Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Covolumes for a Number of Common Gases

P. A. LONGWELL, J. B. OLIN, and B. H. SAGE
California Institute of Technology, Pasadena, Calif.

In the study of chemical reactions in the ballistic piston apparatus (*10*), which is used to subject samples of gases to high pressures and high temperatures for short times, it is necessary to take the pressure-volume-temperature relationships of the gases into account. The conditions in the ballistic piston apparatus range from room temperature at subatmospheric pressure up to 10,000 to 150,000 p.s.i. at temperatures ranging from 1500 to 15,000 degrees Rankine. Because experimental pressure-volume-temperature data are unavailable for most of these ranges of conditions, it is necessary to make use of relationships based on theoretical considerations.

Hirschfelder, Curtiss, and Bird (*7*) treat rather thoroughly the subject of the calculation of equations of state on the basis of statistical-mechanical models and present several equations of state obtained in this manner. These include two which seem suitable for nonpolar gases in the range of conditions of interest. One using a three-shell modification (*11*) of the Lennard-Jones and Devonshire equation of state (*8*) is suitable for the dense gas region. For this calculation a spherical molecule was considered to be confined to a cell and interactions with the three neighboring shells of molecules were taken into account. A virial equation of state with the second and third virial coefficients calculated from the Lennard-Jones (6–12) potential (*4, 5*) is suitable for the region of lower densities. Both equations of state are based on spherically symmetrical potentials. The results summarized by Hirschfelder (*7*) have been used to estimate the equations of state for several gases which have been employed in the ballistic piston apparatus. In all cases the influence of any possible dissociation or decomposition has been neglected and the results shown are for the normal molecular species. These simple considerations lead to estimates of the covolume which may be subject to rather large uncertainties of the order of 25% (*2*) at the higher pressures and temperatures. Even so, the resulting predictions appear to be an improvement over the use of the equation of state of a perfect gas for these conditions.

EQUATIONS OF STATE USED

The virial equation of state as presented by Hirschfelder (*7*) is

$$\frac{P\underset{\circ}{V}}{RT} = Z = 1 + \frac{B^{\star}b_0}{\underset{\circ}{V}} + \frac{C^{\star}b_0^2}{\underset{\circ}{V}^2} + \frac{0.2869b_0^3}{\underset{\circ}{V}^3} + \frac{0.1928b_0^4}{\underset{\circ}{V}^4} \qquad (1)$$

and he tabulates $B^{\star}$ and $C^{\star}$ as functions of t^{*} where

$$t^{*} = \frac{T}{(\epsilon/k)} \qquad (2)$$

Values of the force constants, b_0 and (ϵ/k), given by Hirschfelder for the gases involved have been converted to engineering units and are shown in Table I. Where there was a choice, values derived from equation of state data were selected as most applicable.

The equation of state for dense gases based on the three-shell modifications of the Lennard-Jones and Devonshire equation of state is presented (*7*) in tabular form. The compressibility factor, Z, is tabulated as a function of t^{*} and $(a^{*})^3$, where

$$(a^{*})^3 = \frac{2\sqrt{2}\,\pi}{3b_0}\underset{\circ}{V} \qquad (3)$$

A covolume equation of state such as that considered by Corner (*6*) has advantages for use in connection with the ballistic piston apparatus, particularly if the covolume remains approximately constant. It was therefore decided to utilize the covolume equation of state

$$P(\underset{\circ}{V} - b) = RT \qquad (4)$$

and to determine values of the molal covolume, b, in accordance with Hirschfelder's calculations. The covolume is easily obtained from compressibilities, since

$$b = \left[\frac{Z-1}{Z}\right]\underset{\circ}{V} = \frac{Z-1}{Z\underset{\circ}{\sigma}} \qquad (5)$$

Table I. Force Constants for Various Gases[a]

Gas	b_0, Cu. Ft./Lb. Mole	(ϵ/k), °R.
H_2	0.5073	66.60
He	0.3375	18.40
n-C_6H_{14}	4.169	743
CH_4	1.1238	266.8
NO	0.6407	236
N_2	1.0202	171.09
O_2	0.9250	211.5

[a] Converted from Table 1-A (7).

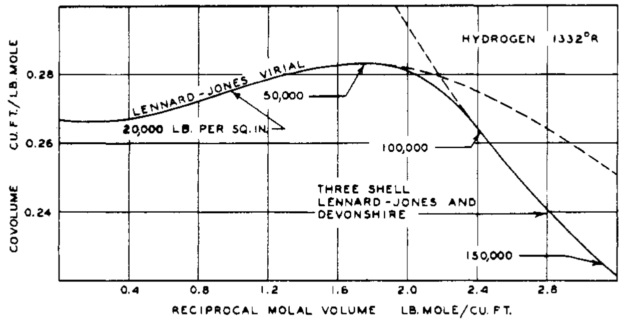

Figure 1. Typical covolumes from equations of state

It is necessary to know covolumes as functions of pressure and temperature in order to determine the covolume of a mixture, using the assumption of ideal solutions (9). Using this latter assumption the covolume for a mixture of gases is given by the relation

$$b = \sum_{k=1}^{n} \underset{o}{n}_k b_k \qquad (6)$$

PROCEDURE

The procedure used to obtain covolumes for pure gases as functions of pressure and temperature was in general as outlined below. Special points are mentioned in discussing individual gases.

1. Using force constants from Table I, compressibility factors Z were calculated for the lower range of the reciprocal molal volume at various temperatures by means of Equation 1 and Hirschfelder's $B^\star$ and $C^\star$. Z's at higher values of reciprocal molal volume were obtained for temperatures in the region of interest from the tabular data for the three-shell modification of the Lennard-Jones and Devonshire equation of state.

2. Covolumes b were calculated for both sets of data obtained above by means of Equation 5.

3. Plots of b vs. $\underset{o}{g}$ at constant temperature were made, with the values from both the virial and the three-shell equations of state on one plot. Since the virial equation was poor at high densities and the three-shell equation was poor at lower densities, it was necessary to draw in a transition curve between the two curves. This step in some cases is probably the source of considerable uncertainty. Figure 1 shows an example wherein the transition between the two curves was quite simple and probably introduces little error beyond that of the two equations of state in their respective domains. On the other hand, Figure 2 shows a case where the proper position of the line bridging the gap between the two curves is subject to considerable uncertainty.

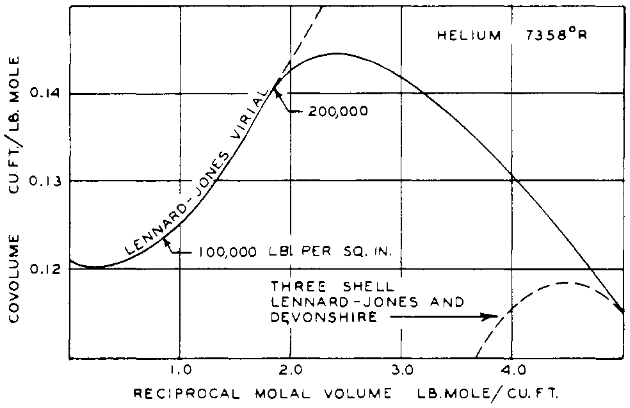

Figure 2. Poor agreement between equations of state

4. The pressure was calculated for various values of reciprocal molal volume at constant temperature using the final smoothed-in curve arrived at in Step 3 in each case. Equation 4 was used for these calculations.

5. The covolume, b, was plotted against log P at constant temperature and smooth curves were drawn.

6. The curves of Step 5 were used to crossplot b vs. log T at constant pressure.

7. Values of b were read at even temperatures and pressures and tabulated.

HYDROGEN

Covolumes for hydrogen were calculated at temperatures of 1332°, 3330°, 6660°, and 26,640° R. and treated as outlined. The curves of b as functions of $\underset{o}{g}$ were easily joined for the two lower temperatures, while those for the upper two temperatures were tending toward the type shown in Figure 2. However, for the latter two cases the pressures at which the smoothed curves depart from the low density virial equations of state are in excess of 150,000 p.s.i. and are thus out of the range normally used. It is believed that little added uncertainty is introduced by the smoothing between the two equations of state for hydrogen. The covolumes resulting are shown in Table II for a temperature range of 1500° to 20,000° R. and pressures from 0 to 200,000 pounds per square inch absolute. The covolume for hydrogen varies only from 0.192 to 0.282 cubic foot per pound mole in this rather large range of conditions.

HELIUM

For helium, the data (7) were so spaced that covolumes were obtained from the three-shell modification of the Lennard-Jones and Devonshire equation of state only at 1840° and 7358° R. Values from the low density virial equation of state were calculated at 1472°, 1840°, 3679°, 5519°,

Table II. Covolumes b for Hydrogen[a]

	Temperature, °R											
P, P.S.I.	1500	2000	2500	3000	4000	5000	6000	8000	10,000	12,500	15,000	20,000
0	0.267	0.265	0.262	0.258	0.250	0.243	0.237	0.227	0.219	0.210	0.203	0.192
5,000	0.267	0.265	0.262	0.258	0.250	0.243	0.237	0.227	0.219	0.210	0.203	0.192
7,000	0.268	0.266	0.262	0.258	0.250	0.243	0.237	0.227	0.219	0.210	0.203	0.192
10,000	0.269	0.266	0.262	0.258	0.250	0.243	0.237	0.227	0.219	0.210	0.203	0.192
15,000	0.271	0.267	0.262	0.258	0.250	0.243	0.237	0.227	0.219	0.210	0.203	0.192
20,000	0.273	0.268	0.263	0.259	0.250	0.243	0.237	0.227	0.219	0.210	0.203	0.192
30,000	0.278	0.272	0.266	0.261	0.251	0.244	0.237	0.227	0.219	0.210	0.203	0.192
50,000	0.282	0.277	0.272	0.266	0.256	0.247	0.239	0.227	0.219	0.210	0.203	0.192
70,000	0.279	0.278	0.275	0.271	0.261	0.251	0.243	0.230	0.221	0.211	0.204	0.192
100,000	0.268	0.276	0.277	0.274	0.266	0.257	0.250	0.236	0.225	0.214	0.206	0.194
150,000	0.231	0.249	0.261	0.269	0.268	0.261	0.255	0.242	0.232	0.221	0.212	0.198
200,000	0.216	0.235	0.248	0.258	0.265	0.260	0.254	0.244	0.236	0.227	0.219	0.204

[a] Cu.ft./lb.mole.

Table III. Covolumes *b* for Helium[a]

P, P.S.I.	Temperature, °R. 1500	2000	2500	3000	4000	5000	6000	8000	10,000	12,500	15,000	20,000
0	0.162	0.155	0.150	0.145	0.137	0.132	0.127	0.120	0.113	0.107	0.103	0.095
5,000	0.160	0.153	0.148	0.143	0.136	0.131	0.126	0.119	0.113	0.107	0.103	0.095
7,000	0.160	0.153	0.148	0.143	0.136	0.131	0.126	0.119	0.113	0.107	0.103	0.095
10,000	0.160	0.153	0.147	0.143	0.136	0.130	0.126	0.119	0.113	0.107	0.103	0.095
15,000	0.161	0.153	0.147	0.142	0.135	0.130	0.126	0.119	0.113	0.107	0.103	0.095
20,000	0.162	0.154	0.148	0.143	0.135	0.130	0.126	0.119	0.113	0.107	0.103	0.095
30,000	0.166	0.156	0.149	0.144	0.136	0.130	0.126	0.119	0.113	0.107	0.103	0.095
50,000	0.170	0.162	0.155	0.149	0.139	0.132	0.127	0.119	0.113	0.107	0.103	0.095
70,000	0.171	0.166	0.160	0.154	0.144	0.136	0.130	0.121	0.114	0.108	0.104	0.096
100,000	0.167	0.166	0.164	0.160	0.150	0.141	0.134	0.124	0.116	0.109	0.104	0.097
150,000	0.158	0.161	0.161	0.159	0.155	0.149	0.143	0.130	0.121	0.113	0.107	0.098
200,000	0.145	0.153	0.155	0.156	0.154	0.151	0.147	0.137	0.127	0.117	0.110	0.100

[a] Cu.ft. /lb.mole.

Table IV. Covolumes *b* for *n*-Hexane[a]

P, P.S.I.	Temperature, °R. 1500	1750	2000	2250	2500	2750	3000	3250	3500	3750	4000
0	-2.53	-1.83	-1.10	-0.42	0.00	0.28	0.49	0.71	0.88	1.03	1.17
1,000	-2.08	-1.45	-0.74	-0.10	0.27	0.50	0.68	0.87	1.02	1.13	1.25
1,500	-1.70	-1.09	-0.43	0.08	0.40	0.62	0.80	0.95	1.09	1.20	1.82
2,000	-1.28	-0.70	-0.17	0.23	0.53	0.73	0.88	1.03	1.15	1.25	1.35
2,500	-0.63	-0.26	0.10	0.44	0.69	0.86	0.96	1.10	1.21	1.30	1.38
3,000	-0.08	0.16	0.40	0.60	0.80	0.96	1.06	1.17	1.27	1.35	1.43
4,000	0.55	0.65	0.77	0.89	1.02	1.17	1.25	1.32	1.40	1.45	1.50
5,000	0.935	0.992	1.053	1.135	1.250	1.390	1.480	1.508	1.525	1.534	1.536
7,000	1.230	1.290	1.360	1.445	1.550	1.625	1.667	1.682	1.688	1.688	1.688
10,000	1.382	1.475	1.562	1.640	1.710	1.780	1.822	1.842	1.850	1.851	1.848
15,000	1.472	1.575	1.665	1.748	1.815	1.880	1.938	1.970	1.993	2.002	2.005
20,000	1.515	1.605	1.688	1.765	1.840	1.912	1.965	2.002	2.027	2.040	2.050
30,000	1.560	1.605	1.660	1.725	1.802	1.880	1.940	1.980	2.005	2.020	2.030
50,000	1.582	1.595	1.615	1.645	1.688	1.735	1.780	1.822	1.860	1.894	1.925
70,000	1.568	1.573	1.585	1.600	1.622	1.648	1.675	1.703	1.732	1.760	1.787
100,000	1.532	1.540	1.547	1.555	1.562	1.567	1.579	1.593	1.610	1.633	1.660
150,000	1.483	1.483	1.485	1.490	1.493	1.498	1.502	1.508	1.512	1.520	1.525
200,000	1.460	1.460	1.460	1.460	1.460	1.460	1.460	1.460	1.460	1.460	1.460

[a] Cu.ft./lb.mole.

and 7358° R. The smoothing between the two curves at 1840° R. was over a moderate range, while the curves for 7358° R. are shown in Figure 2 as an example in which considerable uncertainty may be introduced. As it was desired to compute covolumes over a full range of temperatures and pressure, plots of b vs. log T at constant g were used for both interpolation and extrapolation. Fortunately, these lines were almost straight, so interpolation and extrapolation to 20,000° R. seemed reasonable. However, only for temperatures less than 7500° R. was it necessary to depart from the curve for the virial equation of state in order to reach pressures of 200,000 p.s.i. Thus the extrapolations to the higher temperature were really extrapolations of the virial equation of state. In any event the covolumes for helium are small and errors in them are of relatively less importance than are errors in those for the other gases when mixtures are considered. The covolumes for helium are shown in Table III for temperatures from 1500° to 20,000° R. and pressures up to 200,000 p.s.i.

n-HEXANE

Covolumes were calculated from the two equations of state for temperatures of 1487°, 2230°, 2974°, and 3717° R., and handled in the normal manner. The transition between the two curves was in every case over a relatively short range. Covolumes are tabulated in Table IV for the range of 1500° to 4000° R. and pressures up to 200,000 p.s.i. The variation in covolumes is large in this range. Because the *n*-hexane molecule is far from spherical, the covolumes are probably much less accurate than for the other gases considered.

METHANE

Covolumes were calculated at temperatures of 1334°, 1868°, 2668°, and 5336° R. The transitions between the curves for the two equations of state were in all cases over very small ranges. The covolumes were handled in the established manner and are shown for a range of 1500° to 5000° R. and for pressures up to 200,000 p.s.i. in Table V.

NITRIC OXIDE

Covolumes were calculated at temperatures of 1180°, 2360°, 4720°, 7080°, 11,800°, 18,880°, and 23,600° R. Transitions between curves of the equations of state were over moderately small ranges. Covolumes are shown in Table VI for a range of 1500° to 20,000° R. and up to 200,000 p.s.i. While nitric acid is slightly polar, the dipole moment is very small, values of 0.07 and 0.16 debye being reported (*12*) at ordinary temperatures. As the effect of this small polarity should be insignificant (*7*) at the high temperatures considered here, equations of state for nonpolar gases were employed.

NITROGEN

Covolumes were calculated at temperatures of 1710°, 3420°, 8550°, and 17,100° R. Transitions between curves were over small ranges in all cases and no unusual techniques were used in handling the data. Covolumes for the

Table V. Covolumes *b* for Methane[a]

P, P.S.I.	1500	1750	2000	2250	2500	2750	3000	3250	3500	4000	4500	5000
	Temperature, °R.											
0	0.330	0.399	0.445	0.481	0.504	0.522	0.536	0.550	0.559	0.572	0.583	0.589
2,000	0.368	0.422	0.464	0.494	0.517	0.532	0.544	0.553	0.561	0.573	0.581	0.589
5,000	0.427	0.465	0.492	0.513	0.530	0.542	0.551	0.558	0.565	0.574	0.581	0.587
7,000	0.460	0.490	0.510	0.526	0.538	0.548	0.556	0.563	0.568	0.577	0.583	0.588
10,000	0.498	0.518	0.533	0.543	0.551	0.558	0.563	0.569	0.573	0.580	0.585	0.589
15,000	0.540	0.552	0.559	0.565	0.569	0.572	0.575	0.578	0.581	0.585	0.589	0.592
20,000	0.565	0.573	0.578	0.581	0.583	0.585	0.587	0.588	0.590	0.592	0.594	0.595
30,000	0.585	0.594	0.600	0.603	0.605	0.606	0.607	0.607	0.607	0.607	0.606	0.605
50,000	0.568	0.592	0.606	0.614	0.620	0.622	0.623	0.624	0.624	0.623	0.621	0.619
70,000	0.524	0.552	0.575	0.594	0.608	0.618	0.622	0.625	0.626	0.627	0.626	0.625
100,000	0.481	0.501	0.522	0.543	0.558	0.571	0.581	0.589	0.595	0.606	0.614	0.620
150,000	0.438	0.452	0.467	0.482	0.496	0.508	0.520	0.530	0.541	0.559	0.575	0.590
200,000	0.417	0.423	0.438	0.450	0.460	0.471	0.481	0.491	0.500	0.517	0.532	0.546

[a] Cu.ft./lb.mole.

Table VI. Covolumes *b* for Nitric Oxide[a]

P, P.S.I.	1500	2000	2500	3000	4000	5000	6000	8000	10,000	12,500	15,000	20,000
	Temperature, °R.											
0	0.231	0.274	0.300	0.313	0.330	0.337	0.338	0.336	0.331	0.325	0.319	0.306
5,000	0.239	0.282	0.309	0.323	0.333	0.336	0.336	0.334	0.329	0.323	0.317	0.304
7,000	0.253	0.290	0.311	0.323	0.333	0.335	0.336	0.333	0.329	0.323	0.316	0.303
10,000	0.269	0.299	0.314	0.324	0.333	0.335	0.336	0.333	0.328	0.322	0.316	0.302
15,000	0.293	0.312	0.321	0.327	0.333	0.336	0.336	0.333	0.328	0.322	0.315	0.302
20,000	0.306	0.320	0.328	0.332	0.336	0.338	0.337	0.333	0.327	0.321	0.314	0.302
30,000	0.322	0.332	0.337	0.340	0.342	0.341	0.339	0.333	0.327	0.320	0.313	0.300
50,000	0.334	0.342	0.346	0.348	0.349	0.347	0.344	0.335	0.328	0.320	0.313	0.300
70,000	0.337	0.343	0.346	0.349	0.352	0.350	0.347	0.339	0.331	0.322	0.314	0.301
100,000	0.339	0.344	0.347	0.350	0.353	0.353	0.351	0.343	0.333	0.323	0.316	0.303
150,000	0.341	0.344	0.346	0.350	0.354	0.355	0.353	0.346	0.335	0.323	0.317	0.305
200,000	0.343	0.344	0.344	0.349	0.354	0.355	0.354	0.347	0.336	0.323	0.317	0.306

[a] Cu. ft./lb.mole.

Table VII. Covolumes *b* for Nitrogen[a]

P, P.S.I.	1500	2000	2500	3000	4000	5000	6000	8000	10,000	12,500	15,000	20,000
	Temperature, °R.											
0	0.443	0.493	0.518	0.531	0.538	0.538	0.534	0.521	0.508	0.493	0.481	0.462
5,000	0.488	0.511	0.525	0.533	0.538	0.535	0.530	0.517	0.504	0.490	0.478	0.458
7,000	0.500	0.520	0.531	0.537	0.540	0.536	0.530	0.517	0.504	0.490	0.478	0.458
10,000	0.517	0.529	0.537	0.541	0.541	0.536	0.530	0.517	0.504	0.490	0.478	0.458
15,000	0.537	0.542	0.545	0.546	0.544	0.538	0.531	0.517	0.504	0.490	0.478	0.458
20,000	0.549	0.550	0.551	0.552	0.547	0.539	0.531	0.517	0.504	0.490	0.478	0.458
30,000	0.559	0.561	0.560	0.559	0.553	0.544	0.537	0.518	0.504	0.490	0.478	0.458
50,000	0.542	0.557	0.565	0.568	0.564	0.554	0.545	0.527	0.511	0.495	0.480	0.458
70,000	0.490	0.534	0.556	0.566	0.568	0.562	0.554	0.536	0.520	0.502	0.487	0.462
100,000	0.440	0.488	0.520	0.541	0.557	0.560	0.558	0.546	0.530	0.513	0.496	0.468
150,000	0.416	0.440	0.460	0.477	0.506	0.528	0.542	0.550	0.540	0.524	0.508	0.480
200,000	0.409	0.419	0.430	0.440	0.462	0.490	0.521	0.544	0.540	0.528	0.515	0.491

[a] Cu.ft. /lb.mole.

Table VIII. Covolumes *b* for Oxygen[a]

P, P.S.I.	1500	2000	2500	3000	4000	5000	6000	8000	10,000	12,500	15,000	20,000
	Temperature, °R.											
0	0.372	0.419	0.445	0.463	0.485	0.489	0.486	0.480	0.474	0.466	0.456	0.434
5,000	0.393	0.439	0.465	0.477	0.485	0.484	0.482	0.476	0.470	0.462	0.454	0.434
7,000	0.417	0.448	0.468	0.479	0.486	0.484	0.481	0.475	0.470	0.461	0.452	0.430
10,000	0.446	0.463	0.474	0.482	0.487	0.484	0.481	0.474	0.469	0.460	0.450	0.430
15,000	0.466	0.475	0.482	0.486	0.490	0.486	0.481	0.474	0.467	0.458	0.447	0.429
20,000	0.477	0.487	0.491	0.494	0.494	0.488	0.482	0.473	0.467	0.456	0.446	0.429
30,000	0.485	0.499	0.506	0.509	0.508	0.500	0.488	0.477	0.468	0.456	0.445	0.428
50,000	0.489	0.505	0.513	0.518	0.519	0.511	0.497	0.483	0.474	0.461	0.448	0.428
70,000	0.474	0.497	0.507	0.514	0.520	0.514	0.501	0.489	0.480	0.466	0.452	0.431
100,000	0.446	0.487	0.499	0.508	0.513	0.510	0.504	0.495	0.487	0.475	0.462	0.437
150,000	0.418	0.445	0.461	0.472	0.490	0.502	0.507	0.504	0.497	0.485	0.471	0.448
200,000	0.385	0.408	0.426	0.440	0.465	0.482	0.492	0.501	0.502	0.496	0.483	0.458

[a] Cu. ft. /lb.mole.

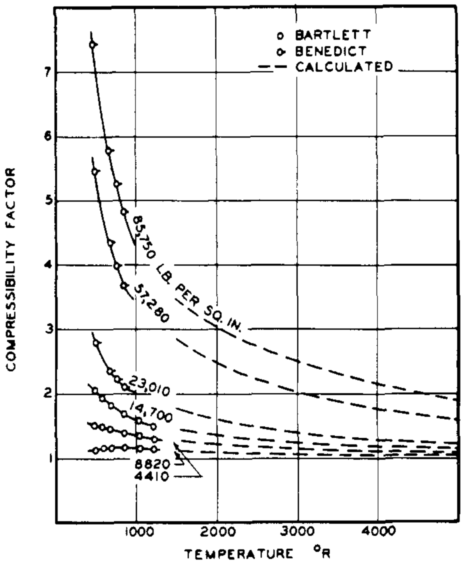

Figure 3. Compressibility of nitrogen

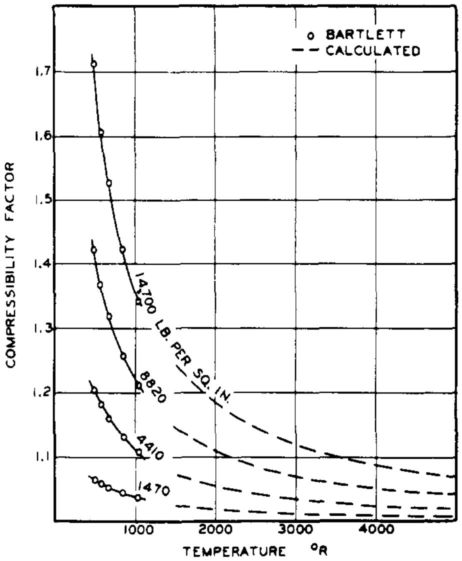

Figure 4. Compressibility of hydrogen

range 1500° to 20,000° R. and pressures up to 200,000 p.s.i. are found in Table VII.

OXYGEN

Covolumes were calculated at temperatures of 1057°, 2115°, 4230°, 6345°, 10,575°, 16,920°, and 21,150° R. The transitions between the curves were over moderately small ranges of reciprocal molal volume. Covolumes are shown for a range of 1500° to 20,000° R. and pressures up to 200,000 p.s.i. in Table VIII.

COMPARISON WITH EXPERIMENTAL DATA

Although experimental pressure-volume-temperature data are not available in the range of conditions for which covolumes were calculated, compressibility factors have been measured for many gases at lower temperatures. In Figure 3 data of Benedict (*3*) and of Bartlett (*1*) for nitrogen are compared with compressibility factors calculated from the covolumes of Table VII. Figure 4 shows Bartlett's data on hydrogen in comparison with compressibility factors calculated using covolumes from Table II, while Figure 5 shows similar information for a 0.75 mole fraction hydrogen –0.25 mole fraction nitrogen mixture. In all three figures the high temperature data corresponding to the covolumes described herein appear to be logical extrapolations of the experimental data for lower temperatures.

PROPERTIES OF COVOLUME EQUATION OF STATE

The equation of state is given by Equation 4 as

$$P(\underset{o}{V} - b) = RT \tag{7}$$

where

$$b = f(P,T) \tag{8}$$

The standard derivatives are

$$\left(\frac{\partial \underset{o}{V}}{\partial T}\right)_P = \frac{R}{P} + \left(\frac{\partial b}{\partial T}\right)_P \tag{9}$$

$$\left(\frac{\partial \underset{o}{V}}{\partial P}\right)_T = -\frac{RT}{P^2} + \left(\frac{\partial b}{\partial P}\right)_T \tag{10}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underset{o}{V}} = \frac{1}{\underset{o}{V} - b}\left[R + P\left(\frac{\partial b}{\partial T}\right)_{\underset{o}{V}}\right] \tag{11}$$

Using these equations, the pressure dependence of the internal energy is given by the relation

$$\left(\frac{\partial \underset{o}{E}}{\partial P}\right)_T = -T\left(\frac{\partial \underset{o}{V}}{\partial T}\right)_P - P\left(\frac{\partial \underset{o}{V}}{\partial P}\right)_T = -T\left(\frac{\partial b}{\partial T}\right)_P - P\left(\frac{\partial b}{\partial P}\right)_T \tag{12}$$

and the change in internal energy due to gas imperfection is given by the equation

$$\underset{o}{E} - \underset{o}{E}^{\circ} = -T\int_0^P \left(\frac{\partial b}{\partial T}\right)_P dP - \int_0^P P\left(\frac{\partial b}{\partial P}\right)_T dP \tag{13}$$

when the integration is performed at constant temperature. Differentiation of Equation 12 with respect to temperature at constant pressure gives

$$\left(\frac{\partial \underset{o}{C}_V}{\partial P}\right)_T = -\left[\left(\frac{\partial b}{\partial T}\right)_P + T\left(\frac{\partial^2 b}{\partial T^2}\right)_P + P\left(\frac{\partial^2 b}{\partial P\,\partial T}\right)\right] \tag{14}$$

For isentropic processes the change in molal volume with temperature at constant entropy is of interest. This partial derivative may be shown to be

$$\left(\frac{\partial \underset{o}{V}}{\partial T}\right)_S = \frac{-\underset{o}{C}_V\left[1 - \frac{P^2}{RT}\left(\frac{\partial b}{\partial P}\right)_T\right]}{P\left[1 + \frac{P}{R}\left(\frac{\partial b}{\partial T}\right)_P\right]} \tag{15}$$

The fugacity is the potential suitable for use when chemical reactions are considered. The fugacity is related to the covolume by

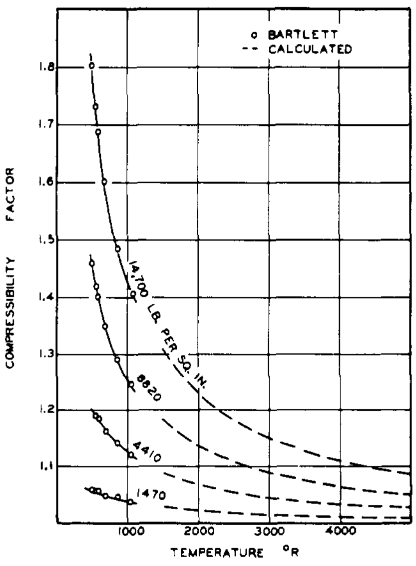

Figure 5. Compressibility of hydrogen-nitrogen mixture

$$\left(\frac{\partial \ln \frac{f^\circ}{P}}{\partial P}\right)_T = \frac{b}{RT} \tag{16}$$

and integration from zero pressure at constant temperature gives

$$\ln \frac{f^\circ}{P} = \frac{1}{RT}\int_0^P b\,dP \tag{17}$$

The Joule-Thomson coefficient is given by

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{-b + T\left(\frac{\partial b}{\partial T}\right)_P}{\underset{o}{C}_P} \tag{18}$$

PROPERTIES FOR CONSTANT COVOLUME

If covolume b is constant, it is evident that most of the relationships considered above are markedly simplified. It is found from Equations 9 and 10 that

$$\left(\frac{\partial \underset{o}{V}}{\partial T}\right)_P = \frac{R}{P} \tag{19}$$

and

$$\left(\frac{\partial \underset{o}{V}}{\partial P}\right)_T = -\frac{RT}{P^2} \tag{20}$$

Equation 12 gives

$$\left(\frac{\partial \underset{o}{E}}{\partial P}\right)_T = 0 \tag{21}$$

Equation 14 reduces to

$$\left(\frac{\partial \underset{o}{C}_V}{\partial P}\right)_T = 0 \tag{22}$$

and it is easily shown that

$$\underset{o}{C}_P - \underset{o}{C}_V = R \tag{23}$$

Equation 15 becomes

$$\left(\frac{\partial \underset{o}{V}}{\partial T}\right)_S = -\frac{\underset{o}{C}_V}{P} \tag{24}$$

and Equations 17 and 18 reduce to

$$\ln \frac{f^\circ}{P} = \frac{bP}{RT} \tag{25}$$

and

$$\mu = -\frac{b}{\underset{o}{C}_P} \tag{26}$$

DISCUSSION

The advantage of the use of covolumes as compared to the use of compressibility factors in representing the equations of state in the region of high temperature and pressure lies in the relative constancy of the covolume over large ranges of temperature and pressure. Inspection of the tabulated covolumes shows that the variation of covolume with respect to temperature and pressure is moderate for all except *n*-hexane. The latter deviates markedly, showing negative covolumes in the low-pressure-low-temperature region, which can be attributed to its relatively high critical temperature.

Spherically symmetrical potentials were assumed in the derivations of both the virial equation of state and the three-shell modification of the Lennard-Jones and Devonshire equation of state. This assumption is probably good for all the gases treated except *n*-hexane; the latter molecule would not be expected to have a spherical potential and therefore the tabulated covolumes for *n*-hexane are considered to be much less valid than those for the other gases. However, the results predicted here are primarily estimates and are subject to rather large uncertainties but appear to yield results more descriptive of actuality than the equation of state of a perfect gas.

NOMENCLATURE

$(a^*)^3 = (2\sqrt{2}\pi \underset{o}{V})/(3b_0)$
$B^*(T) = B(T)/b_0$
b = molal covolume, cu. ft./lb. mole
b_0 = force constant, cu. ft./lb. mole
$C^*(T) = C(T)/b_0^2$
$\underset{o}{C}_p$ = molal heat capacity at constant pressure, B.t.u./(lb. mole)(°R.)
$\underset{o}{C}_v$ = molal heat capacity at constant volume, B.t.u./(lb. mole)(°R.)
d = differential operator
$\underset{o}{E}$ = molal internal energy, B.t.u./lb. mole
$\underset{o}{E}^\circ$ = molal internal energy at infinite attenuation, B.t.u./lb. mole
$f(\ )$ = function of
f° = fugacity of component in pure state
H = specific enthalpy, B.t.u. /lb.
k = index of summation
ln = natural logarithm
log = logarithm to the base 10
$\underset{o}{n}_k$ = mole fraction of component k
P = pressure, lb./sq. inch
R = molal gas constant, (lb.)(cu.ft.)/(sq. in.)(lb.mole)(°R.)
°R. = degrees Rankine
S = specific entropy, (B.t.u.)/(lb.)(°R.)
T = temperature, °R.
$t^* = T/(\epsilon/k)$
$\underset{o}{V}$ = molal volume, cu.ft./lb.mole
$\underset{o}{Z}$ = compressibility factor, $P\underset{o}{V}/RT$
ϵ/k = force constant, °R.
μ = Joule-Thomson coefficient, °R./(lb./sq. in.)
$\sum_1^n$ = summation of n terms
$\underset{o}{\sigma}$ = reciprocal molal volume, lb. mole/cu. ft.
∂ = partial differential operator
$\int$ = integration operator

LITERATURE CITED

(1) Bartlett, E. P., Cupples, H. L., Tremearne, T. H., *J. Am. Chem. Soc.* **50**, 1275 (1928).
(2) Beattie, J. A., Amdur, I., private communication.
(3) Benedict, Manson, *J. Am. Chem. Soc.* **59**, 2233 (1937).
(4) Bird, R. B. Spotz, E. L., University of Wisconsin, **CM. 599** Project NORD 9938, May 10, 1950.
(5) Bird, R. B., Spotz, E. L., Hirschfelder, J. O., *J. Chem. Phys.* **18**, 1395 (1950).
(6) Corner, J., "Theory of the Interior Ballistics of Guns," Wiley, New York, 1950.
(7) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(8) Lennard-Jones, J. A., Devonshire, A. F., *Proc. Roy. Soc.* (*London*) **A163**, 53 (1937).
(9) Lewis, G. N., *J. Am. Chem. Soc.* **30**, 668 (1908).
(10) Longwell, P. A., Reamer, H. H., Wilburn, N. P., Sage, B. H., *Ind. Eng. Chem.* **50**, 603 (1958).
(11) Wentorf, R. H., Buehler, R. J., Hirschfelder, J. O., Curtiss, C. F., *J. Chem. Phys.* **18**, 1484 (1950).
(12) Wesson, L. G., "Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948.

Received for review September 9, 1957. Accepted February 7, 1958.