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SOME PHYSICAL PROPERTIES OF COMPRESSED GASES
I. NITROGEN*

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Abstract

The writers have adjusted and extrapolated the *compressibility data* obtained by Bartlett and his collaborators on nitrogen, so that very accurate *p-v-T data from* -70 *to 600° and up to 1200 atm.* are available. A suitable graphical scheme has been devised for obtaining the derivatives $(dv/dp)_T$, $(dv/dT)_p$, $(d^2v/dT^2)_p$ at any point in order that some of the physical properties of the gas can be calculated. This graphical scheme depends on the relation of $\alpha \equiv RT/p - v$ and $\Delta \equiv v(pv/RT - 1)$ to p,v,T, and on the relations of the derivatives of α and Δ to the derivatives of v. Errors in the estimation of the slope of an α or Δ curve at any point introduce much smaller errors into the derivatives of v, since the derivatives of α and Δ enter as correction terms to the derivatives of v just as α and Δ are corrections to v itself.

A *graphical process is used as originally in MS for adjusting the p-v-T* data and all the physical properties derived from it. This process is based on the assumption that surfaces such as p-v-T; α-v-T; or Δ-v-T are smooth and hence that the curves in any family of isotherms or isobars show related characteristics. It throws most of the adjustment on v, where it belongs, since the measurements of p and T are much more accurate than those of v. Such an adjustment enhances the precision of the compressibility data and of the calculations made from it.

The *specific volume, density, coefficients* $(-p/v)(dv/dp)_T$ *and* $(T/v)(dv/dT)_p$, *fugacity*, C_p, $C_p - C_v$, C_v, and μ are calculated and shown in curves and a table for the fourteen pressures and twelve temperatures in the range studied. *Inversion pressures and temperatures* are read from the μ vs. p isotherms and the μ vs. T isobars.

The calculations of C_p agree well with the experimental values of Krase and Mackey, who worked at 30, 100, 125, 150° up to 700 atm. and at 50° to 800 atm. The agreement is probably within the experimental error, but the trends of the two sets suggest that a real difference may exist. At 30° the calculated C_p drift below the experimental values at pressures above 400 atm., becoming 0.13 cal/mole · deg low at 700 atm. At 50° the agreement is good to 800 atm. At 100, 125, 150° the calculated C_p drift above the experimental values, but the disagreement reaches only 0.2 cal/mole · deg at 600 and 700 atm.

As one might expect, $C_p - C_v$ approaches R at all temperatures as the pressure approaches zero. In general, $C_p - C_v$ increases at any particular pressure as the temperature decreases. $C_p - C_v$ shows a strong maximum at about 200 atm. at the lowest temperatures. With increasing temperature this maximum comes at higher and higher pressures, and gradually disappears. The C_v vs. T isobars show some curious tendencies. C_v along the 20 atm. isobar stays constant and equal to 2.50 R from -70 to 100°C, then it rises slowly to 5.15 cal/mole · deg at 600°. Along the 40, 60, 80, and 100 atm. isobars, C_v drops a few hundredths of a cal/mole · deg below 2.50 R at $-70°$. the drop being greater the greater the pressure. Along the 200 atm and higher pressure isobars, C_v rises as the temperature falls below 50°, and the rise is steeper the greater the pressure. At 600°C_v is about 5.18 cal/mole deg or 2.61 R for all pressures.

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RECENT extensions of compressibility data on several gases to 1000 atm. from −70 to 300° and 400° published by Bartlett[1] and his collaborators at this laboratory have made possible the calculation of such physical properties as pressure and temperature coefficients of volume expansion, fugacity, change in heat capacity with pressure, difference between the heat capacity at constant pressure and that at constant volume, Joule-Thomson coefficient, and inversion temperatures and pressures, all at the various temperatures and pressures throughout the range of experimentation and as much further as extrapolations can safely be made.

With extrapolations made by a method to be described, we have reliable compressibility data on nitrogen from −70 to 600° up to 1200 atm. The physical properties of this gas might be expected to show some interesting properties over such a wide range, and we have endeavored to investigate them.

In order to calculate these physical properties from compressibility data it is necessary to evaluate the derivatives $(dv/dp)_T$, $(dv/dT)_p$, $(d^2v/dT^2)_p$ wherever desired. Analytical or graphical methods can be devised for this purpose. Perhaps the best analytical method of getting $(dv/dp)_T$ over a limited pressure range is to write pv as a power series in p along an isotherm. However, no set of coefficients can be found that will satisfactorily follow the trend of pv for nitrogen through the whole range of pressures along any isotherm; one set of constant seems to hold fairly well to some intermediate pressure, depending on the temperature, and another set is necessary from this pressure on up to 1000 atm. This introduces a discontinuity, and the intermediate pressure is thus at the ends of the two ranges. End points are the least trustworthy and we usually get two values for $(dv/dp)_T$ at the discontinuity, and it is then necessary to resort to graphical methods to smooth out the disagreement. The same difficulty exists in getting $(dv/dT)_p$; v^2 expressed as a power series in T seems to fit at low pressures, v as a power series in T seems to fit at high pressures; so there is a break at the intermediate pressure again. These empirical formulas are satisfactory for first derivatives but not for second derivatives except over a limited range. Jakob[2] used them to get the change in heat capacity of air up to 200 atm. from −80 to 250.° He recognized that at the highest temperatures his calculation of $(d^2v/dT^2)_p$ showed evidence of being untrustworthy. Drs. E. P. Bartlett and H. L. Cupples of this laboratory used Jakob's scheme with nitrogen up to 1000 atm. and the difficulties mentioned above were encountered, but by calling on graphical determinations at certain points they obtained results that were valuable, though probably not as reliable as those gotten by the method to be described. We have made free use of some of the ideas in their unpublished manuscript.

The ideal way to obtain these physical properties would be through an

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[1] Bartlett, J. Amer. Chem. Soc. **49**, 687 (1927); **49**, 1955 (1927); Bartlett, Cupples, Tremearne, ibid. **50**, 1275 (1928); Bartlett, Cupples, Tremearne, Hetherington, ibid. **52**, 1363 (1930); Bartlett, Hetherington, Kvalnes, Tremearne, ibid. **52**, 1374 (1930); Kvalnes and Gaddy, ibid. **53**, 394 (1931).

[2] Max Jakob, Zeits. f. Techn. Physik, **4**, 460 (1923).

equation of state, but this should not be attempted at pressures and temperatures where it appears not to give trustworthy results. Extensive calculations have been made only with the Beattie-Bridgeman[3,4] formula, but the ranges of temperature and pressure covered in the present paper probably far exceed the limits of validity of any existing equation of state. Since the calculation of the constants in the Beattie-Bridgeman formula for high pressure data on nitrogen were made, further work by the writers[5] has shown that its constants are different above and below the critical density for hydrogen and a 3:1 mixture of hydrogen and nitrogen. The calculations with nitrogen[4] were carried only a trifle beyond the critical density and it is possible that if higher densities had been included a different set of constants would have been indicated for densities above critical. If this second set had been introduced the formula would doubtless have been found to fit better at high pressures than was concluded in our paper, but calculations of the desired physical properties at medium and high pressures are surely more reliable when made by the graphical method about to be described. By it no discontinuities are introduced and the precision can be estimated by the regularity of the graphs of the quantities evaluated.

The authors of the Beattie-Bridgeman equation of state have used it to find the heat capacities and Joule-Thomson coefficients of air and ammonia[6] at ordinary temperatures and relatively low pressures, where the increase ΔC_p in heat capacity is usually a small fraction of the heat capacity at 1 atm. C_p is computed by calculating the change ΔC_p in heat capacity with pressure and adding it to the value of C_p at 1 atm., and when $\Delta C_p/C_p$ is small, large errors in ΔC_p are overlooked when observed and calculated values of C_p are compared.

After studying the α and Δ curves for nitrogen, we decided that it is expecting too much of any formula that it should follow the trends of the p-v-T data as faithfully through the whole range as is desired for determining the physical properties sought after. The following graphical process was developed in the hope of obviating some of the difficulties with analytical methods.

The v vs. T isobars are nearly straight lines from -70 to 600° even to 1200 atm., but by plotting residuals their curvature can be measured easily. If the gas were perfect, the v vs. T isobars would be straight lines through the origin having slopes inversely proportional to the pressure. Any departure from the perfect gas law is evidenced by residuals such as

$$\Delta \equiv v(pv/RT - 1) \tag{1}$$

and

$$\alpha \equiv RT/p - v \tag{2}$$

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[3] Beattie and Bridgeman, Proc. Amer. Acad. Arts Sci. **63**, 229 (1928); J. Amer. Chem. Soc. **49**, 1665 (1927); ibid. **50**, 3133 (1928); and later papers.

[4] Deming and Miss Shupe, J. Amer. Chem. Soc. **52**, 1382 (1930).

[5] Deming and Miss Shupe, J. Amer. Chem. Soc. March 1931 (two papers).

[6] Oscar C. Bridgeman, Phys. Rev. **34**, 527 (1929); James A. Beattie, Phys. Rev. **34**, 1615 (1929); James A. Beattie, Phys. Rev. **35**, 643 (1930).

being different from zero; likewise any departure of $(-p/v)\,(dv/dp)_T$ and $(T/v)\,(dv/dT)_p$ from unity is evidenced by $(d\Delta/dp)_T$, $(d\alpha/dp)_T$, $(d\Delta/dT)_p$, $(d\alpha/dT)_p$ being different from zero. Fig. 1 shows how straight the 200 atm. v vs. T isobar is, how much curvature the corresponding Δ and α curves have, and that their shapes are different. There are relations between the slopes of the v vs. T, Δ vs. T, and α vs. T isobars; likewise there are relations between the slopes of v vs. p, pv vs. p, Δ vs. p, α vs. p, Δ vs. ρ (density) isotherms. The relations between these are as follows:

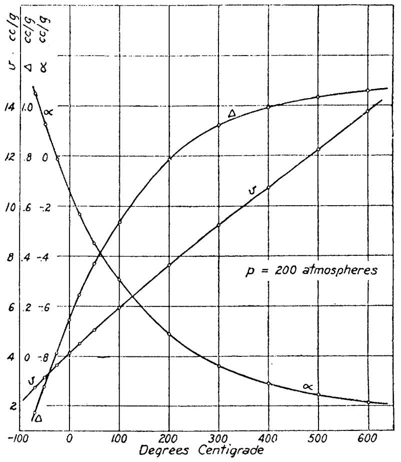

Fig. 1. Graphs of v, Δ, and α vs. T with p constant. This shows that the Δ and α curves have great curvature compared with the v vs. T curve, and that the Δ and α curves are of very different shape.

$$(T/v)(dv/dT)_p = \frac{pv/RT + (T/v)(d\Delta/dT)_p}{1 + 2\Delta/v} \tag{3}$$

$$(T/v)(dv/dT)_p = RT/pv - (T/v)(d\alpha/dT)_p \tag{4}$$

$$(-\,p/v)(dv/dp)_T = 1 - \rho(dpv/dp)_T \tag{5}$$

$$(-\,p/v)(dv/dp)_T = RT/pv + (p/v)(d\alpha/dp)_T \tag{6}$$

$$(-\,p/v)(dv/dp)_T = \frac{pv/RT - (p/v)(d\Delta/dp)_T}{1 + 2\Delta/v} \tag{7}$$

$$(-\,p/v)(dv/dp)_T = -\,pv/RT(2\Delta/v + 1 + \rho^2(d\Delta/d\rho)_T) \tag{8}$$

$$(d^2v/dT^2)_p = -\,(d^2\alpha/dT^2)_p \tag{9}$$

$$(2\Delta/v + 1)(d^2v/dT^2)_p = (d^2\Delta/dT^2)_p - \frac{2p}{RT}\,\frac{(\Delta/T - (d\Delta/dT)_p)^2}{(2\Delta/v + 1)^2}\,. \tag{10}$$

A 1 percent error in estimating the slope of an α vs. T or a Δ vs. T isobar may mean only a few hundredths percent error in $(dv/dT)_p$, since by Eqs. (3) and (4) the slopes $(d\alpha/dT)_p$ and $(d\Delta/dT)_p$ enter as correction terms to the slope that the v vs. T isobar would have if the gas were perfect, just as α and Δ are correction terms to v by Eqs. (1) and (2). Likewise, any error in the determination of $(-p/v)\ (dv/dp)_T$ is diminished according to Eqs. (5), (6), (7), (8). The different families of isobars and isotherms have quite different appearances, so the effect on $(-p/v)\ (dv/dp)_T$ or $(T/v)\ (dv/dT)_p$ of any personal error in estimating the slope of a curve on account of its having a particular shape may be balanced out at that point by a determination from some other curve of different shape. It was not noticeable that the determinations of these derivatives from the α curves were consistently higher or lower than those from the Δ curves or any others.

In order to determine $(d^2v/dT^2)_p$ one can plot $(dv/dT)_p$ vs. T isobars and read the slope at the desired point. Or, one can plot $(d\alpha/dT)_p$ or $(d\Delta/dT)_p$ vs. T isobars, and from the slope of these curves and the relations between $(d^2v/dT^2)_p$ and $(d^2\alpha/dT^2)_p$ or $(d^2\Delta/dT^2)_p$, one can determine $(d^2v/dT^2)_p$. Both methods were used; the results agreed well, and their averages at the various points are shown in Fig. 2.

The most probable positions of observed points lie on the most plausible graph (curve or surface) that can be drawn from them. The most probable values are not uniquely determined by a graphical method, because they depend on the weight assigned by the investigator to various essentials. An adjustment by least squares depends on the weights assigned to the observations so it, too, is subject to the taste and judgment of the computer or observer. Schemes of curve fitting or adjusting that give unique results are incapable of weighting the observations and of throwing the adjustment where it belongs. This has been discussed in two papers by the senior author.[7]

We adopted as a working principle that, in the range investigated, all surfaces such as p, v, T; Δ, p, T; α, p, T; $(d\alpha/dT)_p$, p, T; etc.; have no sharp ridges nor breaks; accordingly all families of isobars and isotherms should be smooth curves without sharp bends or cusps. All the curves in a given family should show their relationship one to another since they can be considered as sections all cut from the same surface, so that each helps to regulate the drawing of the others. The p-v-T data themselves were adjusted by first drawing smooth curves through the Δ vs. p isotherms and reading off Δ from them, then by plotting these Δ against T with p constant and smoothing these curves for the final values of Δ. The specific volumes were calculated from these final values of Δ. The precision of adjusted observations is strengthened by a wide range of temperature and pressure, such as that studied in this work.

The final values shown in the table and curves were smoothed with respect to temperature and pressure, except where they had been derived from others that had already been smoothed. The regularity of the points on the Δ and α curves attests to the high precision of the compressibility data and gave promise that thermodynamic calculations derived from them should be reliable.

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[7] W. Edwards Deming, Proc. London Phys. Soc. **42,** 97 (1930); Phil. Mag. **11,** 146 (1931).

TABLE I. *Some physical properties of compressed nitrogen derived from experimental data on compressibility.*

1 t °C	2 p atm	3 v cc/g	4 ρ g/cc	5 f atm	6 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$	7 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$	8 ΔC_p cal/mole°	9 μ °/atm
−70°	20	28.50	.03508	19.22	1.053	1.162	.50	.627
	40	13.71	.07294	36.91	1.075	1.347	1.12	.592
	60	8.840	.1131	53.31	1.075	1.530	1.79	.538
	80	6.460	.1548	68.66	1.052	1.682	2.46	.470
	100	5.082	.1968	83.18	1.004	1.806	3.13	.408
	200	2.725	.3669	152.1	.717	1.564	5.17	.128
	300	2.150	.4652	227.2	.514	1.162	5.19	.029
	400	1.896	.5273	319.2	.403	.918	5.10	−.013
	500	1.743	.5738	433.0	.345	.776	5.04	−.033
	600	1.642	.6090	575.5	.309	.675	5.00	−.045
	800	1.508	.6630	976.2	.280	.551	4.97	−.057
	1000	1.421	.7035	1596	.250	.459	4.93	−.065
	1100	1.388	.7204	2021	.250	.408	4.89	−.070
	1200	1.358	.7365	2545	.250	.356	4.81	−.074
−50°	20	31.75	.03149	19.48	1.031	1.129	.45	.559
	40	15.50	.06452	37.92	1.048	1.259	.93	.511
	60	10.13	.09872	55.49	1.048	1.381	1.43	.463
	80	7.492	.1335	72.38	1.030	1.477	1.92	.405
	100	5.952	.1680	88.75	1.000	1.560	2.41	.355
	200	3.139	.3186	168.4	.775	1.462	3.76	.136
	300	2.394	.4178	255.1	.590	1.158	3.85	.035
	400	2.068	.4836	357.8	.472	.937	3.84	−.012
	500	1.878	.5325	483.4	.397	.799	3.77	−.035
	600	1.753	.5705	638.1	.360	.699	3.72	−.050
	800	1.591	.6284	1063	.313	.578	3.66	−.064
	1000	1.485	.6736	1701	.286	.491	3.61	−.072
	1100	1.443	.6928	2127	.286	.449	3.56	−.076
	1200	1.408	.7103	2645	.286	.404	3.48	−.081
−25°	20	35.75	.02798	19.70	1.018	1.094	.36	.470
	40	17.65	.05666	38.80	1.025	1.191	.75	.424
	60	11.66	.08578	57.43	1.025	1.266	1.14	.383
	80	8.694	.1150	75.69	1.008	1.328	1.53	.339
	100	6.950	.1439	93.70	.900	1.377	1.90	.298
	200	3.645	.2744	183.6	.830	1.363	2.95	.134
	300	2.704	.3698	281.4	.653	1.149	3.12	.040
	400	2.287	.4372	395.5	.540	.961	3.02	−.008
	500	2.046	.4888	532.4	.455	.831	2.91	−.035
	600	1.890	.5291	697.6	.415	.732	2.81	−.052
	800	1.695	.5901	1121	.353	.608	2.72	−.069
	1000	1.567	.6382	1784	.325	.526	2.66	−.078
	1100	1.516	.6598	2205	.325	.491	2.62	−.081
	1200	1.473	.6789	2703	.320	.457	2.53	−.085
0°	20	39.67	.02521	19.84	1.010	1.068	.29	.387
	40	19.72	.05071	39.38	1.010	1.128	.60	.344
	60	13.11	.07627	58.72	1.005	1.183	.92	.308
	80	9.828	.1018	77.91	.993	1.235	1.24	.277
	100	7.886	.1268	97.05	.978	1.265	1.53	.247
	200	4.139	.2416	194.6	.850	1.281	2.34	.125
	300	3.020	.3311	301.3	.696	1.136	2.55	.043

TABLE I. (Cont'd.) *Some physical properties of compressed nitrogen derived from experimental data on compressibility.*

1 t °C	2 p atm	3 v cc/g	4 ρ g/cc	5 f atm	6 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$	7 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$	8 ΔC_p cal/mole°	9 μ °/atm
	400	2.510	.3984	424.2	.590	.983	2.48	−.005
	500	2.217	.4510	569.2	.510	.863	2.37	−.033
	600	2.032	.4922	741.8	.466	.765	2.30	−.052
	800	1.798	.5560	1194	.390	.639	2.20	−.071
	1000	1.650	.6060	1834	.360	.557	2.13	−.080
	1100	1.591	.6286	2246	.360	.530	2.08	−.082
	1200	1.543	.6481	2732	.350	.503	2.01	−.084
20°	20	42.74	.02340	19.92	1.003	1.055	.25	.325
	40	21.33	.04688	39.70	1.001	1.099	.50	.291
	60	14.23	.07027	59.41	.995	1.140	.75	.263
	80	10.70	.09347	79.12	.983	1.182	.99	.236
	100	8.604	.1162	99.06	.970	1.199	1.22	.211
	200	4.524	.2210	201.0	.860	1.223	2.05	.114
	300	3.271	.3058	313.1	.720	1.117	2.32	.043
	400	2.693	.3713	441.5	.628	.994	2.33	−.002
	500	2.360	.4238	591.8	.550	.880	2.27	−.031
	600	2.146	.4659	768.9	.500	.786	2.22	−.051
	800	1.880	.5318	1226	.417	.660	2.13	−.071
	1000	1.717	.5823	1861	.387	.580	2.06	−.080
	1100	1.654	.6047	2265	.387	.554	2.03	−.082
	1200	1.601	.6248	2737	.373	.534	1.98	−.083
50°	20	47.33	.02113	20.01	.998	1.037	.19	.248
	40	23.72	.04217	40.05	.992	1.070	.37	.228
	60	15.87	.06301	60.18	.984	1.099	.54	.208
	80	11.97	.08356	80.44	.975	1.125	.71	.188
	100	9.639	.1038	100.9	.961	1.138	.86	.169
	200	5.078	.1969	207.5	.845	1.151	1.46	.094
	300	3.640	.2747	325.4	.753	1.092	1.77	.038
	400	2.967	.3371	459.7	.670	.995	1.88	−.001
	500	2.572	.3888	615.4	.597	.895	1.90	−.003
	600	2.320	.4311	796.4	.540	.808	1.89	−.050
	800	2.010	.4974	1254	.456	.688	1.83	−.071
	1000	1.821	.5492	1878	.423	.611	1.78	−.080
	1100	1.748	.5720	2268	.418	.588	1.76	−.081
	1200	1.688	.5925	2719	.402	.566	1.74	−.083
100°	20	54.87	.01822	20.08	.995	1.023	.12	.162
	40	27.59	.03624	40.36	.987	1.041	.24	.149
	60	18.52	.05400	60.87	.975	1.052	.35	.138
	80	14.00	.07143	81.64	.965	1.064	.46	.126
	100	11.29	.08856	102.1	.953	1.078	.56	.114
	200	5.955	.1679	213.7	.881	1.078	1.01	.058
	300	4.243	.2357	337.0	.791	1.037	1.33	.020
	400	3.421	.2924	476.8	.716	.974	1.53	−.010
	500	2.928	.3416	636.3	.652	.896	1.63	−.035
	600	2.612	.3828	819.2	.601	.828	1.67	−.052
	800	2.225	.4494	1271	.515	.720	1.70	−.072
	1000	1.994	.5014	1867	.471	.649	1.77	−.080
	1100	1.909	.5239	2232	.463	.623	1.86	−.083
	1200	1.836	.5447	2649	.445	.597	1.98	−.085

TABLE I. (Cont'd.) *Some physical properties of compressed nitrogen derived from experimental data on compressibility.*

1 t °C	2 p atm	3 v cc/g	4 ρ g/cc	5 f atm	6 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$	7 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$	8 ΔC_p cal/mole°	9 μ °/atm
200°	20	69.82	.01432	20.15	.990	1.008	.07	.075
	40	35.21	.02840	40.62	.980	1.013	.14	.063
	60	23.68	.04223	61.45	.970	1.017	.21	.053
	80	17.93	.05578	82.63	.960	1.017	.27	.044
	100	14.48	.06905	104.2	.950	1.017	.33	.035
	200	7.637	.1309	218.8	.895	1.003	.59	.002
	300	5.389	.1856	346.3	.835	.970	.79	−.022
	400	4.287	.2333	489.0	.775	.923	.94	−.041
	500	3.622	.2761	649.4	.720	.875	1.05	−.056
	600	3.192	.3133	829.7	.675	.828	1.15	−.067
	800	2.655	.3767	1261	.601	.748	1.30	−.082
	1000	2.333	.4286	1804	.550	.672	1.41	−.092
	1100	2.217	.4511	2126	.537	.644	1.46	−.095
	1200	2.120	.4718	2485	.516	.610	1.51	−.098
300°	20	84.64	.01181	20.18	.990	1.003	.05	.010
	40	42.70	.02342	40.71	.980	1.003	.09	.002
	60	28.73	.03480	61.62	.970	.997	.14	−.006
	80	21.75	.04597	82.92	.960	.997	.18	−.012
	100	17.57	.05692	104.6	.951	.992	.22	−.018
	200	9.230	.1083	219.6	.907	.969	.39	−.042
	300	6.467	.1546	346.7	.858	.934	.53	−.058
	400	5.098	.1962	487.4	.808	.894	.64	−.071
	500	4.277	.2338	643.1	.762	.860	.73	−.077
	600	3.735	.2678	815.7	.722	.825	.81	−.084
	800	3.060	.3268	1218	.658	.751	.91	−.096
	1000	2.657	.3764	1709	.607	.694	.98	−.103
	1100	2.509	.3985	1994	.594	.665	1.00	−.105
	1200	2.387	.4190	2306	.570	.642	1.02	−.107
400°	20	99.39	.01006	20.17	.991	.976	.03	−.043
	40	50.12	.01995	40.69	.983	.996	.07	−.047
	60	33.71	.02967	61.56	.975	.990	.10	−.051
	80	25.50	.03921	82.81	.968	.983	.13	−.055
	100	20.59	.04858	104.4	.960	.983	.16	−.058
	200	10.76	.09289	218.6	.915	.949	.28	−.074
	300	7.502	.1333	343.6	.874	.916	.40	−.082
	400	5.879	.1701	480.6	.832	.889	.45	−.088
	500	4.912	.2036	630.7	.791	.855	.51	−.094
	600	4.263	.2346	795.1	.755	.828	.56	−.097
	800	3.456	.2893	1172	.700	.767	.63	−.105
	1000	2.976	.3360	1621	.650	.714	.67	−.110
	1100	2.798	.3574	1876	.635	.693	.69	−.112
	1200	2.653	.3770	2154	.612	.670	.70	−.113
500°	20	114.1	.008765	20.16	.991	.997	.02	−.068
	40	57.50	.01739	40.65	.985	.990	.04	−.072
	60	38.65	.02588	61.47	.975	.982	.06	−.076
	80	29.22	.03422	82.63	.969	.982	.08	−.080
	100	23.57	.04242	104.1	.960	.974	.09	−.082
	200	12.27	.08149	217.1	.921	.943	.17	−.093
	300	8.521	.1174	339.9	.885	.912	.24	−.098

TABLE I. *Some physical properties of compressed nitrogen derived from experimental data on compressibility.*

1 t °C	2 p atm	3 v cc/g	4 ρ g/cc	5 f atm	6 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$	7 $\left(\frac{Tdv}{vdT}\right)_p$	8 ΔC_p cal/mole°	9 μ °/atm
	400	6.651	.1504	473.3	.847	.889	.29	−.101
	500	5.530	.1808	618.2	.812	.858	.34	−.104
	600	4.783	.2091	775.6	.780	.835	.38	−.107
	800	3.848	.2599	1131	.728	.781	.44	−.112
	1000	3.290	.3039	1547	.682	.736	.48	−.115
	1100	3.084	.3242	1781	.665	.715	.49	−.116
	1200	2.916	.3429	2033	.644	.698	.50	−.116
600°	20	128.8	.007766	20.15	.992	.995	.01	−.083
	40	64.87	.01542	40.60	.985	.987	.03	−.087
	60	43.57	.02295	61.36	.976	.987	.04	−.090
	80	32.93	.03037	82.43	.969	.978	.05	−.093
	100	26.54	.03768	103.9	.961	.978	.06	−.095
	200	13.77	.07264	215.8	.926	.943	.11	−.101
	300	9.528	.1050	336.6	.891	.917	.15	−.106
	400	7.409	.1350	466.9	.860	.891	.19	−.110
	500	6.141	.1628	607.4	.829	.864	.23	−.114
	600	5.294	.1889	758.9	.800	.838	.26	−.116
	800	4.234	.2362	1097	.746	.792	.31	−.117
	1000	3.604	.2775	1488	.707	.753	.33	−.119
	1100	3.369	.2968	1705	.691	.737	.34	−.119
	1200	3.177	.3148	1938	.670	.720	.35	−.119

In most p-v-T determinations, the measurement of v is subject to greater error than those of p and T. The Δ and α curves are large scale deviation graphs of residuals of volume and they greatly magnify any error in v, so it is possible to smooth out any irregularities that may be in the original data, and put the adjustment where it belongs. Δ can probably be smoothed to within 0.005 cc/g; and since $(dv/d\Delta)_{p,T} = 1/(2pv/RT - 1)$, the smoothed specific volumes should be accurate to within 0.005 cc/g except in the extrapolated region and in the small range where $pv < RT$.

After considerable practice in laying a straight edge tangent at various points along a curve where the slopes are definitely known, it was found possible to estimate the slope at any point within half a percent, in trial after trial. It thus seemed that our various families of curves represented the most likely course of the p-v-T relations, and that the required derivatives could be gotten very accurately by mechanical means.

The tables published by Bartlett *et al.* show compressibility factors $pv/(pv)_s$ at the different pressures and temperatures. The denominator $(pv)_s$ is the value of pv at S.T.P. In order to find the specific volume of the gas it is required to know the volume of 1g at S.T.P. Birge gives 22414.1 cc as the volume of a mole of an ideal gas at S.T.P.

$pv/(pv)_s$ at 1 atm. is close to 1/1.00046. The gas used by Bartlett contained 0.9993 nitrogen and 0.0007 inert gas, presumably argon; the apparent molecular weight is therefore taken as 28.025. The volume adopted for 1 g at S.T.P. is accordingly $22414.1/1.00046 \times 28.025 = 799.42$ cc, and the value of RT at 0° is $22414.1/28.025 = 799.79$ cc atm./g. When one of Bartlett's compressibility factors is divided by the pressure and multiplied by 799.42 the result is the volume in cc of 1 g of the gas at the given temperature and pressure.

Some of the temperatures listed by Bartlett *et al.* were not integral; further a calibration of their thermocouple by the Bureau of Standards showed that the temperatures published[1] as $-25°$, $-50°$, $-70°$ should have been $-24.99°$, $-49.93°$, $-69.90°$. We have made the slight alterations necessary to change his data to integral temperatures by a sensitive method of interpolation.[5]

At pressures below 100 atm. we used a compilation deduced by Dr. Bartlett from all the available data, chiefly from Amagat, the Reichsanstalt, and the cryogenic laboratory at Leiden, since Bartlett worked at the low pressures only to tie his results with those of previous observers. This compilation was kindly furnished us by Dr. Bartlett in a private communication. Our Δ vs. p isotherms give an easy and reliable means of interpolating to even pressures—one has only to read off Δ at any desired p and calculate v therefrom; accordingly we list results at 20, 40, 60, 80, 100 atm. rather than at the odd pressures one gets by converting meters of Hg to atm.

The Δ vs. p isotherms also give a reliable method of extrapolating to higher pressure; since the original ten isotherms constitute a family of curves, one can not go far wrong in extending them a reasonable distance. This was done and values of Δ were read at 1100 and 1200 atm. The specific volumes calculated at these pressures are probably not in error by 0.01 cc/g, judging from the regularity of the Δ vs. p isotherms and the values of $(dv/d\Delta)_{p,T}$ in this region. In the same way the Δ vs. T isobars give a means of extrapolating to temperatures higher than 400°. Values of Δ were read from the extended isobars at 500 and 600°. In order to estimate the error of the extrapolations, the Δ vs. T isobars were first plotted only to 300° and were extrapolated to 400° and the Δ read at that temperature. Later the observations at 400° were plotted and the smoothed Δ read. The two sets of specific volumes calculated from these two sets of Δ agreed closely, the probable error being 0.17 percent.

The value of these extrapolations, if they are reliable, must be considerable. To extend the experiments to 1200 atm. and 600° would entail enormous expense and labor. Calculations at 1100 atm. and 500° were included, because with them, at least, there should not be any risk. All the calculations in the extrapolated region tied on to the others satisfactorily, so it seems safe to assume that they were made successfully.

The final values of the physical properties at the twelve temperatures and fourteen pressures are shown in the table, or in the figures. Their preparation and implications will now be discussed.

Column 3 shows the specific volumes, which were calculated from the adjusted values of Δ through Eq. (1). The densities in column 4 are the reciprocals of the specific volumes.

The fugacities in column 5 were computed from the smoothed values of α by Lewis and Randall's[8] graphical method.

In columns 6 and 7 the pressure and temperature coefficients of volume expansion are shown. The reason for listing $-(p/v)\ (dv/dp)_T$ and not $-(1/v)\ (dv/dp)_T$ is that the former is dimensionless, and this fact facilitates changing units. Thus if one wishes to get the pressure coefficients at 100° for pressures in meters Hg, one has only to plot the values in column 6 for the 100° isotherm against p in atmospheres, and then graduate the scale of abscissas in the new units of pressure; one can then read $-(p/v)\ (dv/dp)_T$ for any number of meters Hg. The ordinates need not be changed in any way because they are dimensionless. Another advantage is that we can see at a glance how far this coefficient departs from unity, which is the value it would have if the gas were perfect. $(T/v)\ (dv/dT)_p$ was listed for the same reasons. The pressure coefficients of column 6 were adjusted from determinations given by the pv vs. p, α vs. p, Δ vs. p, and Δ vs. ρ isotherms through Eqs. (5), (6), (7), (8); the temperature coefficients of column 7 were adjusted from determinations given by the α vs. T and Δ vs. T isobars through Eqs. (3) and (4). The unsmoothed values at any point determined by the different methods nearly always agreed closely; when they disagreed more than 1 percent even at the highest pressures we went back and reconsidered the curves. Particular care was given to the determinations of $(T/v)\ (dv/dT)_p$, because this derivative enters to the second power in the calculation of $C_p - C_v$ and because it is used to get $(d^2v/dT^2)_p$, which enters into the calculation of ΔC_p.

Probably the most important properties that result from these calculations are C_p and C_v. For this reason extreme care was exercised to obtain the greatest possible precision for ΔC_p, which is shown in column 8. This depends on $(d^2v/dT^2)_p$ through the thermodynamic equation

$$(dC_p/dp)_T = -\ T(d^2v/dT^2)_p, \tag{11}$$

which when integrated along an isotherm gives

$$C_p = C_p' + \int_{p'}^{p} -\ T(d^2v/dT^2)_p dp. \tag{12}$$

C_p' is the heat capacity at pressures p'. The $-T(d^2v/dT^2)_p$ vs. p isotherms are shown in Fig. 2. The area under a given isotherm between any two abscissas is the change in C_p between those abscissas. The values of ΔC_p obtained by Eq. (12) from the curves in Fig. 2 were smoothed with respect to temperature and pressure before being listed in column (8).

In drawing the curves of Fig. 2 it was necessary to know something about their course in the region $0 < p < 20$, since p' was 1 atm. In an extremely rarefied condition the gas would have some characteristics of a perfect gas. The question has been raised by the writers[9] whether $(d^2v/dT^2)_p$ and $(dC_p/dp)_T \rightarrow 0$ as $p \rightarrow 0$, as they would if the heat capacity of the actual gas at very low pres-

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[8] Lewis and Randall, Thermodynamics, pp. 192 to 195, McGraw-Hill (1923).

[9] Deming and Miss Shupe, Phys. Rev. **37**, 220 (1931).

sure behaves like that of a perfect gas. For the calculations in this paper we have assumed that $(dC_p/dp)_T \neq 0$ at $p=0$, and for its value we have used, wherever it seemed feasible, the one given by the Beattie-Bridgeman equation of state with constants determined[4] from these same compressibility data. In Fig. 2 are shown the graphs of $-T(d^2v/dT^2)_p$ vs. p isotherms. The points are the averages of determinations made from the α vs. T and Δ vs. T isobars through Eqs. (3), (4), (9), (10). The curves given by Beattie's formula[6] are shown dashed and they are drawn as far as the equation of state might be expected to hold, namely, as far as the critical density. At 100, 200, 300, and 400° the dashed curves seem to be the best curves that could be drawn to the points shown.

The curves in Fig. 2 for 20, 50, and 100° are not quite flat from 20 to 100 atm. This is the range of pressure considered by Hoxton[10] in discussing the variation of the heat capacity of oxygen at 26° obtained in the experiments of Workman.[11] Hoxton speaks of a "change in c_p per atmosphere relative to its value at one atmosphere, the temperature being constant and taken as 26°C," and says that Workman found this quantity $\delta \equiv (dC_p/dp)_T/C_p'$ to be constant and equal to 0.00165 parts per atm. This implies that for oxygen the $(dC_p/dp)_T$ vs. p 26° isotherm is flat. There are reasons to expect C_p for nitrogen and oxygen to be similar in some ranges of temperature and pressure; e.g., their C_p values at one atmosphere for various temperatures are sometimes[12] expressed by the same formula, and Jakob's results for air are very similar to ours for nitrogen in some respects (*vide infra*). Our curves in Fig. 2 show that δ for nitrogen should decrease slightly with pressure. Taking 0.0178 and 0.0125 as the average ordinates for the 20° and 50° isotherms from

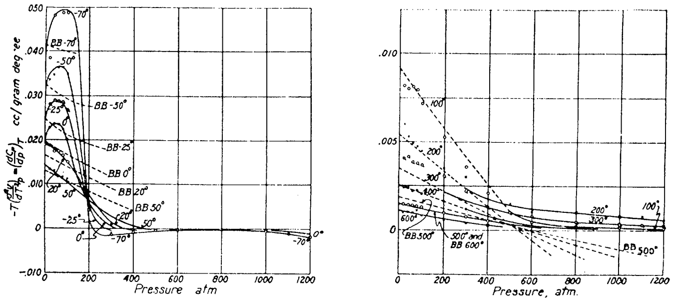

Fig. 2. $(dC_p/dp)_T$ vs. p isotherms. The full lines are drawn to the points determined from the p-v-T data. The dashed curves are given by the Beattie-Bridgeman equation of state, and are drawn as far as the critical density. Where only the dashed line is shown, the Beattie-Bridgeman values were accepted. To avoid confusion, some of the curves are not drawn at high pressures. The area under a particular curve between any two pressures is the change in heat capacity (in cc atm./g deg.) between these two pressures, at that temperature.

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[10] L. G. Hoxton, Phys. Rev. **36**, 1091 (1930).

[11] E. J. Workman, Phys. Rev. **36**, 1183 (1930).

[12] E. D. Eastman, Specific Heats of Gases at High Temperatures, Bureau of Mines Techn. Paper 445 (1929).

20 to 100 atm. in Fig. 2, and interpolating linearly to 26°, δ turns out to be 0.00164 parts per atm. for nitrogen, very nearly what it is for oxygen.

In order to find C_p from Eq. (12) it is necessary to adopt values of C_p' at some pressure p' for the different temperatures. Several formulas have been devised to express C_p at 1 atm. as a function of T. As far as we know none of these is expected to extend to temperatures much below 20°. For C_p' at the low temperatures we finally accepted Brinkworth's[13] three values, which are 6.91, 6.92, 7.20 at 10, −78, −183°. A smooth curve through these points met Partington and Shilling's[14] formula very well at 30°, so we constructed a curve through Brinkworth's three points and points calculated from Partington and Shilling's formula above 30°, and from this curve read the values for C_p' that are listed below.

$t°C$	−70	−50	−25	0	20	50
C_p' (1 atm.)	6.92	6.91	6.91	6.91	6.91	6.92
$t°C$	100	200	300	400	500	600
C_p'	6.94	6.98	7.01	7.05	7.09	7.13

Eastman's formula would not join on to Brinkworth's points satisfactorily. At 200° Eastman's and Partington and Shilling's formulas differ by 0.1 cal/mole·deg. As the temperature increases the disparity widens even more, which shows that more precise direct calorimetric measurements of C_p at 1 atm. are needed.

It is difficult to estimate the accuracy of the ΔC_p, which are shown in column 8. The relation of the curves and points in Fig. 2 suggests that the precision of the calculations is greatest at the highest pressures. The calculated values of C_p agree well with the experimental values of Mackey and Krase.[15] They worked to 700 atm. at 30, 100, 125, 150° and to 800 atm. at 50°. Their points have been inserted in Fig. 4, so that observed and calculated values can be compared at a glance. The dashed curves represent calculated values obtained by interpolating along C_p vs. T isobars. At 50° the agreement is excellent through the entire range of experiment. At 30° the calculated values run below the experimental ones above 400 atm., and at 100, 125, 150° the calculated values lie above the experimental ones throughout the entire range. While the discrepancy is probably not greater anywhere than the experimental error of the calorimetric measurements, the trend of the calculated curves is definitely away from the experimental points above and below the 50° isotherm. An incorrect assumption for C_p at 1 atm. would result in a constant distance between an experimental and a calculated isotherm. A constant difference above, say, 100 atm. might mean that the corresponding isotherm in Fig. 2 is incorrectly drawn between 0 and 100 atm. But we are at a loss to account for the *constantly widening* gap between the calculated and experimental points at 30° above 350 atm., and for that at 100, 125, and 150.° The precision of the points in Fig. 2 does not diminish

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[13] J. H. Brinkworth, Proc. Roy. Soc. **A111**, 124 (1926).

[14] Partington and Shilling, The Specific Heats of Gases, p. 145, D. van Nostrand (1924).

[15] B. H. Mackey and Norman W. Krase, J. Ind. and Eng. Chem. **22**, 1060 (1930).

with increasing pressure, and they could hardly be *consistently* in error by so great an amount as to account for the widening gaps. It thus seems impossible that the discrepancy can be laid to the calculations from the p-v-T data.

Witkowski's curves[16] for air go only to 100 atm., but it is interesting to note that the hump that appears in Fig. 3 at the lowest temperatures appears in his curves for $-100°$ and lower temperatures; also that the pressure at which the hump appears decreases as the temperature decreases with both air and nitrogen.

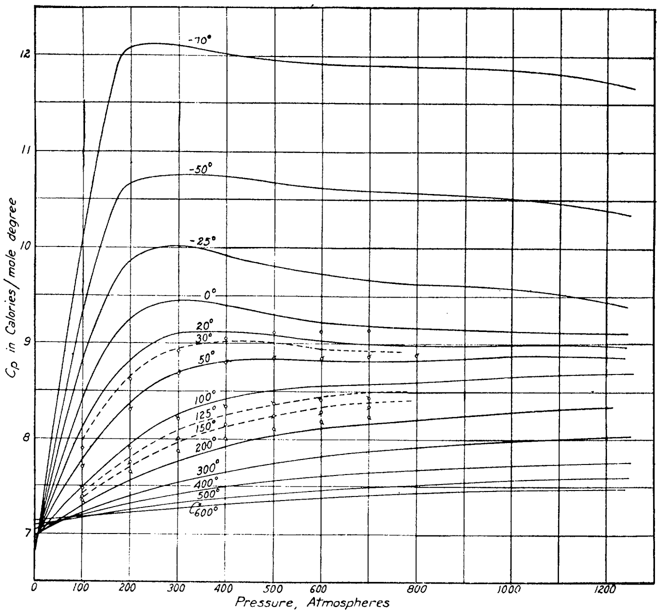

Fig. 3. Variation of C_p for nitrogen with pressure. Mackey and Krase's values ○ 30°, ♂50°, ↖○100°, ↙○125°, ○↘150°.

Comparison with Jakob's[2] calculations of C_p for air show agreement within a few percent at 100 and 200° through 200 atm., and within a few percent at $-50°$ and 50 atm.

$$C_p - C_v = -T(dv/dT)_p^2/(dv/dp)_T. \tag{13}$$

Since the derivatives used in Eq. (13) have already been evaluated, $C_p - C_v$ can be calculated at each pressure and temperature. The results are shown in Fig. 4. In view of the precision claimed for the first derivatives, the error in $C_p - C_v$ should not exceed 0.3 percent, which is about as close as the graph can be read. It will be noticed that these curves all run toward the ordinate

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[16] Witkowski, Phil. Mag. **42**, 1 (1896). These curves are shown in Partington and Shilling's book, p. 154.

R as p approaches zero. It was found that our values of $C_p - C_v$ for nitrogen agree closely with Jakob's for air; for example, our 100 atm. isobar almost coincides with his for 100 kg/cm² throughout his entire range of temperature. Our $C_p - C_v$ values were smoothed with respect to temperature and pressure.

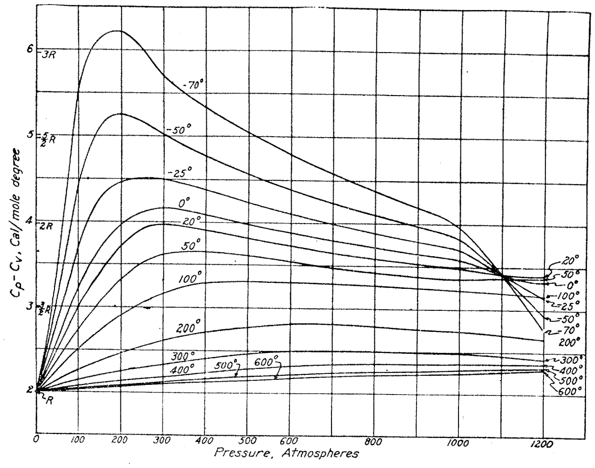

Fig. 4. The variation of $C_p - C_v$ for nitrogen with pressure at various temperatures.

The values of $C_p - C_v$ from which Fig. 4 was plotted were subtracted from the values of C_p in Fig. 3 to get the C_v graphed in Fig. 5. It will be seen that

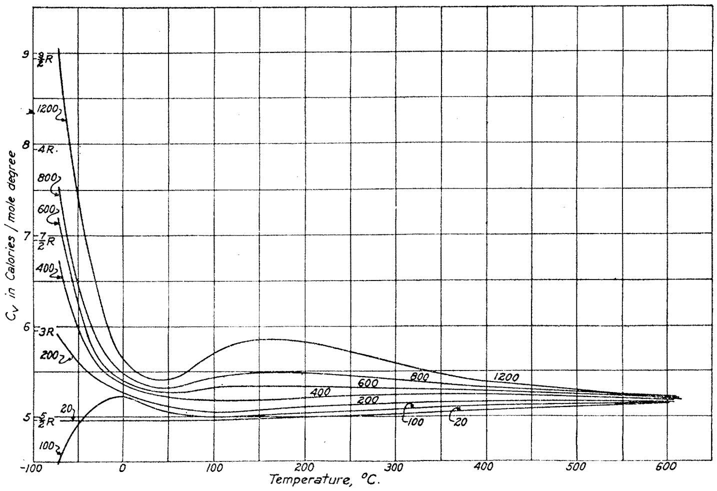

Fig. 5. Variation of C_v for nitrogen with temperature at constant pressure. The numbers on the isobars denote atmospheres.

C_v at 20 atm falls from 5.15 cal/mole·deg (2.59 R) at 600° to 2.50 R at 100°, and it stays there as the temperature is lowered to −70°. An increase in pressure lowers C_v at $-70°$ until 100 atm. is reached; at 200 atm. and higher, C_v rises as the temperature falls below 20°, and the rise is steeper the higher the pressure. Above 400° it is evident that C_v is approaching the same value for all pressures; at 600° C_v is about 5.18 cal/mole·deg or 2.61 R from 20 to 1200 atm. Jakob's calculated values of c_v for air, when plotted, show the same behavior at low temperatures for his entire pressure range, which included 200 kg/cm^2. His 200 kg/cm^2 isobar would fall off faster than his 100 kg/cm^2, instead of rising like the 200 atm. isobar in Fig. 5; but 200 kg/cm^2 is at the end of his pressure range and he lays no claim for accuracy there, so it can only be conjectured how C_v for air compares with C_v for nitrogen above 100 atm. Various explanations of this behavior in Fig. 5 have been considered, but they will not be discussed here because we prefer to present results only.

The Joule-Thomson coefficient can be calculated from the equation

$$\mu C_p = T(dv/dT)_p - v \qquad (14)$$

by using the values already found for C_p and $(dv/dT)_p$. They are listed in column 9. The inversion temperatures for the various pressures are where the μ vs. T isobars cross the ordinate $\mu = 0$, and the inversion pressures for the various temperatures are where the μ vs. p isotherms cross the ordinate $\mu = 0$. The inversion curve, Fig. 6, is plotted from the inversion points so obtained. There are no existing data on the Joule-Thomson coefficient for nitrogen, so a comparison with observed values is not yet possible. Roebuck's[17] values for air give the inversion points marked x on Fig. 6.

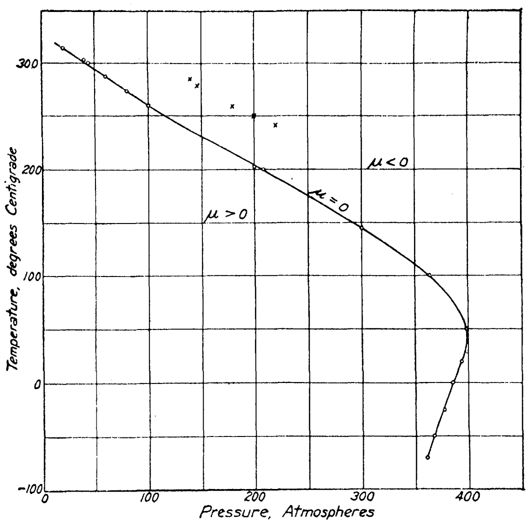

Fig. 6. Inversion curve for nitrogen. The points were read from the μ vs. T isobars and the μ vs. p isotherms. μ denotes Joule-Thomson coefficient $\mu = (dT/dp)_H$. x denotes Roebuck's inversion points for air.

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[17] Roebuck, Proc. Amer. Acad. Arts Sci. **60,** 535 (1925); **64,** 314 (1930) International Critical Tables **5,** 144, first edition.

If the results derived in the present paper are a step toward the determination of the heat capacity and other physical properties of gases, the importance of compressibility data must be recognized. The calculations in this paper were made by two people in nine weeks time. Compressibility data on a number of gases are now available; their physical properties will be determined as rapidly as possible and will appear in subsequent papers. The method will doubtless undergo changes that will result in greater precision.

This work was undertaken at the suggestion of Dr. Edward P. Bartlett, formerly of this laboratory. We have enjoyed the encouragement and willing cooperation from him and the staff at this laboratory throughout the course of the work. We wish also to acknowledge indebtedness to Professor James A. Beattie of the Massachusetts Institute of Technology for his interest in the work, especially in the heat capacity at low pressures, and to Professor L. G. Hoxton of the University of Virginia for his encouragement and many helpful suggestions.

Note added in proof, February 16, 1931: Some results on C_p for nitrogen to be read by E. J. Workman at the New York meeting of the American Physical Society on February 26, 1931 make possible further comparison between the present calculations and experimentally obtained results. Workman has obtained $C_p:C_p'$ at 30, 60, 90, 130 kg/cm^2 at 26° and 60°C. C_p read from the original tracing of Fig. 3 at these points gives the following comparison. *W* denotes Workman, *D* denotes Deming and Miss Shupe. 6.916 and 6.926 cal/mole deg were adopted for C_p' at 26° and 60°.

	p kg/cm^2	p atm.	26°C $C_p:C_p'$	60°C $C_p:C_p'$
W	30	31	1.0443	1.0324
D			1.05	1.04
W	60	62	1.0900	1.0665
D			1.10	1.07
W	90	93	1.1332	1.0990
D			1.15	1.11
W	130	134.5	1.1863	1.1395
D			1.21	1.15