 4i-8. THE SECOND VIRIAL COEFFICIENT OF OXYGEN AND ITS TEMPERATURE DERIVATIVES

T , K	B , cm ³ /mol	$T dE/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol	T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol
100.00	-197.5	3.3	-1,201	210.00	-44.8	104	-259
102.00	-190.1	3.7	-1,141	220.00	-40.1	97	-240
104.00	-183.1	3.2	-1,087	230.00	-35.9	91	-223
106.00	-176.5	3.9	-1,036	240.00	-32.1	86	-208
108.00	-170.3	3.6	-989	250.00	-28.7	81	-195
110.00	-164.4	3.4	-946	260.00	-25.6	77	-184
112.00	-158.9	3.3	-906	273.15	-22.0	72	-171
114.00	-153.6	2.3	-868	280.00	-20.2	69	-164
116.00	-148.6	2.3	-833	300.00	-15.7	63	-148
120.00	-139.3	2.5	-770	320.00	-11.8	58	-135
124.00	-130.9	2.9	-715	340.00	-8.4	53	-124
128.00	-123.2	2.5	-667	360.00	-5.5	49	-114
132.00	-116.2	2.2	-624	373.15	-3.7	47	-109
136.00	-109.7	2.0	-585	380.00	-2.9	46	-106
140.00	-103.8	2.0	-551	400.00	-0.6	43	-99
144.00	-98.3	1.0	-520	405.88	0.0	42	-97
148.00	-93.2	1.2	-492	450.00	4.1	37	-85
154.00	-86.2	1.0	-454	500.00	7.7	32	-74
160.00	-79.9	1.3	-422	550.00	10.6	29	-65
166.00	-74.2	1.0	-393	600.00	12.9	25	-58
172.00	-69.1	1.2	-368	700.00	16.5	21	-48
178.00	-64.3	1.3	-346	800.00	19.1	18	-41
184.00	-60.0	1.2	-326	1000.00	22.4	13	-31
190.00	-56.0	1.2	-308	1200.00	24.5	10	-25
200.00	50.0	1.2	-281	1400.00	25.9	8	-20

potential functions. For the second virial coefficient, this range is given approximately by $0.6 < T/T_{B, \text{Boyle}} < 3.0$. We have included a table (Table 4i-17) of experimental Boyle temperatures to facilitate the conversion of these numbers into experimental temperatures for the various gases studied. The second result mentioned states, in effect, that one should not use Eq. (4i-4) with a potential function determined by data entirely contained in the insensitive range to predict $B(T)$ outside that range; nor should one use the resulting potential function in other theories. On the other hand, potential functions determined with data entirely outside the insensitive range can be used in an extrapolation to predict $B(T)$ values within that range.

4i-7. Construction of the Tables. Using linear and nonlinear [8] least-squares techniques, calculated second virial coefficients based on the function (4i-5) were

fitted to the experimental second virial coefficient data for eight substances. Each value of m was taken to define a separate potential, with ϵ and σ in (4i-5) the adjustable parameters for the fit. The value of m was varied until the standard deviation of the fit was a minimum. The "best" $m - 6$ potential was used to generate a table of B , $T dB/dT$ and $T^2 d^2B/dT^2$ values at various temperatures. Furthermore, it was used for extrapolation beyond the range of experimental data. Such extrapolations are indicated in each case by a dashed line across the tables.

TABLE 4i-9. THE SECOND VIRIAL COEFFICIENT OF DRY CO₂-FREE AIR AND ITS TEMPERATURE DERIVATIVES

T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol	T , K	B , cm ³ /mol	$T dB/dT$, cm ³ /mol	$T^2 d^2B/dT^2$, cm ³ /mol
100.00	-167.3	318	-935	210.00	-34.5	95	-230
102.00	-161.2	307	-893	220.00	-30.2	89	-214
104.00	-155.3	295	-854	230.00	-26.4	84	-200
106.00	-149.8	285	-818	240.00	-22.9	79	-187
108.00	-144.6	275	-785	250.00	-19.8	75	-176
110.00	-139.6	266	-754	260.00	-16.9	71	-166
112.00	-134.9	258	-725	273.15	-13.5	66	-155
114.00	-130.4	249	-698	280.00	-11.9	64	-150
116.00	-126.0	242	-673	300.00	-7.7	58	-136
118.00	-122.0	235	-649	320.00	-4.1	54	-124
120.00	-118.2	228	-627	340.00	-1.0	50	-114
124.00	-110.9	215	-586	346.81	0.0	48	-111
128.00	-104.3	204	-550	360.00	1.7	46	-106
132.00	-98.1	193	-517	373.15	3.4	44	-101
136.00	-92.5	184	-488	380.00	4.2	43	-98
140.00	-87.3	176	-462	400.00	6.3	40	-92
144.00	-82.5	168	-438	450.00	10.7	35	-79
148.00	-78.0	161	-416	500.00	14.1	30	-69
152.00	-73.8	154	-396	550.00	16.8	27	-61
156.00	-69.9	148	-378	600.00	19.0	24	-55
160.00	-66.2	142	-361	650.00	20.8	21	-50
166.00	-61.1	134	-339	700.00	22.3	19	-45
172.00	-56.5	127	-319	800.00	24.7	16	-38
178.00	-52.2	121	-301	900.00	26.4	14	-33
184.00	-48.3	115	-284	1000.00	27.8	12	-29
190.00	-44.7	110	-270	1200.00	29.7	9	-23
200.00	-39.3	102	-248	1400.00	30.9	7	-19

Equation (4i-4) and the procedures described above were used for the quantum gases He, H₂, and D₂ as well. In these cases, however, the methods were used only to facilitate smoothing and interpolation of virial data. For H₂O, D₂O, and CO₂ a potential of the form (4i-5) was found to be inadequate. These substances were therefore treated as were the quantum gases; that is, the methods outlined were used only for smoothing and interpolation. The tables prepared for these six substances consist only of smoothed experimental $B(T)$ values, with no extrapolations attempted. Tables of $T dB/dT$ and $T^2 d^2B/dT^2$ are not given, nor are potential parameters used in the smoothing process reported since they are without clear meaning. Since the $B(T)$ tables for these six substances are so closely tied to the experimental values, minor departures from smoothness in the tables may be detected.

Third virials, in all cases, were obtained by graphical interpolation of the (refitted) experimental values for C . They are summarized in Table 4i-16.

Table 4i-17 contains values for the Boyle temperature and the inversion temperature. In those cases where the form (4i-5) for the intermolecular potential applies, the potential parameters and the value of m are summarized in Table 4i-18.

We note that the optimum value of m is much closer to 18 than to the popular value of 12.

4i-8. Accuracy of the Tables. From a computational point of view, in all cases, the temperature spacing is sufficiently fine to allow for an interpolation to be made

TABLE 4i-10. THE SECOND VIRIAL COEFFICIENT OF HYDROGEN

T , K	B , cm ³ /mol	T , K	B , cm ³ /mol
24.00	-112.8	74.00	-12.9
25.00	-106.2	78.00	-10.9
26.00	-100.3	82.00	-8.9
27.00	-94.8	86.00	-7.2
28.00	-89.6	90.00	-5.7
29.00	-85.0	100.00	-2.5
30.00	-80.7	110.00	-0.0
31.00	-76.7	110.04	0.0
32.00	-73.0	120.00	2.0
33.00	-69.5	130.00	3.7
34.00	-66.2	140.00	5.1
35.00	-63.2	150.00	6.4
36.00	-60.2	160.00	7.6
38.00	-55.0	170.00	8.6
40.00	-50.3	180.00	9.5
42.00	-46.2	190.00	10.2
44.00	-42.5	200.00	10.8
46.00	-39.2	250.00	13.0
48.00	-36.2	273.15	13.7
50.00	-33.4	300.00	14.4
54.00	-28.6	350.00	15.3
58.00	-24.5	373.15	15.6
62.00	-21.0	400.00	15.9
66.00	-17.9	420.00	16.1
70.00	-15.2		

using a quadratic formula without the introduction of errors. Furthermore, linear interpolation can be used without introducing an error of more than 0.3 cm³/mol in $B(T)$ owing to the neglect of quadratic terms. It should be noted that where B , $T dB/dT$, and $T^2 d^2 B/dT^2$ are available, a Taylor series expansion can be used for interpolation.

It is much harder to assess the absolute accuracy of the tables in any general way. Where data from many sources are available for one substance, as is the case for most of the noble gases and for nitrogen, one usually finds discrepancies up to 1.5 cm³/mol in B and up to 30 percent in C between data from different laboratories. Discrepancies in B may become much larger at temperatures below critical. The main source

TABLE 4i-11. THE SECOND VIRIAL COEFFICIENT OF DEUTERIUM

T , K	B , cm ³ /mol	T , K	B , cm ³ /mol
84.00	-10.4	200.00	10.2
88.00	-8.7	220.00	11.3
92.00	-7.0	240.00	12.2
96.00	-5.6	260.00	12.8
100.00	-4.2	273.15	13.1
110.00	-1.3	280.00	13.2
115.00	0.0	300.00	13.5
120.00	1.0	320.00	14.0
130.00	3.0	340.00	14.4
140.00	4.6	360.00	14.7
150.00	6.0	373.15	14.9
160.00	7.1	380.00	15.0
170.00	8.1	400.00	15.2
180.00	8.9	420.00	15.5
190.00	9.5		

TABLE 4i-12. THE SECOND VIRIAL COEFFICIENT OF WATER VAPOR (H₂O)

T , K	B , cm ³ /mol	T , K	B , cm ³ /mol
432.00	-311.2	500.00	-176.2
434.00	-304.5	505.00	-170.4
436.00	-298.1	510.00	-165.0
438.00	-291.9	515.00	-160.0
440.00	-285.5	520.00	-155.3
442.00	-279.7	530.00	-146.7
444.00	-273.9	540.00	-139.1
446.00	-268.5	550.00	-132.0
448.00	-263.2	560.00	-125.3
450.00	-258.2	570.00	-119.0
452.00	-253.4	580.00	-113.1
454.00	-248.9	590.00	-107.6
456.00	-244.7	600.00	-102.5
458.00	-240.5	610.00	-97.6
460.00	-236.5	620.00	93.0
462.00	-232.6	630.00	-88.6
464.00	-228.9	640.00	-84.4
466.00	-225.4	650.00	-80.4
468.00	-222.1	660.00	-76.6
470.00	-218.5	670.00	-72.9
475.00	-210.2	680.00	-69.4
480.00	-202.5	690.00	-66.1
485.00	-195.4	700.00	-62.9
490.00	-188.6	710.00	-59.9
495.00	-182.2	720.00	-57.0

of oxygen data (L. A. Weber) is particularly precise, ~ 0.1 cm³/mol in B , and agrees with the others within combined precision. For hydrogen and deuterium, problems with the temperature scale between 100 and 274 K may cause errors in B as large as 0.5 cm³/mol. For H₂O and D₂O, there is only one source for which the precision ranges from several cm³/mol at the lower temperatures to 0.2 cm³/mol at the higher ones. For CO₂, discrepancies of several cm³/mol in B exist between data of different sources, and for CH₄, of 0.7 cm³/mol in B and of 10 percent in C .

TABLE 4i-13. THE SECOND VIRIAL COEFFICIENT OF HEAVY WATER VAPOR (D₂O)

T , K	B , cm ³ /mol	T , K	B , cm ³ /mol
32.00	-314.5	500.00	-177.6
34.00	-307.8	505.00	-171.8
36.00	-301.3	510.00	-166.3
38.00	-295.0	515.00	-161.1
40.00	-288.6	520.00	-156.4
42.00	-282.6	530.00	-147.7
44.00	-276.9	540.00	-140.0
46.00	-271.3	550.00	-132.8
48.00	-265.9	560.00	-126.1
49.00	-260.8	570.00	-119.6
52.00	-255.9	580.00	-113.6
54.00	-251.4	590.00	-108.1
56.00	-247.0	600.00	-103.0
58.00	-242.8	610.00	-98.0
60.00	-238.8	620.00	-93.3
62.00	-234.8	630.00	-88.8
64.00	-231.1	640.00	-84.6
66.00	-227.6	650.00	-80.6
68.00	-224.2	660.00	-76.7
70.00	-220.5	670.00	-73.1
75.00	-212.2	680.00	-69.5
80.00	-204.4	690.00	-66.2
85.00	-197.2	700.00	-63.0
90.00	-190.3	710.00	-59.9
95.00	-183.8	720.00	-57.0

4i-9. Use of the Tables. The averaged virials presented here can be used for calculations of precise PV products at low pressures. However, in the process of separately averaging and rounding the second and third virials, correlations in their experimental errors have been obliterated; thus, they cannot be used to represent the PVT data from which they were derived within experimental precision over the entire density range. If precise PVT values are needed at higher densities, it is usually preferable to interpolate in the original data.

The tables of virials and their temperature derivatives can be used to calculate the initial density dependence of other thermodynamic properties [2].

TABLE 4i-14. THE SECOND VIRIAL COEFFICIENT OF CARBON DIOXIDE (CO₂)

<i>T</i> , K	<i>B</i> , cm ³ /mol	<i>T</i> , K	<i>B</i> , cm ³ /mol
250.00	-181.8	420.00	-52.6
255.00	-174.1	430.00	-49.1
260.00	-166.8	440.00	-45.9
265.00	-160.0	450.00	-42.8
270.00	-153.5	460.00	-40.0
273.15	-149.7	480.00	-34.7
275.00	-147.4	500.00	-30.0
280.00	-141.7	520.00	-25.8
285.00	-136.2	540.00	-21.9
290.00	-131.1	560.00	-18.4
295.00	-126.2	580.00	-15.3
300.00	-121.5	600.00	-12.4
310.00	-112.8	620.00	-9.8
320.00	-104.8	640.00	-7.4
330.00	-97.5	660.00	-5.1
340.00	-90.8	680.00	-3.1
350.00	-84.7	700.00	-1.3
360.00	-79.0	714.81	0.0
370.00	-73.8	750.00	2.7
373.15	-72.2	800.00	6.0
380.00	-68.9	850.00	8.8
390.00	-64.4	900.00	11.1
400.00	-60.2	950.00	13.0
410.00	-56.3	1000.00	14.6

TABLE 4i-15. THE SECOND VIRIAL COEFFICIENT OF METHANE AND ITS TEMPERATURE DERIVATIVES

T, K	$B,$ cm^3/mol	$T dB/dT,$ cm^3/mol	$T^2 d^2B/dT^2,$ cm^3/mol	T, K	$B,$ cm^3/mol	$T dB/dT,$ cm^3/mol	$T^2 d^2B/dT^2,$ cm^3/mol
110.00	-334.0	671	-2,244	210.00	-95.3	193	-505
112.00	-322.2	643	-2,132	220.00	-86.6	179	-463
114.00	-311.0	618	-2,029	230.00	-78.9	167	-428
116.00	-300.5	594	-1,934	240.00	-72.0	157	-397
118.00	-290.5	571	-1,846	250.00	-65.8	147	-369
120.00	-281.1	550	-1,764	260.00	-60.2	139	-346
122.00	-272.2	531	-1,688	270.00	-55.2	131	-324
124.00	-263.7	512	-1,617	273.15	-53.6	129	-318
126.00	-255.6	495	-1,551	280.00	-50.5	124	-306
128.00	-248.0	479	-1,490	290.00	-46.3	118	-289
130.00	-240.7	464	-1,432	300.00	-42.3	113	-273
132.00	-233.7	449	-1,378	320.00	-35.4	103	-247
134.00	-227.0	435	-1,327	340.00	-29.4	94	-225
136.00	-220.7	422	-1,280	360.00	-24.2	87	-207
140.00	-208.8	398	-1,193	373.15	-21.2	83	-196
144.00	-197.9	377	-1,115	380.00	-19.7	81	-191
148.00	-187.8	357	-1,046	400.00	-15.7	76	-177
152.00	-178.5	340	-984	450.00	-7.4	65	-150
156.00	-169.9	323	-928	500.00	-1.1	56	-130
160.00	-161.9	309	-877	509.66	0.0	55	-126
164.00	-154.5	295	-831	550.00	4.0	50	-114
168.00	-147.5	282	-789	600.00	8.1	45	-102
172.00	-141.0	271	-751	650.00	11.5	40	-92
176.00	-134.9	260	-716	700.00	14.3	37	-83
180.00	-129.2	250	-683	800.00	18.8	31	-70
184.00	-123.8	241	-653	900.00	22.1	26	-61
188.00	-118.7	232	-626	1000.00	24.7	23	-53
192.00	-113.9	224	-600	1100.00	26.8	20	-47
196.00	-109.4	216	-576	1300.00	29.8	16	-39
200.00	-105.1	209	-554	1500.00	31.9	13	-32

TABLE 4i-16. THE THIRD VIRIAL COEFFICIENTS OF VARIOUS SUBSTANCES
 (C in units of $10^2\text{cm}^6/\text{mol}^2$)

T, K	He	Ne	Ar	Kr	Xe	N_2	O_2	Air	H_2	D_2	H_2O	D_2O	CO_2	CH_4
25	14.0					
30	16.0					
35	14.3					
40	12.1					
45	10.7					
50	9.6					
55	8.9					
60	2.7	4	8.4					
70	2.5	4	7.4					
80	2.4	4	7	6.9					
90	2.3	4	9	6.4					
100	2.2	4	12	6.1	6				
110	2.1	3	16	5.9	5				
120	2.0	3	20	5.7	5				
130	1.9	3	23	5.5	5				
140	1.8	3	25	28	5.4	5				
150	1.7	3	23	26	5.3	5				
160	1.6	3	22	26	23	24	5.2	5				
180	1.5	3	20	21	20	21	5.0	5				
200	1.3	3	18	19	17	19	4.8	5				
220	1.2	3	16	33	...	17	15	18	4.6	5				
240	1.1	3	15	30	...	16	13	17	4.5	5				
260	1.1	3	13	28	...	15	12	16	4.4	5				
273	1.1	3	12	27	62	15	11	15	4.2	5	57	29
280	1.0	3	12	26	59	15	11	15	4.1	5	56	28
300	1.0	2	11	24	54	14	10	15	3.9	5	52	26
320	1.0	2	11	23	50	14	...	14	3.6	5	49	24
340	0.9	2	10	21	46	14	...	14	3.4	5	45	22
360	0.8	2	9	20	41	13	3.2	5	42	21
380	0.8	2	9	19	36	13	3.0	4	38	19
400	0.7	2	9	18	34	13	2.9	4	36	18
420	0.7	...	9	18	32	12	3	32	17
440	8	17	30	12	16
460	8	16	28	12	16
480	8	16	26	12	15
500	7	15	24	12	-100	-150	...	15
525	7	15	22	-53	-64	...	14
550	7	14	20	-17	-20	...	14
575	7	14	18	+2	0	...	14
600	7	13	9	8	...	13
650	13	12	12
700	12	10	12

TABLE 4i-17. THE BOYLE TEMPERATURE AND THE INVERSION TEMPERATURE OF VARIOUS SUBSTANCES

Substance	Boyle temperature, K	Inversion temperature, K
Helium	22.64	
Neon	122.11	231.42
Argon	411.52	779.91
Krypton	575.00	1089.72
Xenon	768.03	1455.79
Nitrogen	327.22	620.63
Oxygen	405.88	764.43
Air	346.81	658.79
Hydrogen	110.04	
Deuterium	115.30	
Carbon dioxide	714.81	
Methane	509.66	967.81

TABLE 4i-18. POTENTIAL PARAMETERS FOR THE $m - 6$ POTENTIAL OF SELECTED SUBSTANCES

Substance	m	$\epsilon/k, K$	$b_0 \left(= \frac{2\pi N}{3} \sigma^3 \right)$ cm ³ /mol
Neon	18	47.74	22.83
Argon	18	160.87	43.74
Krypton	18	224.78	53.78
Xenon	18	300.29	73.82
Nitrogen	21	139.41	54.41
Oxygen	21	172.93	44.49
Air	21	147.76	50.95
Methane	21	217.14	57.96

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Experimental PVT data from sources marked by an asterisk were fitted.

Table 4i-2: Helium

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Table 4i-3: Neon

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Table 4i-4: Argon

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