

The Joule-Thomson Effect in Nitrogen

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The measurements were made with the same apparatus and procedure as in the case of argon. The effect of the known impurities in the nitrogen, namely argon and oxygen, can be safely neglected. The data for the isenthalpic curves are given in detail and are plotted. The values of the Joule-Thomson coefficient, μ , over the field (-150 to 300°C and 1 to 200 atmos.) are calculated, plotted and tabulated as functions of pressure and temperature. Both

upper and lower branches of the inversion curve are measured and the whole inversion curve plotted. The isenthalpic curves, the Joule-Thomson coefficient, and the inversion curve in nitrogen are exceedingly like the corresponding phenomenon in air and in argon. C_p is spread over the pressure range and agrees well with the values of Deming and Shupe, and of Mackey and Krase.

THE measurements on the Joule-Thomson effect in air,^{1,2} in helium^{3,4} and in argon⁵ are here extended to nitrogen. They cover the now customary range of pressure (1 to 200 atmos.) and of temperature (-150°C to 300°C). The apparatus is the same as that used for measuring argon. Reference is made to the argon and earlier articles for details of both apparatus and methods.

NITROGEN SUPPLY

Air Reduction Company commercial nitrogen was purchased for these measurements. It was stated to contain 0.1–0.2 percent of oxygen and 0.25–0.5 percent of argon, as well as traces of hydrocarbon vapors from their compressor oil. Analysis made by bringing samples of the gas in contact with hot metallic calcium, showed the argon present to be below 0.2 percent.

To determine the effect of these small argon impurities on the nitrogen data, pure argon was added to the nitrogen in small measured amounts, and runs made with these mixtures at 25, 50 and 75°C . Extrapolation of these data to low percentages of argon showed that the percentage change in the drop in temperature for a drop in pressure of 120 atmos. was approximately equal to the percent of argon in the mixture. As the analyses showed 0.13 percent of argon impurity, the error from this impurity falls well below the 0.5 percent error estimated for these Joule-Thomson measurements.

There is less difference between the critical temperatures of oxygen and nitrogen than of argon and nitrogen so that it seems safe to assume that the effect of the smaller percent of oxygen present as impurity will also fall below the 0.5 percent.

The preparation of very pure nitrogen by cracking of ammonia was considered carefully but was not attempted since: (1) Such freedom from impurity, as indicated above, was hardly necessary; (2) the time and labor involved were considerable; and (3) the risk of handling the required quantities of hydrogen in our location was not desirable.

We hope soon to make comprehensive measurements on the Joule-Thomson effect in mixtures of nitrogen and argon. Experimental evidence bearing on the effect of this neglect of argon impurity in the nitrogen will be available in the report on the mixture work.

APPARATUS

In the work on air, serious difficulty was experienced in obtaining zero temperature drop across a plug permeable enough to give a negligible pressure drop. The observed result is a shift of the initial point off the isenthalpic curve. As suggested,¹ a heater coil was wound around the thermostat tank to increase the homogeneity of the bath temperature.

For the work above room temperature with helium, argon and nitrogen, use was made of a flat heater coil which was placed directly below the plug support. The current through this heater was adjusted to maintain zero reading of a thermocouple having one junction against the

¹ Roebuck, Proc. Am. Acad. **60**, 537 (1925).

² Roebuck, Proc. Am. Acad. **64**, 287 (1930).

³ Roebuck and Osterberg, Phys. Rev. **43**, 60 (1933).

⁴ Roebuck and Osterberg, Phys. Rev. **45**, 332 (1934).

⁵ Roebuck and Osterberg, Phys. Rev. **46**, 785 (1934).

plug support and the other in the bath liquid. These two heaters appear to have lessened materially the number of instances in which the initial point falls seriously off the isenthalp.

This situation is often complicated by uncertainty in the next two or three points down the isenthalp. If the same plug is to be used for the whole curve, the flow at these points may not be large enough to submerge the effect of heat leaks. It is often necessary to use a more permeable plug to duplicate the high pressure section of the isenthalp. In the present work this was required near both extremes of temperature.

It is noteworthy that the life of the fiber packing in the compressor is greatly prolonged by changing the lubricating water frequently to avoid alkali accumulation.

EXPERIMENTAL RESULTS

The data are given in Table I. The individual experimental runs are referred to by their approximate bath temperatures. The last temperature and pressure readings in a run are, respectively, the bath temperature and the inlet high pressure. The temperatures are in the hydrogen centigrade scale, and the pressures in atmospheres absolute.

About half of the runs were completely repeated at least once with a different plug, and most of the runs were repeated over part of their range. Out of 75 runs actually made, 46 have been selected for publication.

ISENTHALPIC CURVES

The data from Table I are plotted in Fig. 1. The curves below that at -50°C are plotted to half the temperature scale of those above. In the upper group the temperature scale is broken and the curves crowded together. Confusion has been avoided by not attempting to show every point from Table I. They were all used, however, in the working drawing from which Fig. 1 was traced.

The data for the vapor pressure curve, shown dashed in Fig. 1, are taken from the International Critical Tables. The points for an isenthalp which has intersected the vapor pressure curve follow along the vapor pressure curve. Since

many runs were continued below this intersection, the resulting mass of points is not plotted in Fig. 1. The points fall into a narrow band whose width is such as might be expected from experimental errors.

The points which belong to the isenthalps entering the vapor pressure curve from below show a tendency to fall below the vapor pressure curve whereas the corresponding points of the isenthalps entering from above do not. A volatile impurity of lower critical temperature than that of nitrogen can be expected to produce this tendency. This explanation appears reasonable in the case of the larger tendency in argon⁵ in which nitrogen was the known volatile impurity. It fits also in the case of carbon dioxide⁶ where air acted as the known volatile impurity.

With air this observed tendency was rather large but there was no known suitable volatile impurity. With nitrogen the tendency is much smaller though still observable and a suitable known impurity is likewise lacking. Failing this explanation, it would seem that there are either instrumental or systematic (i.e., whether the two methods measure in all particulars the same phenomenon) differences between the two methods of obtaining the vapor pressure curve. A thorough study of carbon dioxide containing various impurities is expected to lead to a better understanding of the situation.

Theory⁷ requires that the isenthalp through the critical point shall be tangent to the vapor pressure curve at the critical point. The -120° isenthalp falls very close to this particular isenthalp.

The curves intersecting the vapor pressure curve from the left, starting at T_c , meet it at a small and decreasing angle, till finally a particular isenthalp grazes the vapor pressure curve. Below this point of tangency and between the grazing isenthalp and the vapor pressure curve the isenthalps must come out of the vapor pressure curve, as in the case of the -97° isenthalp, Fig. 1. This situation is well known in throttling calorimetric work with steam⁸ and is indicated for carbon dioxide by Burnett.⁶

The maximum observed drop in temperature

⁶ E. S. Burnett, Bull. of Univ. of Wis. 9, No. 6 (1926).

⁷ A. G. Worthing, Phys. Rev. 33, 256 (1911).

⁸ H. N. Davis, Proc. Am. Acad. 45, 241 (1910).

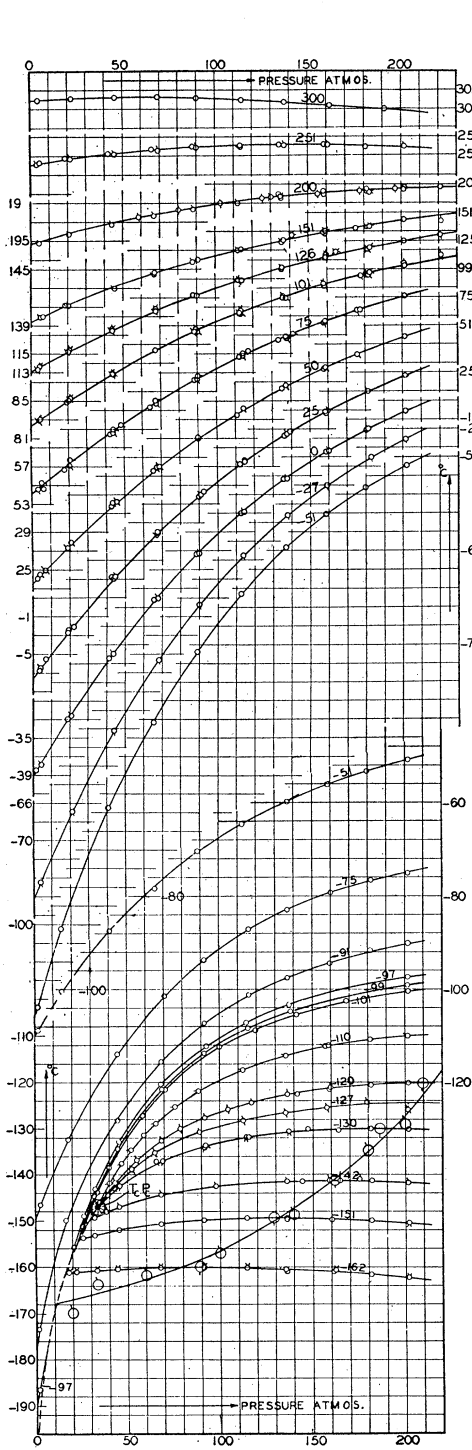


FIG. 1. t as a function of p at constant enthalpy.

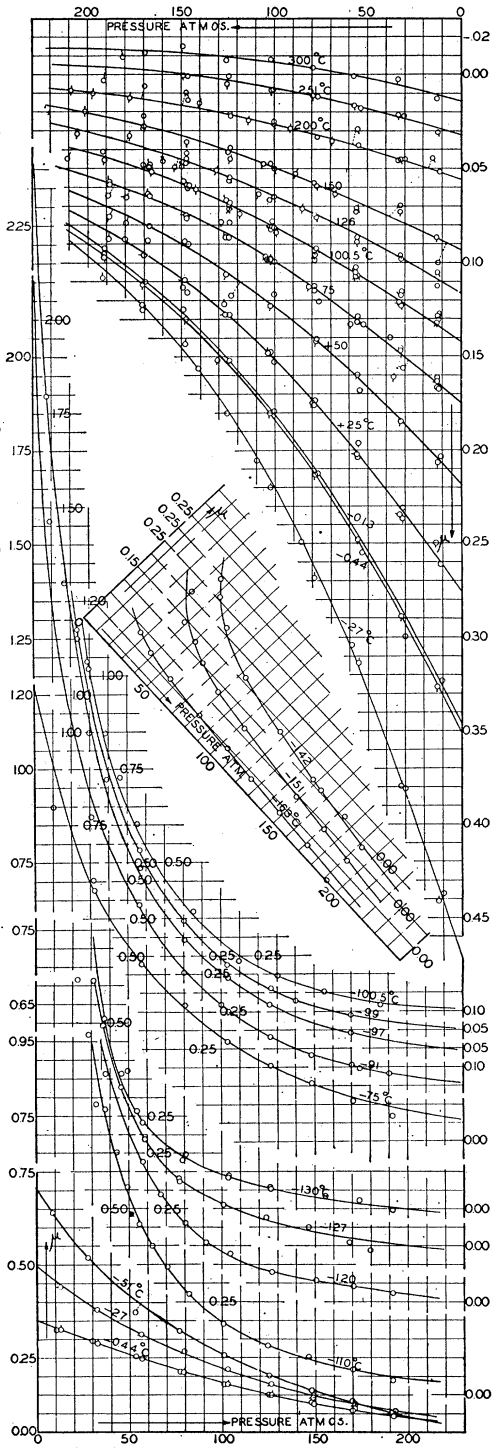


FIG. 2. μ as a function of p at constant enthalpy.

across the plug is 87°C and the maximum value of μ 2.32°C/atmos. These values are smaller than the corresponding values (120° and 3.0°C/atmos.) for argon.⁵

The same precautions as those taken with argon again proved sufficient to prevent the plug clogging from introducing uncertainty except in the lower ends of the -50°, -75° and -91° isenthalps.

Comparison of this whole group of isenthalps (Fig. 1) for nitrogen with the corresponding groups for air^{1, 2} and for argon,⁵ shows remarkable similarity between them. The comparison immediately suggests that the theorem of corresponding states will fit at least approximately. Scattered numerical examples from these measurements show that this theorem may be applied to the Joule-Thomson effect with approximately the same precision as to p v data. A systematic application of this theorem to our data is in progress.

JOULE-THOMSON COEFFICIENT, $\mu \equiv (dt/dp)_h$

As in previous papers,^{1, 5} the numerical values of μ are obtained by taking the ratio of the successive and corresponding differences of temperature and of pressure for each experimental run. These values of μ are plotted against the corresponding average pressure to give the isenthalpic curves of Fig. 2. To avoid confusion these curves are plotted in groups and, occasionally, to shifted scales. This family of isenthalpic curves is more complex than the corresponding family for argon. Each curve was obtained from the data of the original isenthalp (Fig. 1) designated by the same approximate bath temperature.

From the curves of Fig. 2 the values of μ for a series of selected pressures were picked off and the corresponding temperatures obtained from the isenthalpic curves of Fig. 1. These values of μ and t are plotted in Fig. 3 as isopiestic. It was necessary to shift these isopiestic apart since μ shifts very slowly in a part of the field. The ordinate scale is indicated for each isopiestic. As in the case of air, the critical isopiestic (33.5 atmos.) has been plotted.

As indicated by the work of Burnett,⁶ the critical isopiestic is tangent to the "Limit Curve"

at the critical point. Thus the slope of the vapor pressure curve at the critical point⁷ ($T_{c\mu_c}$, Fig. 3) is common to the critical isopiestic and to the limit curve. The slope of the vapor pressure curve as a function of temperature is the curve plotted with square points. The limit curve (long dashed line in Fig. 3) enters at the lower left-hand edge of the diagram, bends upward so as to pass vertically through the critical point, and leaves at the point $\mu = 2.20$.

The points for locating the limit curve were obtained by determining the slopes of the isenthalps of Fig. 1 at the points at which they strike the vapor pressure curve. The p and t of each intersection was read from Fig. 1. The corresponding isenthalp of Fig. 2 was then extrapolated to the value of p as read from Fig. 1, and μ for this pressure picked off. These values of μ are plotted against the corresponding temperatures as the triangles in Fig. 3. In the resulting limit curve, the upper branch, rising from the critical point, is associated with the steep isenthalps intersecting the vapor pressure curve from above. The lower branch, descending from the critical point, is associated with the flat isenthalps intersecting the vapor pressure curve from below.

The discontinuity in μ when a point moves along an isopiestic across the vapor pressure curve in Fig. 1, e.g., along the 20 atmosphere isopiestic is represented in Fig. 3 by the vertical dotted line between the upper and lower branches of the limit curve. As the chosen isopiestic moves to lower pressures in Fig. 1, the dotted line in Fig. 3 moves to the left. Presently a pressure is reached at which a particular one of the upper isenthalps of Fig. 1 is tangent to the vapor pressure curve. At this pressure the corresponding isopiestic, the upper branch of the limit curve, and the curve of the slopes of the vapor pressure curve intersect (Fig. 3, point P). The upper branch of the limit curve will probably rise continually to the triple point pressure.

Final values of μ for the range of these experiments were read from the curves of Fig. 3 before it was inked and are listed in Table II.

Deming and Shupe⁹ have calculated the values of μ for nitrogen from the p v measurements of Bartlett and co-workers. Their corrected values

⁹ Deming and Shupe, Phys. Rev. **37**, 638 (1931).

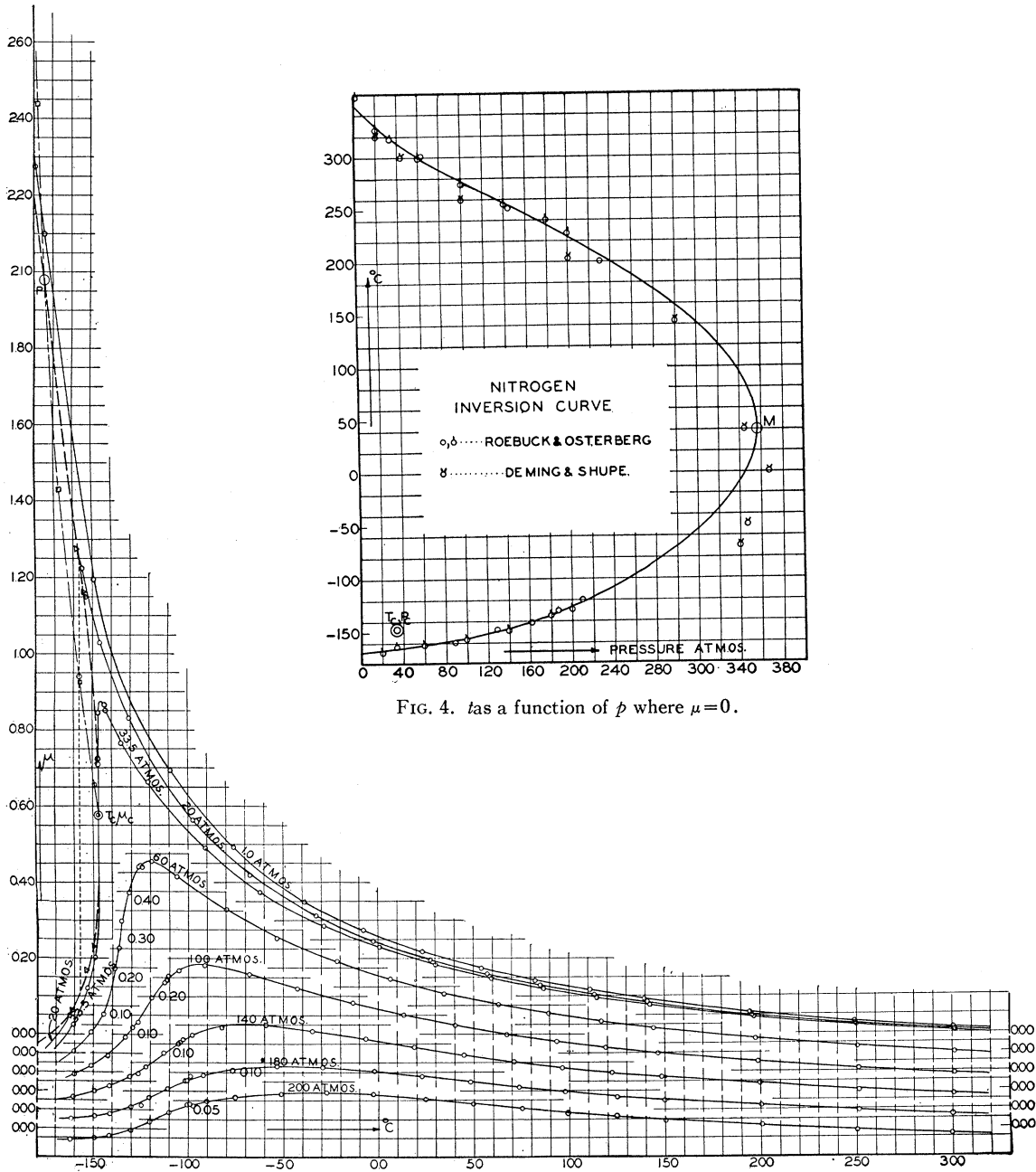


FIG. 4. t_{as} as a function of p where $\mu=0$.

FIG. 3. μ as a function of t at constant pressure.

are given in the article which just precedes this. Comparison of these values with ours shows that when the high percentage divergences where μ is small are omitted, the average numerical percentage divergence and the average percentage difference are, respectively, 5.2 and 2.4

percent. The numerical divergences between the μ 's where μ is small average only 0.007°C/atmos. Their values of μ are greater than ours at low temperatures, but become slightly smaller at the highest temperatures. These differences show no clearly marked trend with pressure. Con-

TABLE II. Final values of μ from Fig. 3.

$t \setminus p$	1	20	33.5	60	100	140	180	200
300°C	0.0135	0.0095	0.0050	-0.0010	-0.0070	-0.0120	-0.0150	-0.0160
250	0.0320	0.0250	0.0225	+0.0160	+0.0075	+0.0015	-0.0030	-0.0050
200	.0540	.0460	.0420	0.0365	.0260	.0170	+0.0100	+0.0075
150	.0840	.0755	.0715	.0615	.0480	.0350	.0250	.0225
125	.1035	.0945	.0880	.0770	.0615	.0460	.0345	.0320
100	.1250	.1140	.1070	.0955	.0760	.0580	.0460	.0415
75	.1505	.1380	.1300	.1165	.0930	.0735	.0580	.0535
50	.1795	.1660	.1575	.1415	.1150	.0910	.0730	.0660
25	.2145	.2000	.1905	.1690	.1380	.1100	.0875	.0780
0	.2570	.2420	.2310	.2040	.1660	.1310	.1020	.0900
-25	.3120	.2925	.2775	.2475	.1975	.1510	.1120	.0950
-50	.3840	.3625	.3370	.2995	.2315	.1695	.1155	.0940
-75	.4870	.4535	.4200	.3640	.2680	.1770	.1090	.0840
-87.5	.5525	.5095	.4730	.4020	.2825	.1675	.0980	.0760
-100	.6280	.5785	.5355	.4430	.2810	.1425	.0800	.0620
-112.5	.7190	.6645	.6050	.4880	.2375	.0980	.0515	.0375
-125	.8280	.7725	.6870	.4945	.1475	.0530	.0200	.0070
-137.5	.9650	.9100	.7910	.2500	.0685	.0210	-0.0040	-0.0140
-150	1.225	1.097	.1775	.0620	.0215	-0.0025	-0.0180	-0.0255
-160	1.580	0.0730	.0330	.0075	-0.0075	-0.0160	-0.0235	-0.0295
-170	1.940	-0.0075	-0.0360					
-180	2.315							

sidering the precision required in Bartlett's work and the difficulties in Deming and Shupe's calculation, the above agreement must be considered remarkable.

INVERSION CURVE $\mu=0$

The data for plotting the inversion curve for nitrogen are obtained from: (a) the estimated points of zero slope on the isenthalpic curves of Fig. 1; (b) the points of zero μ on the isenthalpic curves of Fig. 2; and (c) the points of zero μ on the isopiestic curves of Fig. 3. These data are plotted in Fig. 4. The three groups of data are mutually consistent.

To this are added data from the work of Deming and Shupe⁹ to serve as a guide in connecting the upper and lower branches of the inversion curve. This carries the meeting point M of the two branches to a higher pressure than our data alone had suggested. This is in agreement also with the results of Porter's¹⁰ analysis of the experimental data of Amagat on nitrogen.

Along the upper branch the data of Deming and Shupe⁹ fall consistently near our curve, but below M their data diverge from it.

The data from this smooth curve have been picked off and are assembled in Table III. The maximum pressure is 376 atmospheres falling at 40°C.

The data for the low pressure end of the upper branch were obtained by a moderate extrapolation, and lead quite definitely to the indicated

TABLE III. Data from the inversion curve, $\mu=0$.

$t^\circ\text{C}$ Upper	p (atmos.)	$t^\circ\text{C}$ Lower	$t^\circ\text{C}$ Upper	p (atmos.)	$t^\circ\text{C}$ Lower
348.0	1		212.5	220	-117.2
330.0	20	-167.0	187.0	260	-96.4
299.6	60	-162.4	158.7	300	-68.7
277.2	100	-156.5	121.3	340	-35.3
256.5	140	-148.0	93.7	360	-10.0
235.0	180	-134.7	40.0	376	+40.0

turn upward. Ignoring the upward turn shifts the 1 atmosphere reading to 334°C. In some of our unpublished inversion curves for nitrogen-helium mixtures the low pressure ends of the upper branches have been determined with greater certainty than in nitrogen, but show no upward turn at low pressure. This casts doubt upon the reality of the upward turn in nitrogen.

The low temperature branch is shown also in Fig. 1 since the isenthalps in this part of the field are plotted without relative displacement. This part of the nitrogen curve resembles that for air² more closely than the straighter curve for argon.⁵ Nitrogen and air are the only substances for which parts of both branches of the inversion have been measured. These two inversion curves resemble each other strongly.

In the group of substances (air, O₂, A, CH₄, CO) whose critical temperatures are above that of N₂ the upper branch of the inversion curve falls largely or completely above our temperature range. In the group of substances (Ne, H₂, He) whose T_c 's fall below that of N₂, the lower branch of the inversion curves falls completely below our temperature range. The fall in p_c accompanying that in T_c , is estimated to bring

¹⁰ A. W. Porter, Phil. Mag. (6) 19, 891 (1910).

the whole upper branch of H₂ within our temperature and pressure range.

SPECIFIC HEAT C_p

The data on the specific heat of nitrogen are much more satisfactory than those for argon.

Deming and Shupe⁹ select a series of values of C_p at one atmosphere to cover the range -70 to 600°C. For the sake of ready comparison we have used their values to spread C_p over our pressure range by the method described in the air articles.^{1, 2} These values were plotted in Fig. 5, and the data of Table IV were read from the smooth curves of the working drawing. C_p at 1 atmos. cannot be spread at low temperatures because of the conditions set up by the critical state as explained earlier in detail.^{1, 2}

The values of C_p calculated by Deming and Shupe⁹ and those measured by Mackey and Krase¹¹ are compared with ours in Table V which contains a representative group of values selected to cover the common field. The data of Deming and Shupe are in italics, of Mackey and Krase in black face, and of the writers in ordinary type. The two former have been reduced to cal./g°C by the divisor 28.025 given by Deming and Shupe.

Examination of Table V shows agreement within the expected error. Our variations from Deming and Shupe show no regular trend,

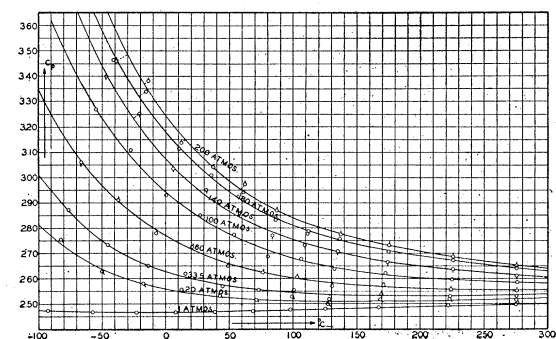


FIG. 5. C_p as a function of t at constant pressure.

¹¹ Mackey and Krase, J. Ind. and Eng. Chem. 22, 1060 (1930).

TABLE IV. C_p in cal./g°C as a function of pressure and temperature.

p	$t^\circ\text{C}$	-100	-50	0	50	100	150	200	300
1		.2473	.2466	.2466	.2469	.2476	.2484	.2490	.2501
20		.2813	.2636	.2557	.2522	.2510	.2507	.2510	.2523
33.5		.3010	.2748	.2626	.2569	.2543	.2533	.2530	.2538
60		.3345	.2967	.2769	.2658	.2601	.2573	.2560	.2556
100			.3233	.2942	.2775	.2680	.2627	.2602	.2581
140			.3438	.3071	.2865	.2754	.2687	.2648	.2605
180			.3577	.3179	.2943	.2810	.2735	.2688	.2629
200				.3243	.2986	.2841	.2759	.2706	.2690

TABLE V. Comparison of C_p for nitrogen, data from Deming and Shupe⁹ (italics) Mackey and Krase¹¹ (black face) and authors (ordinary).

p	$t^\circ\text{C}$	-50	0°C	50	100	150	200	300
1		0.2466 <i>.2466</i> <i>.2466</i>	0.2466 <i>.2466</i> <i>.2466</i>	0.2469 <i>.2469</i> <i>.2469</i>	0.2476 <i>.2476</i> <i>.2476</i>	0.2484 <i>.2483</i> <i>.2483</i>	0.2490 <i>.2490</i> <i>.2490</i>	0.2501 <i>.2501</i> <i>.2501</i>
20		.2636 <i>.2629</i> <i>.2629</i>	.2557 <i>.2569</i> <i>.2569</i>	.2522 <i>.2537</i> <i>.2537</i>	.2510 <i>.2519</i> <i>.2519</i>	.2507 <i>.2510</i> <i>.2510</i>	.2510 <i>.2516</i> <i>.2516</i>	.2523 <i>.2519</i> <i>.2519</i>
50					.2573 <i>.2573</i> <i>.2573</i>			
60		.2967 <i>.2978</i> <i>.2978</i>	.2769 <i>.2794</i> <i>.2794</i>	.2658 <i>.2662</i> <i>.2662</i>	.2601 <i>.2601</i> <i>.2601</i>	.2573 <i>.2573</i> <i>.2573</i>	.2560 <i>.2566</i> <i>.2566</i>	.2556 <i>.2551</i> <i>.2551</i>
100		.3233 <i>.3226</i> <i>.3226</i>	.2942 <i>.3012</i> <i>.3012</i>	.2775 <i>.2755</i> <i>.2755</i>	.2680 <i>.2669</i> <i>.2669</i>	.2627 <i>.2626</i> <i>.2626</i>	.2602 <i>.2608</i> <i>.2608</i>	.2581 <i>.2580</i> <i>.2580</i>
200			.3243 <i>.3307</i> <i>.3307</i>	.2986 <i>.2990</i> <i>.2990</i>	.2841 <i>.2826</i> <i>.2826</i>	.2759 <i>.2733</i> <i>.2733</i>	.2706 <i>.2701</i> <i>.2701</i>	.2690 <i>.2640</i> <i>.2640</i>

averaging only 0.2 percent with a maximum of 2.8 percent. These are about the same as the differences shown on the plot between the curves and the unsmoothed values. Our values of C_p are uniformly larger than those of Mackey and Krase by an average of 0.6 percent with a maximum of 1.1 percent.

Such agreement between data obtained by three radically different methods justifies considerable confidence in the results. It adds also to the confidence with which the values of Deming and Shupe at higher temperatures and pressures may be used.

It is a pleasure to acknowledge our indebtedness to the Wisconsin Alumni Research Foundation for financial aid providing for relief from teaching and for adequate assistance.

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We plan to measure next mixtures of argon with helium and of argon with nitrogen, and to make a thorough study of carbon dioxide.