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Critical Temperatures, Pressures, and Volumes of Hydrogen, Deuterium, and Hydrogen Deuteride

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The critical temperatures, pressures, and volumes of H_2, HD, and D_2 have been determined by measuring short sections of P–V isotherms in the neighborhood of the critical points. The H_2 and D_2 samples were catalyzed to ortho-para equilibrium at 20.4° K and are designated e-H_2 and e-D_2. For e-H_2 the values found are $T_c=32.9_{94}$° K, $P_c=12.7_{70}$ atm, and $V_c=65.5$ cm^3 mole^{-1}. For HD the corresponding values are 35.9_{08}° K, 14.6_{45} atm, and 62.8 cm^3 mole^{-1}; for e-D_2 the values are 38.2_{62}° K, 16.2_{82} atm, and 60.3 cm^3 mole^{-1}. A method of correlating isotherm data for different substances, based on the use of graphs of log P versus log V, is described.

1. Introduction

The present paper and the accompanying one on vapor pressures and dew-point pressures [1] [3] comprise a full report of a program of determination of properties of the hydrogens undertaken at the National Bureau of Standards early in 1950. The situation with regard to critical data at that time was very similar to the situation with regard to vapor pressures above 1 atm; the field having been neglected from the time of the last Leiden measurements [2] in 1917, until very recently, when White, Friedman, and Johnston [3] published critical data for normal hydrogen, and a preliminary report [4] was made of the present work.

2. Experimental Methods

The measurements were made with an apparatus used previously in an investigation of the vapor pressure of oxygen [5]. Minor modifications are mentioned in [1]. Pressure exerted by the hydrogen in the equilibrium chamber was transmitted out of the cryostat through a small metal tube that connected to one end of a U-tube of stainless steel (½-in. outside diameter). The lower-part of the U-tube contained mercury, and the arm not filled with hydrogen contained water through which the pressure was transmitted to oil and thence to the piston gage with which pressures were measured. By means of a pump, water could be forced into or removed from the line. This caused the mercury to rise in one side of the U-tube and to fall in the other, thus varying the space available for hydrogen in the U-tube and causing material to flow into or out of the equilibrium chamber. This made it possible to measure the sample in the equilibrium chamber at different molar volumes.

The experimental data are given in tables 1, 2, and 3. All observations are numbered in chronological order, with the run number preceding the decimal point. The directly observed (unadjusted) values of temperature and pressure are given in columns 2 and 3 of each table. Temperature variation among the points of a given isotherm was small; nonetheless, corrections were made to bring each group to a common temperature. This was accomplished by using appropriate values of $(1/P)(dP/dT)$ obtained whenever possible from tables 5, 6, and 7 of [1], which give log P as a function of $1/T$. Above the range of these tables, estimated values of $(1/P)(dP/dT)$ were used. The correction is exact only where two phases are present in the equilibrium chamber, but fortunately this is the place where the corrections are most important. Adjusted values of T and P are given in columns 4 and 5 of the tables. The adjustments seldom changed the pressure by more than 1 mm Hg.

The molar volume corresponding to each observation is the effective volume of the equilibrium chamber divided by the number of moles of hydrogen present in it when the observation was made. This quantity, V, is given in column 6 of the tables. The effective volume of the equilibrium chamber and the volumes of the various parts of the pressure-transmitting line were determined in a separate series of experiments. The number of moles of sample confined in the equilibrium chamber and in the pressure-transmitting line, including the U-tube, was determined separately for each run. For each observation of a given run, the number of moles not in the equilibrium chamber was computed by means of the gas laws, and subtracted from the total number to give the quantity actually inside the chamber.

All the necessary knowledge of volumes may be obtained after the apparatus is assembled, provided the inside diameter of the U-tube is known.

If n moles of gas are confined in a volume V_1 at temperature T_1, they satisfy the equation $PV_1=nRT_1Z_1$, where the compressibility factor Z accounts for the deviation of the gas from ideality. If the volume containing the gas is not all at uniform temperature it must be divided into subvolumes. The number of moles of gas in the ith subvolume is

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[3] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Isotherms of* e-H_2

Observations of the dependence of pressure on volume in the critical region

Observation number	T (unadjusted)	P (unadjusted)	T (adjusted)	P (adjusted)	V
	° K	mm Hg	° K	mm Hg	cm^3 $mole^{-1}$
18.6a	32.8935	9654.4	32.893 ($T/T_c=0.99694$)	9653.7	52.07
18.6b	32.8933	9579.8		9579.4	55.24
18.6c	32.8933	9566.8		9566.4	58.61
19.1g	32.8936	9564.4		9563.6	60.69
18.6d	32.8932	9566.1		9565.8	62.50
19.4h	32.8897	9556.0		9560.6	62.86
19.4i	32.8943	9561.1		9559.7	66.09
18.6e	32.8933	9565.9		9565.5	66.95
19.4j	32.8938	9560.8		9559.7	70.23
18.6f	32.8933	9566.0		9565.6	71.84
19.4k	32.8936	9558.2		9557.4	76.81
19.4l	32.8936	9554.6		9553.8	80.55
18.5a	33.0455	9925.1	33.045 ($T/T_c=1.00155$)	9924.4	52.20
18.5b	33.0463	9837.0		9835.1	55.35
19.3h	33.0453	9815.2		9814.8	56.58
18.5c	33.0455	9799.7		9799.0	58.87
19.3i	33.0453	9784.2		9783.8	61.95
18.5d	33.0458	9786.7		9785.6	62.79
18.5g	33.0452	9782.5		9782.2	65.12
18.5e	33.0457	9778.8		9777.8	67.44
19.3j	33.0453	9774.5		9774.1	67.49
19.3k	33.0453	9768.7		9768.3	71.47
18.5f	33.0460	9769.3		9767.9	72.70
19.3l	33.0456	9756.3		9755.4	76.09
19.3m	33.0456	9731.6		9730.7	81.17
17.5e	33.2935	10733	33.293 ($T/T_c=1.00906$)	10732	[a] 48.76
16.12a	33.2933	10755		10755	[a] 48.77
19.2q	33.2928	10417		10417	52.21
18.4l	33.2963	10390		10385	52.26
17.5f	33.2933	10334		10334	[a] 53.49
16.12b	33.2928	10324		10324	[a] 53.50
18.4m	33.2931	10244		10244	56.04
19.2r	33.2928	10238		10238	56.52
16.12c	33.2944	10193		10191	[a] 58.99
19.2s	33.2925	10177		10178	60.24
18.4n	33.2935	10175		10174	60.47
19.2t	33.2925	10136		10137	64.97
16.12d	33.2939	10136		10135	[a] 65.63
18.4o	33.2925	10133		10134	65.74
17.5g	33.2942	10105		10103	[b] 70.68
18.4p	33.2931	10091		10091	72.40
19.2u	33.2925	10076		10077	74.47
17.5h	33.2935	10055		10054	[b] 77.56
19.2v	33.2922	10008		10009	82.38
17.5i	33.2967	9963		9958	[b] 86.28
17.5j	33.2938	9798		9797	[b] 96.60
17.5k	33.2938	9543		9542	[b] 108.67

[a], [b] No measurements of mass of material were made corresponding to the two groups of observations marked respectively by a and b. Masses were determined as described in the text, from the superposition of graphs.

TABLE 2. *Isotherms of* HD

Observations of the dependence of pressure on volume in the critical region

Observation number	T (unadjusted)	P (unadjusted)	T (adjusted)	P (adjusted)	V
	° K	mm Hg	° K	mm Hg	cm^3 $mole^{-1}$
3.16b	35.033	9844	35.033 ($T/T_c=0.97563$)	9844	59.48
3.16c	35.033	9841		9841	63.60
3.16a	35.033	9841		9841	68.10
3.16d	35.034	9843		9842	73.23
3.16e	35.034	9841		9840	81.75
5.2h	35.7499	10889	35.749 ($T/T_c=0.99557$)	10888	57.76
5.2g	35.7494	10886		10885	60.91
5.2f	35.7494	10889		10888	64.12
5.2d	35.7486	10887		10888	67.68
5.2e	35.7496	10885		10884	67.84
5.2c	35.7487	10886		10886	72.11
5.2b	35.7486	10880		10881	75.72
5.2a	35.7491	10860		10860	82.59
5.3a	35.8798	11095	35.880 ($T/T_c=0.99922$)	11095	57.83
5.3b	35.8796	11091		11092	61.04
5.3c	35.8798	11089		11089	64.68
5.3d	35.8796	11091		11092	69.36
5.3e	35.8795	11078		11079	74.15
5.3f	35.8795	11056		11057	78.75
5.3g	35.8793	11021		11022	82.68
3.17d	36.022	11319	36.023 ($T/T_c=1.00320$)	11321	59.86
3.17e	36.023	11308		11308	63.22
3.17c	36.023	11298		11298	66.89
3.17b	36.023	11257		11257	75.71
3.17a	36.023	11132		11132	86.76
4.10b	36.250	11715	36.250 ($T/T_c=1.00952$)	11715	57.88
4.10c	36.251	11684		11682	60.84
4.10a	36.251	11648		11646	65.15
4.10d	36.250	11626		11626	67.87
4.10e	36.250	11603		11603	70.61
4.10f	36.249	11565		11567	74.39
4.10g	36.249	11508		11510	79.05
4.10h	36.249	11427		11429	84.35

given by $n_iR=PV_i/T_iZ_i$, and summing over all subvolumes

$$nR=R\sum_i n_i=P\sum_i (V_i/T_iZ_i). \qquad (1)$$

With all the volumes V_i at the same known temperature (room temperature), and with enough gas in the apparatus to obtain convenient pressures, the position of the mercury meniscus in the U-tube was varied and the resulting changes in P observed. In this way the total volume occupied by the sample was found to be

$$\sum_i V_i(\text{cm}^3)=84.66-0.0968h_1, \qquad (2)$$

where h_1 was the scale reading in millimeters of the mercury meniscus in the arm of the U-tube containing hydrogen. Previously, when the apparatus had been used to measure the vapor pressure of oxygen [5], similar measurements had given 84.45 for the constant term. The agreement is considered satisfactory. Having obtained eq 2, the effective volume of the cryostat was determined by noting the pressure, first with all volumes at room temperature, and again after cooling the cryostat with liquid air, and applying eq 1 to the results. The volume was found to be 5.88 cm^3.

Once the volumes were known, the number of moles of gas confined could be determined from any set of pressure and temperature readings, provided none of the sample was condensed. Normally, such a determination was made at the completion of each run, after the cryostat had warmed to liquid-air temperature and the pressure had risen to 25 to 35 atm. The molar volume V corresponding to each individual observation of the run could then be computed by summing eq 1 over all volumes except that of the cryostat itself, and subtracting the result from the total number of moles in the system. The temperature of the U-tube was indicated by a mercury-in-glass thermometer. The table of Z-values given by Woolley, Scott, and Brickwedde [6] was used for all three gases. The table is for H_2, but was considered adequate for HD and D_2 also, in view of the fact that other quantities involved in the calculation were not known with very high accuracy.

In two instances we failed to make any measurement of the total mass of sample in the system. The two groups of observations involved are for the highest isotherm of e-H_2 and are indicated in table 1. Calculations of the molar volume were made for these observations in the usual way, except that the unknown total number of moles appeared as an arbitrary constant. Graphs of pressure versus

TABLE 3. *Isotherms of* e-D_2

Observations of the dependence of pressure on volume in the critical region

Observation number	T (unadjusted)	P (unadjusted)	T (adjusted)	P (adjusted)	V
	° K	mm Hg	° K	mm Hg	$cm^3\ mole^{-1}$
6.21c	37.1983	10708	37.199 (T/T_c=0.97222)	10709	63.74
6.21a	37.1988	10709		10709	70.60
6.21b	37.1991	10708		10708	80.73
7.4a	38.2029	13969	38.203 (T/T_c=0.99846)	13969	40.19
7.4b	38.2036	12292		12291	52.48
8.6a	38.2038	12276		12275	56.44
8.6b	38.2031	12272		12272	63.04
6.22c	38.2017	12274		12276	64.20
6.22a	38.2022	12272		12273	72.35
6.22b	38.2018	12163		12165	84.13
8.7a	38.3978	12630	38.398 (T/T_c=1.00355)	12630	54.12
8.7b	38.3979	12610		12610	57.15
8.7c	38.3978	12599		12599	60.49
8.7d	38.3977	12588		12588	64.25
8.7e	38.3977	12570		12570	68.57
8.7f	38.3977	12536		12536	73.34
7.5a	38.5556	15010	38.556 (T/T_c=1.00768)	15011	40.30
7.5b	38.5552	14236		14237	42.20
7.5c	38.5554	13654		13655	44.33
7.5d	38.5558	13295		13295	46.58
7.5e	38.5554	13106		13107	48.94
8.4a	38.5563	13003		13002	50.74
7.5f	38.5556	12991		12992	51.85
7.5g	38.5554	12952		12953	53.46
8.4b	38.5566	12907		12906	55.57
8.4c	38.5566	12866		12865	60.28
8.4d	38.5565	12827		12826	65.72
8.4e	38.5563	12742		12742	73.99
7.6a	38.8794	15981	38.880 (T/T_c=1.01615)	15982	40.37
7.6b	38.8766	15075		15082	42.40
7.6c	38.8795	14421		14422	44.67
7.6d	38.8794	14017		14018	47.05
7.6e	38.8794	13775		13776	49.53
8.5a	38.8801	13666		13666	50.86
7.6f	38.8794	13608		13609	52.66
7.6g	38.8791	13545		13547	54.50
8.5b	38.8807	13492		13491	55.91
8.5c	38.8801	13399		13399	60.87
8.5d	38.8801	13312		13312	66.54
8.5e	38.8806	13155		13154	75.23
7.7a	39.1990	16937	39.199 (T/T_c=1.02449)	16937	40.45
7.7b	39.1985	15878		15879	42.58
7.7c	39.1988	14113		14113	55.40
6.23c	39.1981	13839		13841	64.74
6.23a	39.1995	13627		13626	73.54
6.23b	39.1980	13211		13213	87.00
6.24a	40.1960	14876	40.196 (T/T_c=1.05055)	14876	74.98
6.24b	40.1959	14151		14151	89.63
6.25a	41.2076	16066	41.208 (T/T_c=1.07700)	16067	76.42
6.25b	41.2085	15020		15019	92.33

number of moles of hydrogen in the equilibrium chamber were made on transparent paper for these data (with the zero of abscissas undetermined); and a similar graph was made of the rest of the data of the isotherm, for which the zero of abscissas was known. The graphs of the "unknown" data were superposed in turn on the graph of the "known" data, and moved along the axis of abscissas until known and unknown graphs merged into a single continuous curve. By comparing the two abscissa scales the total number of moles of sample employed in each unknown run was determined.

3. Analysis of the Data

The preliminary analysis of the isotherms was carried out in the usual way by plotting P versus V for each modification of hydrogen, drawing in the liquid-vapor domes, and taking the highest point of each dome as the critical point of that particular modification. It was difficult to determine the positions of the domes with the desired accuracy, however, so we sought some method of correlating the data for the three kinds of hydrogen in order to obtain more accurate critical constants for all. If the critical temperature and pressure of each variety were known, P/P_c could be plotted versus V/V_c with all three modifications on the same graph; and, if the law of corresponding states were obeyed all the isotherms would form a single family. Since only approximate values of P_c and V_c were available, this method of correlation could be used only by a process of successive approximations. However, it was recognized that this difficulty could be avoided by taking logarithms. If log (P/P_c) were plotted versus log (V/V_c), the isotherms of the three modifications would, of course, form a single family just as they would when the variables were P/P_c and V/V_c. But a graph of log (P/P_c) versus log (V/V_c) differs from a graph of log P versus log V only by a translation of $-$log P_c along the axis of ordinates and of $-$log V_c along the axis of abscissas. Hence, if separate graphs of log P versus log V for each modification are prepared on transparent stock, it should be possible to superpose them in such a way as to form a single family of isotherms, to draw a single liquid-vapor dome for the family, and thus to obtain critical constants for the three modifications with improved absolute accuracy and much greater relative accuracy than could otherwise be obtained.

The result of applying this type of correlation is shown in figure 1. The three sets of data were initially plotted on three separate sheets of tracing cloth and superposed for viewing by transmitted light. The graphs were shifted relative to each other along the axes of coordinates until they most nearly blended into a single family. The relation between the various coordinate scales was then noted and all the data plotted on a single sheet. On this graph the liquid-vapor dome was drawn and the critical point selected. The coordinates of this point with respect to the three original graphs give log P_c and log V_c for the three modifications of hydrogen. The corresponding critical temperatures were found by substituting each value of P_c into the appropriate vapor-pressure table (table 5, 6, or 7) of [1]. The critical constants are given in table 4. Values of the compressibility factor $Z=PV/nRT$ at the critical point are included. After the critical constants had been determined, T/T_c was computed for each isotherm of figure 1, and coordinate scales in terms of log (P/P_c) and log (V/V_c) were substituted for those originally used, so that the same scales could be used for all three modifications.

TABLE 4. *Critical constants of* e-H_2, HD, *and* e-D_2

	T_c	P_c			V_c	$P_c V_c/RT_c$
	°K	mm Hg	atm	$psia$	$cm^3 mole^{-1}$	
e-H_2---	32.994	9,705	12.770	187.67	65.5	0.309
HD---	35.908	11,130	14.645	215.22	62.8	.312
e-D_2---	38.262	12,374	16.282	239.27	60.3	.312

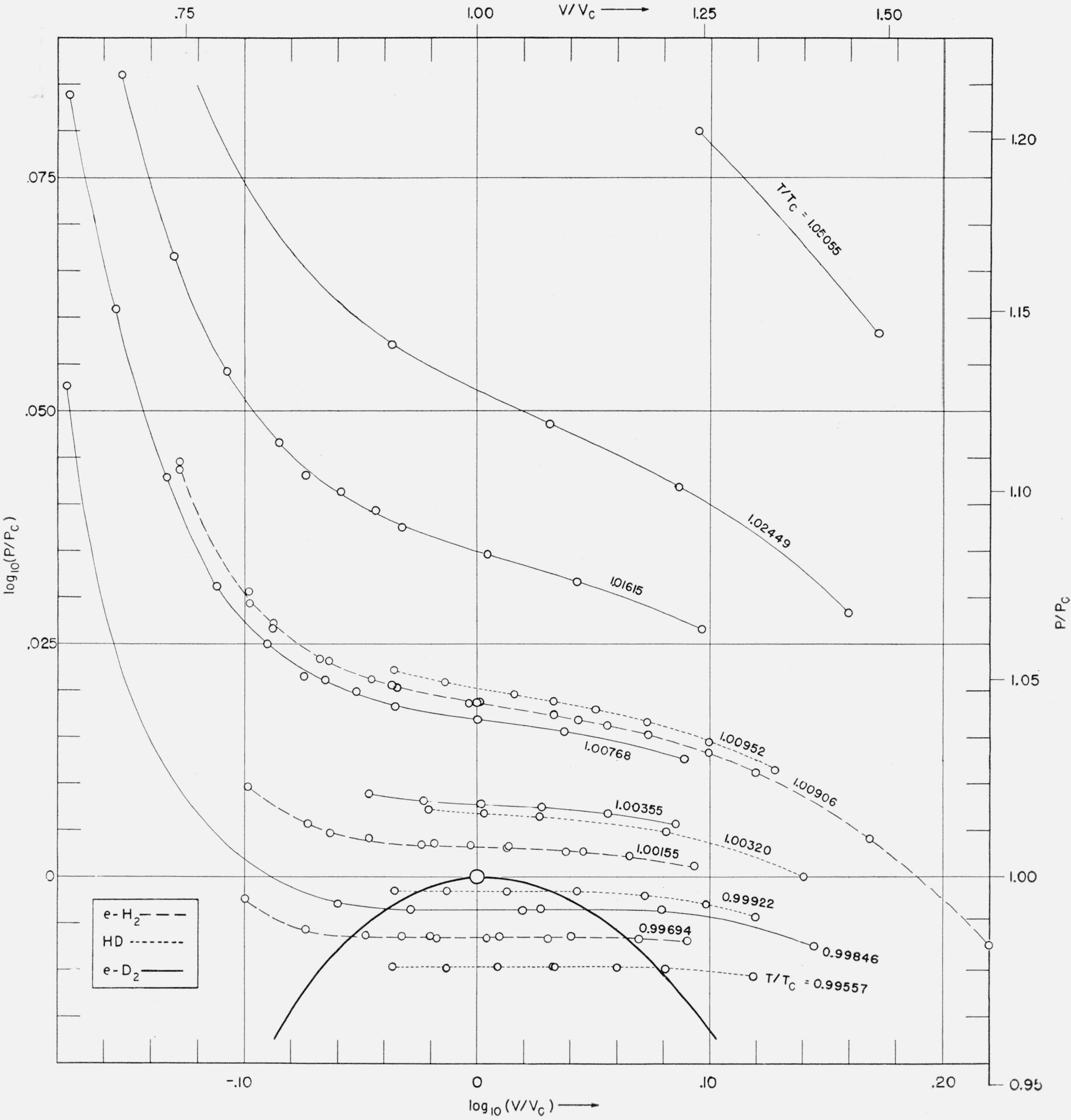

FIGURE 1. *Isotherms of* e-H_2, HD, *and* e-D_2 *in the neighborhood of the critical point.*

To help in properly drawing the liquid-vapor dome, several other sets of isotherm data were plotted on log P versus log V graphs and compared with our own results by superposition. The data plotted included those of Michels, Blaisse, and Michels for CO_2 [7], and those of Onnes, Crommelin, and Cath for hydrogen [2]. The isotherm data in the latter paper are given graphically rather than numerically, so the coordinates of the plotted points and of various points on the dome had to be read from the published graph. The dome drawn in figure 1 is in agreement with that of the Leiden observers within the accuracy of the observations. The CO_2 data could not be satisfactorily superposed on our hydrogen data because the dome was too wide. It was estimated that if for CO_2 one should plot log P versus 0.81 log V, the resulting graph could be superposed satisfactorily on the hydrogen graph. The difference in dome-shape of hydrogen and CO_2 is undoubtedly real. It would be interesting to compare the critical regions of other triatomic molecules, such as N_2O and SO_2 with that of CO_2, to see the extent to which triatomic molecules follow one law of corresponding states and diatomic molecules another.

The vapor-pressure tables of [1] are believed to be accurate near the critical point to ±8 mm Hg in the case of e-H_2 and e-D_2, and to ±15 mm Hg in the case of HD. The uncertainties of the critical constants are greater than these values, however, because they include the additional uncertainty in locating the proper spot on figure 1 to choose as the critical point. It is estimated that the critical point selected is uncertain by ±0.001 in log (P/P_c). This is equivalent to ±22 mm Hg for e-H_2, ±26 mm Hg for HD, and ±28 mm Hg for e-D_2. To these may be added the estimated uncertainties in the vapor-pressure tables, giving (after rounding off) ±30 mm Hg for e-H_2, ±40 mm Hg for HD, and ±35 mm Hg for e-D_2. Using values of dP/dT from the accepted vapor-pressure tables of [1], these uncertainties are approximately equivalent to ±20 mdeg for e-H_2 and e-D_2, and to ±25 mdeg for HD. An additional allowance of ±20 mdeg must be made for uncertainty in the temperature scale.

The position of the critical point in figure 1 is uncertain by perhaps ±0.005 in log (V/V_c), which is equivalent to slightly more than 1 percent in V. Errors in determining the volumes of the equilibrium chamber and the various parts of the pressure-transmitting line are not included in this figure. These would affect the determinations of the total mass of material employed in each run, and would introduce a systematic error into log (V/V_c). An uncertainty of ±2 percent is thought to be adequate to cover errors due to all causes. The relative errors of the critical volumes of the three varieties are much smaller than the total errors. This type of error may be estimated from the accuracy with which the three original log P-log V graphs could be correctly superposed. It is estimated that the ratio of any two critical volumes is correct to 5 per mille. The relative accuracy of any two critical pressures is probably 1 per mille, and that of any two critical temperatures about 3 parts in 10,000.

The published critical data for hydrogen were summarized by Pickering [8] in 1926. He selected as best values: $t_c = -239.9°$ C, $P_c = 12.8$ atm, and $\rho_c = 0.0310$ g cm^{-3} (equivalent to $V_c = 65.0$ cm^3 mole^{-1}). These are essentially the values of Onnes, Crommelin, and Cath [2] for the critical temperature and pressure and that of Mathias, Crommelin, and Onnes [9], for the critical density. In [2] the critical temperature is given both in centigrade and in Kelvin units ($-239.91°$ C$=33.18°$ K). Since the Leiden authors were unaware of the necessity of controlling ortho-para compositions, we may assume that they worked with normal (normal=0.25 parahydrogen, 0.75 orthohydrogen; see [1]) hydrogen, possibly with an appreciable conversion in the direction of equilibrium hydrogen. In the recent determination of critical constants at Ohio State University [3], normal hydrogen was also employed, so there are no published data exactly comparable with ours. The Ohio State values are $T_c = 33.24_4°$ K, and $P_c = 12.797$ atm.

The above critical points are shown in figure 3 of [1], which is a graph of deviations of observed vapor pressures from an accepted vapor-pressure table. Note that the n-H_2 data in this graph are not to be expected to give zero deviations because the table from which deviations are calculated represents not n-H_2 but e-H_2. To our knowledge there are no previous measurements of the critical constants of HD and e-D_2 with which our results may be compared.

The valuable assistance of Dino Zei and Raymond A. Nelson in making the measurements is acknowledged.

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WASHINGTON, April 27, 1951.