columns maintained a nearly constant difference of height except near the closed end of the capillary. After correcting for the small pressure of uncondensable gases, the difference of height was found to be 2.6 cm. The vapor pressure of water at the same temperature is 2.65 cm.

Summary

Hydrogen molecules have been activated by collisions with electrons of known energy and made to react with copper oxide. It is found that reaction begins at 11.4 volts. At the same time Franck current-potential curves show a resonance point at 11.4 volts. This agrees with the recent value of 11.6 volts for the first resonance potential of the hydrogen molecule as obtained from spectroscopy. It is concluded, therefore, that the first step in the activation process at low voltages is the formation of a resonated hydrogen molecule.

No evidence is found that 3- to 5-volt electrons dissociate hydrogen molecules.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY]

THE CONCENTRATION OF WATER VAPOR IN COMPRESSED HYDROGEN, NITROGEN AND A MIXTURE OF THESE GASES IN THE PRESENCE OF CONDENSED WATER

BY EDWARD P. BARTLETT

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Recently developed commercial processes involving the use of gases under pressures of several hundred atmospheres have aroused keen interest in the physical properties of compressed gases. Not only does engineering design depend upon these properties, but accurate data concerning them must be available for a complete scientific understanding of the process itself.

In the synthetic preparation of ammonia from hydrogen and nitrogen the efficiency and life of the catalyst as well as the purity of the product depend upon the purity of the gases. Of possible impurities, water vapor is always present. It has been customary to calculate the water vapor content of "indifferent" gases in contact with a liquid by assuming the application of the perfect gas law both to gas and vapor, and the constancy of the vapor pressure of a liquid with temperature, but neglecting the effect of pressure. The volume per cent. of water vapor at temperature T in any indifferent gas and at any pressure is thus expressed

$$(\text{Volume \% of water vapor})_T = (100p)/(760P)_T \quad (1)$$

where p is the vapor pressure of water at T in millimeters of mercury and P is the total pressure in atmospheres. If a portion of the compressed gas in equilibrium with condensed water be removed from contact with water and allowed to expand, the volume per cent. of water vapor in the expanded gas will be identical with that calculated for the compressed gas.

It has been recognized that the above assumptions are inaccurate and several attempts have been made to develop a more accurate formula.

All known gases deviate from the perfect gas law at high pressures. If pv/p_0v_0 represents the ratio of the pressure-volume product at pressure p to the pressure-volume product at pressure p_0 at temperature T, then the above formula should be written

$$(\text{Volume \% of water vapor in expanded gas})_T = \left(\frac{100p}{760P}\cdot\left(\frac{pv}{p_0v_0}\right)_P\right)_T \qquad (2)$$

Secondly if the indifferent gas in contact with the liquid be assumed to be a membrane permeable to vapor but not to the liquid, the effect of pressure on the vapor pressure of the liquid may be calculated from Poynting's relation[1]

$$\left(\frac{\mathrm{d}p}{\mathrm{d}P}\right)_T = \left(\frac{V}{v}\right)_T \qquad (3)$$

where p is the vapor pressure of the liquid at the temperature T, P the total pressure, V the specific volume of the liquid at T and v the specific volume of the vapor at T. This expression is evaluated by placing

$$V = V_0(1 - \beta P) \qquad (4)$$

where β is the compressibility factor of the liquid at T and V_0 is the specific volume of the liquid at T and at saturation pressure. In case the vapor content is so small as to show but slight deviation from the perfect gas law

$$v = RT/p \qquad (5)$$

Where such is not the case v must be derived from an established equation of state for the vapor.

The expression

$$\left(\frac{\mathrm{d}p}{p\mathrm{d}P}\right)_T = \left(V_0\,\frac{(1-\beta P)}{RT}\right)_T \qquad (6)$$

is integrated between p_0 and P where p_0 is the saturation pressure at T, and solved for p/p_0 at P.[2]

Equation 2 may now be written

$$\left(\begin{matrix}\text{Volume \% of water}\\ \text{vapor in expanded gas}\end{matrix}\right)_T = \left(\frac{100p}{760P}\cdot\left(\frac{pv}{p_0v_0}\right)_P\cdot\left(\frac{p}{p_0}\right)_P\right)_T \qquad (7)$$

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[1] Poynting, *Phil. Mag.*, [IV] 12, 32 (1881).

[2] When v is derived from Callendar's equation of state for water vapor

$$v = 4.548\ T/p - 26.3\left(\frac{373}{T}\right)^{\frac{10}{3}} + 1.0$$

a transcendental equation results, which is mathematically inconvenient to solve. A solution of this expression for the minimum specific volume of water vapor observed in this investigation (5872 cc. with nitrogen at 50° and 1000 atm.) gives results which differ from those obtained by the use of the perfect gas law by less than 0.5%. Because this difference is well within the limits of experimental error, it has been assumed that water vapor in these small concentrations conforms to the ideal gas laws.

Quantitative studies of liquid-gaseous systems of this type have been made by Sander[3] on ether and carbon dioxide, by Pollitzer and Strebel[4] on water and air, hydrogen or carbon dioxide at pressures below 200 atmospheres and by McHaffie[5] on a sodium sulfate-air system at the transition point of the sulfate. Larson and Black in this Laboratory[6] have made an extensive study of a liquid ammonia-hydrogen-nitrogen system at pressures to 1000 atmospheres. As observed results obtained by these investigators do not even qualitatively correspond to results calculated by Equation 7, a further study of indifferent gas-liquid systems is important. The present investigation comprizes a study of the water vapor content of a compressed 3:1 mixture of hydrogen and nitrogen in contact with liquid water at 25°, 37.5° and 50° and a similar study of compressed hydrogen and compressed nitrogen at 50° at pressures to 1000 atmospheres.

Method

The dynamic method of determining vapor pressures has been modified for use at high pressures. The gas is bubbled through water in a system maintained at constant temperature and pressure. The saturated compressed gas is expanded through a needle valve kept at the temperature of the bath and the expanded gas is dehydrated by means of phosphorus pentoxide at liquid-air temperature. The volume of the expanded gas is determined by means of a gas meter or by a gas holder of known capacity. The gain in weight of the phosphorus pentoxide tubes represents the water vapor in the known volume of expanded gas. The volume of the compressed gas is calculated from the pv/p_0v_0 data for the gas under investigation, and the free space, or space between the molecules of the gas, is calculated by subtracting from the actual volume, the volume occupied by the molecules.

Experimental Procedure and Method of Calculation

The 3:1 mixture of hydrogen and nitrogen is prepared by burning electrolytic hydrogen with air. The burned gas passes over a copper de-oxidizer and through a water condenser to a gas compressor. The compressed gas is freed from oil in a charcoal trap and stored at 200 atmospheres.[7]

The hydrogen used in this investigation was made by the electrolysis of potassium hydroxide solution. The nitrogen was from fractionated liquid air guaranteed 99.8% pure and containing insufficient oxygen to be detected by combustion analysis with pure hydrogen. These gases are stored in cylinders and during use are connected to the system at *A* (Fig. 1).

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[3] Sander, *Z. physik. Chem.*, **78**, 513 (1912).

[4] Pollitzer and Strebel, *ibid.*, **110**, 768 (1924).

[5] McHaffie, *Phil. Mag.*, [VII] **1**, 561 (1926).

[6] Larson and Black, THIS JOURNAL, **47**, 1015 (1925).

[7] For flow sheet of this apparatus and description of burner see Ernst. Reed and Edwards, *Ind. Eng. Chem.*, **17**, 775 (1925).

From *A* the gases enter the hydraulic booster pump,[8] where they are compressed to the desired pressure. A de-oxidizer at 350° removes traces of oxygen, and an ice-cooled condenser most of the water vapor. By the proper manipulation of Valves *F*, *G* and *H*, the gas may be purified still further by passage through a condenser at the temperature of liquid air. This refinement can be employed only with the hydrogen.

A dead-weight pressure gage sensitive to 0.1 atmosphere is attached to the system at this point. During an experiment the pressure is maintained constant, with the piston under rotation.

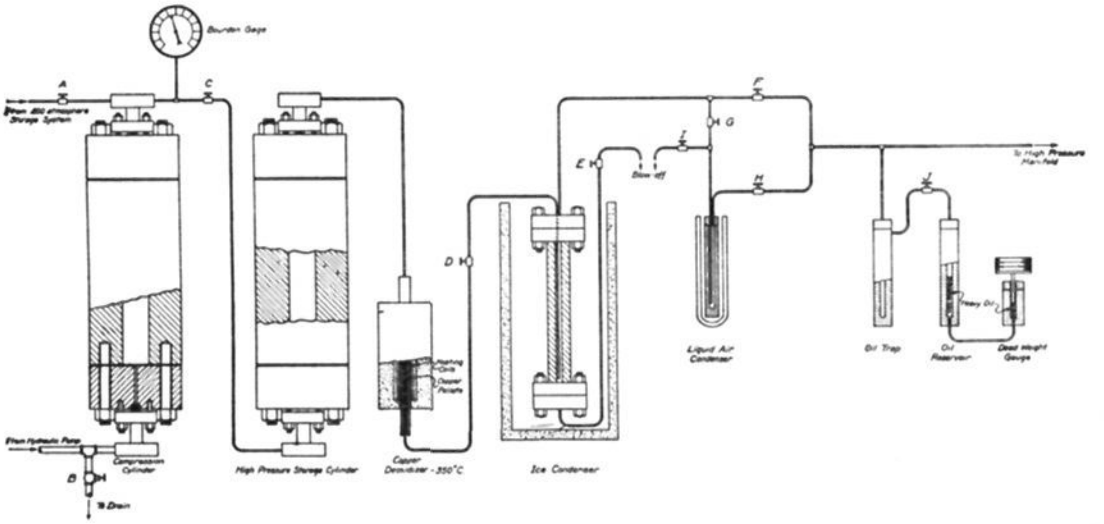

Fig. 1.—Compression cylinders and purification train for hydrogen and nitrogen under high pressure.

The humidifiers are double steel bottles so arranged that the gas must bubble through the liquid. The first pair of bottles is maintained at 5° above or below the final temperature of saturation, alternating on successive runs in order to detect failure to attain equilibrium. No variations in results have been traceable to this source. The humidifiers are followed by a spray catcher tightly packed with fine-mesh copper gauze. *B* is the expansion valve, kept at bath temperature in order to avoid heat effects. *C* is a safety valve kept open to the air while the flow of gas through *B* is being adjusted. The overflow trap, at first supplied with a pure, heavy, mineral oil, but later with mercury, is an important link in the system. It acts as a safety valve and also determines the pressure, and hence the weight, of the gases confined in the absorption tubes. Care is taken to maintain the liquid level constant. The pressure is about 3 cm. of mercury.

From *D* the gases may be by-passed through a pre-drying train of phosphorus pentoxide tubes, one or two of which are immersed in liquid air, or conveyed directly to the absorption trains, here shown in parallel. At

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[8] For a description of the pump and high-pressure equipment used in this investigation see Ernst, *Ind. Eng. Chem.*, **18**, 664 (1926).

high pressure when the flow of compressed gas through the liquid is very slow, the gas flow is divided at *F* and *G*, and two determinations are made during the same period of time.

The absorption tubes, about 15 cm. long, are filled with glass beads coated with phosphorus pentoxide and held in place by glass-wool plugs. Their weight is about 75 g. The first two tubes are immersed in liquid air and the third tube is used to catch any snow or spray; 90 to 100% of the water vapor is caught in the first tube. The third tube seldom changes in weight more than a few tenths of a milligram. The absorption tubes are flushed with pre-dried gas for two hours or more before the first

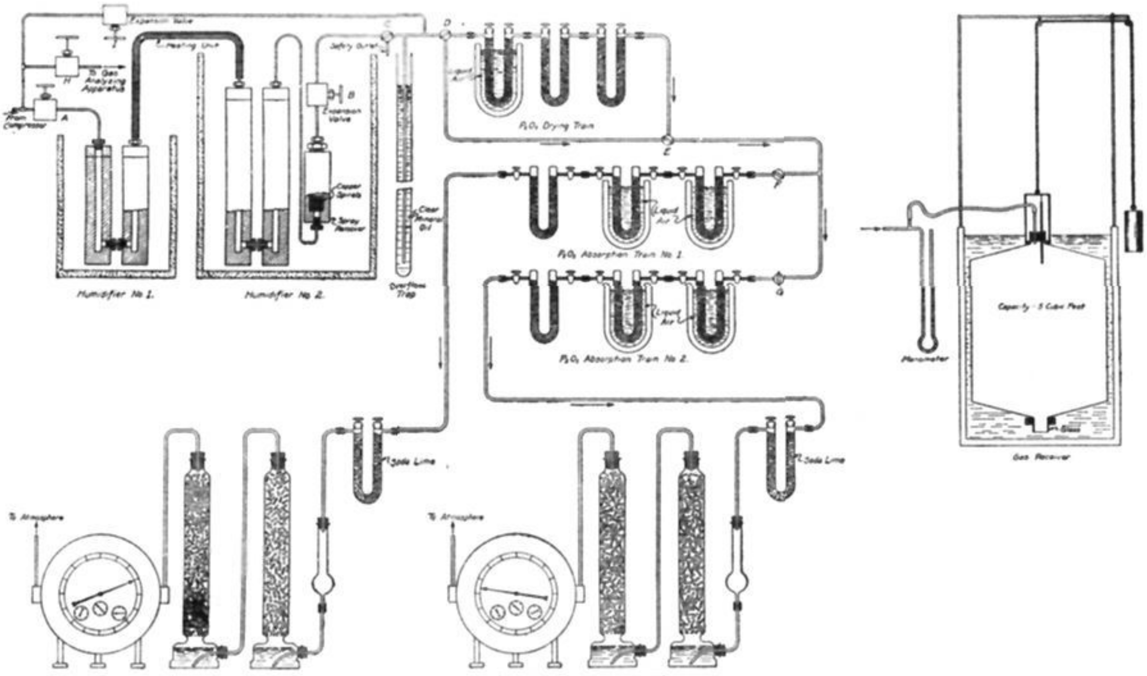

Fig. 2.—Humidifiers, absorption trains and gas-measuring devices for determination of vapor pressure of water.

weighing. After absorption of water vapor they are allowed to come to room temperature with the stopcock at the outlet end of the series closed, and are then flushed with 30 liters of pre-dried gas to remove adsorbed material other than water vapor. The 2–3 mg. lost during this flushing is probably mostly adsorbed nitrogen.

During a run, the stopcocks of the absorption tubes are protected from the mass of condensed moisture, due to the low temperature of the liquid air, by toy balloons which fit snugly around the barrels. Weighings are made with the use of a counterpoise and the usual precautions incident to careful weighings are observed. The maximum error of weighing is not greater than 0.2 mg., ordinarily reproducible, after hours of standing, to less than 0.5 mg. The average mean error on the three tubes should not exceed 1 mg.

The volume of the expanded gas is measured by means of a wet meter or by a large calibrated gas holder shown in the insert (Fig. 2). The dry gas is humidified before entering the meter. Frequent calibration of the meter showed a maximum variation of 1%. As the average of hourly readings of temperature and pressure were used in calculating the volume of dry gas passing through the meter, no other large error of calculation is involved. On account of lack of temperature control throughout its volume, a similar error may be introduced into measurements made with the gas holder. The mean error from all sources in this investigation probably does not exceed 1%.

A single illustration is given to make clear the method by which derived data in the tables were calculated from observed data.

Total pressure (absolute)	1000 atmos.
Temperature of humidifiers (absolute)	323.1°
Time of run	10 hours, 45 min.
Volume of expanded gas indicated by meter	566.57 liters
Av. temperature of wet meter	21.7°
Av. barometric pressure	752.6 mm.
Volume of dry gas at 25° and 760 mm	562.35 liters
Increase in wt. of P_2O_5 tubes	43.1 mg.
Volume of water vapor	0.0585 liter
Total volume of expanded gas with water vapor	562.41 liters
Volume of compressed gas, assuming perfect gas laws	0.5624 liter
Wt. of water per liter (W_1)	76.65 mg.
pv/p_0v_0 for a 3:1 mixture at 25° and 1000 atm	1.7378
Actual volume of compressed gas (0.5624×1.7378)	0.9773 liter
Weight of water per liter of actual volume (W_2)	44.10 mg.
Molecular diameter, hydrogen	2.40×10^{-8} cm.
Molecular diameter, nitrogen	3.38×10^{-8} cm.
Volume of hydrogen molecules per liter	1.780×10^{-4} liters
Volume of nitrogen molecules per liter	4.972×10^{-4} liters
Volume of hydrogen and nitrogen molecules, 3:1 mixture	2.578×10^{-4} liters
Volume of molecules in 562.41 liters of mixture	0.1450 liter
Volume of free space ($0.9773 - 0.1450$)	0.8323 liter
Wt. of water per liter of free space (W_3)	51.79 mg.
Wt. of water vapor per liter under saturation pressure assuming perfect gas laws (W_0)	22.80 mg.
Actual weight of water vapor per liter under saturation pressure (W)[a]	23.03 mg.

[a] Knoblauch, "Tabellen und Diagramme für Wasserdampf," München, 1923, p. 28.

Experimental Results

Explanation of Data Tables.—Table I contains a typical set of data collected at 25°. Col. 3 shows the measured amount of expanded gas which passed through the absorption tubes, calculated to standard pressure and to the temperature of the experiment. The pv/p_0v_0 values given in Col. 4 are from data collected in this Laboratory. It is the ratio of the volume actually occupied by a given quantity of the gas at the temperature of the experiment to the volume it would occupy if it were a perfect gas at the temperature of the experiment. Col. 5 indicates the actual volume of compressed gas used in the experiment and Col. 6 the weight of water vapor collected. Col. 7 shows the volume of the gas molecules themselves. Results given in Cols. 8, 9 and 10 are calculated from the data given in

TABLE I

WATER-VAPOR CONTENT OF 3:1 HYDROGEN-NITROGEN GAS MIXTURE IN EQUILIBRIUM WITH LIQUID WATER AT HIGH PRESSURES

Temp., 25°.

Molecular diameter of H_2 = 2.40×10^{-8}; of N_2 = 3.38×10^{-8}.[a] Volume of molecules per liter in 3:1 hydrogen-nitrogen mixture = 0.2578 cc. at 760 mm., 25°.

1 Expt. no.	2 Total press., atm.	3 Vol. of expanded gas, liters (25°)	4 $\frac{pv}{p_0v_0}$	5 Vol. of compressed gas (liters actual)	6 Wt. of H_2O vapor, mg.	7 Vol. of moles, liters	8 Mg. of H_2O per liter (perfect gas vol.)	9 Mg. of H_2O per liter (actual gas vol.)	10 Mg. per liter (free space)
Satn. press.							(22.80)[b]	(23.03)	(23.03)
22	100	292.6	1.058	3.094	82.3	0.0754	28.13	26.60	27.26
23		280.1		2.963	79.6	.0722	28.41	26.87	27.54
							(28.54)	(26.73)	(27.40)
20	200	283.0	1.118	1.582	49.6	.0730	35.05	31.35	32.86
21		288.4		1.612	49.5	.0743	34.33	30.70	32.19
							(34.69)	(31.02)	(32.52)
16	300	286.8	1.192	1.139	38.6	.0739	40.38	33.89	36.24
17		287.1		1.140	39.0	.0740	40.75	34.20	36.57
18		566.2		2.249	76.6	.1459	40.59	34.06	36.43
							(40.57)	(34.05)	(36.41)
19	400	571.0	1.266	1.807	62.7	.1472	43.93	34.69	37.76
24A		564.7		1.788	64.6	.1456	45.76	36.13	39.34
24B		557.3		1.764	62.4	.1436	44.79	35.37	38.50
27A		567.1		1.795	62.3	.1462	43.95	34.71	37.78
27B		556.6		1.762	61.8	.1435	44.41	35.07	38.18
32A		567.8		1.797	62.3	.1464	43.89	34.66	37.73
32B		561.3		1.777	63.5	.1447	45.25	35.74	38.91
							(44.57)	(35.23)	(38.31)
28A	600	572.8	1.424	1.359	54.3	.1435	56.89	39.95	44.82
28B		565.3		1.341	53.7	.1476	57.00	40.03	44.91
							(56.95)	(39.99)	(44.86)
14	800	558.2	1.581	1.104	46.7	.1439	66.92	42.32	48.66
15		577.1		1.141	47.4	.1487	65.72	41.56	47.78
30A		562.1		1.111	47.5	.1449	67.61	42.75	49.16
30B		555.4		1.098	46.7	.1432	67.26	42.53	48.91
							(66.88)	(42.29)	(48.63)
10	1000	560.2	1.738	0.9735	43.8	.1444	78.19	44.99	52.83
11		557.2		.9683	43.2	.1436	77.11	44.37	52.05
31A		562.4		.9773	43.1	.1450	76.64	44.10	51.79
31B		563.7		.9796	43.4	.1453	76.99	44.30	52.02
29A		567.1		.9855	42.5	.1462	74.95	43.13	50.64
							(76.78)	(44.18)	(51.87)

[a] Kaye and Laby, "*Physical and Chemical Constants*," 1918, p. 33.

[b] Data in parentheses are average values.

the first seven columns, and represent milligrams of water per liter of compressed gas, first assuming the operation of the laws of perfect gases, then making correction to actual volume and finally to the volume of "free space."

Table II records a summary of similar data for hydrogen and nitrogen at 50°. Table III contains a summary of data obtained with approximately a 3:1 hydrogen-nitrogen gas mixture at 50°, 37.5° and 25°. The last column in these tables contains values calculated from Poynting's relation governing the effect of pressure on the vapor pressure of a liquid. Data from Table II are given in the form of curves in Fig. 3, and the amounts of water vapor per liter of actual volume of nitrogen, hydrogen and the 3:1 mixture of these gases at 25°, 37.5° and 50° are plotted in Fig. 4.

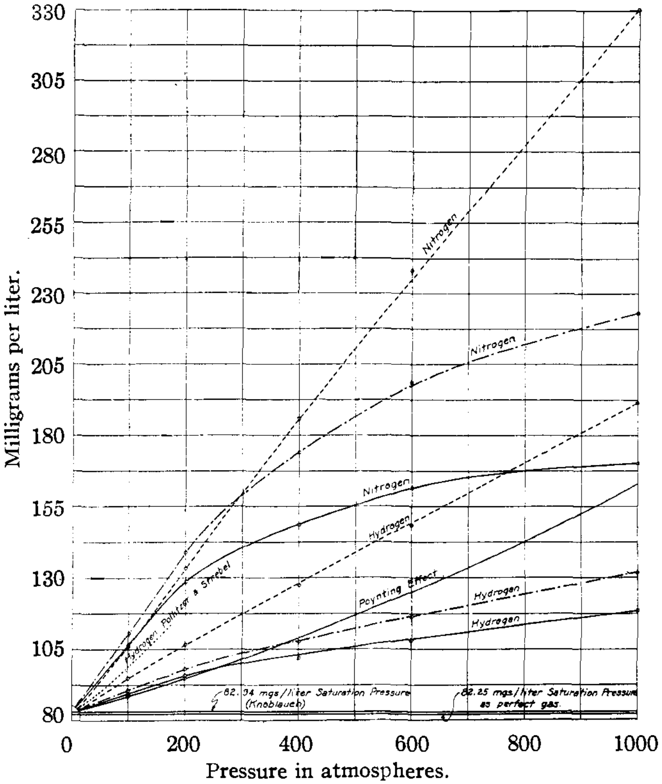

Fig. 3.—Water vapor content of hydrogen and nitrogen in contact with liquid water at high pressures at 50°. – – – – Calcd. to perfect gas volume. ——— Calcd. to actual volume. — · — · — Calcd. to free space.

Table IV presents a summary of the data from this investigation. The values given for mg. per liter of compressed gas are taken directly from the smoothed curves of Fig. 4. A small correction is added to the values for the approximately 3:1 mixture at 50° and 37.5° to make the figures conform to a gas mixture of exactly 3:1 composition. The mg. per liter of gas expanded after contact with liquid water at high pressure is calculated from these data by use of the equation

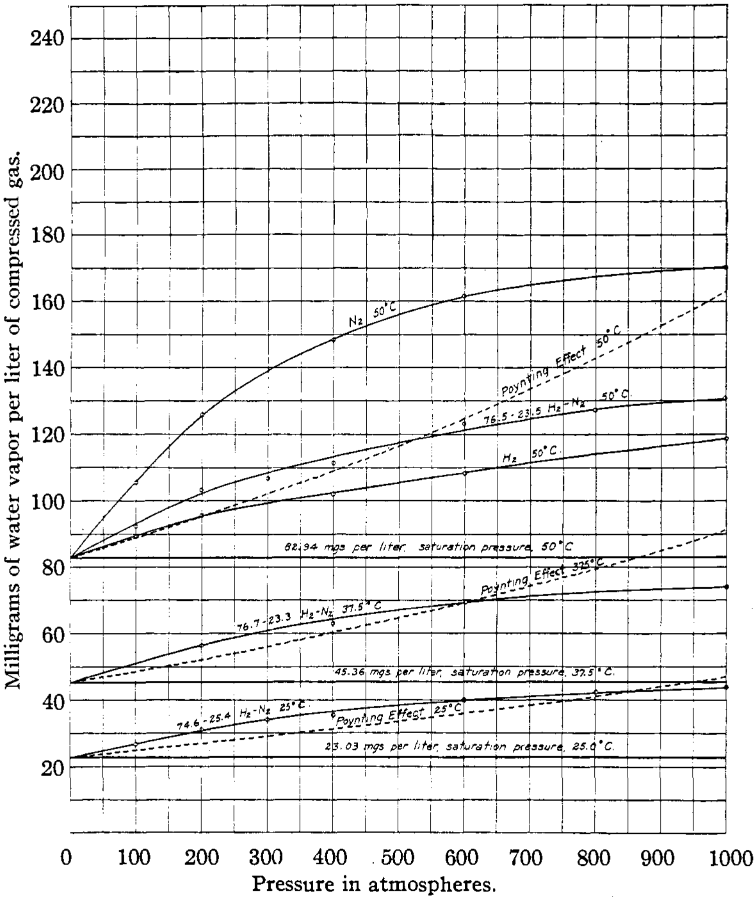

Fig. 4.—Water-vapor content of compressed gases in contact with liquid water, 25.0°, 37.5°, 50.0°.

$$(W_E)_T = \left(\frac{W_c}{P}\left(\frac{pv}{p_0v_0}\right)_P\right)_T \text{ or } \left(\frac{W_E}{W_c} = \frac{v}{v_0}\right)_T \tag{8}$$

where W_E is the mg. per liter of expanded gas, W_c the mg. per liter of compressed gas, P the total pressure and pv/p_0v_0 the compressibility factor at pressure P and temperature T.

The volume per cent. of water vapor in the expanded gas given in Table IV and also in Fig. 5 has been calculated by means of the perfect gas laws, using the weight of water given by Equation 8. Results shown on the dotted-line curves are calculated by means of Equation 7.

Discussion of Results

The data in Table II and the curves of Fig. 3 demonstrate the following. (1) The water vapor content in a compressed gas is a function of the properties of the gas. Volume for volume at 1000 atmospheres' pressure and at 50°, nitrogen will hold 44% more water vapor than will hydrogen. (2) The difference in water-vapor content of the gases is not explained by a difference in free space. Under conditions stated in (1), 69% more water vapor is present per unit of free space between molecules of nitrogen than between molecules of hydrogen. (3) There is no apparent relationship between observed results and results calculated by Poynting's relation. (4) Qualitatively, results of this investigation on hydrogen at 50° verify the findings of Pollitzer and Strebel.[4,9]

TABLE II

OBSERVED AND CALCULATED WATER-VAPOR CONTENT OF HYDROGEN AND NITROGEN IN EQUILIBRIUM WITH LIQUID WATER AT HIGH PRESSURES

Temp., 50°

Vol. of molecules per liter of hydrogen at 760 mm. and 50° = 0.1639 cc. Vol. of molecules per liter of nitrogen 760 mm. 50° = 0.4577 cc.

		Hydrogen mg. per liter				Nitrogen mg. per liter			
Pressure, atm.	pv/p_0v_0	Perfect gas vol.	Actual vol.	Free space	pv/p_0v_0	Perfect gas vol.	Actual vol.	Free space	Poynting effect, calcd.
Satn. press.	...	82.25	82.94	82.94	...	82.25	82.94	82.94	....
100.0	1.060	95.0	89.1	90.5	1.006	106.1	105.4	110.5	88.83
200.0	1.117	106.7	95.5	98.4	1.058	133.2	125.9	138.4	95.13
400.0	1.250	127.3	101.8	107.5	1.251	185.5	148.3	173.7	108.98
600.0	1.370	148.0	108.0	116.4	1.476	238.4	161.5	198.5	124.91
1000.0	1.615	191.6	118.7	132.0	1.940	330.5	170.3	223.0	162.81

The data of Table III and Fig. 4 show the following. (1) The effect of a compressed 3:1 hydrogen-nitrogen gas mixture on the water content of the gas phase in contact with liquid water is greater at 50° than at 25° but the proportional effect is greater at the lower temperature. At 1000

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[9] The quantitative difference between the results obtained on hydrogen in the two investigations at low pressures may be explained partly by the experimental method employed. Pollitzer and Strebel depended upon the large capacity of a cylinder of compressed gas to prevent an appreciable change of pressure during an experiment. However, between 200 and 100 atmospheres the average increase in water-vapor content per liter of expanded gas amounts to 0.8% for each atmosphere lowering of pressure. If 160 liters of expanded hydrogen were drawn from a cylinder of 40 liters' capacity at a pressure of 200 atmospheres, the pressure must have dropped at least five atmospheres. Secondly, Pollitzer and Strebel located the expansion valve outside the thermostat. The heat of the expanding gas may have been conducted through the connecting tube to particles of unvaporized water, thus establishing equilibrium at a temperature higher than that of the thermostat. Either of these causes would tend to produce water concentrations higher than have been obtained in the present investigation.

atmospheres and 50° the compressed gas accounts for 47.66 mg. or 57.5% increase in water content per liter; at 25° corresponding values are 21.17 mg. and 91.6%, respectively. (2) The proportional effect of the compressed gas at 37.5° (64.5%) is not the mean of values obtained at 25° and 50°. Extrapolation indicates that at 0° the compressed gas may increase the water content 4- or 5-fold. (3) At 50° the water-vapor content of a 3:1 mixture of hydrogen and nitrogen could have been calculated, within experimental limits of accuracy, as a linear function of gas composition from the water content of pure hydrogen and pure nitrogen (rule of Leduc). The greatest deviation observed is less than 1%. It is probable that this observation applies at other temperatures.

TABLE III

OBSERVED AND CALCULATED WATER-VAPOR CONTENT OF AN APPROXIMATELY 3:1 HYDROGEN-NITROGEN GAS MIXTURE IN EQUILIBRIUM WITH LIQUID WATER

Temp., 25°, 37.5°, 50°

	74.6:25.4 H_2-N_2 25°			76.7:23.3 H_2-N_2 37.5°			76.5:23.5 H_2-N_2 50°		
Pressure, atm.	pv/p_0v_0	Mg., per liter	Poynting effect, calcd.	pv/p_0v_0	Mg., per liter	Poynting effect, calcd.	pv/p_0v_0	Mg., per liter	Poynting effect, calcd.
Satn. press.	...	23.03	..	...	45.36	..	...	82.94	...
100.0	1.058	26.7	24.8	...	..	..	1.053	92.3	88.8
200.0	1.118	31.0	26.7	1.115	56.5	52.3	1.112	103.3	95.1
300.0	1.192	34.1	28.7	...	..	..	1.181	106.3	101.8
400.0	1.266	35.2	30.9	1.258	62.9	60.2	1.251	111.4	109.0
600.0	1.424	40.0	35.7	1.411	69.3	69.3	1.398	123.2	124.9
800.0	1.581	42.3	41.2	...	..	..	1.547	127.2	142.6
1000.0	1.738	44.2	47.5	1.717	74.6	91.3	1.697	130.6	162.8

The results tabulated in Table IV and Fig. 5 are calculated from the data already discussed and are presented as working tables and to emphasize the large discrepancy between calculated and observed results.

TABLE IV

WEIGHT OF WATER VAPOR PER LITER OF COMPRESSED GAS, PER LITER OF GAS EXPANDED FROM HIGH PRESSURE CONTACT WITH LIQUID WATER AND THE VOLUME PERCENT. OF WATER VAPOR IN THE EXPANDED GAS, CALCULATED FROM DATA IN TABLES III AND IV

	Hydrogen, 50°			Nitrogen, 50°		
Pressure, atm.	Mg./liter, compressed gas	Mg./liter, expanded gas	Vol. % water vapor	Mg./liter compressed gas	Mg./liter expanded gas	Vol. % water vapor
Satn. press.	82.94	82.94	....	82.94	82.94	....
100	89.2	0.9455	0.1391	106.5	1.0713	0.1576
200	95.6	.5339	.0785	128.7	0.6808	.1001
300	100.0	.3957	.0582	141.0	.5415	.0796
400	103.0	.3218	.0473	148.7	.4651	.0684
500	105.8	.2776	.0408	155.6	.4238	.0623
600	108.5	.2477	.0364	161.5	.3973	.0584
700	111.2	.2273	.0334	165.0	.3748	.0551
800	113.5	.2118	.0312	167.7	.3580	.0527
900	116.0	.2001	.0294	169.5	.3435	.0505
1000	118.7	.1917	.0282	170.3	.3304	.0486

TABLE IV (*Concluded*)

	3:1 H_2-N_2, 50°			3:1 H_2-N_2, 37.5°			3:1 H_2-N_2, 25°		
Pressure, atm.	Mg./l. compressed gas	Mg./l. expanded gas	Vol. % water vapor	Mg./l. compressed gas	Mg./l. expanded gas	Vol. % water vapor	Mg./l. compressed gas	Mg./l. expanded gas	Vol. % water vapor
Satn. press.	82.94	82.94	....	45.36	45.36	....	23.03	23.03	....
100	93.7	0.9868	0.1451	51.5	0.5428	0.0768	26.8	0.2835	0.0385
200	103.4	.5749	.0846	56.9	.3172	.0449	30.8	.1721	.0234
300	109.0	.4290	.0631	61.0	.2411	.0341	34.0	.1351	.0183
400	113.5	.3540	.0521	64.5	.2028	.0287	36.5	.1155	.0157
500	118.0	.3120	.0460	67.2	.1793	.0254	38.3	.1030	.0140
600	121.9	.2840	.0417	69.4	.1632	.0231	39.8	.0945	.0128
700	125.0	.2625	.0386	71.2	.1512	.0214	41.2	.0884	.0120
800	127.7	.2470	.0362	72.5	.1417	.0200	42.2	.0834	.0113
900	130.0	.2342	.0344	73.3	.1336	.0189	43.2	.0797	.0108
1000	131.2	.2226	.0328	74.5	.1279	.0181	44.2	.0768	.0104

No simple thermodynamic relationships serve adequately to explain the phenomena observed in systems of the type described in this report. McHaffie[5] suggests that "activity" rather than partial pressure of the vapor should be employed in the Poynting relation (Equation 3) and that the activity depends upon the properties of the indifferent gas. Pollitzer

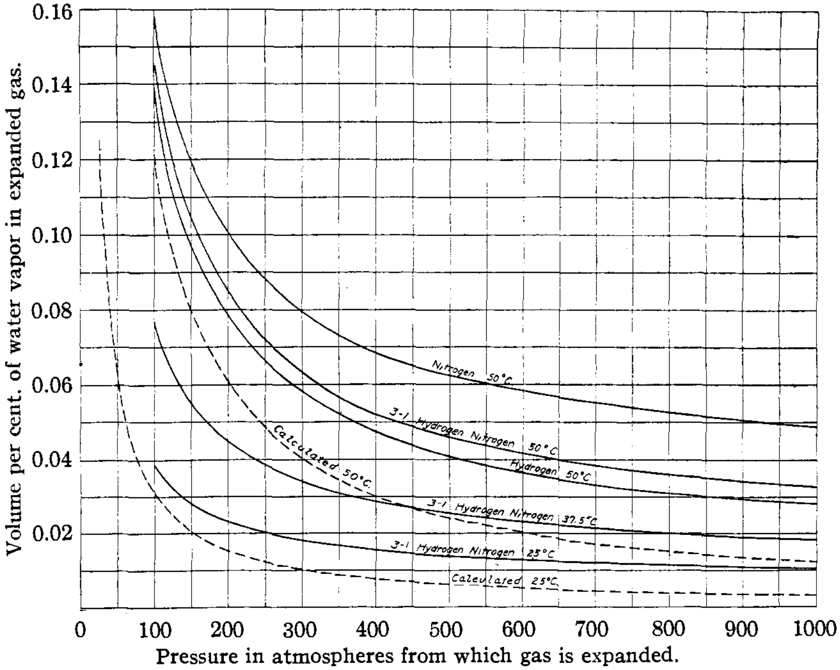

Fig. 5.—Volume per cent. of water vapor in gases expanded from high-pressure contact with liquid water, 25.0°, 37.5°, 50.0°.

and Strebel[4] believe that the indifferent gas exerts an attractive force on the molecules of the vapor and that a measure of this force is the difference in molal heat of vaporization of the liquid in vacuum and in the presence of the indifferent gas. The numerical value of both "activity" and "attractive force" must, however, be derived from observed data. An explanation based on the association of water molecules is tenable but not yet established.[10]

Observed results may be most easily correlated by assuming the compressed gas to be solvent for the liquid. The liquid-gas system is then a two component system analogous to a liquid-liquid system in which the two components are mutually soluble but under certain conditions separate into two phases (for instance, water and ether). There is abundant evidence of the solubility of both solids and liquids in gases heated above their critical temperature.[11]

Roozeboom[12] discussing the phenomenon from the viewpoint of the Gibbs phase rule points out that at constant temperature with increasing pressure the solubility of each phase in the other increases until at the "critical pressure" the two phases become identical. Above this pressure the gas and liquid are miscible in all proportions. This critical phenomenon for a number of gas-liquid mixtures has been observed,[11] but the only quantitative data known to the author are the result of a study by Sander[3] on the system carbon dioxide–ether. While the critical pressures of liquid ammonia–gas and liquid water–gas systems which have been studied in this Laboratory must be far above 1000 atmospheres at the temperatures employed, 20° to 50°, the analogy is striking between the phenomena observed in these systems and those presented by Sander for the carbon dioxide–ether system at a pressure well below the critical pressure. Data concerning the composition of the liquid phase at high pressure in both the ammonia–gas and water–gas systems are needed and the vapor content of still other compressed gases should be determined before a more complete discussion of compressed gases as solvents is presented.

Much credit for the success of this investigation is due to the hearty coöperation of the entire staff of the Fixed Nitrogen Research Laboratory. I am highly indebted to Dr. J. A. Almquist for suggestion and council, and to my assistant, T. H. Tremearne, whose efficient aid and unstinted generosity of time and labor have made possible the collection of the extensive data.

[10] Winkelmann, *Wied. Ann.*, **9**, 208 (1880). Wilsmore, *Trans. Faraday Soc.*, **3**, 85 (1907). Bose, *Z. Elektrochem.*, **14**, 269 (1908). Oddo, *Gazz. chim. ital.*, [1] **45**, 319 (1915). Kendall, This Journal, **42**, 2477 (1920).

[11] Hannay and Hogarth, *Proc. Roy. Soc.*, **30**, 178 (1880); *J. physique*, [1] 9, 415 (1880). Cailletet, *ibid.*, [1] 9, 193 (1880). Villard, *ibid.*, [3] **5**, 453 (1896).

[12] Roozeboom, "Die Heterogenen Gleichgewichte, Braunschweig, **1904**, vol. 2, pt. 1, p. 99.

Summary

The actual water-vapor content of saturated compressed gases is larger than is calculated by the usual method in which temperature effects are alone considered and the volume is calculated by means of the laws of a perfect gas. The maximum observed effect in this investigation was with nitrogen at 50° and 1000 atmospheres. In this case the effect of pressure is to increase the water content 4-fold as computed by the usual method, or 2-fold if allowance is made for deviation from the laws of a perfect gas. In every case studied, the amount of water vapor increased with pressure but not in proportion to the increase in density of the gas. In the case cited above, the water-vapor content increased 2-fold while the density increased 516-fold.

The magnitude of the phenomenon depends on the nature of the gas. Under the above conditions a liter of nitrogen will hold 44% more water vapor than the same volume of hydrogen. The amount of water vapor in the 3:1 hydrogen-nitrogen mixture could have been interpolated, using the Leduc rule of additive volumes at constant temperature and pressure, from results obtained with nitrogen and hydrogen.

The application of certain dynamic principles to this phenomenon has been attempted, but as yet quantitative relationships have not been detected between observed and calculated results. Qualitatively, the phenomenon may be correlated, in the absence of an adequate theoretical treatment, by assuming the compressed gas to act as a solvent for water vapor.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

THE ELECTRODE EQUILIBRIUM IN THE WESTON STANDARD CELL

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There are some peculiarities in the action of the Weston standard cell which have not been satisfactorily explained. Newly prepared cells sometimes have abnormally high electromotive forces which decrease slowly as time goes on, and sometimes do not stop decreasing at any particular value.[1] Well aged cells are not always constant in electromotive force. Shaw and Reilley[2] found that a number of cells decreased 6 to 8 mmv. a year for ten years. When the contents of the cathode com-

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[1] (a) Hulett, *Trans. Am. Electrochem. Soc.*, **14**, 84 (1908); (b) *Phys. Rev.*, **25**, 16 (1907). (c) Smith, *Trans. Roy. Soc. London*, **207**, 407 (1908). (d) Vosburgh, THIS JOURNAL, **47**, 1257 (1925).

[2] Shaw and Reilley, *Trans. Roy. Soc. Canada*, [iii] **13**, 171 (1919).