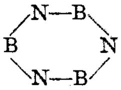
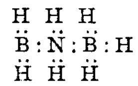
a B–N–B pattern of linking, rather than of those containing B–B bonds; the B–N–B skeleton explains why the compound, when heated, gives good yields of $B_3N_3H_6$, a substance containing the  ring; its rapid hydrolysis in acid solution to give five volumes of hydrogen suggests the existence of five B–H bonds.

Finally, attention is called to a recent paper by S. H. Bauer,[14] who, at our suggestion, investigated the electron diffraction of the vapor of this compound, and concluded that the data obtained can be explained only by the existence of a B–N–B skeleton for the molecule.

Acknowledgment.—We wish to express our thanks to the Research Corporation, for providing the liquid nitrogen used in a large part of this work.

Summary

The new volatile compound B_2H_7N (b. p. 76.2°; m. p. −66.5°) was prepared by the action of diborane upon its "diammoniate." The new substance is hydrolyzed easily in acid solution, to give five volumes of hydrogen, two equivalents of boric acid, and one equivalent of ammonium ion. Its thermal decomposition (slow at room temperature) produces diborane and a solid of undetermined character. It reacts with an equal gas volume of trimethylamine, to form a stable white solid; on heating with an excess of that amine, this product yields borine trimethylammine. With ammonia, B_2H_7N forms the stable solid $B_2H_7N{\cdot}NH_3$, which, on heating to 200°, gives a good yield of triborine triamine ($B_3N_3H_6$). The ammonia addition product reacts with sodium in liquid ammonia to liberate one equivalent of hydrogen; the residue after thorough removal of the solvent corresponds to the formula $NaNH_2{\cdot}B_2H_7N$.

The structure  $\begin{array}{c}\mathrm{H}\ \ \mathrm{H}\ \ \mathrm{H}\\ \ddot{\mathrm{B}}:\ddot{\mathrm{N}}:\ddot{\mathrm{B}}:\mathrm{H}\\ \ddot{\mathrm{H}}\ \ \ddot{\mathrm{H}}\ \ \ddot{\mathrm{H}}\end{array}$ is proposed for the compound, and although this specific picture is not considered definitely proved, it is shown to interpret satisfactorily all of the physical and chemical properties of the substance.

CHICAGO, ILL. RECEIVED APRIL 11, 1938

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[14] S. H. Bauer, THIS JOURNAL, **60**, 524 (1938).

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Compressibilities of Hydrogen and of Four Mixtures of Hydrogen and Nitrogen at 0, 25, 50, 100, 200 and 300° and to 1000 Atmospheres

BY R. WIEBE AND V. L. GADDY

This is a continuation of work in this Laboratory on the compressibilities of hydrogen, nitrogen and their mixtures.[1] A summary of work previous to 1930 was given by Bartlett. Townend and Bhatt measured the isotherms of hydrogen at 0 and 25° to 600 atm.[2] Isothermal measurements on hydrogen between 0 and 100° and up to 1000 atm. were made by Michels, *et al.*[3] Michels and Gerver recalculated the compressibility data of Kohnstamm and Walstra on hydrogen at 15.5 and 20° between 1000 and 2000 atm.[4] Isotherms of nitrogen between 0 and 150° and at pressures from 20 to 80 atm. were determined by Michels, *et al.*[5] This latter work was continued up to 400 atm. by Otto, Michels and Wouters.[6] A further extension to 3000 atm. including a calculation of the thermodynamic properties was made by Michels, *et al.*[7] W. Edwards Deming and Lola S. Deming have calculated the thermodynamic properties of hydrogen and nitrogen.[8]

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[1] (a) Bartlett, THIS JOURNAL, **49**, 687; 1955 (1927); (b) Bartlett, *et al.*, *ibid.*, **50**, 1275 (1928); (c) **52**, 1363 (1930). Dr. Bartlett has kindly informed me that in Ref. 1b the column of figures for the compressibility of a 3:1 mixture of hydrogen and nitrogen at 99.85° was wrongly transcribed and should be as follows:

Press., atm.	Old figures	Correct
1	1.3656	1.3656
50	1.3992	1.4027
100	1.4298	1.4364
200	1.5068	1.5170
300	1.5870	1.5975
400	1.6700	1.6799
600	1.8412	1.8472
800	2.0130	2.0168
1000	2.1865	2.1865

Also in the same table, for 300 atmospheres and 0°, the figures have been transposed.

Old figure	Correct figure
1.0264	1.2064

[2] Townend and Bhatt, *Proc. Roy. Soc.* (London), **A134**, 502 (1931).

[3] Michels, Nijhoff and Gerver, *Ann. Phys.*, **12**, 562 (1932).

[4] Michels and Gerver, *ibid.*, [5] **16**, 745 (1933).

[5] Michels, Wouters and De Boer, *Physica*, **1**, 587 (1934).

[6] Otto, Michels and Wouters, *Physik. Z.*, **35**, 97 (1934).

[7] Michels, Wouters and De Boer, *Physica*, **3**, 585 597 (1936).

[8] Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931). *ibid.*, **40**, 848 (1932); Deming and Deming, *ibid.*, **45**, 109 (1934).

Since in the previous investigations on hydrogen some disagreement exists among the different observers, we have repeated most of their measurements.

Apparatus and Procedure.—Figure 1 shows the low pressure part of the apparatus and the high pressure pipet. Before each run the connecting tube between pipet outlet valve M and stopcock G is open to the atmosphere through J. The 4-bulb buret A of 3000-cc. capacity is filled with mercury, stopcocks H, K and J are closed, and gas at some definite temperature and pressure is expanded from D through valve M. The whole volume is brought to atmospheric pressure by means of the oil-manometer F. Stopcock G is now closed and the gas is confined to the 4-bulb buret A. The mercury levels are now adjusted to calibration marks between the bulbs. Since usually two combinations of bulbs are possible, the one giving a pressure nearest to that of the atmosphere is selected. After opening H, manometer E is adjusted so that the mercury surface in the right arm just touches the tip of pin L. This assures a constant volume between H and L. The first two or three samples have to be discarded; after that the manometer will show the actual experimental variation, since the manometer volume is small compared with the gas volume in A. Any slight change in atmospheric pressure between closing of stopcock J and adjusting of oil-manometer F introduces only a negligible error since here again the volume of the connecting tube is small. Even a smaller volume is exposed to possible changes in room temperature. B is a coil to bring the incoming gas rapidly to the temperature of C. The large thermostat C was kept at 25 ± 0.01° while the temperature of the thermostat containing D was varied from 0 to 300°. Toluene and mercury filled regulators were used to cover the range between 0 and 200° while at 300° a thyratron control was used.[9] We used the control only for an auxiliary immersion heater; the voltage across the heating coils was that of the unregulated 110 a. c. voltage mains. It was possible to maintain the temperature within a few one-hundredths of a degree with little trouble. The true temperatures were measured with platinum resistance thermometers built according to specifications by Myers.[10] The thermometers were calibrated both at this Laboratory and at the Bureau of Standards with identical results. At 100 and 200° Crisco, or its equivalent, was used for bath liquid; while at 300° a lead–tin mixture was found satisfactory.

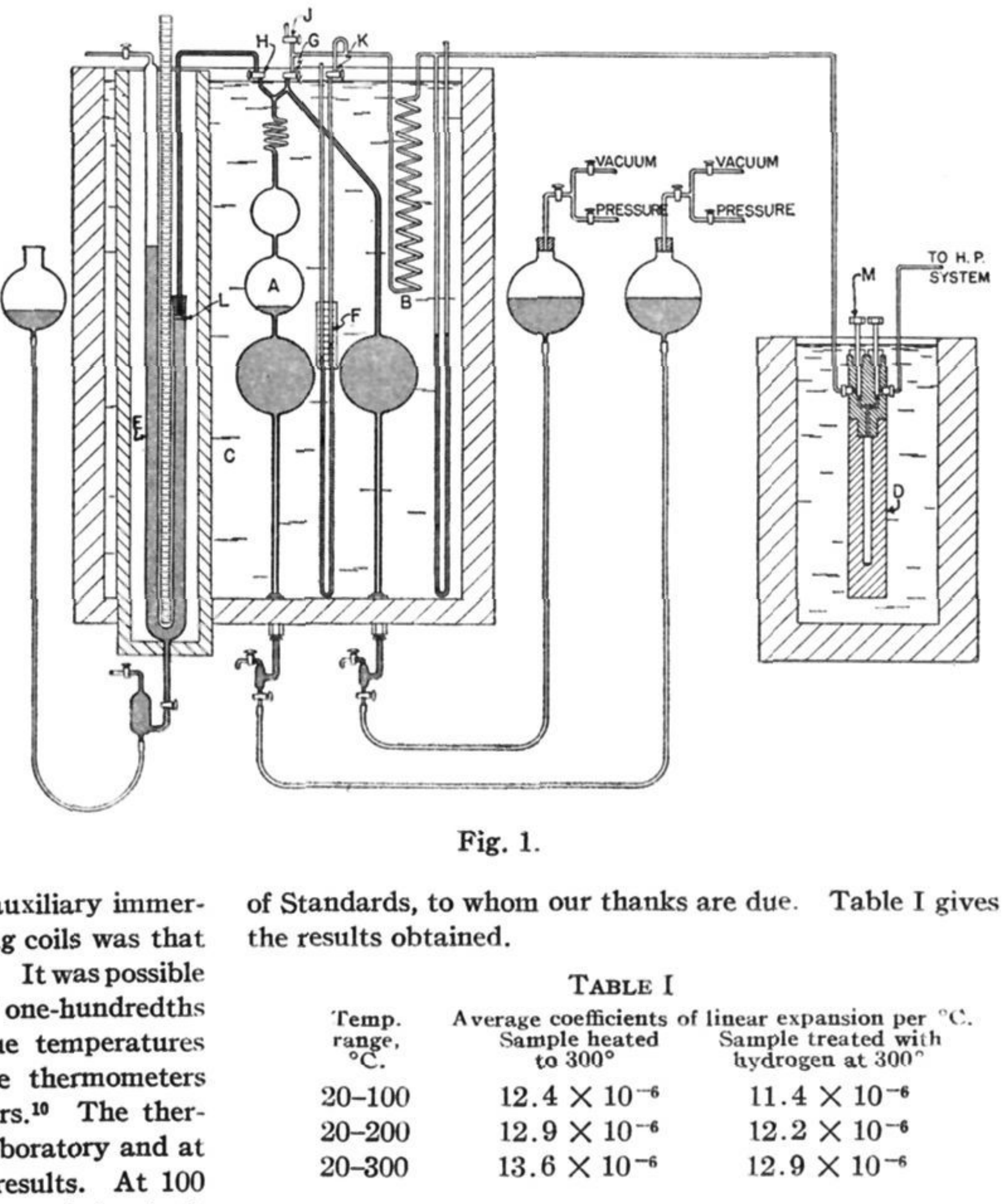

Fig. 1.

Our 200 and 1500 atmosphere piston gages were compared at 100 atm. with the National Bureau of Standards gage,[11] and it was found that only one of the pistons had developed a change of one part in 10,000 since August, 1935. The acceleration of gravity at the laboratory is taken to be 980.091 cm./sec.[2] The pressures are given in international atmospheres. The thermal conductivity and an accurate combustion method[12] were used to analyze the gas mixtures. The latter method was the more satisfactory in our case.

The high pressure volume was measured at 25 and 100° and at 100 atm. in a slightly modified steel pipet by displacing mercury by gas. The mercury was withdrawn, weighed and the volume calculated. The pressure coefficient was obtained from the work of Smith and Keyes.[13] From several determinations the compressibility of hydrogen was determined at 25 and 100°, and 100 atmospheres. These values were used as reference points throughout this work. The average coefficients of linear expansion of our steel (C 0.49%, Cr 2.48%, V 0.25%, Mn 0.68%) were determined by Dr. Peter Hidnert of the National Bureau of Standards, to whom our thanks are due. Table I gives the results obtained.

TABLE I

Temp. range, °C.	Average coefficients of linear expansion per °C. Sample heated to 300°	Sample treated with hydrogen at 300°
20–100	12.4×10^{-6}	11.4×10^{-6}
20–200	12.9×10^{-6}	12.2×10^{-6}
20–300	13.6×10^{-6}	12.9×10^{-6}

The results of Table I show a decided influence of hydrogen on steel. The sample used in determining the linear coefficient of expansion had been exposed to extreme conditions. In actual practice the thickness of the pipet walls (2.5 cm.) and the short time exposure at 300° and 1000

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[9] Zabel and Hancox, *Rev. Sci. Instruments*, **5**, 28 (1934).

[10] Myers, *Bur. Standards J. Research*, **9**, 807 (1932).

[11] Meyers and Jessup, *ibid.*, **6**, 1061 (1931).

[12] Shepherd, *ibid.*, **6**, 121 (1931).

[13] Smith and Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 313 (1934).

TABLE II

EXPERIMENTAL *pv* VALUES

P, atm.	Hydrogen	87.44 : 12.56 H_2:N_2 mixture	75.56 : 24.44 H_2:N_2 mixture	51.74 : 48.26 H_2:N_2 mixture	26.12 : 73.88 H_2:N_2 mixture	Nitrogen
			0°			
25	1.0152	1.0136		1.0062	0.9999	0.9910[b]
50	1.0311	1.0293	1.0265	1.0165	1.0038	.9853[b]
100	1.0641	1.0613	1.0572	1.0416	1.0191	.9857[a]
200	1.1327	1.1311	1.1273	1.1081	1.0789	1.0363[a]
400	1.2761[a]	1.2829	1.2863	1.2837	1.2728	1.2566[a]
600	1.4221[a]	1.4411	1.4558	1.4802	1.5023	1.5251[a]
800	1.5668[a]	1.5994	1.6282	1.6820	1.7382	1.7984[a]
1000	1.7086[a]	1.7563	1.7989	1.8824	1.9727	2.0676[a]
			25°			
25	1.1072	1.1063		1.1015	1.0945	
50	1.1235	1.1224	1.1202	1.1130	1.1020	1.0877[a]
100	1.1572	1.1563	1.1529	1.1425	1.1236	1.0969[a]
200	1.2271	1.2273	1.2249	1.2127	1.1894	1.1546[a]
400	1.3705	1.3794	1.3849	1.3878	1.3817	1.3699[a]
600	1.5158	1.5372	1.5542	1.5816	1.6076	1.6326[a]
800	1.6595	1.6948	1.7245	1.7822	1.8414	1.9030[a]
1000	1.8013	1.8508	1.8945	1.9817	2.0743	2.1710[a]
			50°			
25	1.1993[b]			1.1949		1.1848[b]
50	1.2162[b]	1.2145	1.2134	1.2079	1.1997	1.1882[a]
100	1.2496	1.2490	1.2467	1.2394	1.2253	1.2046[a]
200	1.3203	1.3215	1.3209	1.3133	1.2959	1.2692[a]
400	1.4640	1.4745	1.4822	1.4898	1.4887	1.4825[a]
600	1.6090	1.6315	1.6505	1.6836	1.7128	1.7408[a]
800	1.7525	1.7887	1.8202	1.8829	1.9444	2.0086[a]
1000	1.8933	1.9438	1.9894	2.0818	2.1758	2.2756[a]
			100°			
25	1.3827[b]			1.3812		1.3748[b]
50	1.4003	1.3996	1.4009	1.3976	1.3928	1.3853[a]
75	1.4182					
100	1.4358	1.4361	1.4377	1.4343	1.4262	1.4123[a]
200	1.5069	1.5111	1.5148	1.5142	1.5054	1.4889[a]
400	1.6513	1.6661	1.6777	1.6938	1.7021	1.7039[a]
600	1.7955	1.8231	1.8462	1.8868	1.9234	1.9569[a]
800	1.9386	1.9795	2.0159	2.0849	2.1532	2.2209[a]
1000	2.0780	2.1338	2.1844	2.2813	2.3834	2.4857[a]
			200°			
50	1.7659	1.7658	1.7703	1.7702	1.7711	1.7725[c]
100	1.8018	1.8049	1.8097	1.8078	1.8134	1.8115[c]
200	1.8756	1.8822	1.8909	1.9001	1.9057	1.9119[c]
400	2.0206	2.0379	2.0593	2.0858	2.1110	2.1455[c]
600	2.1628	2.1940	2.2264	2.2793	2.3320	2.3961[c]
800	2.3043	2.3496	2.3942	2.4749	2.5590	2.6557[c]
1000	2.4568[c]	2.5027	2.5627	2.6705	2.7876	2.9212[c]
			300°			
50	2.1293	2.1322	2.1323	2.1363	2.1432	2.1469[c]
100	2.1700[c]	2.1703	2.1757	2.1821	....	2.1986[c]
200	2.2393	2.2499	2.2596	2.2755	2.2914	2.3127[c]
400	2.3826	2.4079	2.4294	2.4664	2.5050	2.5506[c]
600	2.5246	2.5648	2.5978	2.6618	2.7315	2.8043[c]
800	2.6653	2.7195	2.7662	2.8581	2.9560	3.0623[c]
1000	2.8026	2.8702	2.9323	3.0554	3.1842	3.3203[c]

[a] Data from Michels, Nijhoff and Gerver, *Ann. Phys.*, **12**, 562 (1932) (Hydrogen); Michels, Wouters and De Boer, *Physica*, **3**, 585 (1936) (Nitrogen). [b] Data from Holborn and Otto, *Z. Physik*, **33**, 1 (1925). [c] Data from Bartlett, *et al.*, THIS JOURNAL, **50**, 1275 (1928).

atm. make it probable that an effect as great as that shown in the table would not occur. It was finally decided to use the equation given by Keyes[14]

$$V_t^{\mathrm{Fe}} = V_0(1 + 3.25 \times 10^{-5}t + 2.85 \times 10^{-8}t^2 - 1.65 \times 10^{-11}t^3)$$

where V_0 is the volume at 0° and V_t the volume at temperature t. This formula gives linear coefficients for the ranges 0–200 and 0–300° which are about the averages of the two sets given in Table I. The possible error in the determination of volume incurred at 0 and 50° is probably not more than one or two parts in 10,000, since the absolute values were known at 25 and 100°. At 200 and 300° the error introduced in V_t^{Fe} using the above equation is estimated between 0.05–0.10%. This does not influence the relative precision of any one isotherm. A change in the value of the reference point will affect all the other values by the same fractional amount.

Our experimental data are shown in Table II, and also data from Bartlett, Michels, and Holborn and Otto, where we have no values of our own. Since the data of Michels for nitrogen were given at odd pressures, we have used his equations to calculate the values given in this table. Dr. Deming expects to calculate the thermodynamic properties of hydrogen–nitrogen mixtures from these data.

We want to thank Dr. E. J. Jones for assistance in setting up our thyratron temperature control and Lola S. Deming (Mrs. W. E. D.) for helping us in our calculations. We also acknowledge the help of Mr. J. R. Dilley, who assisted in the design of the high pressure equipment.

Summary

Previous work since 1930 on the compressibilities of hydrogen, nitrogen and their mixtures has been summarized. A modified Bartlett compressibility apparatus is described. The compressibilities of hydrogen and four hydrogen–nitrogen mixtures have been measured at 0, 25, 50, 100, 200 and 300° and to 1000 atmospheres.

WASHINGTON, D. C. RECEIVED JUNE 6, 1938

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[14] Keyes, Joubert and Smith, *J. Math. Phys. Mass. Inst. Tech.*, 1, 191 (1922).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK AND CO., INC.]

The Hydration of Vitamin B₁

BY W. A. BASTEDO, JR., N. R. TRENNER AND T. J. WEBB

Introduction

The marked deliquescence of vitamin B_1[1] has been recognized by many investigators. The water of crystallization, however, has been given variously in the literature as one-half, one, or approximately one molecule of water (per molecule of vitamin) without regard for the conditions of humidity. The problem of preparing the one or more supposed hydrates in pure form and the measurement of their dissociation pressures was undertaken in these Laboratories. In the beginning the problem proved to be baffling on account of lack of reproducibility. This initial lack of reproducibility in the degree of hydration was attributed finally to variable minor details in the later stages of preparation of the vitamin, such, for example, as solvents used in the precipitation process, methods of removing solvent, etc. After standard procedures having regard for such details had been found, the early difficulties regarding reproducibility disappeared (at least to the extent of 0.1 g. of water per 100 g. of vitamin). The much higher reproducibility obtainable for samples under identical conditions of humidity led to the belief that the remaining difficulty lay in the inherent problem of the reproducibility of the aqueous pressures to which the samples were exposed. The fact that *slight* variations in the aqueous pressures to which the samples were exposed gave rise to appreciably variable water contents of the vitamin indicated immediately that the problem was not one of an ordinary system of hydrates.

Experimental Details and Results

In the first attack on the problem the aqueous pressure to which the samples were exposed was regulated by H_2SO_4–H_2O mixtures in evacuated desiccators at 25 ± 1°.

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[1] Formula of vitamin B_1