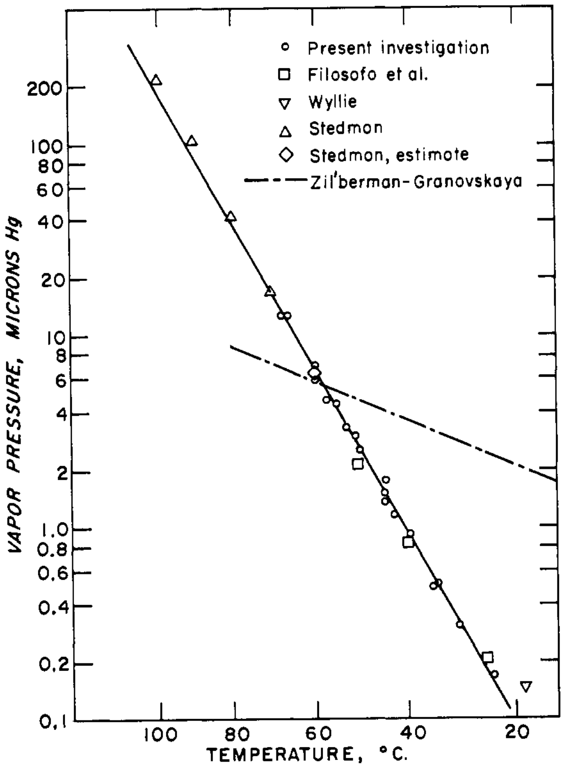

Figure 2. Vapor pressure of glycerol

during weighing intervals. There is the additional possibility of decomposition of the glycerol during the ten successive distillations used for preparation. These probably were simple distillations at atmospheric pressure (b.p. 290° C.) and, since polymerization and decomposition are reported to begin at little over 200° C. (*7*), the purity of the glycerol studied remains in doubt.

To test the effect of minute quantities of water present in the glycerol, an opened sample vial was left in a desiccator for several months and then used for a vapor pressure measurement. The water absorbed, even in this very dry atmosphere, was sufficient to increase the apparent vapor pressure by a factor of five. Thus, it is possible that thorough drying of Wyllie's glycerol could have lowered the measured vapor pressure to coincide with the present study. A prime advantage of the present method thus becomes its ability to obtain weight measurements without exposure of the glycerol to the atmosphere during the weighing process.

NOMENCLATURE

A_o = orifice area, sq. cm.
A_s = surface area of evaporating liquid, sq. cm.
M = molecular weight, grams/gram-mole
P = pressure, dyne/sq. cm.
P_v = vapor pressure, dyne/sq. cm.
P_v' = steady state cell pressure, dyne/sq. cm.
r = radius of effusion canal (orifice), cm.
R = gas content, 8.31×10^7 dyne cm./gram-mole ° K.
t = length of effusion canal (foil thickness), cm.
T = temperature, ° K.
W_b = Clausing factor for orifice, dimensionless
$dW/d\theta$ = rate of weight loss, grams/hour
α = evaporation coefficient, dimensionless

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RECEIVED for review March 26, 1962. Accepted July 2, 1962.

Compressibility Factors of 2,2-Dimethylpropane (Neopentane)

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A STANDARD Burnett apparatus was modified and used to determine the compressibility isotherms of gaseous 2,2-dimethylpropane (neopentane) between 1 atm. and the vapor pressure at 30°, 50°, 75°, 100°, 125°, and 150° C., and between 1 and 70 atm. at 161.5°, 175°, and 200° C. The critical temperature of 2,2-dimethylpropane is 160.60° C. (*1*).

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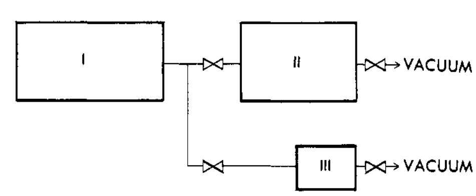

Figure 1. Modified Burnett apparatus

APPARATUS

The Burnett method (*3*) employs two thermostated chambers connected by a valve (Figure 1). The gas under investigation is introduced into V_I while V_{II} is evacuated. The pressure in V_I is measured, whereupon the gas is expanded into V_{II} and the pressure is again measured. The evacuation of V_{II} and expansion of the contents of V_I into it are then repeated until as low a pressure is reached as can be measured precisely. The compressibility factor can then be calculated at each measured pressure according to the relations given below.

With each expansion, the density of the gas drops an equal fraction of the previous density, giving very large pressure intervals at high pressures. If the expansion chamber is made small so that the pressure interval is small, then the pressures become so close together at the lower pressures that an unreasonable number of measurements is required to complete a single run.

To overcome this disadvantage, a third chamber was added to the first two. Initial expansions are made into the new V_{III}, until the pressure intervals become less than the maximum desired. Subsequent expansions are made into V_{II}.

The density of the gas after any expansion into V_{III} is

$$d_i = (1/M)\, d_{i-1}$$

where

$$M = (V_I + V_{III})/V_I$$

Since

$$d = P/zRT$$

$$P_i/z_iRT_i = P_{i-1}/z_{i-1}RT_{i-1}M$$

and

$$z_i = (P_iM/T_i)/(P_{i-1}/z_{i-1}T_{i-1}) \qquad (1)$$

Repeated substitution in the denominator of this expression in terms of the previous expansion ultimately yields

$$z_i = (P_iM^i/T_i)/(P_0/z_0T_0)$$

Let rm be the last expansion into V_{III}, subsequent expansions being made into V_{II}.

$$z_{rm-1} = (P_{rm-1}N/T_{rm-1})/(P_{rm}/z_{rm}T_{rm})$$

$$= (P_{rm-1}M^{rm}N/T_{rm+1})/(P_0/z_0T_0)$$

where

$$N = (V_I + V_{II})/V_I$$

and in general,

$$z_i = (P_iM^rN^{i-r}/T_i)/(P_0/z_0T_0) \qquad (2)$$

where for $i \leqq rm, r = i$, and for $i > rm, r = rm$.

During any particular run, the temperature might vary $\pm 0.05°$ C. To correct for this variation, the temperature of each measurement is retained in Equation 2. When the investigation of a gas is complete, each compressibility is corrected to the nominal isotherm by

$$z_{corr} = z_i + (\partial z/\partial T)_P(T - T_i)$$

where the unsubscripted T is the nominal temperature of the isotherm.

Equation 2 permits calculation of z_i at each measured P_i and T_i provided that M, N, and P_0/z_0T_0 are known. Rearrangement of Equation 2 shows that

$$P_0/z_0T_0 = P_iM^rN^{i-r}/T_iz_i = \lim_{P_i \to 0} P_iM^rN^{i-r}/T_i$$

This limit is determined graphically for each run.

M is determined from a series of expansions into V_{III} carried down to a low pressure. Then from Equation 1

$$M = (P_{i-1}/z_{i-1}T_{i-1})/(P_i/z_iT_i) = \lim_{P_i \to 0} \frac{(P_{i-1}/T_{i-1})}{(P_i/T_i)}$$

N is found by a similar set of expansions into V_{II}. The limits are taken graphically, and once the constants are determined, they remain unchanged until one of the chambers is disturbed.

MATERIALS

2,2-Dimethylpropane of 99.92% purity was obtained from the Phillips Chemical Co. Chromatographic analysis showed the presence of over 15% air (or nitrogen) in the vapor phase. This was removed by freezing the hydrocarbon and evacuating the vapor space. Two such treatments reduced the permanent gas to less than 0.02%.

EXPERIMENTAL

The compressibility cells were thermostated in a stirred oil bath, controlled by a thermistor in conjunction with an a.c. bridge. Temperature control was to $\pm 0.05°$ C. Pressures above 3 atm. were measured with a dead weight (piston) gage; below 3 atm., with mercury manometers. Precision of the pressure measurements was estimated to be $\pm 0.04\%$.

The compressibility factors of 2,2-dimethylpropane are presented in Table I and in Figure 2. No point deviated from the indicated curves by more than 0.15%, except for a few points in obviously serious error, and the points in the critical region. The data overlap the data of Beattie, Douslin, and Levine (2) at temperatures above the critical and are from 0.57 to 1.9% below them.

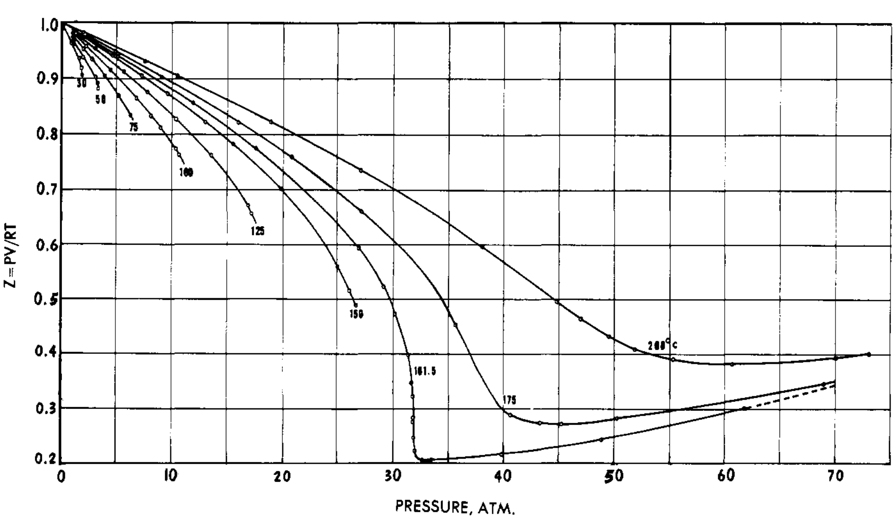

Figure 2. Compressibility factors of 2,2-dimethylpropane

Table I. Isothermal Compressibility Factors of 2,2-Dimethylpropane (Neopentane)

Press., Atm.	Z, Compressibility[a]	Vol., L./G. Mole
	30° C.	
0.9434	0.9643	25.428
1.0555	0.9601	22.626
1.1804	0.9554	20.133
1.3191	0.9500	17.914
1.3510	0.9487	17.469
1.4730	0.9439	15.940
1.6426	0.9366	14.184
1.8553	0.9199	12.334
	50° C.	
0.9948	0.9685	25.813
1.0290	0.9685	24.956
1.1519	0.9648	22.206
1.2472	0.9613	20.437
1.2895	0.9610	19.759
1.4422	0.9563	17.582
1.6111	0.9506	15.644
1.7396	0.9467	14.429
1.7991	0.9446	13.921
2.0084	0.9382	12.387
2.2387	0.9306	11.022
2.4083	0.9253	10.188
2.4937	0.9223	9.807
2.7730	0.9126	8.726
3.0759	0.9008	7.765
3.2837	0.8908	7.193
3.3773	0.8801	6.909
	75° C.	
1.0217	0.9756	27.280
1.0456	0.9742	26.612
1.2792	0.9704	21.670
1.2995	0.9693	21.310
1.4322	0.9656	19.261
1.4672	0.9650	18.788
1.7888	0.9580	15.299
1.8174	0.9571	15.045
2.0008	0.9524	13.599
2.0484	0.9512	13.264
2.4898	0.9414	10.801
2.5290	0.9403	10.622
2.7779	0.9336	9.601
2.8435	0.9321	9.365
3.4378	0.9177	7.626
3.8225	0.9069	6.779
3.9104	0.9051	6.611
4.2411	0.8954	6.032
4.6909	0.8840	5.384
4.6996	0.8829	5.367
5.1977	0.8689	4.7756
5.7342	0.8530	4.2494
6.2626	0.8332	3.8009
6.2832	0.8317	3.7811
	100° C.	
1.0211	0.9808	29.411
1.1451	0.9787	26.170
1.6076	0.9701	18.477
2.2495	0.9585	13.045
2.3346	0.9566	12.547
3.1285	0.9410	9.210
3.2460	0.9391	8.858
4.3195	0.9174	6.503
4.4751	0.9140	6.254
4.9740	0.9039	5.565
5.5189	0.8924	4.9518
5.8966	0.8842	4.5912
6.1107	0.8793	4.4062
6.7540	0.8647	3.9206
7.4495	0.8488	3.4886
7.9162	0.8381	3.2415
8.1942	0.8307	3.1042
8.9864	0.8106	2.7621
9.8187	0.7881	2.4578
10.343	0.7731	2.2886
10.652	0.7608	2.1869
	125° C.	
0.9891	0.9844	32.515
1.0719	0.9827	29.951
1.1098	0.9829	28.932
1.5091	0.9768	21.146
1.5611	0.9762	20.427
2.1155	0.9668	14.930
2.1893	0.9665	14.422
2.9558	0.9537	10.541
3.0579	0.9532	10.182
4.1075	0.9357	7.442
4.2472	0.9347	7.189
5.6621	0.9106	5.254
5.8459	0.9083	5.076
6.4917	0.8975	4.5164
7.1969	0.8853	4.0187
7.7133	0.8759	3.7098
7.9648	0.8718	3.5759
8.7962	0.8568	3.1818
9.6931	0.8402	2.8312
10.326	0.8279	2.6192
10.653	0.8216	2.5192
11.671	0.8009	2.2416
12.740	0.7779	1.9946
13.459	0.7618	1.8492
13.851	0.7526	1.7748
14.990	0.7245	1.5792
16.124	0.6931	1.4052
16.816	0.6722	1.3056
17.176	0.6572	1.2504
	150° C.	
0.9820	0.9878	34.925
1.0665	0.9872	32.135
1.1963	0.9852	28.594
1.3834	0.9825	24.658
1.6827	0.9784	20.188
1.9433	0.9743	17.410
2.3617	0.9695	14.254
2.7252	0.9647	12.292
3.3034	0.9574	10.064
3.8046	0.9509	8.678
4.5982	0.9409	7.105
5.2805	0.9318	6.127
6.3525	0.9178	5.016
7.2682	0.9056	4.3259
8.6898	0.8864	3.5418
9.6200	0.8731	3.1515
9.8828	0.8693	3.0542
10.632	0.8586	2.8042
11.722	0.8424	2.4952
12.892	0.8243	2.2202
13.198	0.8197	2.1564
14.140	0.8046	1.9756
15.459	0.7826	1.7579
16.835	0.7584	1.5642
17.167	0.7526	1.5225
18.259	0.7319	1.3918
19.704	0.7028	1.2384
21.146	0.6711	1.1020
21.454	0.6643	1.0749
22.549	0.6368	0.9806
23.864	0.5997	0.8725
25.049	0.5601	0.7764
25.267	0.5524	0.7589
26.040	0.5158	0.6908
26.090	0.5075	0.6753
	161.5° C.	
0.9710	0.9864	36.232
1.1960	0.9860	29.404
1.3702	0.9827	25.581
1.6840	0.9802	20.760
1.9293	0.9770	18.061
2.3664	0.9725	14.657
2.7906	0.9687	12.752
3.3128	0.9612	10.348
3.7887	0.9564	9.003
4.6172	0.9458	7.306
5.2704	0.9393	6.356
6.3957	0.9250	5.158
7.2767	0.9156	4.4878
8.7752	0.8961	3.6420
9.9379	0.8828	3.1685
11.878	0.8564	2.5714
13.355	0.8377	2.2371
15.758	0.8021	1.8155
17.539	0.7767	1.5794
20.309	0.7299	1.2818
22.260	0.6959	1.1151
25.082	0.6364	0.9050
26.894	0.5936	0.7873
29.163	0.5223	0.6389
30.350	0.4728	0.5559
31.424	0.3973	0.45111
31.737	0.3489	0.39246
31.820	0.3115	0.34921
31.852	0.2773	0.31073
31.853	0.2845	0.31850
31.882	0.2472	0.27649
32.097	0.2215	0.24602
32.619	0.2057	0.22487
33.524	0.2059	0.21891
39.913	0.2180	0.19479
48.826	0.2437	0.17804
61.940	0.3010	0.17333
	175° C.	
1.0517	0.9899	34.610
1.1798	0.9880	30.796
1.2452	0.9865	29.132
1.6624	0.9829	21.743
1.7554	0.9819	20.568
2.3380	0.9760	15.351
2.4666	0.9740	14.522
3.2791	0.9665	10.838
3.4578	0.9641	10.253
4.5814	0.9534	7.652
4.8247	0.9497	7.239
6.3580	0.9342	5.403
6.6942	0.9304	5.111
8.7584	0.9085	3.8145
9.2048	0.9032	3.6084
11.924	0.8733	2.6932
12.502	0.8661	2.5476
15.949	0.8247	1.9015
16.666	0.8152	1.7987
20.820	0.7601	1.3425
21.642	0.7474	1.2700
22.594	0.7340	1.1946
24.417	0.7058	1.0629
26.251	0.6752	0.9458
27.081	0.6603	0.8966
28.074	0.6425	0.8416
29.842	0.6077	0.7488
31.515	0.5711	0.6663
32.209	0.5543	0.6330
33.055	0.5330	0.5929
34.432	0.4940	0.5276
35.633	0.4544	0.46943
36.068	0.4382	0.44695
36.636	0.4161	0.41770
37.510	0.3791	0.37167
38.328	0.3446	0.33072
38.673	0.3317	0.31556
39.253	0.3140	0.29427
40.605	0.2892	0.26185
43.366	0.2749	0.23299
45.274	0.2743	0.22279
50.299	0.2837	0.20732
69.092	0.3466	0.18447
	200° C.	
2.0017	0.9823	19.053
2.8113	0.9751	13.467
3.9374	0.9653	9.519
5.4098	0.9481	6.804
5.4777	0.9492	6.728
7.5092	0.9302	4.8096
7.5943	0.9303	4.7555
10.340	0.9054	3.3995
10.450	0.9048	3.3613
14.077	0.8712	2.4029
14.216	0.8700	2.3759
18.862	0.8251	1.6984
19.029	0.8231	1.6793
24.705	0.7639	1.2005
24.897	0.7612	1.1870
27.012	0.7376	1.0601
29.195	0.7121	0.9468
31.362	0.6857	0.8485
31.437	0.6848	0.8456
33.705	0.6561	0.7552
35.984	0.6255	0.6745
38.072	0.5961	0.6078
38.247	0.5937	0.6024
38.342	0.5922	0.5998
40.376	0.5625	0.5408
40.466	0.5611	0.5382
42.629	0.5285	0.48119
42.644	0.5280	0.48069
44.799	0.4954	0.42931
44.864	0.4948	0.42817
46.982	0.4640	0.38342
47.126	0.4624	0.38099
49.299	0.4347	0.34244
49.531	0.4325	0.33900
51.969	0.4094	0.30584
52.346	0.4068	0.30165
55.423	0.3902	0.27315
56.134	0.3881	0.26841
60.710	0.3816	0.24395
62.114	0.3820	0.23883
70.171	0.3938	0.21788
73.157	0.4003	0.21251

[a] PV/RT.

ACKNOWLEDGMENT

This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to these donors. The materials were donated by the Phillips Chemical Co., and part of the apparatus was a gift of the Socony-Mobil Co.

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RECEIVED for review March 27, 1962. Accepted July 23, 1962.