[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Joule-Thomson Effects in Hydrogen at Liquid Air and at Room Temperatures[1]

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Hydrogen has not been included among those gases for which extensive and reliable measurements of Joule-Thomson coefficients have been carried out.[1a] Some *PVT* data on hydrogen are available, and have been tabulated, and smoothed, by Deming and Shupe,[2] from which Joule-Thomson coefficients may be calculated, but these data are not very reliable over any very wide range of temperature and pressure.

In order to obtain data from which we could compute molal heat contents of hydrogen, as a function of its pressure, at several temperatures, we have measured Joule-Thomson effects in hydrogen, with the apparatus described by Johnston.[3] The method consists, essentially, in measuring the temperature drop when high pressure hydrogen is expanded through a needle valve made from thermally non-conducting materials.

Measurements were made for pressures up to 200 atmospheres and for isotherms at 64, 69, 75, 80 and 288°K.

The present paper reports preliminary results.

Purity of the Hydrogen

The runs were begun with hydrogen of very high purity (less than 0.01 mole per cent. of nitrogen as the only significant impurity), which was prepared by evaporating liquid hydrogen. This hydrogen was recycled, and used over and over again during the first seventy-five or eighty runs. We now suspect that nitrogen impurity may have risen to a few tenths of one per cent. for some of this group of runs but, unfortunately, no further analyses were made on this gas. Our suspicions are based on later findings, that hydrogen in the compressor cycle becomes slowly contaminated by nitrogen which diffuses through the gas holder oil. (Oxygen diffusion, on the other hand, occurs to only an insignificant degree.) The contamination that may have been present during this earliest group of runs is not necessarily progressive with the run number because hydrogen which was lost from time to time, through leaks in the valve stem packing or the compressor piston rod packing, was replaced by more of the pure hydrogen from pure storage cylinders.

When the supply of pure hydrogen was exhausted we continued the runs with ordinary (unliquefied) hydrogen from the ordinary storage cylinders. Nitrogen contamination in this hydrogen varied between one and two-tenths of one per cent. (with oxygen negligible). Any difference in results obtained with this hydrogen and with that used previously was not immediately noticeable to us.

Beginning with run 205 analytical checks were made on the purity of the hydrogen used in the runs. Ordinary tank hydrogen was used, except as noted below, and the nitrogen impurity never exceeded 0.2 of 1%.

Runs 238 to 243 inclusive were run with hydrogen to which nitrogen was purposely added to bring the nitrogen contamination to 0.7 of 1%, in order to get an estimate of the possible influence of this impurity. Results indicate (*cf.* Figs. 2 and 3) that nitrogen contamination raises the ΔT's slightly but that the effect is small even for 0.7 of 1% nitrogen. This result is similar to that found by Roebuck and Osterburg[4] in measurements of the Joule-Thomson effect in helium. These authors found that nitrogen influence was almost negligible up to about 10% nitrogen in helium. We may conclude from our own observations that the influence of nitrogen in hydrogen will have been negligible for those of our runs in which nitrogen contamination cannot have exceeded 0.2 of 1%.

However, nitrogen contamination produces trouble of a different sort in high pressure runs at the lowest temperatures. We experienced this trouble first with run 229 (a 64° run at 102 atm.) in which both pressures and ΔT's fluctuated badly so that we were unable to establish good equilibrium. The same trouble was experienced in a repeat run—run 230. We suspected that solid nitrogen was forming in the valve as a result of the temperature drop that accompanied the expansion. We confirmed this by runs 231 (34 atm. at 64°) and 232 (102 atm. at 75°) and 233 (return to 102 atm. and 64°). In runs 231 and 232 (for which the outlet temperatures remain above 50°K.) no trouble was experienced. Run 233 (for which the outlet temperature was 42°K.) brought a repetition of the difficulty. Analysis of the hydrogen after this run indicated 0.10 of 1% nitrogen, which corresponds to 0.8 mm. of nitrogen partial pressure in the expanded gas and exceeds the saturation vapor pressure over solid nitrogen by a factor of more than two. All of the remaining runs at 64° (runs 244 to 254 inclusive) were made with hydrogen in which the impurity was reduced below 0.01 of 1% by passing the compressed hydrogen through char-

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(1a) *Cf.* ref. 1 of Johnston, THIS JOURNAL, **68**, 2362 (1946); also *cf.* Hoxton, *Phys. Rev.*, **13**, 438 (1919), for a bibliography of earlier work.

(2) W. E. Deming and L. E. Shupe, *ibid.*, **40**, 848 (1932).

(3) H. L. Johnston, THIS JOURNAL, **68**, 2362 (1946).

(4) J. R. Roebuck and H. Osterburg, *Phys. Rev.*, **43**, 60 (1933).

coal, under pressure, at liquid air temperature.[5] No difficulty was experienced after this.

We also gave consideration to error that might be introduced by possible condensation of nitrogen on the high pressure side of the expansion valve. Reference to the published data of Verschoyle[6] indicates, however, that no liquid phase could form for nitrogen percentage lower than about 1.5, at any of our working pressures and temperatures.

Valve and Apparatus Changes

Runs 1 to 38 were made with the lignum vitae valve seat.[3] Runs 39 to 98 were made with the "first lucite valve." This valve was broken through an accident and replaced by an identical valve referred to as the "second lucite valve." Runs 99 to 256 were all made with this latter valve.

When the apparatus was reassembled, after replacing the first lucite valve, the glass dewar in the expansion chamber was broken while soldering the lid. This was not known until the apparatus was opened following run 125. Repeat runs at room temperature (runs 99 to 114, inclusive) agreed reasonably well with those made earlier, for high flow rates, but showed some disagreement at low flow rates. However, new runs at 187 atm. and at 204 atm. (runs 116 to 121 inclusive) yielded ΔT's that were considerably smaller than were expected. This was also true of 170 atm. runs (runs 122–125) which yielded ΔT's about ten per cent. smaller than were measured previously. There was also a marked dependence on flow rate (*cf.* runs 124 and 125).

We make the assumption that correct ΔT's fall off in the *same proportions*, in going from 170 to 204 atm., as are exhibited here among the obvi-

TABLE I

JOULE–THOMSON EFFECTS IN HYDROGEN OVER THE PRESSURE RANGE 250 TO 3000 P.S.I. AND FOR INLET TEMPERATURES OF 64, 69, 75, 80 AND 288 °K.

Run	Press. atm. int. atm.	Flow cubic meters/ minute	Inlet T, °K.	ΔT, °C.
1	34	1.70	288	0.98
2	68	1.70	288	1.94
3	102	1.70	288	3.29
4	136	1.70	288	4.37^{ac}
5	170	1.70	288	5.65^{ac}
6	170	1.00	288	5.62^{ac}
7	170	0.57	288	5.86^{ab}
8	170	.08	288	5.29^{ab}
9	136	.09	288	4.16^{ab}
10	102	.06	288	2.96^{ac}
11	68	.13	288	1.96^{ac}
12	34	.13	288	0.83^{ac}
13	34	.40	288	1.01^{ac}
14	68	.43	288	2.09^{ac}
15	102	.43	288	3.32^{ac}
16	136	.43	288	4.48^{ab}
17	136	.85	288	4.21^{ab}
18	102	.85	288	2.89^{ac}
19	68	.85	288	1.95^{ab}
20	34	1.00	288	0.85^{ab}
21	68	1.70	288	1.83^{ab}
22	68	1.70	288	1.91^{ac}
23	68	0.85	288	1.89^{ab}
24	68	1.75	288	1.96^{ab}
25	68	1.75	288	1.98^{ac}
26a	68	1.70	288	1.95^{ac}
26b	68	0.85	288	2.11^{ac}
26c	68	1.70	288	2.06
27	68	0.85	288	2.13
28	68	.57	288	2.10^{ac}
29	68	.40	288	2.00
30	68	.17	288	2.13
31	68	.17	288	2.15
32	68	.17	288	2.08
33 (Run lost)				
34	68	1.00	288	1.88
35	68	1.70	288	1.91
36	34	0.43	75	−8.34
37	68	.57	75	-14.7^{ac}
38 (Run lost)				
39	68	1.70	288	1.91
40	68	0.50	288	2.06
41	68	1.70	288	1.86
42	68	0.13	288	1.99
43	170	1.70	288	5.44^{aa}
44	170	0.43	288	5.71
45 (Run lost)				
46	136	.57	75	−19.46
47	153	.57	75	-19.7^{aa}
48a	102	.57	75	−18.53
48b	68	.57	75	−15.4
49	85	.51	75	−17.27
50	51	.51	75	-12.05^{aa}
51	34	.61	75	-8.52^{aa}
52	17	.57	75	−4.25
53 (Run lost)				
54	153	.21	75	−19.1
55	136	.23	75	-19.37^{ab}
56	102	.20	75	−17.89
57	85	.18	75	-16.92^{ac}
58	68	.17	75	−14.83
59	51	.18	75	−12.74
60	34	.24	75	-8.55^{aa}
61	17	.21	75	−4.58
62	170	.21	69	−21.38
63 (Run lost)				
64	34	.17	80	-6.85^{aa}
65	34	.20	69	−10.18
66 (Run lost)				
67 (Run lost)				
68 (Run lost)				
69	153	.18	80	−18.46
70	136	.21	80	-18.85^{aa}

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(5) No more than two or three per cent. of the ortho hydrogen is converted into para hydrogen during this process and it converts back to its normal percentage after standing overnight in storage cylinders. This comment is based on our own observations, to be reported in a later paper.

(6) T. T. H. Verschoyle, *Trans. Roy. Soc.*, **A230**, 189–220 (1931).

TABLE I (*Concluded*)

Run	Press. atm. int. atm.	Flow cubic meters/ minute	Inlet T, °K.	ΔT, °C.
71	102	.20	69	−20.39
72	102	.18	80	−16.58[ac]
73	68	.21	69	−17.05
74	68	.20	80	−12.73
75	136	.21	69	−21.63[aa]
76	153	.23	69	−21.67
77	85	.21	69	−19.09
78a	51	.21	69	−14.27[aa]
78b	51	.21	80	−10.97[ab]
79	85	.20	80	−15.86
80	136	.17	80	−18.69
81	119	.20	80	−17.91
82	119	.20	75	−19.72
83	119	.21	69	−21.68[ac]
84	170	.20	69	−21.69[aa]
85	17	.23	69	− 5.41[aa]
86	17	.09	80	− 3.8[aa]
87	17	.20	80	− 3.83
88	170	.20	75	−19.72[aa]
89	170	.20	80	−17.85
90	170	.09	80	−17.7
91	170	.09	75	−19.6
92	170	.09	69	−21.1
93–98				[b]
99–114				[c]
115	34	.85	80	− 6.6[d]
116	187	.20	69	−18.33[e]
117	187	.17	75	−17.18[e]
118a	187	.17	80	−15.2[e]
118b	204	.20	80	−14.74[e]
119	204	.20	75	−16.41[ac,e]
120	204	.20	69	−18.76[e]
121	187	.20	69	−18.92[e]
122	170	.20	69	−18.83[aa,e]
123	170	.20	75	−17.83[e]
124	170	.09	80	−15.9[aa,e]
125	170	.57	80	−18.45[aa,e]
205	68	.85	75	−14.04
206–207 (Runs lost)				
208	34	.85	75	− 8.07
209	68	.85	75	−14.34[aa]
210 (Run lost)				
211	34	.85	75	− 7.76
212	68	.85	75	−14.08
213	68	low	75	−14.33[aa]
214	136	0.85	75	−18.91
215	187	.85	75	−18.37[aa]
216	68	.85	75	−14.12
217	136	.85	75	−19.04
218	136	1.27	75	−19.45
219	136	0.20	75	−19.14
220	136	.21	69	−20.65[aa]
221	68	.10	69	−16.48
222	68	.08	64	−19.65
223	17	.08	64	− 5.52
224	17	.20	64	− 5.51
225	34	.20	64	−10.92[aa]
226	51	.23	64	−15.49
227	68	.15	64	−18.98
228	85	.23	64	−20.95
229	102	.18	64	−21.87[aa]
230	102	.17	64	−22.25[aa]
231	34	.20	64	−10.93
232	102	.25	75	−18.29
233	102	.25	64	−22.19[aa]
234	68	.20	75	−14.82[aa]
235	34	.31	75	− 7.86
236	102	.62	75	−18.04
237	187	.75	75	−19.09
238	187	.62	75	−19.91[g]
239	102	.75	75	−18.59[g]
240	68	.62	75	−14.92[g]
241	34	.51	75	− 8.91[g]
242	136	.51	75	−19.65[g]
243	51	1.02	69	−13.75[g]
244	149	0.45	64	−23.46
245	119	.17	64	−23.41
246	102	.28	64	−22.26
247	197	.23	64	−21.48
248	187	.20	64	−21.73
249	170	.20	64	−22.60
250	136	.25	64	−23.28
251	197	.25	64	−21.14
252	127.5	.20	64	−22.67
253	127.5	.20	64	−23.38
254	34	.23	64	−10.84[aa]

[aa] Fluctuations in readings due to unsatisfactory control of operating conditions, or failure to extend runs to certain thermal equilibrium. (Plotted as large circles on the graphs.) Five minute individual reading of ΔT's showed deviations of more than a microvolt from the mean.

[ab] Thermal equilibrium had apparently not been reached.

[ac] Extended for less than thirty minutes after thermal equilibrium had apparently been reached.

[b] Poor pressure and temperature control, with erratic results, apparently due to some oil that had reached the valve seat and been frozen there.

[c] Runs 99 to 114 were made at room temperature just after installation of the "second lucite valve." Later found that glass dewar in expansion chamber had been broken when apparatus was reassembled.

[d] This run is included in the table (but not plotted in Fig. 3) in order to show the effect of the broken dewar in considerably reducing the measured ΔT's in the runs at liquid air temperature.

[e] Runs 116–125, likewise made with the broken dewar and obviously low, are entered in the table because they show a progressive falling off in ΔT between 170 and 204 atm. The 187 and 204 atm. runs are plotted in Figs. 2, 3 and 4 by "correcting" them through the assumption that they should bear the same ratios to correct 170 atm. values (previously determined) as they here show toward the incorrect 170 atm. values of runs 122–125. Justification for this treatment is provided in later runs with a new dewar in the apparatus (following run 205). We did not know that the dewar was broken until some weeks after the 99–125 series of runs was completed. At the time we attributed the apparent errors to reduction in length of the original 15 meter coil when the apparatus was disassembled after Run 98. This coil was shortened to 7.5 meters when the liquid air trap was inserted but was restored to its original 15 meters following the 99–125 series.

[f] Numberings 126–199 were omitted in the run designations. Runs 200–204, inclusive, were made with a second dewar which was broken while assembling the apparatus. Results were without significance.

[g] These runs were carried out with hydrogen containing 0.7% nitrogen in order to obtain a direct determination of nitrogen influence on the Joule–Thomson cooling.

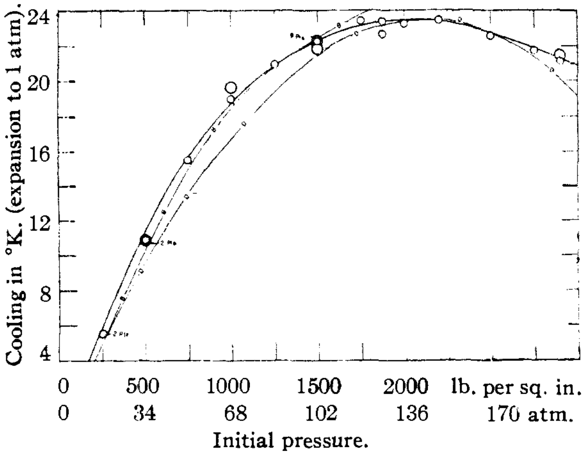

Fig. 1.—Joule–Thomson cooling in hydrogen from an initial 64°K.: experimental, this research, —O—◯—; O, points with good temperature and pressure control; ◯, points of lesser accuracy. Computations from existing charts and tables; Brickwedde, —B—; Deming and Shupe, —D—.

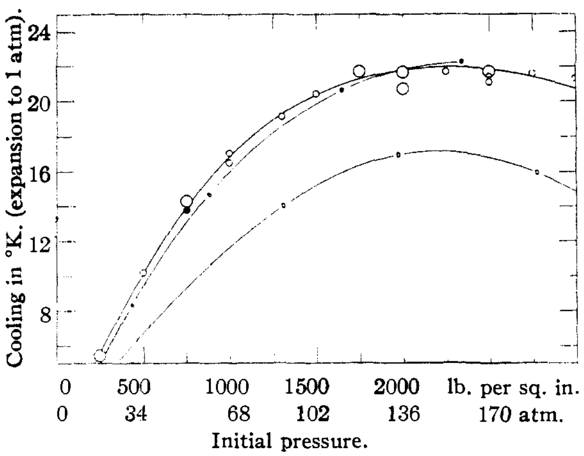

Fig. 2.—Joule–Thomson cooling in hydrogen from an initial 69°K.: experimental, this research, -O-◯-●-◌-; O, point with good pressure and temperature control; ◯, point of lesser accuracy; ◌, *cf.* footnote [e] of Table I; ●, 0.7% N_2 in H_2. Computations from existing charts and tables: Brickwedde, —B—; Deming and Shupe, —D—.

ously incorrect ΔT's. By use of this assumption we obtain the "corrected" values for the 187 and 204 atm. runs that are plotted as broken circles for the 69, 75 and 80° isotherms. Later data (runs 215 and 237) confirm this treatment for the 75° isotherm. The 64° isotherm, taken after the broken dewar was replaced, shows clearly the existence of the maximum at the position at which it is located on the other low temperature isotherms, for which we used the *relative* values above 170 atm., as described above. This confirms the essential correctness of the treatment we employed for those isotherms.

Runs 205 to 256 inclusive were made after the broken dewar was replaced by a new one.

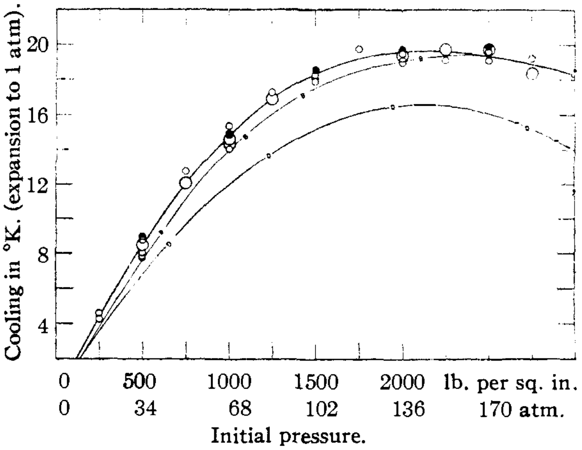

Fig. 3.—Joule–Thomson cooling in hydrogen from an initial 75°K.: experimental, this research, -O-◯-●-◌; O, point with good pressure and temperature control; ◯, point of lesser accuracy; ◌, *cf.* footnote *e* of Table I; ●, 0.7% N_2 in H_2. Computations from existing charts and tables: Brickwedde, —B—; Deming and Shupe, —D—.

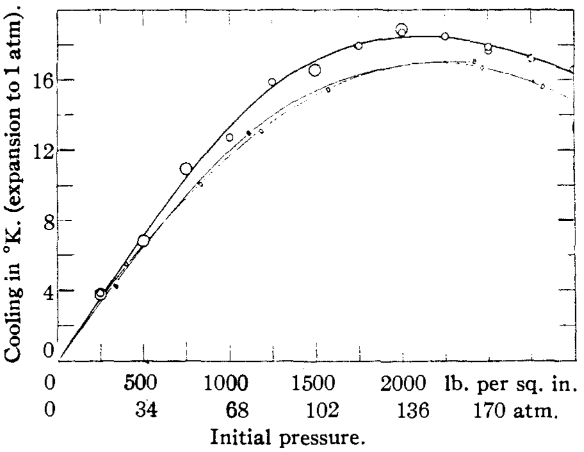

Fig. 4.—Joule–Thomson cooling in hydrogen from an initial 80°K.: experimental, this research, -O-◯-◌-; O, point with good pressure and temperature control; ◯, point of lesser accuracy; ◌, *cf.* footnote [e] of Table I. Computations from existing charts and tables: Brickwedde, —B—; Deming and Shupe, —D—.

Results

Results are tabulated in Table I, and are shown graphically in Figs. 1 to 5, inclusive. Pressures in this table, and in the graphs, are gage pressures.

Table I, with its appended notes, is a complete summary of all of our data with hydrogen. Not all of the data are equally reliable. Runs 1–20 were made with independent readings on Inlet and Outlet thermocouples. ΔT's were computed by plotting the readings of the two thermocouples separately and reading the differences between smooth curves. The procedure of opposing the two thermocouples in a circuit hooked to the potentiometer, so as to read ΔT's directly, was introduced in run 21.

We were inclined, in our early runs, to terminate the runs too soon, on the basis of a misapprehension concerning the rapidity with which thermal equilibrium is reached in the expansion chamber. Eventually, we adopted the procedure of continuing all runs until ΔT's were constant, within rather close limits, for thirty minutes or more.

No cryostat bath was used in the runs at room temperature. As a consequence the actual temperatures at which runs were made varied from 12 to 25°. The ΔT's recorded in the table have been corrected to an inlet temperature of 15° by means of temperature coefficients of the Joule–Thomson effects, computed from hydrogen data of state.[2] The corrections were never larger than 0.3° and were, usually, much less.

Liquid air boiling under reduced pressure was used as cryostat liquid at the four lowest temperatures. The degree of vacuum and the rate of replenishment of liquid air (to maintain a constant bath composition) were both manually controlled. The pressure was also controlled manually. As at room temperature, individual runs were corrected to the respective temperatures entered in the table. Corrections were based on preliminary isobars and isotherms plotted up from the uncorrected data, and were small.

Errors that may have resulted from inlet temperature fluctuations or from possible failure to reach thermal equilibrium, or from varying amounts of nitrogen impurity affect the precision of the data but are not systematic. We believe that the curves drawn in the graphs are reasonably accurate representations of isotherms.

The data of Table I are shown, as isotherms, in Figs. 1 to 4 inclusive. Individual points are plotted for the low temperature isotherms; but for the isotherm at 15°, for which many duplicate points were taken to test possible influence of flow rate, we have averaged the ΔT's for each pressure and plotted average values.

Comparisons with Other Data for Hydrogen

The solid curves in the figures represent our own data. The broken curves represent ΔT's computed from surveys of PVT data in the literature, or from heat content tables based on other indirect data.

Deming and Shupe[2] summarized their review of PVT data for hydrogen at various temperatures and pressures in the form of tables, which included columns in V and Δ as functions of pressure. There Δ is defined by the relationship

$$\Delta = V\,(PV/RT - 1) \qquad (1)$$

Extrapolation of the Δ's at any one temperature to zero pressure yields Δ_0, equal to the constant B in the Virial equation

$$PV = RT + BP + CP^2 + \cdots \qquad (2)$$

The constant C in the same equation—carried through the term in P^2—can be evaluated from the molal V's by the equation

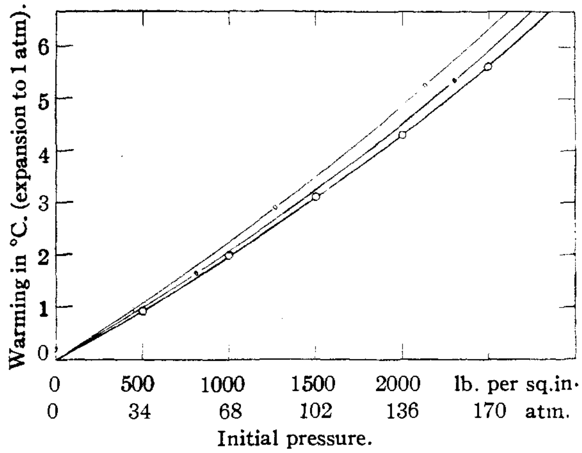

Fig. 5.—Joule–Thomson warming effects from an initial 15°: O, average of experimental points at a single pressure. Computations from existing charts and tables: Brickwedde, —B—; Deming and Shupe, —D—.

$$C = \left(V - B - \frac{RT}{P}\right) \div P \qquad (3)$$

Table II is a table of the B and C constants which we have evaluated in the manner described.

TABLE II

VIRIAL CONSTANTS B AND C FOR HYDROGEN EVALUATED FROM THE TABLES OF DEMING AND SHUPE

T, °K.	B, cc.	C, cc./atm.
58.1	−24.46	0.197
73.1	−13.81	.139
98.1	− 3.06	.073
123.1	2.90	.049
148.1	6.54	.0373
173.1	8.92	.0309
198.1	10.46	.0276
273.1	13.44	.0197
298.1	13.99	.0183

The thermodynamic equation

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \qquad (4)$$

integrates to give

$$H_p - H_0 = [B - T(\mathrm{d}B/\mathrm{d}T)]P + {}^1/_2[C - T(\mathrm{d}C/\mathrm{d}T)]P^2 \qquad (5)$$

when V and its derivative in equation 4 are replaced by the solution for V from the virial equation (equation 2). Equation (5) can also be put into the form

$$H_p - H_0 = \left[B + \frac{2}{T^2}\left(\frac{\mathrm{d}B}{\mathrm{d}\left(\frac{1}{T^2}\right)}\right)\right]P + {}^1/_2\left[C + \frac{2}{T^2}\left(\frac{\mathrm{d}C}{\mathrm{d}\left(\frac{1}{T^2}\right)}\right)\right]P^2 \qquad (6)$$

which is a more convenient form, with the use of virial constants, since plots of both B and C against $(1/T^2)$ approximate to straight lines.

Since the Joule–Thomson expansion is a process at constant heat content, ΔT may be evaluated, for any given initial pressure, by equating the calculated $(H_P - H_0)_T$ to $(H_O - H_I)_{P=0}$ where the O and I refer to outlet and inlet temperatures, respectively. We used a graph of heat contents of ideal hydrogen gas as a function of temperature in order to determine the outlet temperatures, O, that satisfied the equation.

The "Deming" curves on the four graphs were constructed from the tables of Deming and Shupe, in the manner described above. The method of calculation is rigorous within the limitations of the reliability of the PVT data and its representation by a virial equation through the term in P^2.

The "Brickwedde" curves were obtained from Mollier diagrams for hydrogen prepared by Dr. F. G. Brickwedde, R. B. Scott and H. W. Woolley of the U.S. Bureau of Standards, on the basis of his evaluation of data of state in the literature.

It will be noticed that the Deming curves indicate maxima in the low temperature isotherms, that fall at near the correct pressures but that the Brickwedde curves are generally a little nearer to the experimental ones. However, neither of the calculations is as reliable as our direct determinations.

Heat Contents of Hydrogen as a Function of Pressure

We have computed values of $(H_0 - H_P)$ from the smoothed experimental curves of Figs. 1–5. The results are shown in Table III. The pressures in this table are absolute.

Percentage Liquefaction

We have computed percentages of liquefaction, as a function of initial pressure, for 80, 75, 69 and 64° isothermals. These are computed from ΔT's read from the smoothed curves of our experimental data. The results of these computations are graphed in Fig. 6.

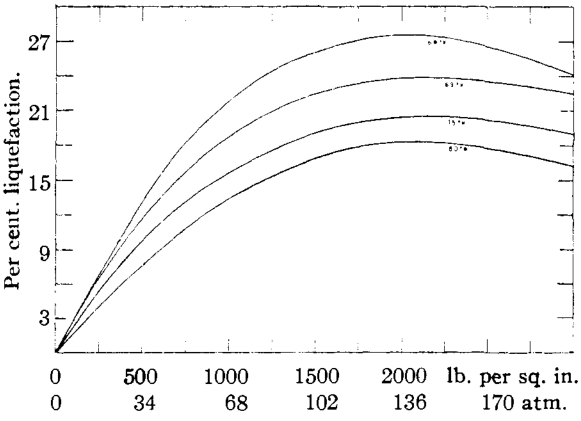

Fig. 6.—Percentage liquefaction of hydrogen as functions of pressure and temperature: isothermals from this research, —.

TABLE III

MOLAR HEAT CONTENTS OF HYDROGEN (CALORIES PER MOLE) AS A FUNCTION OF THE PRESSURE, AT 15°C. AND AT 80°K., 75°K., 69°K. AND 64°K., COMPUTED FROM OUR MEASURED JOULE–THOMSON EFFECTS

Pressure (int. atm.)	$H_p - H_0$ 15°C.	$H_0 - H_p$ 80°K.	$H_0 - H_p$ 75°K.	$H_0 - H_p$ 69°K.	$H_0 - H_p$ 64°K.
13.6	2.47	16.2	18.1	23.0	24.0
27.2	5.01	29.7	35.5	42.8	45.5
40.8	7.69	43.7	50.6	59.7	67.0
54.4	10.9	58.7	62.2	74.1	82.5
68	13.8	68.4	75.6	85.5	94.3
81.6	16.4	77.4	84.2	92.9	103.5
95.2	19.6	84.6	90.8	100.1	110.1
108.8	23.0	89.7	95.4	105.3	114.7
122.4	26.1	93.6	98.4	107.0	117.5
136	29.9	94.7	99.9	110.7	118.9
149.6	33.0	94.8	99.9	111.3	118.4
163.2	36.7	93.3	99.5	111.3	116.8
176.8	40.5	91.4	97.9	111.0	113.8
180.4	44.6	88.3	95.9	109.8	110.1
204	...	84.9	93.9	108.4	106.3

It is interesting to note that these curves indicate relatively little difference in percentage liquefaction over the pressure range 102 to 204 atm. The optimum pressure, from the standpoint of percentage yield appears to be at about 150 atm. The maximum percentage of liquefaction, at 69°K., is just under 24%. This temperature corresponds closely to that at which it is feasible to operate a hydrogen liquefier with liquid air boiling under reduced pressure.

Experience with hydrogen liquefaction in our own laboratory is in good agreement with the above figures. We have found that the optimum pressures for liquefaction lie between about 119 and 187 atmospheres with very little difference in liquefaction rate within this pressure range. In operating our liquefier with an inlet pressure of 150 atm. we have withdrawn, as liquid, 22.5% of the hydrogen delivered to the liquefier. We were not certain of the exact temperature to which this hydrogen was precooled in our liquefier, by liquid air boiling under reduced pressure, but believe that it lay between 65 and 70°K.

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Summary

Joule–Thomson effects in hydrogen have been measured for pressures up to 204 atm. and for isotherms at 64, 69, 75, 80 and 288°K. Measurements were made with the apparatus described by Johnston.[3] The method consists, essentially, in measuring the temperature drop when high pressure hydrogen is expanded through a needle valve made from thermally non-conducting materials.

Each of the low temperature isotherms exhibits a flat maximum at 150–157 atm. pressure. The magnitudes of the Joule–Thomson cooling effects

at the several maxima are as follows: 23.4° for the 64° isotherm; 21.9° for the 69° isotherm; 19.7° for the 75° isotherm; 18.4° for the 80° isotherm.

The 15°C. isotherm rises with a slight upward inflection with an average Joule–Thomson coefficient of approximately two degrees warming per 68 atm. of pressure drop.

Comparisons are made with Joule–Thomson effects computed from hydrogen data of state and other appropriate data.

A table of heat contents, as a function of pressure and of temperature, is computed from the smooth isotherms of our data.

Curves are also given for the thermodynamic efficiency of hydrogen liquefaction as functions of temperature and pressures, computed from our measurements, of the Joule–Thomson effect. Our own experience with a hydrogen liquefier is in good agreement with these curves.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Joule–Thomson Effects in Deuterium at Liquid Air and at Room Temperatures[1]

BY HERRICK L. JOHNSTON, CARROLL A. SWANSON AND HENRY E. WIRTH

In continuation of the program begun with hydrogen,[1a] we have recently measured Joule–Thomson effects in pure deuterium. Measurements were made for pressures up to 190 atmospheres and for temperatures of 64, 69, 75, 80 and 298°K.

Purity of the Deuterium

The deuterium used was prepared by the electrolysis of 99.8% pure heavy water. The deuterium was collected in a small gas holder, over tri-cresyl phosphate as sealing fluid, and was stored under pressure in ordinary steel cylinders.

Oxygen contamination in the electrolytic gas was removed by passing the deuterium over platinized asbestos at 300°, and freezing out the water so formed in a liquid air trap through which the deuterium passed.

Nitrogen or air contamination was removed by passing the deuterium through charcoal at liquid air temperatures, under a pressure of 136 atmospheres. Frequent analyses for nitrogen were carried out in conjunction with the Joule–Thomson runs. For all except the 64° isotherm 0.2 of 1% was set as the maximum limit for impurity. When this limit was reached—due to nitrogen diffusion through the gas holder sealing fluid or due to entrance of air at any other part of the cycle—the gas was repurified before runs were continued. For the runs at 64°K., 0.05% was taken as the upper limit of impurity.

Tri-cresyl phosphate was selected as the gas holder sealing fluid because we have found, in another series of investigations, that the rate of diffusion of nitrogen through tri-cresyl phosphate is much lower than through oil. We have also investigated the rate of isotopic exchange between deuterium gas and tri-cresyl phosphate. In a period of two weeks deuterium which was stored over tri-cresyl phosphate in a small gas holder of the annular ring type (painted inside and out with aluminum paint) exchanged with hydrogen to the extent that the hydrogen content of the stored deuterium increased 0.32 of 1%—or about 0.02 of 1% per day. In the course of our measurements on deuterium, hydrogen contamination may have risen from the original 0.2 of 1% to as much as 0.5 of 1%. This should not be noticeable in the values obtained for the Joule–Thomson effects.

Modifications in the Cycle and in the Operating Conditions

For the Joule–Thomson measurements with deuterium we employed a Rix Type K Compressor in the cycle. This compressor has a normal delivery of 0.17 cubic meter per minute, when operating on hydrogen, and nearly all of our runs were taken with this flow rate through the valve. However, a few of the runs were made with a flow rate of 0.34 cubic meter per minute by putting a larger belt sheave on the motor. These are indicated by a footnote to Table I.

The use of tri-cresyl phosphate as gas holder sealing fluid has been mentioned. The gas holder was of the annular ring type, of fifteen cubic feet capacity and was constructed from tinned copper sheet with strap iron reinforcing.

One thousand pound and 3000 pound Crosby test gages, with 12-inch dials, were used to read the pressures, which were controlled manually. The gages were calibrated against a dead weight gage manufactured by the American Instrument Co. and calibrated by the U.S. Bureau of Standards. These gages replaced the 3000 pound turret gage with $3^{1}/_{2}''$ dial which was used in the measurements on hydrogen.

The most important changes were improvements in temperature control. The coil of 6.35 mm. o.d. copper tubing submerged in the liquid air, which had been reduced to 7.5 meters in the

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(1) Presented before the Symposium on Low Temperature Research, at the Atlantic City meeting of the American Chemical Society, April 10, 1946.

This paper is based on work performed under contract W-7405-eng-93 for the Manhattan Project by the Chemistry Department, The Ohio State University, and the information contained herein will appear in Division III of the Manhattan Project Technical Series.

(1a) H. L. Johnston, Irving I. Bezman and C. B. Hood, THIS JOURNAL, **68**, 2367 (1946).