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Some Physical Properties of Compressed Gases, III. Hydrogen

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The compressibility data on hydrogen taken at the Reichsanstalt, the Leiden, and the Fixed Nitrogen Research Laboratories have been smoothed, averaged, and extrapolated to cover the range −215°C to 500°C and to 1200 atm. A sensitive graphical scheme for getting derivatives makes possible the calculation of some physical properties of gases; those on nitrogen and carbon monoxide have been published. The properties so calculated are specific volume, density, temperature and pressure expansion coefficients, fugacity, C_p, C_p-C_v, C_v, and μ. These are exhibited in graphs and a table that cover the temperature and pressure ranges mentioned above, except that it was not possible to calculate heat capacities and Joule-Thomson coefficient below −75°C. The expansion coefficients $(T/v)(dv/dT)_p$ and $-(p/v)(dv/dp)$ decrease monatonically from unity as the pressure increases from 0 to 1200 atm., along all isotherms within the range studied. This is in contrast with the behavior of nitrogen and carbon monoxide; with these gases the expansion coefficients along isotherms at low and ordinary temperatures at first increase with pressure, then drop back to unity and after that decrease as the pressure is increased. Fugacity is tabulated at integral temperatures and pressures throughout the entire range. The C_p-C_v vs. p isotherms all show a maximum at about 500 atm. At −75°C, C_p increases 0.95 cal./mole deg. as the pressure changes from 0 to 1200 atm. The increase ΔC_p with pressure becomes less as the temperature is raised. At 500°C it amounts to only 0.08 cal./mole deg. in 1200 atm. ΔC_p is several times smaller for hydrogen than for nitrogen or carbon monoxide. The C_v vs. t isobars from 0 to 600 atm. form a family of almost parallel curves. At higher pressures a distinct maximum appears at about 50°C. The Joule-Thomson coefficient is +0.21 deg./atm. at −75° and zero pressure; it is 0 at −75° and 25 atm., and becomes negative at higher pressures. It is 0 at −62° and zero pressure. At higher temperatures it is negative at zero pressure and decreases still further with increase in pressure. μ vs. t isobars and p vs. t μ = constant curves exhibit the calculated values of the Joule-Thomson coefficient. The compressibility data from which these calculations are made are probably for a 1:3 para ortho mixture, though there may be some question about this, particularly at extremely low temperatures. Values for the second virial coefficient are given. They follow the equation $B=17.42+314.7\ T^{-1}-2111\times 10^2 T^{-2}$ cc/mole from −75° to 500°C within 0.05 cc/mole.

THIS is the third of a series of papers on certain physical properties of compressed gases. The two previous publications[1,2] were on nitrogen and carbon monoxide, and the present one deals with hydrogen. The method used is applicable when compressibility data cover a temperature and pressure range so thoroughly that derivatives such as $(dv/dT)_p$ and $(dv/dp)_T$ can be determined in that range.

The method for determining these derivatives has been described in the two previous papers and need not be repeated. It has been supplemented,

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[1] W. Edwards Deming and Lola E. Shupe, Phys. Rev. **37**, 638 (1931).

[2] W. Edwards Deming and Lola E. Shupe, Phys. Rev. **38**, 2245 (1931). The equations, figures, and tables are numbered consecutively through this series of papers.

modified, and refined from time to time to overcome the peculiar obstacles presented by each gas. In particular, for hydrogen it was found that a power series of three and four terms, depending on the temperature range, will fit the $\Delta \equiv v(pv/RT-1)$ vs. T^{-1} isobars from $-215°$ to 300°C, so that differentiation of these gives determinations of derivatives with respect to temperature that are supplementary to the mechanical determinations. Also, the functions $T(dv/dT)_p - v$ and $-p(dv/dp)_T + v$ plotted in isobars and isotherms were found to be well adapted to smoothing the expansion coefficients $(T/v)(dv/dT)_p$ and $-(p/v)(dv/dp)_T$ and for determining $-T(d^2v/dT^2)_p$.

The derivatives $(dv/dT)_p$, $(dv/dp)_T$, $(d^2v/dT^2)_p$ are employed as in the previous work to obtain the desired physical properties, which are presented in Table III and in the graphs.

The compressibility data that we have used for this work were taken chiefly at the Reichsanstalt, the Leiden, and the Fixed Nitrogen Research Laboratories.[3–16] Bartlett's data extend from $-70°$ to 300°C and to 1000 atm. thus constitute by far the most comprehensive measurements over that temperature range. It is probable that all the observers cited were working with a 1:3 para ortho mixture of the two forms of hydrogen. The departure from the 1:3 ratio would be especially slight above -75°C, where our calculations on heat capacity are made.

It is customary to publish p, v, T data in tables showing "compressibility factors" $(pv)/(pv)_s$, the ratio of pv at the given temperature and pressure to the pv product for the same mass of gas at S. T. P. In other words, these tables show the value of pv when v is expressed in Amagat units. The ratio of $(pv)_s : RT_0$ is taken here as 0.99939, as given by William Wild[17] and the I. C. T.; and 22414.1 cc is taken for the volume of a mole of an ideal gas at S. T. P.; whence the factor required to convert volumes in Amagat units to volumes in cc/mole is $22414.1/0.99939 = 22427.8$. The factor 2.0155 converts densities in moles/cc into densities in g/cc.

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[7] Onnes, Crommelin, Smid, Comm. Phys. Lab. Univ. Leiden, No. 146b, or Verslag Akad. Amsterdam, (June 1915).

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[13] Bartlett et al, J. Amer. Chem. Soc. **50,** 1275 (1928).

[14] G. A. Scott, Proc. Roy. Soc. **125 A,** 330 (1929).

[15] Bartlett et al, J. Amer. Chem. Soc. **52,** 1363 (1930).

[16] J. A. Beattie and O. C. Bridgeman, Proc. Amer. Acad. Arts and Sci. **63,** 229 (1928) give an accurate compilation of the data published prior to Bartlett's papers, listed in isochores and isotherms. We have used this extensively.

[17] William Wild, Phil. Mag. **12,** 41 (1931).

TABLE III. *Some physical properties of compressed hydrogen derived from experimental data on compressibility.*

1 p atm.	2 v cc/mole	3 ρ g/liter	4 f atm.	5 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$	6 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$	7 ΔC_p	8 C_p calories/mole degree	9 C_v	10 Δ cc/mole
$t=-75°$ $C_p^*=6.508$ $C_v^*=4.522$									
25	661.4	3.047	25.42	.983	.1000	.08	6.59	4.53	11.19
50	336.7	5.986	51.72	.963	.9965	.15	6.66	4.54	11.90
75	228.7	8.814	78.99	.943	.9895	.22	6.73	4.55	12.53
100	174.8	11.53	107.3	.922	.9800	.29	6.79	4.57	13.16
150	121.3	16.62	167.3	.881	.9546	.40	6.91	4.61	14.41
200	94.67	21.29	232.2	.840	.9250	.49	7.00	4.64	15.57
300	68.31	29.51	379.1	.766	.8611	.64	7.14	4.72	17.78
400	55.30	36.45	552.2	.704	.8004	.72	7.23	4.77	19.93
500	47.52	42.42	756.2	.652	.7458	.77	7.28	4.80	21.91
600	42.36	47.58	996.0	.613	.6957	.80	7.31	4.86	23.86
800	35.84	56.24	1605	.544	.6063	.86	7.37	5.01	27.35
1000	31.95	63.08	2430	.487	.5337	.91	7.42	5.14	30.83
1100	30.54	66.00	2945	.460	.5013	.93	7.44	5.19	32.56
1200	29.38	68.59	3540	.435	.4718	.93	7.44	5.24	34.34
$t=-50°$ $C_p^*=6.660$ $C_v^*=4.674$									
25	744.7	2.707	25.41	.983	.9956	.06	6.72	4.68	12.40
50	378.8	5.321	51.69	.965	.9889	.12	6.78	4.69	13.01
75	257.1	7.841	78.90	.946	.9802	.17	6.83	4.70	13.58
100	196.3	10.27	107.1	.927	.9695	.22	6.88	4.72	14.15
150	135.8	14.84	166.6	.890	.9455	.30	6.96	4.74	15.22
200	105.6	19.08	230.8	.854	.9183	.38	7.04	4.77	16.23
300	75.67	26.64	374.5	.788	.8619	.48	7.14	4.82	18.14
400	60.80	33.15	541.4	.732	.8074	.55	7.21	4.87	19.94
500	51.91	38.83	735.1	.684	.7571	.60	7.26	4.90	21.66
600	46.00	43.82	959.4	.643	.7102	.63	7.29	4.94	23.33
800	38.57	52.26	1517	.579	.6277	.68	7.34	5.07	26.42
1000	34.10	59.11	2252	.524	.5592	.72	7.38	5.18	29.39
1100	32.47	62.08	2700	.502	.5284	.73	7.39	5.24	30.85
1200	31.11	64.78	3211	.478	.4996	.74	7.40	5.28	32.32
$t=-25°$ $C_p^*=6.765$ $C_v^*=4.779$									
25	827.6	2.436	25.40	.984	.9931	.05	6.81	4.79	13.28
50	420.6	4.792	51.63	.967	.9847	.09	6.85	4.80	13.82
75	285.2	7.068	78.74	.949	.9751	.13	6.89	4.80	14.35
100	217.6	9.265	106.7	.932	.9645	.17	6.93	4.81	14.87
150	150.0	13.43	165.8	.898	.9409	.23	7.00	4.83	15.81
200	116.4	17.31	229.1	.865	.9157	.29	7.05	4.85	16.71
300	82.93	24.30	369.6	.806	.8640	.37	7.14	4.89	18.39
400	66.23	30.43	531.0	.755	.8143	.43	7.19	4.92	19.93
500	56.25	35.83	716.0	.709	.7673	.46	7.23	4.95	21.44
600	49.61	40.63	927.6	.671	.7232	.49	7.26	4.99	22.90
800	41.27	48.84	1444	.608	.6472	.53	7.30	5.08	25.64
1000	36.23	55.64	2109	.558	.5821	.56	7.33	5.18	28.22
1100	34.38	58.62	2507	.536	.5526	.57	7.34	5.23	29.47
1200	32.84	61.37	2957	.516	.5253	.57	7.34	5.28	30.72
$t=0°$ $C_p^*=6.841$ $C_v^*=4.855$									
25	910.3	2.214	25.38	.985	.9917	.04	6.88	4.86	13.94
50	462.3	4.360	51.55	.969	.9825	.07	6.91	4.87	14.43
75	313.1	6.437	78.56	.952	.9724	.10	6.94	4.88	14.92
100	238.6	8.447	106.4	.936	.9617	.13	6.97	4.88	15.41
150	164.2	12.27	165.0	.905	.9391	.18	7.03	4.90	16.25
200	127.1	15.86	227.4	.875	.9156	.23	7.07	4.91	17.07
300	90.12	22.37	365.1	.820	.8678	.30	7.14	4.94	18.58
400	71.62	28.14	521.6	.774	.8211	.35	7.19	4.98	19.92
500	60.56	33.28	699.2	.730	.7771	.38	7.22	5.00	21.26
600	53.19	37.90	900.2	.693	.7355	.40	7.24	5.04	22.54
800	43.95	45.86	1383	.634	.6644	.44	7.28	5.11	24.99
1000	38.35	52.56	1993	.586	.6026	.47	7.31	5.20	27.26
1100	36.29	55.54	2354	.567	.5745	.48	7.32	5.26	28.34
1200	34.57	58.30	2757	.548	.5482	.48	7.32	5.30	29.41
$t=25°$ $C_p^*=6.892$ $C_v^*=4.906$									
25	992.8	2.030	25.36	.985	.9910	.03	6.92	4.91	14.45
50	503.8	4.001	51.48	.970	.9814	.06	6.95	4.92	14.91
75	340.9	5.912	78.37	.955	.9712	.08	6.98	4.92	15.36
100	259.6	7.765	106.1	.940	.9606	.11	7.00	4.93	15.82
150	178.3	11.30	164.1	.911	.9389	.15	7.04	4.94	16.60
200	137.7	14.63	225.8	.882	.9165	.19	7.08	4.95	17.35
300	97.26	20.72	360.9	.832	.8719	.24	7.14	4.97	18.73
400	76.97	26.18	513.2	.789	.8280	.28	7.18	5.00	19.90
500	64.85	31.08	684.6	.749	.7864	.31	7.20	5.03	21.10
600	56.75	35.52	876.8	.713	.7480	.33	7.22	5.06	22.23

TABLE III. (*Continued*).

1 p atm.	2 v cc/mole	3 ρ g/liter	4 f atm.	5 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$	6 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$	7 ΔC_p calories/mole degree	8 C_p calories/mole degree	9 C_v calories/mole degree	10 Δ cc/mole
800	46.61	43.24	1332	.656	.6799	.36	7.26	5.12	24.43
1000	40.46	49.82	1899	.611	.6211	.39	7.28	5.21	26.44
1100	38.19	52.77	2229	.593	.5944	.39	7.29	5.25	27.39
1200	36.30	55.53	2596	.576	.5689	.40	7.29	5.30	28.33
			$t=50°$	$C_p^*=6.927$	$C_v^*=4.941$				
25	1075	1.874	25.34	.986	.9906	.02	6.95	4.95	14.85
50	545.2	3.697	51.40	.972	.9809	.05	6.97	4.95	15.28
75	368.6	5.468	78.19	.958	.9708	.07	7.00	4.96	15 71
100	280.4	7.187	105.8	.943	.9605	.09	7.02	4.96	16.15
150	192.3	10.48	163.3	.916	.9394	.12	7.05	4.97	16.87
200	148.3	13.59	224.3	.890	.9181	.15	7.08	4.98	17.57
300	104.3	19.32	357.1	.843	.8762	.20	7.13	5.00	18.81
400	82.30	24.49	505.7	.802	.8349	.24	7.16	5.02	19.88
500	69.12	29.16	671.6	.765	.7960	.26	7.19	5.05	20.96
600	60.30	33.43	856.4	.731	.7595	.28	7.21	5.07	21.97
800	49.26	40.92	1289	.676	.6941	.31	7.24	5.13	23.95
1000	42.56	47.36	1820	.634	.6379	.33	7.26	5.21	25.75
1100	40.09	50.27	2126	.617	.6127	.34	7.26	5.30	26.59
1200	38.03	53.00	2463	.600	.5878	.34	7.27	5.35	27.42
			$t=100°$	$C_p^*=6.969$	$C_v^*=4.983$				
25	1240	1.625	25.31	.988	.9905	.02	6.99	4.99	15.44
50	627.8	3.210	51.26	.975	.9809	.03	7.00	4.99	15.82
75	423.9	4.755	77.88	.962	.9712	.05	7.02	5.00	16.21
100	322.0	6.259	105.2	.949	.9614	.06	7.03	5.00	16.63
150	220.2	9.155	161.9	.924	.9419	.10	7.06	5.01	17.28
200	169.3	11.91	221.6	.901	.9225	.12	7.09	5.01	17.90
300	118.4	17.02	350.6	.861	.8846	.15	7.12	5.03	18.98
400	92.90	21.70	493.2	.824	.8481	.18	7.15	5.05	19.84
500	77.59	25.98	650.3	.791	.8130	.20	7.17	5.07	20.72
600	67.35	29.92	823.1	.760	.7795	.22	7.19	5.09	21.54
800	54.53	36.96	1221	.709	.7192	.24	7.21	5.14	23.16
1000	46.75	43.12	1696	.671	.6676	.26	7.23	5.21	24.62
1100	43.88	45.93	1966	.655	.6443	.26	7.23	5.25	25.30
1200	41.49	48.58	2260	.639	.6218	.26	7.23	5.28	25.97
			$t=200°$	$C_p^*=6.993$	$C_v^*=5.007$				
25	1569	1.285	25.26	.990	.9914	.01	7.00	5.01	16.14
50	792.6	2.543	51.04	.979	.9827	.02	7.01	5.01	16.47
75	534.0	3.775	77.36	.969	.9740	.03	7.02	5.01	16.81
100	404.7	4.980	104.2	.958	.9653	.03	7.03	5.01	17.19
150	275.5	7.316	159.7	.937	.9483	.05	7.04	5.01	17.76
200	211.0	9.554	217.6	.918	.9316	.06	7.05	5.01	18.30
300	146.4	13.77	341.0	.885	.8996	.08	7.08	5.02	19.15
400	113.9	17.70	474.9	.855	.8690	.10	7.09	5.04	19.76
500	94.42	21.35	619.9	.827	.8395	.12	7.11	5.05	20.39
600	81.36	24.77	776.6	.803	.8114	.13	7.12	5.07	20.94
800	65.00	31.01	1128	.757	.7594	.14	7.14	5.11	22.05
1000	55.08	36.59	1534	.724	.7142	.15	7.15	5.16	23.06
1100	51.44	39.18	1759	.708	.6937	.16	7.15	5.18	23.54
1200	48.40	41.65	2000	.696	.6748	.16	7.15	5.21	24.00
			$t=300°$	$C_p^*=7.006$	$C_v^*=5.020$				
25	1898	1.069	25.22	.991	.9923	.01	7.01	5.02	16.53
50	957.1	2.106	50.88	.982	.9846	.01	7.02	5.02	16.84
75	643.8	3.131	76.99	.973	.9769	.02	7.02	5.02	17.14
100	487.2	4.137	103.6	.964	.9692	.02	7.03	5.02	17.50
150	330.6	6.096	158.2	.947	.9542	.03	7.04	5.02	18.04
200	252.4	7.986	214.8	.930	.9395	.04	7.05	5.02	18.52
300	174.1	11.58	334.3	.902	.9115	.06	7.06	5.03	19.24
400	134.8	14.96	462.4	.877	.8849	.07	7.08	5.04	19.70
500	111.1	18.14	599.5	.853	.8595	.08	7.09	5.06	20.15
600	95.28	21.15	745.8	.832	.8352	.09	7.10	5.07	20.54
800	75.40	26.73	1068	.794	.7899	.10	7.11	5.11	21.31
1000	63.38	31.80	1432	.761	.7494	.11	7.12	5.14	22.03
1100	58.98	34.18	1630	.746	.7314	.11	7.12	5.15	22.38
1200	55.29	36.45	1841	.734	.7146	.12	7.12	5.17	22.72
			$t=400°$	$C_p^*=7.029$	$C_v^*=5.043$				
25	2226	.9054	25.19	.992	.9932	.00	7.03	5.04	16.78
50	1122	1.797	50.76	.985	.9863	.01	7.04	5.04	17.06
75	753.4	2.675	76.72	.977	.9794	.01	7.04	5.05	17.35
100	569.5	3.539	103.1	.969	.9726	.02	7.04	5.04	17.69
150	385.6	5.227	157.1	.953	.9591	.02	7.05	5.04	18.21

TABLE III. (*Continued*).

1 p atm.	2 v cc/mole	3 ρ g/liter	4 f atm.	5 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$	6 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$	7 ΔC_p calories/mole degree	8 C_p	9 C_v	10 Δ cc/mole
200	293.7	6.862	212.8	.939	.9461	.03	7.06	5.04	18.66
300	201.7	9.992	329.5	.914	.9213	.04	7.07	5.05	19.29
400	155.5	12.96	453.5	.892	.8977	.05	7.08	5.06	19.65
500	127.8	15.78	585.0	.872	.8750	.06	7.09	5.08	19.99
600	109.1	18.47	724.1	.854	.8534	.07	7.10	5.09	20.25
800	85.77	23.50	1026	.820	.8130	.08	7.11	5.12	20.78
1000	71.65	28.13	1362	.790	.7767	.09	7.12	5.15	21.30
1100	66.50	30.31	1544	.776	.7606	.09	7.12	5.16	21.57
1200	62.19	32.41	1734	.763	.7454	.09	7.12	5.17	21.83
$t=500°$ $C_p^*=7.062$ $C_v^*=5.076$									
25	2554	.7891	25.16	.993	.9938	.00	7.06	5.08	16.94
50	1286	1.568	50.67	.986	.9876	.00	7.07	5.08	17.21
75	863.0	2.336	76.51	.980	.9814	.01	7.07	5.08	17.48
100	651.7	3.093	102.7	.972	.9753	.01	7.07	5.08	17.82
150	440.5	4.575	156.2	.959	.9632	.02	7.08	5.08	18.33
200	335.0	6.017	211.2	.946	.9514	.02	7.08	5.07	18.76
300	229.3	8.791	325.8	.924	.9290	.03	7.09	5.08	19.31
400	176.2	11.44	446.8	.904	.9076	.04	7.10	5.09	19.61
500	144.3	13.96	574.1	.886	.8873	.04	7.11	5.10	19.86
600	123.0	16.39	708.0	.870	.8678	.05	7.11	5.11	20.04
800	96.11	20.97	996.0	.842	.8313	.06	7.12	5.14	20.38
1000	79.91	25.22	1312	.814	.7987	.06	7.12	5.16	20.75
1100	74.01	27.24	1481	.802	.7839	.06	7.13	5.17	20.96
1200	69.07	29.18	1658	.787	.7701	.07	7.13	5.17	21.17

TABLE III. (*Continued*).

1 p atm.	2 v cc/mole	3 ρ g/liter	4 f atm.	6 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$	10 Δ cc/mole
$t=-215°$					
25	168.8	11.94	22.12	1.469	−19.54
$t=-200°$					
25	229.2	8.793	23.75	1.227	−10.45
50	112.9	17.85	45.73	1.319	−6.76
$t=-175°$					
25	321.2	6.275	24.84	1.088	−1.02
50	161.7	12.46	49.69	1.140	.58
75	109.8	18.35	74.88	1.101	2.47
$t=-150°$					
25	408.5	4.934	25.22	1.038	4.31
50	207.4	9.720	51.05	1.061	5.35
75	140.6	14.34	77.64	1.067	6.05
$t=-125°$					
25	493.8	4.082	25.38	1.016	7.60
50	251.3	8.020	51.58	1.023	8.43
75	170.6	11.81	78.70	1.019	8.94
100	131.1	15.37	106.9	1.010	10.27
$t=-100°$					
25	578.0	3.487	25.41	1.004	9.76
50	294.3	6.848	51.71	1.004	10.49
75	199.9	10.08	78.99	.998	11.01
100	153.2	13.16	107.3	.989	11.98

Second virial coefficients

$\Delta = v(pv/RT-1)$ in cc/mole extrapolated to zero pressure

t°C	Δ cc/mole	t°C	Δ cc/mole
−215	−24.46	0	13.44
−200	−13.81	25	13.99
−175	−3.06	50	14.43
−150	2.90	100	15.06
−125	6.54	200	15.81
−100	8.92	300	16.23
−75	10.46	400	16.49
−50	11.77	500	16.66
−25	12.72		

Care has been taken in each entry of the table to give only as many figures as we consider significant. No points are shown on the curves because they are drawn through the plotted points at practically every determination. Each property listed will now be discussed.

Specific volume v, column 2; density ρ, column 3; Δ, column 10 and Fig. 19.

$\Delta \equiv v(pv/RT-1)$ were calculated from the p, v, T data and plotted against p as isotherms and against T^{-1} as isobars. These two families of curves were smoothed and averaged simultaneously, and then extrapolated to higher pressures and temperatures. They were also extrapolated at the low temperature end the short distance from $-70°$ to $-75°$. The resulting smoothed values of Δ were read off at the desired temperatures and pressures. They are listed in column 10.

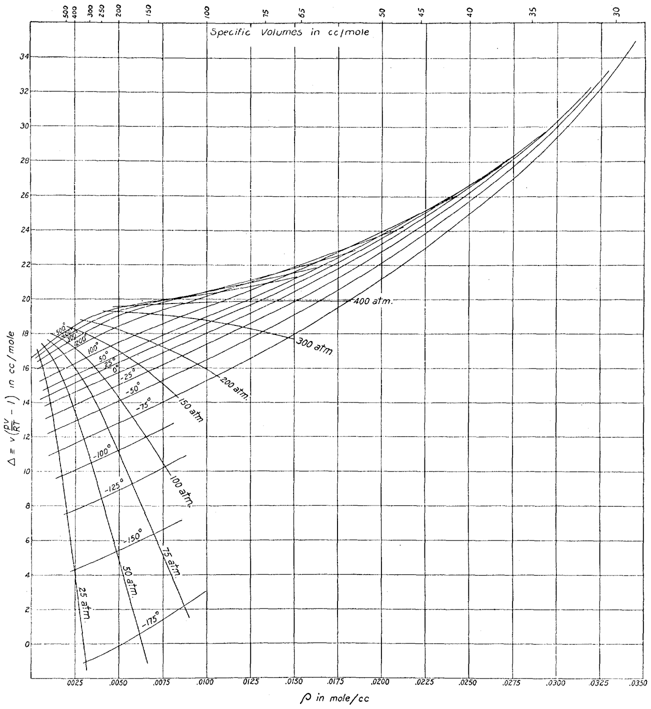

Fig. 19. Δ vs. ρ isotherms and isobars for hydrogen, plotted from column 10 of Table III. By means of this graph one can readily interpolate the p, v, T data. Thus, for $\rho = 0.005$ moles/cc and $p = 50$ atm., the temperature can be roughly estimated as $-153°$ or $-154°$C. By reading off $\Delta = 4.8$ cc/mole, at this point and using $v = 1/\rho = 200$ cc/mole, $p = 50$ atm., $R = 82.049$ cc atm./mole deg., the equation $\Delta = v(pv/RT-1)$ gives $T = 119.02°$, whence $t = 119.02 - 273.18 = -154.16$°C. Isobars above 400 atm. are omitted for clearness.

The second virial coefficients B listed at the end of Table III are the ordinates of the Δ vs. p isotherms at zero pressure, obtained by extrapolation. They follow the equation

$$B = 17.42 + 314.7T^{-1} + 2111 \times 10^2 T^{-2} \text{ cc/mole}$$

from $-75°$ to 500°C within 0.05 cc/mole. The B vs. T^{-1} curve departs considerably from a straight line. This means that second derivatives such as $(d^2v/dT^2)_p$ can not be obtained for hydrogen from van der Waals' equation, even at very low pressures.

Margenau[18] obtained the following equation for the second virial coefficient of a gas:

$$B = b(1 - 0.75y - 0.094y^2 - 0.014y^3 - 0.0019y^4 - 0.00022y^5 - 0.000022y^6 - \cdots) \qquad (27)$$

where

$$b = 2\pi Nd^3/3, \quad y = \beta^2 V_i/d^6kT = 4\pi^2N^2\beta^2V_i/9kb^2T.$$

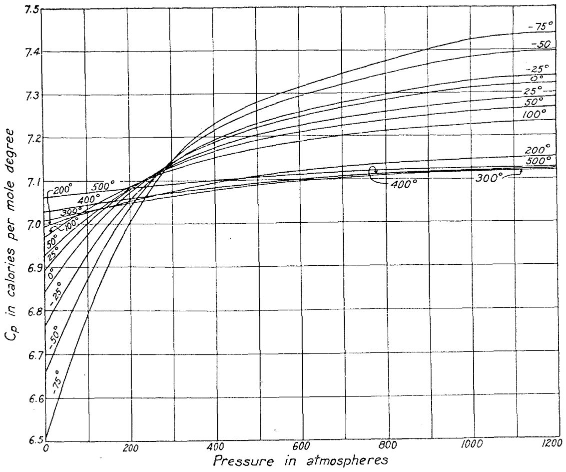

Fig. 20. Hydrogen, C_p vs. p isotherms.

β denotes polarizability of the molecule, V_i is the ionization potential. b is clearly four times the volume of N spheres of diameter d. If N is the number of molecules per mole, b is cc/mole. B can be evaluated by extrapolating the B vs. T^{-1} curve back to $T^{-1}=0$. The value so obtained is $b=17.42$ cc/mole. This with $V_i=15.34$ volts and $\beta=0.777\times10^{-24}$ cc per molecule gives $y=571.4T^{-1}$, for use in Margenau's equation. The values of B so calculated disagree with the experimental ones at the end of Table III. Margenau, having different data to compare with, reached the same conclusion for hydrogen. He pointed out that the zero point energy of H_2 and He probably renders his equation invalid for these gases. This difficulty would not be present in gases having heavier molecules. He found good agreement for N_2, CO, and several others, using the data then available. We later confirmed his conclusions for carbon monoxide[2] after determining b and B from compressibility data.

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[18] Henry Margenau, Phys. Rev. **36**, 1782 (1930).

The relation $\Delta = v(pv/RT - 1)$ when solved for v gives the specific volume for any pressure and temperature at which Δ is known; thus the values of v were calculated. The densities in column 3 are in g/cc and were obtained by dividing 2.0155 by the corresponding v in cc/mole.

The Δ vs. ρ isotherms and isobars in Fig. 19 exhibit the p, v, T data for hydrogen in a form that makes interpolation convenient. Unfortunately the isobars above 400 atm. had to be omitted for clarity; this detracts somewhat from its usefulness at high pressures. This difficulty did not appear with carbon monoxide. A large scale graph can be made by anyone desiring greater accuracy; the necessary coördinates are in Table III. Fig. 19 shows the trends of the departure of hydrogen from the perfect gas law, since Δ is a measure of this deviation.

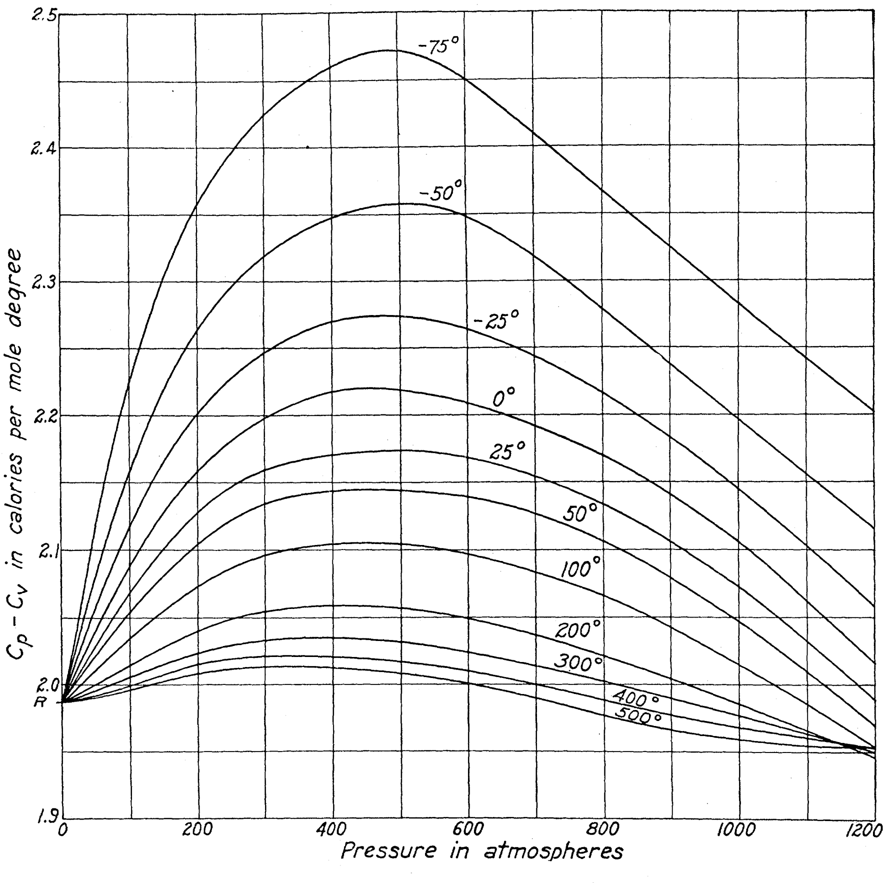

Fig. 21. Hydrogen, $C_p - C_v$ vs. p isotherms.

Fugacity f, column 4.

$\alpha \equiv (RT/pv - 1)$ were plotted in isotherms against p, and the expression

$$f = p \exp\left(-1/RT\right) \int_0^p \alpha dp \qquad (28)$$

was evaluated by mechanical integration.

Expansion coefficients $-(p/v)(dv/dp)_T$ and $(T/v)(dv/dT)_p$, columns 5 and 6.

The Δ vs. p and α vs. p isotherms and the Δ vs. T^{-1} isobars are used to get these coefficients. The two determinations of $-(p/v)(dv/dp)_T$ at each point, obtained through Eqs. (6) and (7), were plotted in isotherms against pressure. The ordinates along these smoothed curves give the values recorded in column 5 of the table.

$(T/v)(dv/dT)_p$ in column 6 were evaluated through Eq. (15). The Δ and $(d\Delta/du)_p$ needed in this equation[19] were obtained from the power series

$$\Delta = a + bu + cu^2$$

that were found to fit the Δ vs. u isobars. a, b, and c are functions of pressure. At 25, 50, 75, and 100 atm. these isobars extended through a longer temperature range and it was necessary to add another term to the series. The values of $(T/v)(dv/dT)_p$ so determined were smoothed by plotting $v[(T/v)(dv/dT)_p - 1]$ against pressure.

Both expansion coefficients $-(p/v)(dv/dp)_T$ and $(T/v)(dv/dT)_p$ decrease monotonically from unity as the pressure increases from 0 to 1200 atm., along all isotherms within the range studied. This is in contrast with the behavior of nitrogen and carbon monoxide; with these gases the expansion coefficients along isotherms at low and ordinary temperatures at first increase with pressure, then drop back to unity and after that decrease as the pressure is increased.

ΔC_p, and the heat capacity C_p, columns 7 and 8 and Fig. 20.

ΔC_p is the change in C_p caused by a change in pressure at constant temperature. It is obtained through the thermodynamic equation

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

which when integrated between 0 and p along an isotherm gives

$$C_p = C_p^* + \Delta C_p = C_p^* + \int_0^p -T(d^2v/dT^2)_p dp. \qquad (12)$$

C_p^* is the heat capacity at zero pressure, and it is necessary to assume some value for it at each temperature in order to complete the calculations. In this matter we have sought the advice of Dr. W. M. D. Bryant of the Ammonia Division of the E. I. du Pont de Nemours Company, and have proceeded in the following manner. Giauque[20] calculated the heat capacity of hydrogen from 0°K to 298.1°K by utilizing spectroscopic data. This calculation does not depend on the behavior of a rigid molecular model, but includes the slight increase in heat capacity caused by molecular stretching. The rotational energy of hydrogen at low temperatures varies markedly with the ratio

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[19] For convenience in writing derivatives, T^{-1} will be denoted by u.

[20] W. F. Giauque, J. Amer. Chem. Soc. **52**, 4821 (1930). Giauque's value at 225°K is evidently in error.

of para to ortho hydrogen. It is probable that the p, v, T data, at least those at -70°C and above, were taken with a 1:3 para ortho mixture, since the ratio changes very slowly at low pressures in the absence of a catalyst. It is not known whether the rate of change increases much with pressure.

Hydrogen does not take on its full rotational heat until it reaches about 400°K. At this temperature the vibrational heat is extremely small but it attains appreciable values with sufficient increase in temperature. At high temperatures (above 400°K), where the molecule has taken up its full rotational heat capacity, the equation[21,22,23]

$$C_p{}^* = 6.954 + \phi(6100/T) + 0.00008T \text{ cal./mole deg.} \qquad (29)$$

probably gives the most reliable values. $6.954 = 7R/2$, the translational and rotational heat. $\phi(6100/T)$ is the Planck-Einstein function $R(6100/T)^2 e^{6100/T}/(e^{6100/T}-1)^2$, which takes care of vibrational energy. The term 0.00008 T is a correction for the small stretching, and was derived by Witmer from spectroscopic data. The characteristic temperature 6100°K was obtained by Eucken also from spectroscopic data. Rasetti[24] obtained 5960°K from the Raman spectrum, and this is in good agreement.

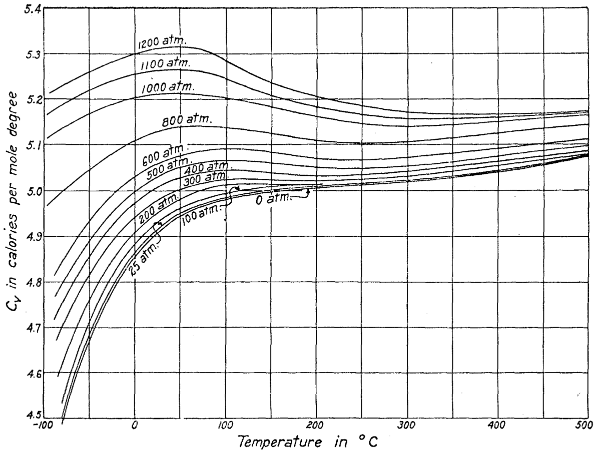

Fig. 22. Hydrogen, C_v vs. t isobars.

A curve of Giauque's values from 15°K to 298.1°K joins perfectly on to one calculated from Eq. (29) for temperatures above 400°K. Ordinates read from a curve so constructed gave the values of $C_p{}^*$ used for this work. We here express our thanks to Dr. Bryant for his advice in selecting values of $C_p{}^*$.

As with nitrogen and carbon monoxide, the ΔC_p were obtained by a mechanical integration under the $-T(d^2v/dT^2)_p$ vs. p isotherms. The ordinates along these isotherms were calculated from the Δ curves by the relation

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[21] A. Eucken, Wien-Harms Handbuch der Experimental Physik, Vol. VIII, part I, p. 445.

[22] E. Justi, Zeits. f. Tech. Mech. und Thermo. **2**, 120 (1931).

[23] E. E. Witmer, Proc. Nat. Acad. Sci., **12**, 238 (1926).

[24] F. Rasetti, Phys. Rev. **34**, 367 (1929).

$$-T(d^2v/dT^2)_p = -\frac{2u^2(d\Delta/du)_p + u^3(d^2\Delta/du^2)_p}{1+2\rho\Delta} + \frac{2pu}{R}\,\frac{(\Delta + ud\Delta/du)_p^{\,2}}{(1+2\rho\Delta)^3}. \quad (30)$$

The second derivative $(d^2\Delta/du^2)_p$ occurring here was obtained by differentiating the power series $\Delta = a+bu+cu^2$ that were found to fit the Δ vs. u isobars, and also by mechanical differentiation. These values of $-T(d^2v/dT^2)_p$ were found to agree well with determinations gotten by mechanical differentiation of the $v[(T/v)(dv/dT)_p-1]$ vs. T isobars. They were smoothed by plotting them in isobars against T^{-2} before they were plotted in isotherms against pressure for the determination of ΔC_p by mechanical integration. The factor 0.02421 converts cc atm./mole deg. into cal./mole deg.

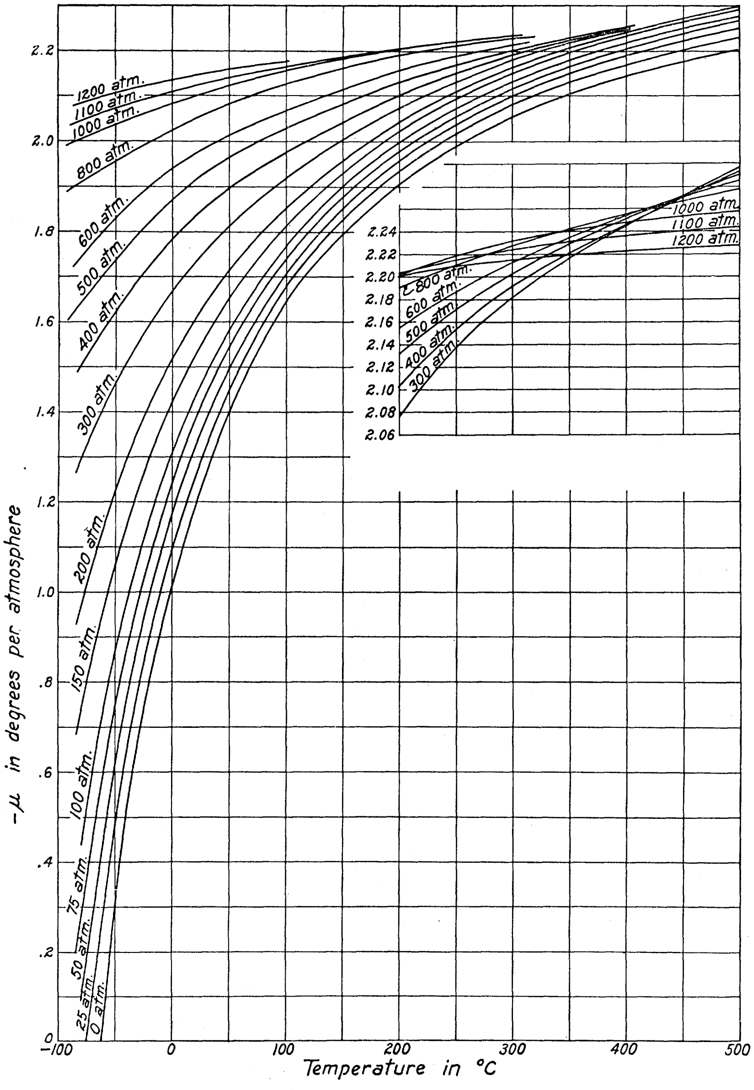

Fig. 23. Hydrogen, μ vs. t isobars.

The quantity $C_p - C_v$, Fig. 21; the heat capacity C_v, column 9 and Fig. 22.

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

Since the derivatives in columns 5 and 6 have been determined it is a simple matter to calculate $C_p - C_v$. This subtracted from C_p gives C_v. Some of the C_v vs. t isobars are drawn in Fig. 22. These are highly interesting for theoretical work on the behavior of hydrogen molecules at various temperatures and pressures.

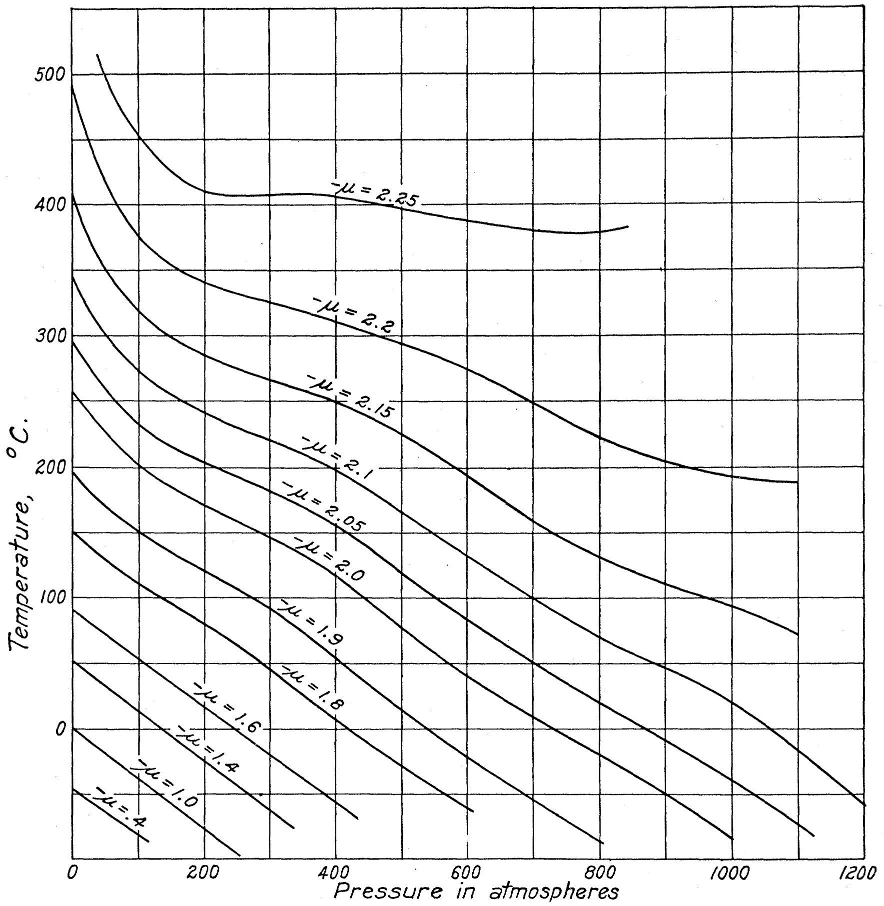

Fig. 24. Hydrogen, t vs. p, μ = constant curves. μ is given in centigrade degrees per atm. $\mu = (dt/dp)_H$.

The Joule-Thomson coefficient μ, Figs. 23 and 24.

The Joule-Thomson coefficient was calculated from

$$\mu p C_p = (T/v)(dv/dT)_p - 1 \tag{14}$$

at each point, and the values so obtained are shown in Figs. 23 and 24. The inversion temperature for zero pressure appears to be about −62°.