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Vapor Pressures of Hydrogen, Deuterium, and Hydrogen Deuteride and Dew-Point Pressures of Their Mixtures[1]

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The vapor pressures of H_2, HD, and D_2 have been measured from near their triple points to their critical points. The H_2 and D_2 samples were catalyzed to ortho-para equilibrium at 20.4° K. Tables suitable for interpolation have been prepared to represent the results both in centimeter-gram-second and in engineering units.

Measurements of dew-point pressures of several binary mixtures have been made at several pressures below atmospheric. Observed pressures were about 3 percent above those predicted by the law of ideal solutions.

1. Introduction

Many papers dealing with the vapor pressures of various isotopic varieties of hydrogen have appeared since Dennison [1][3] correctly explained the behavior of ortho and para forms in 1927, and since Urey, Brickwedde, and Murphy [2] announced the concentration of deuterium in 1932. So far as we are aware, however, no measurements extending above the range of ordinary mercury manometry had been reported until quite recently, when White, Friedman, and Johnston [3] published data for normal hydrogen extending up to the critical point, and a preliminary report of the present work appeared [4]. Grilly [5] has measured the vapor pressures of the normal varieties of hydrogen, deuterium, and tritium up to approximately 3 atm. Vapor pressures of mixtures had been neglected, there being no information on deviations from the laws of ideal solutions other than that published by Woolley, Scott, and Brickwedde [6, p. 454] for mixtures of ortho and para hydrogen.

The present paper, and one on critical constants [7], being published simultaneously, comprise a full report of a program of determination of the properties of the hydrogens undertaken at the Bureau early in 1950. The work reported in this paper consisted of two parts: the measurement of vapor pressures of H_2, HD, and D_2 from low pressures to their critical points; and the measurement of the dew points of a number of binary mixtures of the same substances at pressures below 1 atm. The vapor-pressure measurements and the dew-point measurements were performed with different apparatuses, and are discussed separately, the vapor-pressure measurements being presented in section 2 and the dew-point measurements in section 3. Except for a few preliminary measurements, all the vapor pressures reported for H_2 and D_2 are for samples catalyzed to ortho-para equilibrium at the boiling point of normal hydrogen (20.4° K). Hydrogen so catalyzed (0.979 para-H_2, 0.021 ortho-H_2) has been designated e-H_2 [6]. Likewise, deuterium catalyzed to equilibrium at 20.4° K (0.022 para-D_2, 0.978 ortho-D_2) is designated e-D_2. It is worth while to emphasize that e-H_2 and e-D_2 were in ortho-para equilibrium only at 20.4° K, and that the composition did not change as the temperature was raised or lowered during the course of the measurements. It had been hoped to measure the vapor pressure of normal, or high-temperature-equilibrium hydrogen (0.25 para-H_2, 0.75 ortho-H_2) and deuterium (0.3333 para-D_2, 0.6667 ortho-D_2), but time did not permit. There are no separate ortho and para varieties of HD.

2. Vapor-Pressure Measurements

2.1. Apparatus and Methods

The apparatus and methods were substantially the same as those recently used to measure the vapor pressure of oxygen and are described in reference [8]. The diaphragm cell used for part of the work on oxygen was not employed.

After part of the present work was completed, it was noted that the floating nickel sleeves and magnetic detectors were not indicating correctly the difference in height of the two mercury meniscuses inside the stainless steel U-tube. This was verified by taking X-ray pictures of the meniscuses. The nickel sleeve at the Hg-H_2O interface (height h_2) was found to be functioning properly, supported entirely above the mercury by the surface tension of the latter. The sleeve at the Hg-H_2 interface (height h_1), however, had been wetted by the mercury and had sunk into it. Measurements affected by this difficulty were calculated from the value of h_2 only, by using a curve of h_1+h_2 versus h_2 plotted from data taken before the trouble developed. There was a considerable range of overlap of the piston-gage measurements with the mercury manometer and the mercury manometer-barometer measurements, in which the various methods were cross-checked from time to time.

The resistance thermometer (L14) that developed a leak during the O_2 measurements was removed and replaced by L11 and L28. With the exception of a few check measurements, all the temperatures in the

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

Present NBS scale is .010°K lower than the L11 scale at all temperature

Present scale is .010°K
L11 is .010°K too high

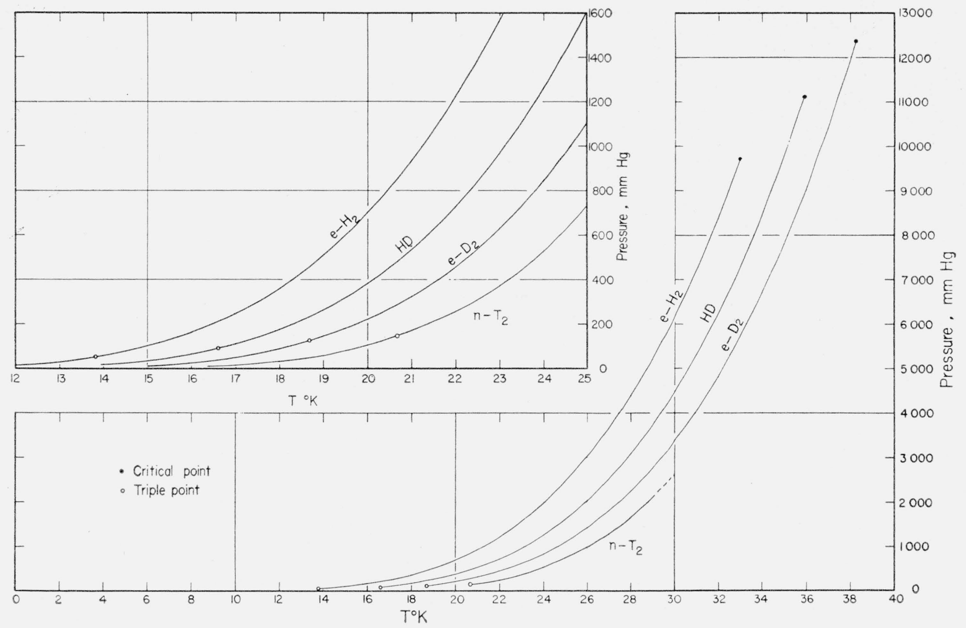

FIGURE 1. *A comparison of the vapor pressures of ordinary hydrogen, hydrogen deuteride, deuterium, and tritium.*

present work were measured with platinum resistance thermometer L11. This thermometer is one of the original group used to define the Bureau's temperature scale below 90° K. Its calibration is discussed in [9].

One improvement was made over the methods used in the oxygen measurements. Rather than make alternate measurements of pressure and of thermometer resistance, it was found more accurate and more convenient to observe the resistance thermometer continuously, keeping the piston gage balanced, until conditions had been steady for several minutes. A valve in the pressure-transmitting line was then closed, after which all the readings associated with the pressure measurement could be made at leisure.

The method of computing pressures was the same as that used for O_2 except that no correction was made for the hydrostatic pressure of hydrogen vapor. The maximum correction (at the critical point) in the case of O_2 was 6.5 mm Hg. It was estimated that the corresponding figure for D_2 would be about 1 mm Hg, with the values for HD and H_2 proportionately less.

Preparation and purity of the samples. The H_2 was taken from the supply generated by electrolysis of H_2O for use in this laboratory's hydrogen liquefier. The HD was prepared for us by Abraham Fookson, Philip Pomerantz, and Edwin H. Rich, who used the reaction

$$LiAlH_4+4D_2O \longrightarrow LiOD+Al(OD)_3+4HD.$$

The D_2 was obtained from the Stuart Oxygen Co. Both the HD and the D_2 were purified by distillation by Fookson, et al. A more complete report of their work is published elsewhere [10].

A number of samples taken at various stages of the vapor-pressure measurements were submitted to the Mass Spectrometry Section of the Bureau for analysis. The results are presented in connection with the discussion of the measurements on each particular substance.

2.2. Ortho-para Catalysis

The catalyst was Nd_2O_3 furnished by the Bureau's Inorganic Chemistry Section. It was a pale blue powder prepared by firing neodymium oxalate at 800° C. To avoid contaminating the H_2 with D_2, the catalyst used for D_2 was removed and replaced by a fresh sample before measurements on H_2 were begun. Each sample was contained in a cylindrical glass chamber of about 1.6-cm inside diameter and 15-cm^3 volume. Connections were made by two glass tubes, one ending at the top and the other near the bottom of the chamber. About 10 cm^3 of catalyst was placed in each chamber and confined with plugs of glass wool. The catalyst was prepared for use by evacuating for several hours near 440° C, and flushing with small portions of the H_2 (or D_2) to be measured. It was surrounded by liquid hydrogen before use, after which the entire sample of H_2 or D_2 to be measured was condensed on it. A toepler pump was used to circulate the gas so that all the material would come in contact with the catalyst. When gas was transferred from the catalyzing chamber to the cryostat, it was removed through the tube extending to the bottom of the chamber, so that only material that had been in close contact with the catalyst would be obtained. During the catalytic conversion, samples were condensed in the cryostat from time to time and their vapor pressures were observed; they were then recirculated until no further change in vapor pressure was observed. The time required to reach ortho-para equilibrium in the presence of the catalyst at 20.4° K appeared to be short compared to the time required to introduce and remove the sample.

2.3. The Data

Figure 1 gives a general picture of the temperature dependence of the vapor pressures of e-H_2, HD, e-D_2, and n-T_2. The curve for tritium is plotted from the data of Grilly [5]; the rest are our own data. On the scale of this graph, curves for different ortho-para compositions of the same isotope would scarcely be distinguishable.

The experimental data are given in tables 1, 2, 3, and 4. The first three contain the measurements on e-H_2, HD, and e-D_2, respectively. Table 4 contains the results of the first run, which was made on an uncatalyzed sample of D_2 taken directly from the supply cylinder. Presumably this sample was normal D_2, and since no other measurements were made on n-D_2 these preliminary data are being reported. The supply was analyzed by mass spectrometer, the mole fraction of D_2 being 0.99_2; and that of HD, 0.008. The data of table 4 are plotted in figure 3.

Column 1 of each table contains the run number (preceding the decimal point) and the observation number (following the decimal point) of each datum. Runs are numbered chronologically, as are the observations of a given run. Column 2 of each table shows the type of pressure-measuring equipment used. This was either a mercury manometer (Hg), mercury manometer plus barometer (HgB), or piston gage (PG). Columns 3 and 4 of each table contain the observed temperature and the corresponding observed pressure. From the original data in tables 1, 2, and 3, three new tables (5, 6, and 7) were derived giving values of $\log_{10}P$ at uniform values of $200/T$, for e-H_2 HD, and e-D_2, respectively. These tables are suitable for interpolation, and represent the results in essentially the same way that an equation might represent them. Deviations of the experimental data from these tables are given in the final columns of tables 1, 2, and 3. These deviations are plotted in figure 2. Consecutive points of each run have been joined by straight lines where this could be done without cluttering the graphs too much. A few of the deviations were too large to fall within the range of the graphs. Each of these is indicated by a line extending in the direction of the missing point, and the corresponding deviation can be found in table 1, 2, or 3. Near the critical point, where isotherms were also measured, all points inside the liquid-vapor dome are included. Where there was more than one point of a run on the horizontal portion of an isotherm, the temperature and pressure given in tables 1, 2, or 3 were obtained by averaging.

After the single run on uncatalyzed (normal) D_2, the measurements on HD were begun. Having no ortho and para forms, this substance requires no catalyst, but the measurements were complicated by slow conversion of HD into H_2 and D_2. This is shown best in figure 2 by the rise in pressure in the neighborhood of 31° K between successive runs. When liquid hydrogen was not available to keep the cryostat cold, it was our practice not to return the sample to the supply bulb, but to lower the mercury meniscus, h_1, so that the sample occupied most of one arm of the stainless steel ∪-tube. Returning the material to the supply bulb would have made it necessary to remeasure the mass in use for each successive run, and would have lowered the reproducibility of data obtained in the critical region. The pressure of the confined sample rose to about 30 atm when the cryostat rose to liquid-air temperatures. It is thought that the breakdown of HD to form H_2 and D_2 occurred principally during periods when most of the sample was inside the stainless steel tube and all of it was at relatively high pressure. In addition to stainless steel, the HD was in contact with nickel, copper, brass, and silver-solder. On completion of the measurements on HD, two samples were taken for mass-spectrometer analysis, one from the 5-liter glass bulb containing the unused portion of the original supply, and another from the sample on which measurements had been made. The analysis of the first sample was 0.99_8 HD, 0.001 H_2, and 0.001 D_2, in substantial agreement with an earlier analysis made at the time of distillation.

TABLE 1. *Observations of the vapor pressure of* e-H_2

The column headed ΔP contains deviations of the observed values from table 5.

Observation number	Pressure-measuring system	T	P (observed)	ΔP (observed − calculated)
		°*K*	*mm* Hg	*mm* Hg
14.1	Hg	17.8294	338.4	−0.1
14.2	Hg	18.5812	442.1	−.3
14.3	Hg	19.1245	530.7	−.1
14.4	Hg	20.0401	707.7	−.1
14.5	Hg	20.4069	789.6	.2
14.6	Hg	20.5118	813.7	−.2
14.7	Hg	16.9549	241.4	−.2
14.8	Hg	20.2648	757.1	.1
14.9	HgB	20.5167	815.2	.1
14.10	HgB	20.8655	900.7	.0
14.11	HgB	21.2046	989.8	−.1
15.1	HgB	20.9513	922.1	−.6
15.2	HgB	21.3379	1026.8	.2
15.3	PG	23.6441	1827.1	−.5
15.4	PG	24.4501	2189.4	−.1
15.5	PG	24.9003	2414.1	1.7
15.6	PG	25.5711	2773.5	0.2
15.7	PG	26.1980	3142.6	−.7
15.8	PG	26.7811	3517.5	.4
15.9	PG	27.4083	3952.7	.0
15.10	PG	28.3858	4705.7	.8
15.11	PG	29.3956	5583.9	.2
15.12	PG	30.3776	6544.6	.5
15.13	PG	31.4021	7660.2	−4.9
16.3	Hg	16.9752	243.1	−0.5
16.4	Hg	15.8414	149.7	−.3
16.5	PG	22.2604	1308.4	.2
16.6	PG	22.9058	1534.9	−.2
16.7	PG	25.0473	2488.5	.0
16.8	PG	27.8744	4299.6	−.2
16.9	PG	29.9173	6080.2	−.3
16.10	PG	30.9020	7102.8	.8
16.11	PG	31.8910	8255.1	7.7
17.1	PG	22.2800	1313.8	−0.9
17.2	PG	22.5792	1416.1	−1.0
17.3	PG	28.8797	5121.5	0.2
17.4	PG	31.0820	7302.5	1.5
18.1	PG	20.9534	922.5	−0.7
18.2	PG	21.6873	1127.2	−.4
18.3	PG	25.8955	2960.3	−.4
[a] 18.6	PG	32.8933	9566.2	3.1
19.1	PG	32.8936	9564.4	0.6
[b] 19.4	PG	32.8926	9559.3	−2.9
19.5	PG	32.6457	9219.5	−2.2
19.6	PG	32.3853	8875.1	0.3
19.7	PG	32.1392	8557.7	−.5

[a] Average of four observations.

[b] Average of three observations.

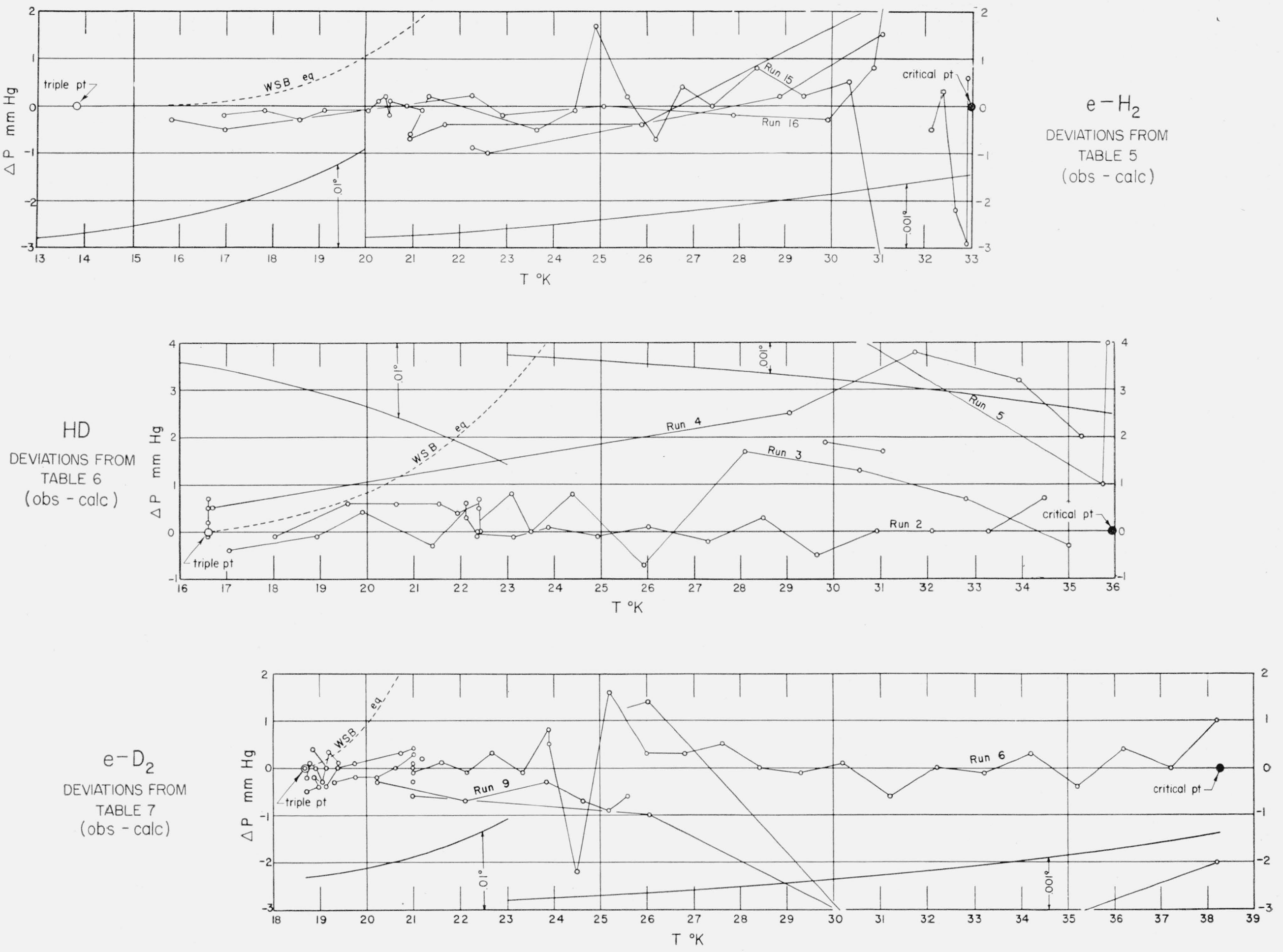

FIGURE 2. *Deviations of the experimental data in tables 1, 2, and 3 from tables 5, 6, and 7, respectively.*

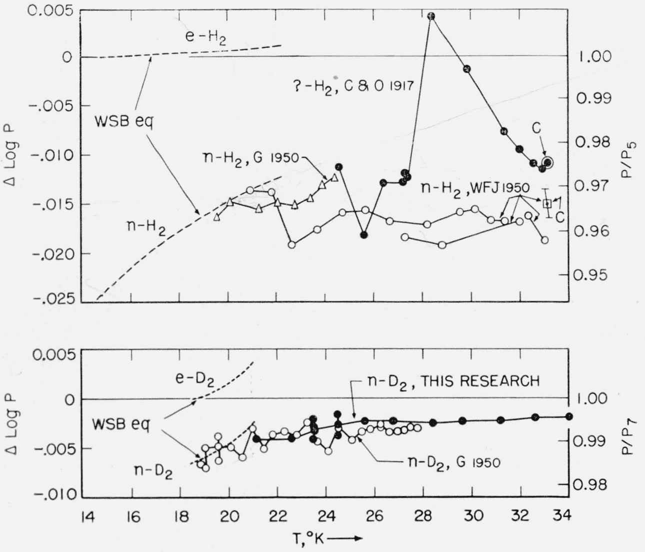

FIGURE 3. *Published vapor-pressure data compared with tables 5 and 7.*

Above: Published data for n-H_2 compared with table 5. Δlog P=log P (observed) minus log P (table 5). $P/P_5=P$ (observed) / P (table 5). Below: Published data for n-D_2 compared with table 7. Δlog P=log P (observed) minus log P (table 7). $P/P_7=P$ (observed) / P (table 7). Note that agreement is not to be expected, since in each case the table refers to the *equilibrium* variety, whereas the plotted points are the normal variety. The lower graph contains one set of data obtained in this research—those of table 4. C & O, Cath and Onnes; G, Grilly; WFJ, White, Friedman, and Johnston. C, Critical point.

TABLE 2. *Observations of the vapor pressure of* HD

The column headed ΔP contains deviations of the observed values from table 6.

Observation number	Pressure-measuring system	T	P (observed)	ΔP (observed−calculated)
		° *K*	*mm* Hg	*mm* Hg
2. 1	Hg	17. 046	114. 5	−0. 4
2. 2	Hg	18. 935	257. 6	−. 1
2. 3	Hg	19. 895	368. 5	. 4
2. 4	Hg	21. 388	604. 5	−. 3
2. 5a	Hg	22. 121	755. 3	. 3
2. 5b	PG	22. 121	755. 6	. 6
2. 6a	Hg	22. 364	810. 2	−. 1
2. 6b	PG	22. 364	810. 3	. 0
2. 7	PG	23. 108	997. 9	−. 1
2. 8	PG	23. 861	1218. 2	. 1
2. 9	PG	24. 920	1584. 0	−. 1
2. 10	PG	26. 024	2042. 4	. 1
2. 11	PG	27. 288	2673. 9	−. 2
2. 12	PG	28. 492	3393. 1	. 3
2. 13	PG	29. 652	4202. 9	−. 5
2. 14	PG	30. 889	5208. 5	. 0
2. 15	PG	32. 098	6344. 7	. 0
2. 16	PG	33. 285	7623. 9	. 0
2. 17	PG	34. 489	9105. 5	. 7
3. 1	PG	31. 049	5351. 5	1. 7
3. 2	PG	29. 814	4328. 3	1. 9
3. 3	Hg	18. 007	176. 6	−0. 1
3. 4	Hg	19. 580	329. 2	. 6
3. 5	Hg	20. 638	475. 7	. 6
3. 6	Hg	21. 554	637. 4	. 6
3. 7	Hg	21. 933	714. 6	. 4
3. 8a	PG	22. 394	817. 8	. 5
3. 8b	Hg	22. 394	818. 0	. 7
3. 8c	PG	22. 395	817. 6	. 0
3. 9	PG	23. 090	993. 9	. 8
3. 10	PG	23. 506	1110. 4	. 0
3. 11	PG	24. 390	1393. 1	. 8
3. 12	PG	25. 919	1994. 4	−. 7
3. 13	PG	28. 096	3144. 8	1. 7
3. 14	PG	30. 565	4931. 8	1. 3
3. 15	PG	32. 814	7096. 6	0. 7
[a] 3. 16	PG	35. 0334	9842. 1	−. 3
4. 2a	Hg	[b] 16. 5958	93. 2	. 7
4. 2b	Hg	[b] 16. 5966	93. 0	. 5
4. 2c	Hg	[b] 16. 5982	93. 0	. 5
4. 4a	Hg	[b] 16. 5990	92. 9	. 3
4. 4b	Hg	[b] 16. 5982	92. 5	−. 1
4. 5	Hg	16. 6718	96. 5	. 5
4. 6	PG	29. 035	3759. 6	2. 5
4. 7	PG	31. 763	6017. 5	3. 8
4. 8	PG	33. 948	8418. 3	3. 2
4. 9	PG	35. 276	10188	2
5. 1	PG	30. 374	4775. 8	4. 2
[c] 5. 2	PG	35. 7493	10887	1
[d] 5. 3	PG	35. 8797	11090	4

[a] Average of five observations.

[b] Triple point.

[c] Average of six observations.

[d] Average of two observations.

The analysis of the material removed from the cryostat, however, was 0.971 HD, 0.015 H_2, and 0.014 D_2. A calculation showed that this amount of decomposition of HD would raise the vapor pressure about twice as much as was actually observed. This is not surprising, for one would expect a fractionation of the isotopic impurities as the measurements proceeded. Run 2 was made immediately after introduction of HD into the apparatus, and hence presumably before any appreciable decomposition had occurred. Therefore it has been given a much greater weight than any of the other runs in determining the table to represent the vapor pressure of HD.

The measurements on e-D_2 were made following removal of HD from the apparatus. It was found desirable to recatalyze both e-D_2 and e-H_2 to ortho-para equilibrium at 20.4° K whenever any substantial part of the sample had been at room temperature for periods longer than an hour or two. On some occasions the change of vapor pressure resulting from catalysis of previously uncatalyzed samples was observed, and found to be in substantial agreement with the differences in vapor pressure of normal and equilibrium varieties found by Brickwedde and Scott [6, p. 452]. On removal from the apparatus the mass-spectrometer analysis of the sample was 0.995 D_2 and 0.005 HD. We were somewhat disappointed in this purity, but have no reason to

TABLE 3. *Observations of the vapor pressure of* e-D_2

The column headed ΔP contains deviations of the observed values from table 7.

Observation number	Pressure-measuring apparatus	T	P (observed)	ΔP (observed−calculated)
		° *K*	*mm* Hg	*mm* Hg
6. 1d	Hg	20. 9914	323. 1	0. 0
6. 1e	Hg	20. 9909	323. 1	. 1
6. 1f	Hg	20. 9909	322. 9	−. 1
6. 2	Hg	21. 6127	402. 0	. 1
6. 3	Hg	22. 1477	480. 5	−. 1
6. 4	Hg	22. 6805	570. 1	. 3
6. 5	Hg	23. 3317	694. 7	−. 1
6. 6a	PG	23. 8950	819. 2	. 8
6. 6b	Hg	23. 8953	818. 9	. 5
6. 7	PG	24. 4938	964. 4	−2. 2
6. 8	PG	25. 1942	1165. 6	1. 6
6. 9	PG	25. 9961	1424. 5	0. 3
6. 10	PG	26. 7961	1723. 6	. 3
6. 11	PG	27. 5954	2064. 5	. 5
6. 12	PG	28. 3966	2450. 9	. 0
6. 13	PG	29. 3002	2945. 8	−. 1
6. 14	PG	30. 1943	3501. 4	. 1
6. 15	PG	31. 1991	4209. 2	−. 6
6. 16	PG	32. 1980	5008. 4	. 0
6. 17	PG	33. 1984	5910. 1	−. 1
6. 18	PG	34. 1968	6920. 7	. 3
6. 19	PG	35. 1947	8048. 2	−. 4
6. 20	PG	36. 1982	9311. 3	. 4
[a]6. 21	PG	37. 1987	10708	0
6. 22c	PG	38. 2017	12274	1
7. 1	Hg	20. 9935	323. 1	−0. 2
7. 2	PG	26. 0185	1433. 4	1. 4
7. 3	PG	32. 2375	5036. 8	−5. 3
8. 1	Hg	20. 9875	322. 0	−0. 6
8. 2	PG	26. 0569	1444. 5	−1. 0
8. 3	PG	32. 2532	5051. 4	−4. 1
[b]8. 6	PG	38. 2034	12274	−2
9. 1	Hg	20. 9927	323. 3	0. 1
9. 15	Hg	20. 2347	243. 3	−. 3
9. 16	Hg	22. 1128	474. 4	−. 7
9. 17	Hg	23. 8370	804. 6	−. 3
9. 18	HgB	24. 6055	995. 7	−. 7
9. 19	HgB	25. 1752	1157. 5	−. 9
9. 20	HgB	25. 5973	1289. 5	−. 6
10. 1	Hg	20. 9991	324. 3	. 3
10. 2	Hg	20. 6377	283. 8	. 0
10. 3	Hg	20. 2178	241. 8	−. 2
10. 4	Hg	19. 7467	200. 7	−. 2
10. 5	Hg	19. 3116	167. 7	−. 3
10. 7	Hg	21. 1878	346. 8	. 2
11. 1a	Hg	20. 9935	323. 0	−. 3
11. 1b	Hg	20. 9944	323. 7	. 3
12. 1	Hg	21. 0145	326. 2	. 4
12. 2	Hg	20. 7220	293. 1	. 3
12. 3	Hg	19. 7457	200. 9	. 1
12. 4	Hg	19. 3730	172. 4	. 0
12. 5	Hg	19. 1332	155. 4	−. 4
12. 6	Hg	18. 8678	138. 7	−. 2
12. 7	Hg	18. 9821	145. 6	−. 4
12. 8	Hg	18. 7098	129. 1	−. 5
13. 1	Hg	19. 3963	174. 2	. 1
13. 2	Hg	19. 2038	160. 8	. 3
13. 3	Hg	19. 0467	149. 8	−. 3
13. 4	Hg	18. 9056	141. 2	. 0
13. 5	Hg	18. 7684	132. 9	. 1
13. 6	Hg	18. 7063	129. 2	−. 2
13. 20	Hg	19. 1459	156. 9	. 0
13. 21	Hg	18. 8379	137. 5	. 4

[a] Average of three observations.

[b] Average of two observations.

TABLE 4. *Observations of the vapor pressure of* n-D_2

Assumed to be n-D_2 because no catalyst was used

Observation number	Pressure-measuring system	T	P (observed)
		° *K*	*mm* Hg
1.1	Hg	21.124	335.6
1.2	Hg	22.612	552.5
1.3a	Hg	23.563	738.2
1.3b	PG	23.560	737.3
1.3c	PG	23.510	729.0
1.3d	Hg	23.511	725.5
1.4a	HgB	24.545	974.1
1.4b	PG	24.546	976.9
1.4c	HgB	24.560	975.6
1.5	PG	25.596	1283.0
1.6	PG	26.787	1710.6
1.7	PG	28.454	2466.1
1.8	PG	29.639	3131.4
1.9	PG	31.216	4201.0
1.10	PG	32.604	5337.2
1.11	PG	34.110	6800.6

doubt the accuracy of this analysis. Some memory effect was present in the mass spectrometer, but this was eliminated by use of a reference sample, which, by repeated runnings, was found to have a purity of 0.998 D_2. Analysis of our sample was then made by comparing it with the reference sample. We feel that the sample was at least as pure as the analysis indicated. No correction has been made for impurity.

A large number of measurements were made on e-D_2 near the triple point, both on the solid and on the liquid. Unfortunately, the apparatus was found to be poorly suited to rapid work in this region. Unless the apparatus was cooled very slowly, a section of the pressure-transmitting tube would become colder than the equilibrium chamber and the tube would become plugged with solid. As a result, the fraction of the observations below the triple point that were obviously bad was so large that all have been rejected. Just above the triple point the situation was better, but a considerable number of observations have been rejected. The deviations of the rejected points were almost all very large compared to those of the points plotted in figure 2. They were almost always negative, indicating that the plug of solid in the tube remained for some time below the temperature of the equilibrium chamber.

Before introducing H_2, the final substance, into the apparatus, the catalyzing chamber used for e-D_2 was removed and a similar one containing fresh catalyst substituted. No attempt was made to carry the measurements on e-H_2 very near to the triple point. When removed from the apparatus, the sample on which measurements had been made was analysed by mass spectrometer. The analysis was 0.999 H_2 and 0.001 HD. The only known source of deuterium contamination was desorption of the previous sample from the interior of the apparatus, which would hardly be expected to yield 1 per mill of HD. However, 1 per mill is the estimated uncertainty of the mass-spectrometer analyses, so this amount of HD is hardly a cause for concern.

2.4. Deriving the Smoothed Tables

Tables 5, 6, and 7, used in lieu of equations to represent the vapor-pressure-versus-temperature relation for each substance, were derived from the original data by the use of deviation plots. Various forms of equation were used. For e-H_2, for example, the equation of Woolley, Scott, and Brickwedde [6, p. 454] was used below about 28° K, in which range the observed values of $\log_{10}P$ do not deviate from the equation by more than about 0.00300. Between 28° and the critical point a different form of equation was used that had a smaller curvature near the critical point. Deviations of the observations from the equations were plotted versus the temperature, with a considerable range of overlap of the two equations. Smooth curves were drawn through the points. On these the temperatures corresponding to the values of $200/T$ appearing in table 5 were marked. At each of these temperatures the ordinate ($\log_{10}P_{\text{obs}}-\log_{10}P_{\text{calc}}$) was read and recorded. The equation was evaluated at the same temperatures and the ordinates of the smooth deviation curve added to the corresponding values of the equation.

The resulting table was differenced to third differences on an Underwood-Sundstrand automatic accounting machine. The table was smoothed by inspection of the differences, and redifferenced. The final result was table 5. Similar procedures, with minor variations, led to tables 6 and 7. For HD, the equation

$$\log_{10} P=A+(B/T)+C\left(\frac{100}{T}-D\right)^{\alpha}$$

was used throughout the entire liquid range. Above 24° K it represents the data almost within the experimental error, and the deviations at lower temperatures are small enough for satisfactory plotting. The value of D used was 2.5, or approximately $90/T_c$, and the exponent, α, was 0.71.

Tables 5, 6, and 7 are given in pressure units of millimeters of mercury, atmospheres, and pounds per square inch absolute; and in temperature units of degrees Kelvin and Rankine having been prepared in this form for inclusion in the NBS-NACA series of Tables of Thermal Properties of Gases [11]. For purposes where accurate interpolation is not necessary, it is more convenient to have tables with T as argument rather than $200/T$. Hence table 8, giving vapor pressures of all three varieties at temperature intervals of 1 deg K has been calculated from tables 5, 6, and 7. Table 9 contains the triple points and boiling points. Critical points are given in reference [7].

2.5. Comparison With Previous Work

The survey paper of Woolley, Scott, and Brickwedde [6], which appeared in 1948, contains an adequate summary of vapor-pressure data for the hydrogens published up so that time. Their paper

TABLE 5. *Vapor pressure of liquid* e-H_2 (*for interpolation*)

Interpolation with $200/T$ as argument is more accurate and also more convenient than interpolation with T as argument. Linear interpolation introduces no significant errors below about 23° K. Between 23° and 30° K linear interpolation is slightly inferior to higher-order interpolation, and above 30° K higher-order interpolation should be used if accurate values are required

$\frac{200}{T}$	T	$\mathrm{Log}_{10}P$			Δ	T	$\frac{360}{T}$
° K^{-1}	° *K*	*mm Hg*	*atm*	*psia*		° *R*	° R^{-1}
14.5	13.793	(1.7176)	[a] (8.8368)	(0.0040)	242	24.828	14.5
14.4	13.889	1.7418	8.8610	.0282	242	25.000	14.4
14.3	13.986	1.7660	8.8852	.0524	242	25.175	14.3
14.2	14.085	1.7902	8.9094	.0766	242	25.352	14.2
14.1	14.184	1.8144	8.9336	.1008	243	25.532	14.1
14.0	14.286	1.8387	8.9579	.1251	243	25.714	14.0
13.9	14.388	1.8630	8.9822	.1494	244	25.899	13.9
13.8	14.493	1.8874	9.0066	.1738	244	26.087	13.8
13.7	14.599	1.9118	9.0310	.1982	244	26.277	13.7
13.6	14.706	1.9362	9.0554	.2226	244	26.471	13.6
13.5	14.815	1.9606	9.0798	.2470	245	26.667	13.5
13.4	14.925	1.9851	9.1043	.2715	245	26.866	13.4
13.3	15.038	2.0096	9.1288	.2960	245	27.068	13.3
13.2	15.152	2.0341	9.1533	.3205	246	27.273	13.2
13.1	15.267	2.0587	9.1779	.3451	247	27.481	13.1
13.0	15.385	2.0834	9.2026	.3698	246	27.692	13.0
12.9	15.504	2.1080	9.2272	.3944	247	27.907	12.9
12.8	15.625	2.1327	9.2519	.4191	247	28.125	12.8
12.7	15.748	2.1574	9.2766	.4438	248	28.346	12.7
12.6	15.873	2.1822	9.3014	.4686	248	28.571	12.6
12.5	16.000	2.2070	9.3262	.4934	249	28.800	12.5
12.4	16.129	2.2319	9.3511	.5183	249	29.032	12.4
12.3	16.260	2.2568	9.3760	.5432	250	29.268	12.3
12.2	16.393	2.2818	9.4010	.5682	250	29.507	12.2
12.1	16.529	2.3068	9.4260	.5932	250	29.752	12.1
12.0	16.667	2.3318	9.4510	.6182	251	30.000	12.0
11.9	16.807	2.3569	9.4761	.6433	251	30.253	11.9
11.8	16.949	2.3820	9.5012	.6684	252	30.508	11.8
11.7	17.094	2.4072	9.5264	.6936	252	30.769	11.7
11.6	17.241	2.4324	9.5516	.7188	253	31.034	11.6
11.5	17.391	2.4577	9.5769	.7441	254	31.304	11.5
11.4	17.544	2.4831	9.6023	.7695	254	31.579	11.4
11.3	17.699	2.5085	9.6277	.7949	255	31.858	11.3
11.2	17.857	2.5340	9.6532	.8204	255	32.143	11.2
11.1	18.018	2.5595	9.6787	.8459	256	32.432	11.1
11.0	18.182	2.5851	9.7043	.8715		32.728	11.0
11.0	18.182	2.58506	9.70425	.87144	2564	32.728	11.0
10.9	18.349	2.61070	9.72989	.89708	2571	33.028	10.9
10.8	18.519	2.63641	9.75560	.92279	2578	33.334	10.8
10.7	18.692	2.66219	9.78138	.94857	2585	33.646	10.7
10.6	18.868	2.68804	9.80723	.97442	2591	33.962	10.6
10.5	19.048	2.71395	9.83314	1.00033	2598	34.286	10.5
10.4	19.231	2.73993	9.85912	1.02631	2606	34.616	10.4
10.3	19.417	2.76599	9.88518	1.05237	2613	34.951	10.3
10.2	19.608	2.79212	9.91131	1.07850	2621	35.294	10.2
10.1	19.802	2.81833	9.93752	1.10471	2628	35.644	10.1
10.0	20.000	2.84461	9.96380	1.13099	2637	36.000	10.0
9.9	20.202	2.87098	9.99017	1.15736	2646	36.364	9.9
9.8	20.408	2.89744	0.01663	1.18382	2654	36.734	9.8
9.7	20.619	2.92398	.04317	1.21036	2663	37.114	9.7
9.6	20.833	2.95061	.06980	1.23699	2672	37.499	9.6
9.5	21.053	2.97733	.09652	1.26371	2682	37.895	9.5
9.4	21.277	3.00415	.12334	1.29053	2692	38.299	9.4
9.3	21.505	3.03107	.15026	1.31745	2702	38.709	9.3
9.2	21.739	3.05809	.17728	1.34447	2712	39.130	9.2
9.1	21.978	3.08521	.20440	1.37159	2723	39.560	9.1
9.0	22.222	3.11244	.23163	1.39882	2735	40.000	9.0
8.9	22.472	3.13979	.25898	1.42617	2746	40.450	8.9
8.8	22.727	3.16725	.28644	1.45363	2758	40.909	8.8
8.7	22.989	3.19483	.31402	1.48121	2770	41.380	8.7
8.6	23.256	3.22253	.34172	1.50891	2783	41.861	8.6
8.5	23.529	3.25036	.36955	1.53674	2797	42.352	8.5
8.4	23.810	3.27833	.39752	1.56471	2810	42.858	8.4
8.3	24.096	3.30643	.42562	1.59281	2825	43.373	8.3
8.2	24.390	3.33468	.45387	1.62106	2839	43.902	8.2
8.1	24.691	3.36307	.48226	1.64945	2854	44.444	8.1
8.0	25.000	3.39161	.51080	1.67799	2869	45.000	8.0
7.9	25.316	3.42030	.53949	1.70668	2886	45.569	7.9
7.8	25.641	3.44916	.56835	1.73554	2903	46.154	7.8
7.7	25.974	3.47819	.59738	1.76457	2919	46.753	7.7
7.6	26.316	3.50738	.62657	1.79376	2936	47.369	7.6
7.5	26.667	3.53674	.65593	1.82312	2954	48.001	7.5
7.4	27.027	3.56628	.68547	1.85266	2973	48.649	7.4
7.3	27.397	3.59601	.71520	1.88239	2993	49.315	7.3
7.2	27.778	3.62594	.74513	1.91232	3016	50.000	7.2
7.1	28.169	3.65610	.77529	1.94248	3040	50.704	7.1

TABLE 5. *Vapor pressure of liquid* e-H_2 (*for interpolation*)—Continued

$\frac{200}{T}$	T	$\mathrm{Log}_{10}P$			Δ	T	$\frac{360}{T}$
° K_{-1}	° *K*	*mm Hg*	*atm*	*psia*		° *R*	° R^{-1}
7.0	28.571	3.68650	0.80569	1.97288	3066	51.428	7.0
6.9	28.986	3.71716	.83635	2.00354	3092	52.175	6.9
6.8	29.412	3.74808	.86727	2.03446	3119	52.942	6.8
6.7	29.851	3.77927	.89846	2.06565	3146	53.732	6.7
6.6	30.303	3.81073	.92992	2.09711	3173	54.545	6.6
6.5	30.769	3.84246	.96165	2.12884	3205	55.384	6.5
6.4	31.250	3.87451	.99370	2.16089	3247	56.250	6.4
6.3	31.746	3.90698	1.02617	2.19336	3303	57.143	6.3
6.2	32.258	3.94001	1.05920	2.22639	3381	58.064	6.2
6.1	32.787	3.97382	1.09301	2.26020	3487	59.017	6.1
6.0	33.333	(4.00869)	(1.12788)	(2.29507)	3629	60.000	6.0
5.9	33.898	(4.04498)	(1.16417)	(2.33136)		61.016	5.9

[a] Figures in parentheses are extrapolated values, to facilitate interpolation.

contains equations and tables giving what the authors judged to be the best values of the vapor pressures of e-H_2, n-H_2, HD, e-D_2, and n-D_2 up to about 1 atm. Tables 5, 6, and 7 are consistent with the triple-point temperatures and pressures accepted by Woolley, Scott, and Brickwedde (WSB) [6, p. 453]. On the basis of the present data alone, slightly different triple points are obtained for HD and e-D_2 (the triple point of e-H_2 was not measured), but the differences are so small that the WSB triple points have been retained. It has not, however, been possible to retain the same boiling points. Above the triple points, the WSB vapor pressures are higher than the present ones. This is shown by the three dotted curves in figure 2 labeled WSB equation. If expressed in terms of temperature, the deviations of the WSB equations for e-H_2 and HD from tables 5 and 6 are nearly the same, both equations being about 4 mdeg low at 19° K and 9 mdeg low at 22° K. Such a discrepancy is probably due to a difference in temperature scales. In this connection it should be pointed out that most of the data on which the WSB equations are based were taken *before* this Bureau's temperature scale [9] below 90° K was established. They were for the most part expressed as differences of vapor-pressures of different modifications, as a function of the vapor pressure of a particular modification. Part of the WSB data, however, related the resistance of thermometer L6 or L3 to the vapor pressure of hydrogen (generally e-H_2), and these were used to establish the temperatures of all the measurements. A discrepancy of up to 9 mdeg between the present temperature scale and that of the WSB equations seems large, but it unquestionably exists.

The deviation of the WSB equation for e-D_2 from the present results increases much more rapidly than the deviations for e-H_2 and HD. However, the WSB data for e-D_2 covered a range of less than 2 degrees K (18.691° to 20.4° K), whereas their measurements on liquid HD covered a range of nearly 4 degrees K, and on liquid e-H_2 of more than 6 degrees K. It is not surprising that the equation based on the

TABLE 6. *Vapor pressure of liquid* HD (*for interpolation*)

Interpolation with 200/T as argument is more accurate and also more convenient than interpolation with T as argument. Linear interpolation introduces no significant errors below about 25° K. Between 25° and 32° K linear interpolation is slightly inferior to higher-order interpolation, and above 32° K higher-order interpolation should be used if accurate values are required.

$\frac{200}{T}$	T	$\mathrm{Log}_{10}P$			Δ	T	$\frac{360}{T}$
° K^{-1}	° *K*	*mm Hg*	*atm*	*psia*		° *R*	° R^{-1}
12.1	16.529	(1.9516)	[a] (9.0708)	(0.2380)	295	29.572	12.1
12.0	16.667	1.9811	9.1003	.2675	296	30.001	12.0
11.9	16.807	2.0107	9.1299	.2971	297	30.253	11.9
11.8	16.949	2.0404	9.1596	.3268	297	30.508	11.8
11.7	17.094	2.0701	9.1893	.3565	297	30.769	11.7
11.6	17.241	2.0998	9.2190	.3862	298	31.034	11.6
11.5	17.391	2.1296	9.2488	.4160	299	31.304	11.5
11.4	17.544	2.1595	9.2787	.4459	298	31.579	11.4
11.3	17.699	2.1893	9.3085	.4757	299	31.858	11.3
11.2	17.857	2.2192	9.3384	.5056	300	32.143	11.2
11.1	18.018	2.2492	9.3684	.5356	300	32.432	11.1
11.0	18.182	2.2792	9.3984	.5656	301	32.728	11.0
10.9	18.349	2.3093	9.4285	.5957	301	33.028	10.9
10.8	18.519	2.3394	9.4887	.6258	301	33.334	10.8
10.7	18.692	2.3695	9.4589	.6559	302	33.646	10.7
10.6	18.868	2.3997	9.4887	.6861	303	33.962	10.6
10.5	19.048	2.4300	9.5492	.7164	303	34.286	10.5
10.4	19.231	2.4603	9.5795	.7467	304	34.616	10.4
10.3	19.417	2.4907	9.6099	.7771	304	34.951	10.3
10.2	19.608	2.5211	9.6403	.8075	305	35.294	10.2
10.1	19.802	2.5516	9.6708	.8380	305	35.644	10.1
10.0	20.000	2.5821	9.7013	.8685		36.000	10.0
10.0	20.000	2.58207	9.70126	.86845	3057	36.000	10.0
9.9	20.202	2.61264	9.73183	.89902	3063	36.364	9.9
9.8	20.408	2.64327	9.76246	.92965	3070	36.734	9.8
9.7	20.619	2.67397	9.79316	.96035	3077	37.114	9.7
9.6	20.833	2.70474	9.82393	.99112	3084	37.499	9.6
9.5	21.053	2.73558	9.85477	1.02195	3091	37.895	9.5
9.4	21.277	2.76649	9.88568	1.05298	3097	38.299	9.4
9.3	21.505	2.79746	9.91665	1.08384	3104	38.709	9.3
9.2	21.739	2.82850	9.94769	1.11488	3111	39.130	9.2
9.1	21.978	2.85961	9.97880	1.14599	3119	39.560	9.1
9.0	22.222	2.89080	0.00999	1.17718	3128	40.000	9.0
8.9	22.472	2.92208	.04127	1.20846	3137	40.450	8.9
8.8	22.727	2.95345	.07264	1.23983	3148	40.909	8.8
8.7	22.989	2.98493	.10412	1.27131	3156	41.380	8.7
8.6	23.256	3.01649	.13568	1.30287	3165	41.861	8.6
8.5	23.529	3.04814	.16733	1.33452	3176	42.352	8.5
8.4	23.810	3.07990	.19909	1.36628	3188	42.858	8.4
8.3	24.096	3.11178	.23097	1.39816	3199	43.373	8.3
8.2	24.390	3.14377	.26296	1.43015	3208	43.902	8.2
8.1	24.691	3.17585	.29504	1.46223	3218	44.444	8.1
8.0	25.000	3.20803	.32722	1.49441	3229	45.000	8.0
7.9	25.316	3.24032	.35951	1.52670	3243	45.569	7.9
7.8	25.641	3.27275	.39194	1.55913	3255	46.154	7.8
7.7	25.974	3.30530	.42449	1.59168	3267	46.753	7.7
7.6	26.316	3.33797	.45716	1.62435	3281	47.369	7.6
7.5	26.667	3.37078	.48997	1.65716	3297	48.001	7.5
7.4	27.027	3.40375	.52994	1.69013	3311	48.649	7.4
7.3	27.397	3.43686	.55605	1.72324	3326	49.315	7.3
7.2	27.778	3.47012	.58931	1.75650	3342	50.000	7.2
7.1	28.169	3.50354	.62273	1.78992	3358	50.704	7.1
7.0	28.571	3.53712	.65631	1.82350	3375	51.428	7.0
6.9	28.986	3.57087	.69006	1.85725	3394	52.175	6.9
6.8	29.412	3.60481	.72400	1.89119	3415	52.942	6.8
6.7	29.851	3.63896	.75815	1.92534	3438	53.732	6.7
6.6	30.303	3.67334	.79253	1.95972	3461	54.545	6.6
6.5	30.769	3.70795	.82714	1.99433	3486	55.384	6.5
6.4	31.250	3.74281	.86200	2.02919	3514	56.250	6.4
6.3	31.746	3.77795	.89714	2.06433	3546	57.143	6.3
6.2	32.258	3.81341	.93260	2.09979	3579	58.064	6.2
6.1	32.787	3.84920	.96839	2.13558	3614	59.017	6.1
6.0	33.333	3.88534	1.00453	2.17172	3654	60.000	6.0
5.9	33.898	3, 92188	1.04107	2.20826	3700	61.016	5.9
5.8	34.483	3.95888	1.07807	2.24526	3757	62.069	5.8
5.7	35.088	3.99645	1.11564	2.28283	3829	63.158	5.7
5.6	35.714	4.03474	1.15393	2.32112	3919	64.285	5.6
5.5	36.364	(4.07393)	(1.19312)	(2.36031)	4031	65.455	5.5
5.4	37.037	(4.11424)	(1.23343)	(2.40062)		66.667	5.4

[a] Figures in parentheses are extrapolated values, to facilitate interpolation.

TABLE 7. *Vapor pressure of liquid* e-D_2 (*for interpolation*)

Interpolation with 200/T as argument is more accurate and also more convenient than interpolation with T as argument. Linear interpolation introduces no significant errors below about 27° K. Between 27° and 33.5° K linear interpolation is slightly inferior to higher-order interpolation, and above 33.5° K higher-order interpolation should be used if accurate values are required.

$\frac{200}{T}$	T	$\mathrm{Log}_{10}P$			Δ	T	$\frac{360}{T}$
° K^{-1}	° *K*	*mm* Hg	*atm*	*psia*		° *R*	° R^{-1}
10.8	18.519	(2.0753)	(9.1945)	(0.3617)	337	33.334	10.8
10.7	18.692	2.1090	9.2282	.3954	338	33.646	10.7
10.6	18.868	2.1428	9.2620	.4292	338	33.962	10.6
10.5	19.048	2.1766	9.2958	.4630	339	34.286	10.5
10.4	19.231	2.2105	9.3297	.4969	340	34.616	10.4
10.3	19.417	2.2445	9.3637	.5309	341	34.951	10.3
10.2	19.608	2.2786	9.3978	.5650	341	35.294	10.2
10.1	19.802	2.3127	9.4319	.5991	342	35.644	10.1
10.0	20.000	2.3469	9.4661	.6333	342	36.000	10.0
9.9	20.202	2.3811	9.5003	.6675	344	36.364	9.9
9.8	20.408	2.4155	9.5347	.7019	344	36.734	9.8
9.7	20.619	2.4499	9.5691	.7363	344	37.114	9.7
9.6	20.833	2.4843	9.6035	.7707	346	37.499	9.6
9.5	21.053	2.5189	9.6381	.8053		37.895	9.5
9.5	21.053	2.51889	9.63808	.80527	3461	37.895	9.5
9.4	21.277	2.55350	9.67269	.83988	3464	38.299	9.4
9.3	21.505	2.58814	9.70733	.87452	3468	38.709	9.3
9.2	21.739	2.62282	9.74201	.90920	3472	39.130	9.2
9.1	21.978	2.65754	9.77673	.94392	3476	39.560	9.1
9.0	22.222	2.69230	9.81149	.97868	3483	40.000	9.0
8.9	22.472	2.72713	9.84632	1.01351	3490	40.450	8.9
8.8	22.727	2.76203	9.88122	1.04841	3497	40.909	8.8
8.7	22.989	2.79700	9.91619	1.08338	3504	41.380	8.7
8.6	23.256	2.83204	9.95123	1.11842	3512	41.861	8.6
8.5	23.529	2.86716	9.98635	1.15354	3519	42.352	8.5
8.4	23.810	2.90235	0.02154	1.18873	3527	42.857	8.4
8.3	24.096	2.93762	.05681	1.22400	3536	43.373	8.3
8.2	24.390	2.97298	.09217	1.25936	3546	43.902	8.2
8.1	24.691	3.00844	.12763	1.29482	3555	44.444	8.1
8.0	25.000	3.04399	.16318	1.33037	3564	45.000	8.0
7.9	25.316	3.07963	.19882	1.36601	3574	45.569	7.9
7.8	25.641	3.11537	.23456	1.40175	3585	46.154	7.8
7.7	25.974	3.15122	.27041	1.43760	3596	46.753	7.7
7.6	26.316	3.18718	.30637	1.47356	3607	47.369	7.6
7.5	26.667	3.22325	.34244	1.50963	3616	48.001	7.5
7.4	27.027	3.25941	.37860	1.54579	3626	48.649	7.4
7.3	27.397	3.29567	.41486	1.58205	3636	49.315	7.3
7.2	27.778	3.33203	.45122	1.61841	3648	50.000	7.2
7.1	28.169	3.36851	.48770	1.65489	3662	50.704	7.1
7.0	28.571	3.40513	.52432	1.69151	3676	51.428	7.0
6.9	28.986	3.44189	.56108	1.72827	3690	52.175	6.9
6.8	29.412	3.47879	.59798	1.76517	3706	52.942	6.8
6.7	29.851	3.51585	.63504	1.80223	3725	53.732	6.7
6.6	30.303	3.55310	.67229	1.83948	3745	54.545	6.6
6.5	30.769	3.59055	.70974	1.87693	3765	55.384	6.5
6.4	31.250	3.62820	.74739	1.91458	3785	56.250	6.4
6.3	31.746	3.66605	.78524	1.95243	3807	57.143	6.3
6.2	32.258	3.70412	.82331	1.99050	3831	58.064	6.2
6.1	32.787	3.74243	.86162	2.02881	3861	59.017	6.1
6.0	33.333	3.78104	.90023	2.06742	3892	60.000	6.0
5.9	33.898	3.81996	.93915	2.10634	3925	61.016	5.9
5.8	34.483	3.85921	.97840	2.14559	3961	62.069	5.8
5.7	35.088	3.89882	1.01801	2.18520	3998	63.158	5.7
5.6	35.714	3.93880	1.05799	2.22518	4038	64.285	5.6
5.5	36.364	3.97918	1.09837	2.26556	4085	65.455	5.5
5.4	37.037	4.02003	1.13922	2.30641	4151	66.667	5.4
5.3	37.736	4.06154	1.18073	2.34792	4268	67.925	5.3
5.2	38.462	(4.10422)	(1.22341)	(2.39060)	4437	69.232	5.2
5.1	39.216	(4.14859)	(1.26778)	(2.43497)		70.589	5.1

shortest range of experimental data is the least satisfactory for extrapolation.

There appear to be no other data at higher pressures for e-H_2, HD, or e-D_2. There are, however, data for n-H_2 and n-D_2 with which a comparison can be made. Figure 3 shows such a comparison. The upper diagram refers to H_2, the base line being table 5, which represents our results for e-H_2. It will be

Table 8. *Vapor pressures of liquid* e–H_2, HD, *and* e–D_2 *at intervals of 1 degree K*

T	20.4° K e-H_2 (0.21% o-H_2) P			Hydrogen deuteride, HD P			20.4° K e-D_2 (97.8% o-D_2) P			T
				Solid						
° K	*mm* Hg	*atm*	*psia*	*mm* Hg	*atm*	*psia*	*mm* Hg	*atm*	*psia*	° R
10	1.93	0.00254	0.0373	0.28	0.00037	0.0054	0.05	0.00007	0.0010	18.0
11	5.62	.00739	.109	.99	.00130	.0191	.21	.00028	.0041	19.8
12	13.9	.0183	.269	2.94	.00387	.0569	.75	.00099	.0145	21.6
13	30.2	.0397	.584	7.46	.00982	.144	2.20	.00289	.0425	23.4
14	-------	--------	--------	16.8	.0221	.325	5.57	.00733	.108	25.2
15	-------	--------	--------	34.4	.0453	.665	12.6	.0166	.244	27.0
16	-------	--------	--------	65.2	.0858	1.261	26.0	.0342	.503	28.8
17	-------	--------	--------	------	--------	--------	49.6	.0653	.959	30.6
18	-------	--------	--------	------	--------	--------	88.7	.1167	1.715	32.4
				Liquid						
14	58.8	0.0774	1.137	------	--------	--------	-------	--------	--------	25.2
15	100.3	.1320	1.939	------	--------	--------	-------	--------	--------	27.0
16	161.1	.2120	3.115	------	--------	--------	-------	--------	--------	28.8
17	246.0	.3237	4.757	112.4	0.1479	2.173	-------	--------	--------	30.6
18	360.3	.4741	6.967	176.2	.2318	3.407	-------	--------	--------	32.4
19	509.5	.6704	9.852	264.2	.3476	5.109	147.1	0.1936	2.844	34.2
20	699.2	.9200	13.520	382.0	.5026	7.387	222.3	.2925	4.299	36.0
21	935.3	1.2307	18.086	534.9	.7038	10.343	324.1	.4264	6.267	37.8
22	1223.7	1.6101	23.663	728.5	.9586	14.087	457.8	.6024	8.852	39.6
23	1570.5	2.0664	30.369	969.0	1.2750	18.737	628.8	.8274	12.159	41.4
24	1981.8	2.6076	38.322	1262.3	1.6609	24.409	843.1	1.1093	16.303	43.2
25	2463.8	3.2418	47.642	1614.5	2.1243	31.219	1106.6	1.4561	21.398	45.0
26	3022.9	3.9775	58.45	2031.5	2.6730	39.283	1425.6	1.8758	27.567	46.8
27	3665.1	4.8225	70.87	2519.4	3.3150	48.717	1806.1	2.3764	34.924	48.6
28	4396.8	5.785	85.02	3084.6	4.0587	59.65	2253.5	2.9651	43.576	50.4
29	5227	6.877	101.07	3732.8	4.9116	72.18	2774.3	3.6504	53.65	52.2
30	6162	8.108	119.16	4470.8	5.883	86.45	3374.7	4.4404	65.26	54.0
31	7210	9.486	139.41	5306	6.982	102.61	4062.0	5.345	78.55	55.8
32	8383	11.031	162.10	6246	8.219	120.79	4842.4	6.372	93.64	57.6
33	-------	--------	--------	7301	9.607	141.18	5723	7.530	110.66	59.4
34	-------	--------	--------	8480	11.157	163.97	6712	8.832	129.79	61.2
35	-------	--------	--------	9796	12.889	189.42	7819	10.288	151.19	63.0
36	-------	--------	--------	------	--------	--------	9051	11.909	175.02	64.8
37	-------	--------	--------	------	--------	--------	10418	13.708	201.45	66.6
38	-------	--------	--------	------	--------	--------	11943	15.714	230.94	68.4

Table 9. *Triple points and boiling points of* e-H_2, HD, *and* e-D_2

The triple points are the same as those of Woolley, Scott, and Brickwedde [6]

Modification	Triple point					Normal boiling point, *T*	
	T	*P*			*T*		
	° *K*	*mm* Hg	*atm*	*psia*	° *R*	° *K*	° *R*
e-H_2	13.81_3	52.8	0.0695	1.02	24.86_3	20.27_8	36.50_0
HD	16.60_4	92.8	.1221	1.79	29.88_7	22.14_3	39.85_7
e-D_2	18.69_1	128.5	.1691	2.48	33.64_4	23.63_7	42.45_7

seen from the auxiliary ordinate scale at the right-hand side of the graph that from the critical point down to the boiling point the vapor pressure of n-H_2 is about 3.5 percent lower than that of e-H_2, but that at lower temperatures the percentage difference increases. This is shown by the dotted line that represents the WSB equation for n-H_2. The data plotted include those of Cath and Onnes [12]. These are chiefly of historical interest, since the measurements were reported in 1917 before the existence of the ortho and para forms was recognized. The other data are all very recent, being those of Grilly [5], and of White, Friedman, and Johnston [3, 13]. The lower diagram refers to D_2, the base line being table 7, which represents our results for e-D_2. The data plotted in this graph are those of Grilly [5], and those of the present research given in table 4. In both researches the material was uncatalyzed and was assumed therefore to be n-D_2. In confirmation of this assumption it may be noted that at 21° K $[P(\text{e-}D_2)-P(\text{n-}D_2)]$ computed from figure 3 is roughly equal to the same quantity computed from the appropriate WSB vapor-pressure equations. The lack of complete agreement could be due to partial conversion of the n-D_2, but is just as likely to be due to incipient failure of the equations at the ends of their ranges. Above the boiling point, the vapor pressure of n-D_2 is about 0.5 percent lower than that of e-D_2. At lower temperatures the percentage difference increases.

It is possible to use table 5 for calculations involving n-H_2 by drawing a smooth curve to represent the values of $P(\text{n-}H_2)/P$(table 5). In a similar way table 7 may of course be used for calculations involving n-D_2.

2.6. Accuracy

The discussion of the accuracy of pressure measurements given in reference [8] is applicable to the present results. The uncertainties in the temperature scale are somewhat greater here than in the measurements on oxygen, but since the same temperature scale was used for all the measurements, the relative accuracy of the temperatures is quite high. The e-H_2 and e-D_2 tables are more accurate than the HD table because of the decomposition of the latter during the measurements. The pressures given for e-H_2 and e-D_2 are believed to be accurate to 0.2 or 0.3 mm Hg up to about 1 atm. Above 1 atm the uncertainty gradually increases, reaching perhaps ±8 mm Hg near the critical points. For HD the pressures up to 1 atm are probably equally accurate, but above 1 atm the uncertainty is larger, gradually increasing to perhaps ±15 mm Hg near the critical point. Uncertainty in the temperature scale is perhaps ±20 m deg.

3. Dew-Point Pressures of Mixtures

Since no information on the vapor pressures of mixtures of H_2, HD, and D_2 appears in the literature, it was thought worth while to determine approximately how far such mixtures depart from ideal solution behavior, even to the limited precision and within the limited range of temperature and composition allowed by the time available for this work. Experimental dew-point pressures of mixtures were compared with those predicted by the law of ideal solutions and discrepancies greater than the experimental error were found. Significant deviations from ideality in mixtures of ortho- and para-H_2 have been previously observed by Woolley, Scott and Brickwedde [6, p. 454].

3.1. The Law of Ideal Solutions

The applicability of the law of ideal solutions to a liquid mixture at a given temperature can be tested by measuring the dew-point pressure, at the given temperature, of a gaseous mixture of the same components in a known composition. In the derivation of the appropriate equation, the following symbols will be used: x_i, mole fraction of the ith component in the liquid phase; y_i, mole fraction of the ith component in the vapor phase; P_{oi}, vapor pressure of the ith component in pure form; P_v, total pressure of the vapor in equilibrium with the liquid mixture; $Z_i(P)$, value of PV/RT for the ith component in pure form at the pressure P, all at the same temperature. The law of ideal solutions states that in the vapor that is in equilibrium with an ideal liquid solution the partial pressure of the ith component is equal to x_iP_{oi}. Assuming that this partial pressure is also equal to y_iP_v, we have

$$x_iP_{oi}=y_iP_v. \tag{1}$$

Equating the sum of the y's to unity yields the expression for the vapor pressure of an ideal solution;

$$P_v=\Sigma x_iP_{oi}. \tag{2}$$

In the dew-point experiment the y's rather than the x's are known, and therefore the proper form of the expression is that obtained by equating the sum of the x's to unity;

$$1/P_v=\Sigma y_i/P_{oi}. \tag{3}$$

A more rigorous expression of the law would result from using fugacities in place of pressures in eq 1, but this refinement seems to have a negligible effect on P_v in the present instances. In an approximation sufficiently good to show the order of magnitude of the effect of using fugacities [see 14, p. 197 to 199, 221 to 227], eq 1 becomes

$$x_iP_{oi}Z_i(P_{oi})=y_iP_vZ_i(P_v). \tag{4}$$

By this substitution, eq 3 is changed to

$$1/P_v=\Sigma y_iZ_i(P_v)/P_{oi}Z_i(P_{oi}). \tag{5}$$

In order to evaluate eq 5 we take values of $Z(P)$ for H_2 and D_2 from reference [6] and, in the absence of experiemental values for HD, assume $Z(P)$ for HD equal to the mean of the values for H_2 and D_2. Values of P_v calculated from eq 5 differ from those calculated from eq 3 by only about 0.2 mm Hg, which is small compared to the experimental deviations from ideality.

3.2. Apparatus and Method

The equipment consisted of a 3-liter gas reservoir (which also served as a mixing bulb), a 140-cm^3 temperature-controlled chamber, and a combination mercury pump and mercury manometer. There were three functions for the latter, first to measure the pressure in the reservoir during mixing, second to transfer measured quantities of gas from the reservoir to the constant-temperature chamber, and third to measure the pressure in the chamber. A vacuum-type adiabatic calorimeter that had been previously constructed at this laboratory by R. B. Scott [15] was used as the isothermal chamber. The connection of these components is shown in figure 4.

A run proceeded as follows. One component of the mixture to be tested was admitted to the reservoir (at room temperature), and the reservoir pressure was measured. Then the second component was admitted and the pressure again measured, the mercury level in the manometer being adjusted to keep the reservoir volume constant. The composition of the mixture was deduced from these pressures taking into consideration the slight isotopic impurities in the individual components as determined by mass-spectrometer analysis. (There were traces of HD in the D_2 samples and of H_2 and D_2 in the HD samples.) The gaseous mixture was allowed to flow into the chamber until the chamber pressure was about 30 mm Hg less than the expected dew-point pressure. A selected volume of the pump-manometer was then filled with gas from the reservoir, the quantity being determined by the pressure difference in the pump before and after filling. This

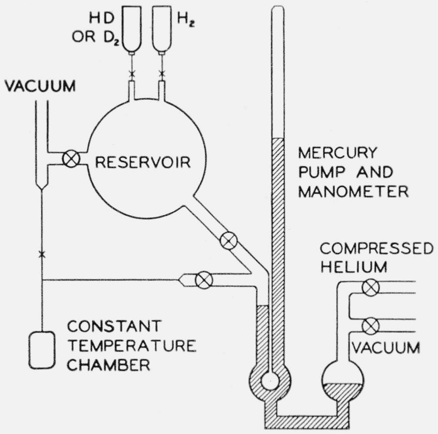

FIGURE 4. *Schematic drawing of the apparatus used in the dew-point pressure measurements.*

quantity was then pumped into the chamber, and the chamber pressure was remeasured. Before each reading of the chamber pressure the chamber was brought to the temperature of the run and the mercury was brought to a selected level. Each reading was repeated after several minutes to make sure that equilibrium had been attained. By repeating this pumping operation a series of points of chamber pressure versus added quantity of mixture was obtained. Temperatures for all points in a run were equal within about 0.00 $_3$ deg K to the average for the run. The thermometer used was L18, which has been calibrated against the Bureau's temperature scale [9], and which after these experiments checked satisfactorily at the ice point.

3.3. Results

Figure 5 is an example of a curve obtained in the manner described above. The dew-point pressure is taken to be the pressure at the intersection of the extrapolations of the two straight-line portions of the curve. Although the values of the abscissas are in error by that quantity of added material that went into the uncooled dead space of the apparatus (about 2% of the total quantity), the error is linear in terms of the pressure and hence has no effect upon the ordinate of the point of intersection. Manometer readings must be multiplied by 0.995 to convert to standard millimeters of mercury.

The results of seven runs are presented in table 10. Calculated pressures are taken from eq 3, using vapor pressures from reference [6, p. 454]. The ortho-para compositions are assumed to correspond to equilibrium at high temperature since no catalyst was used. This assumption is supported by the single-component dew-point pressures (runs E and H) observed with this apparatus. If these two pressures were plotted on the graphs of figure 3 they would fall within 0.0015 (in units of $\Delta\log_{10}P$) of the WSB curves for n-D_2 and n-H_2, respectively. The tabular entry $x_2(H_2)$ is calculated from eq 1.

Principal sources of error are (1) in $P_{obs.}$ the uncertainty in extrapolating the two straight lines to their intersection and (2) in $P_{calc.}$ the uncertainty in the composition. Estimated errors in $P_{obs.}$ are shown in the table. They are greater for the H_2-D_2 mixtures than for the H_2-HD mixtures because of the greater slope of the two-phase part of the isotherms of the former. Compositions of mixtures determined in the mass spectrometer differed from those determined by mixing pressures by an amount sufficient to cause the errors shown in the tabulated values of $P_{calc.}$ Mass-spectrometer compositions were thought to be slightly less reliable due to memory effect and to isotopic exchange in the spectrometer. The over-all estimated error is the sum of the errors in $P_{obs.}$ and $P_{calc.}$

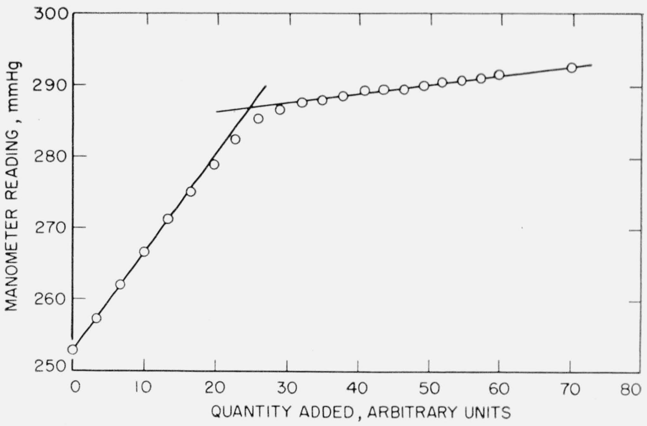

FIGURE 5. *Data of a run for the determination of the dew-point pressure of a mixture.*

Run L, 0.752 H_2, 0.248 HD, T=18.00° K.

TABLE 10. *Dew-point pressures of mixtures of* H_2, HD, *and* D_2 *in standard mm* Hg

Run	E	F	G	H	J	K	L
T(° K)	20.04	19.00	20.00	18.01	18.005	17.03	18.00
$y_1(H_2)$	0	0.499	0.440	1.00	0.503	0.503	0.752
y_2(HD)	0.008	.004	.004	0	.496	.496	.248
$y_3(D_2)$	.992	.497	.556	0	.001	.001	0
$x_1(H_2)$	----	.23	.20	----	.34	.33	0.61
$P_{01}(H_2)$	----	490.8	675.7	347.2	346.5	238.1	345.9
P_{02}(HD)	388.2	264.7	382.8	----	176.8	114.1	176.4
$P_{03}(D_2)$	223.5	145.1	219.9	----	87.5	50	-----
P_v,calc	224.3	224 ±2	313 ±2	347.2	234 ±2	154 ±2	279 ±2
P_v,obs	223.5	234 ±2	322 ±2	348.2	240 ±1	158 ±1	286 ±1
ΔP	−0.8	10 ±4	9 ±4	1.0	6 ±3	4 ±3	7 ±3
$100\Delta P/P$	−.35	4.4	2.8	0.3	2.5	2.6	2.5

Observed pressures are seen to be about 3 percent above those calculated from eq 3, with an estimated error in the deviations of about ±50 percent.

3.4. Discussion

The reason for the rounding of the experimental curves in the region of saturation is not clear, but several possibilities may be considered. These will be discussed with reference to the curve for pure H_2 (fig. 6) in which the rounding also occurs.

First consider the effect of nonideality of the gaseous hydrogen. This will cause the data to depart from a straight line in the same direction as that observed, but is much too small to account for the actual departure. A plot of the isotherm based on a three-term virial equation with the coefficients

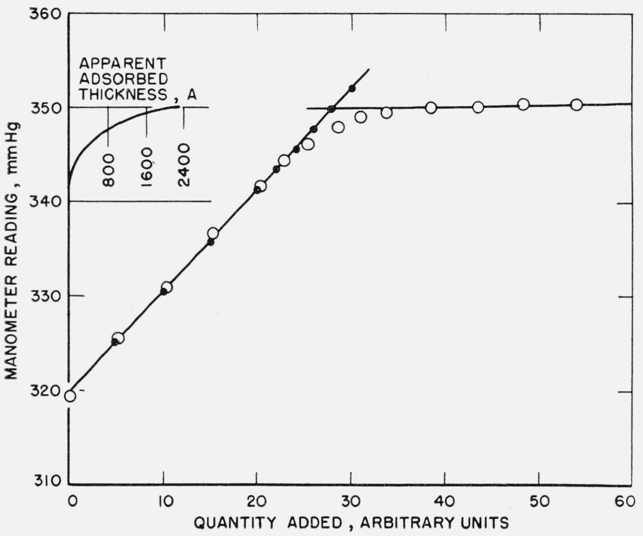

FIGURE 6. *Data of a run using pure H_2 in the dew-point pressure apparatus.*

Run H, T=18.01° K, ●, from virial equation, ○, experimental.

taken from [6, p. 396] is superimposed on the experimental curve. The scale of the abscissa has been adjusted to force the two curves to match in position and slope at one point (330 mm Hg). The significant comparison is that while the virial-based isotherm falls within 0.1 mm Hg of a straight line, the experimental curve deviates more than 3 mm Hg from its extrapolated linear portion. It is of course possible that the three-term virial equation is inadequate to cover peculiar effects, such as molecular aggregation, at pressures very close to saturation.

A more likely cause of the rounding is adsorption of the gas on the walls of the container. (For a discussion of this phenomenon see [16, p. 317 to 329]). Assuming that the horizontal departure of the experimental curve from the straight line corresponds to the quantity of material adsorbed, that the effective adsorbing surface is equal to the macroscopic surface area in the chamber, and that the density of adsorbed material is the same as that of the liquid, the thickness of the adsorbed layer is, as shown in figure 6, up to about 2000 A near saturation. This appears to be excessive; however, the effective surface area is probably many times the macroscopic area, due to surface roughness, and there is in addition the possibility of capillary adsorption. The surface material was tinned copper sheet and tinned copper tubing. The chamber volume contains many baffles and also a close-wound helix of copper tubing, so the existence of many crevices at contact points of parts of the structure is quite probable. It seems reasonable that these conditions could account for the large apparent adsorption thickness. If we can accept the adsorption explanation, then the intersection of the extrapolated straight lines is the correct dew point for the mixtures.

The making of the measurements was greatly assisted by George T. Furukawa, Raymond A. Nelson, and Dino Zei.

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