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The equilibrium attained for the system hydrogen, bromine vapor and hydrogen bromide under the influence of the corona discharge

J. J. Canfield
Iowa State College

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THE EQUILIBRIUM ATTAINED FOR THE SYSTEM HYDROGEN, BROMINE
VAPOR AND HYDROGEN BROMIDE UNDER THE INFLUENCE
OF THE CORONA DISCHARGE.

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42-17

By

J. J. Canfield

A Thesis Submitted to the Graduate Faculty
for the Degree of
Doctor of Philosophy

Major Subject: Physical Chemistry

Approved:

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In Charge of Major Work

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Graduate Dean

Iowa State College

1926

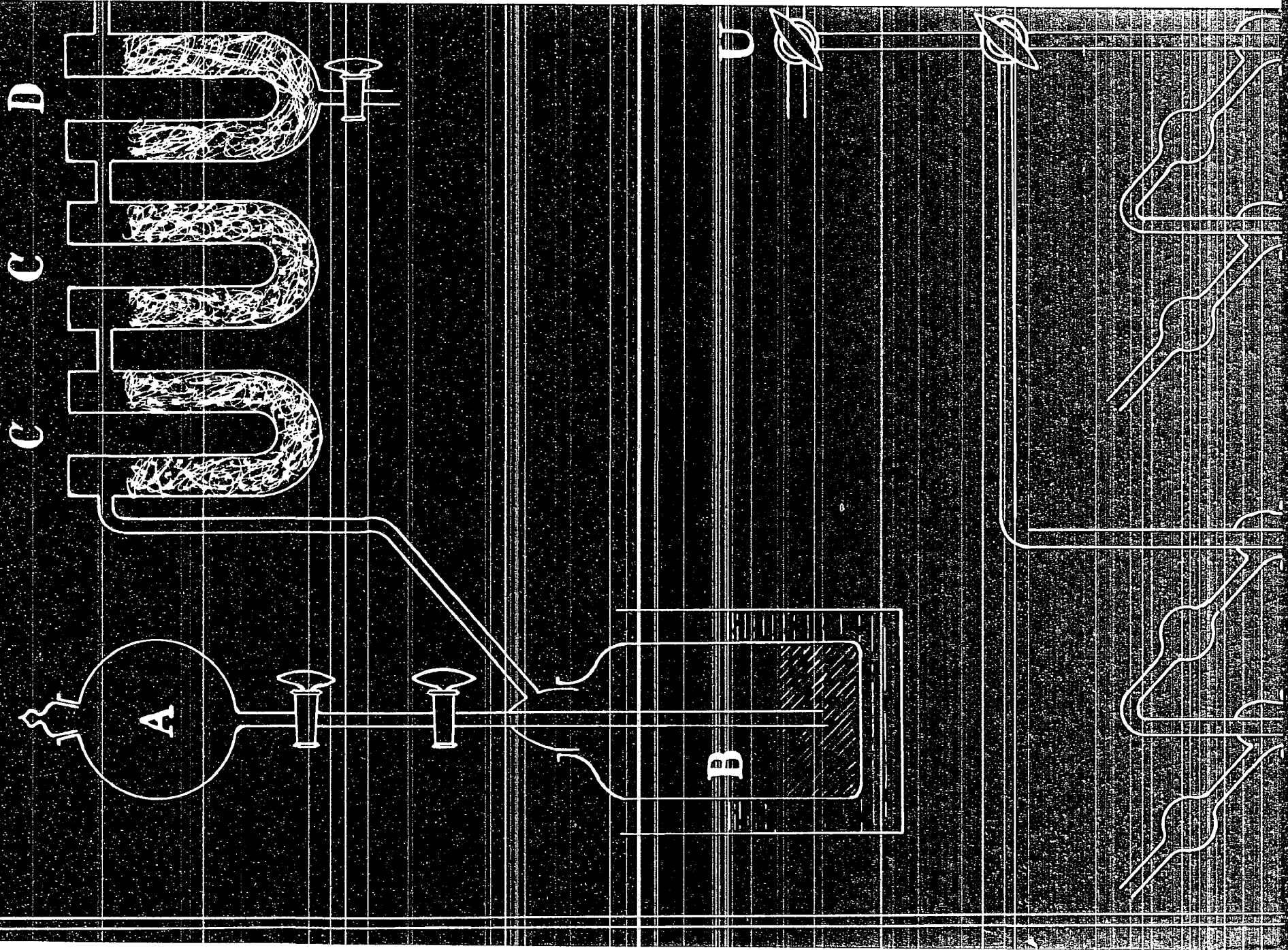
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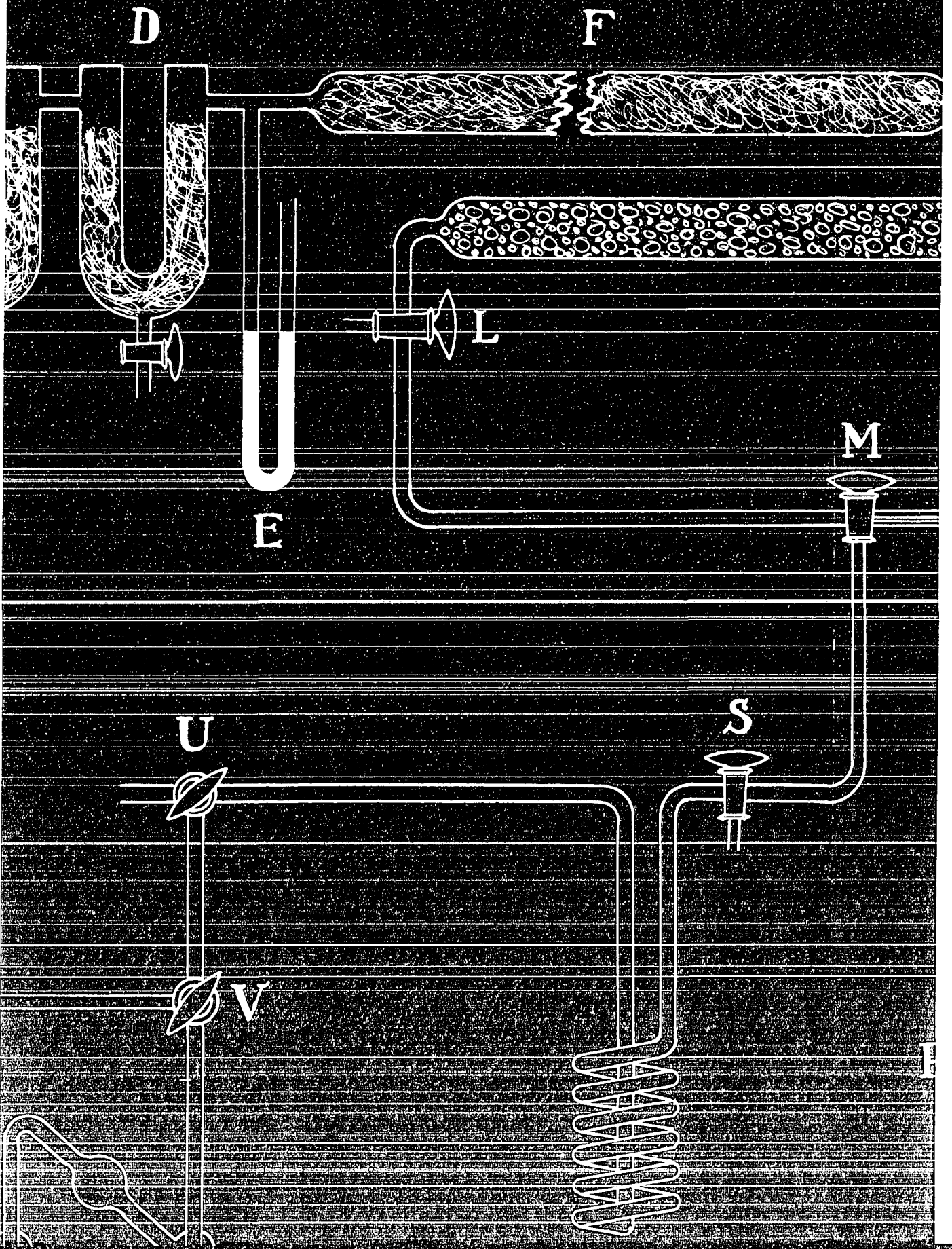
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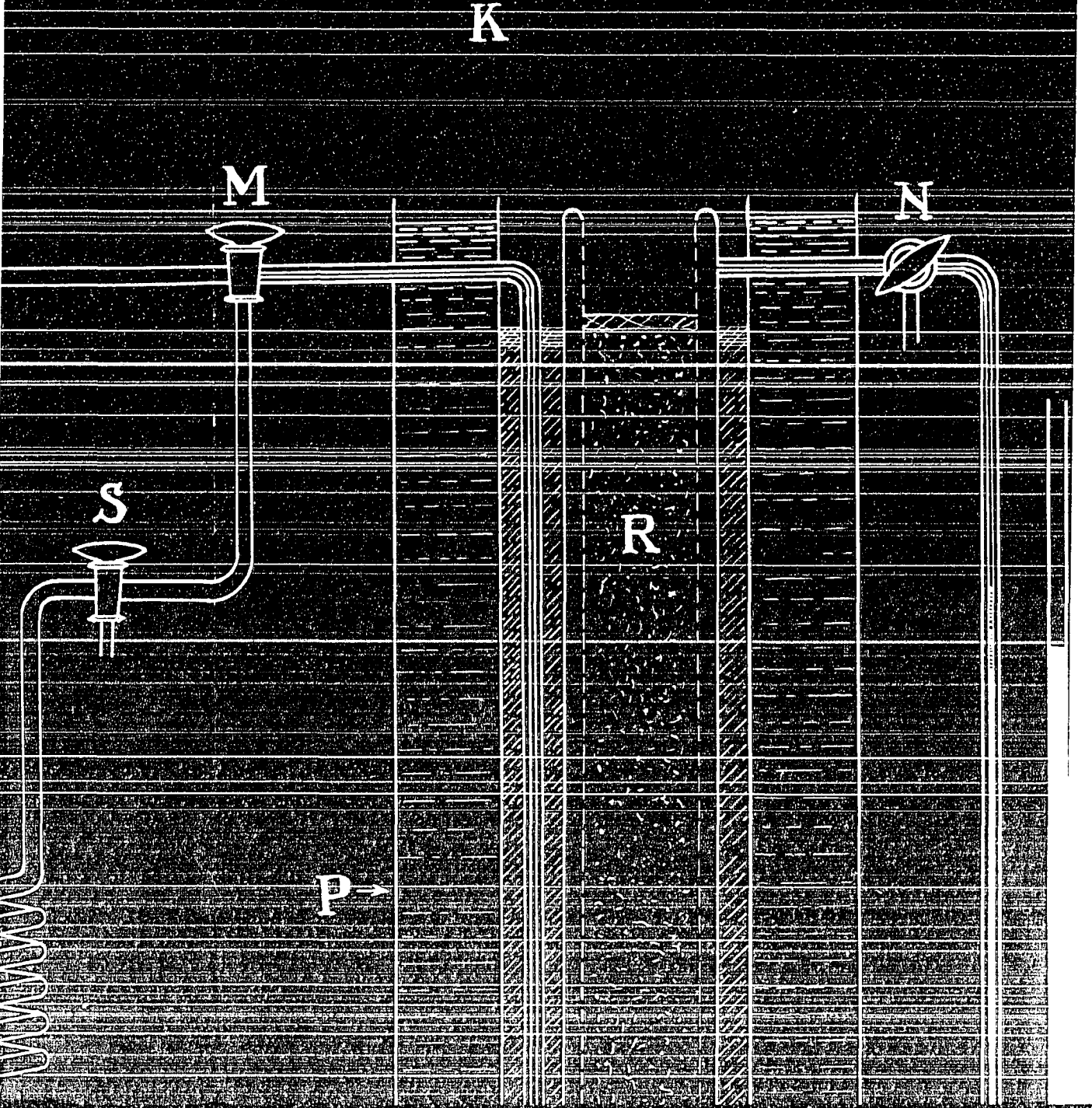
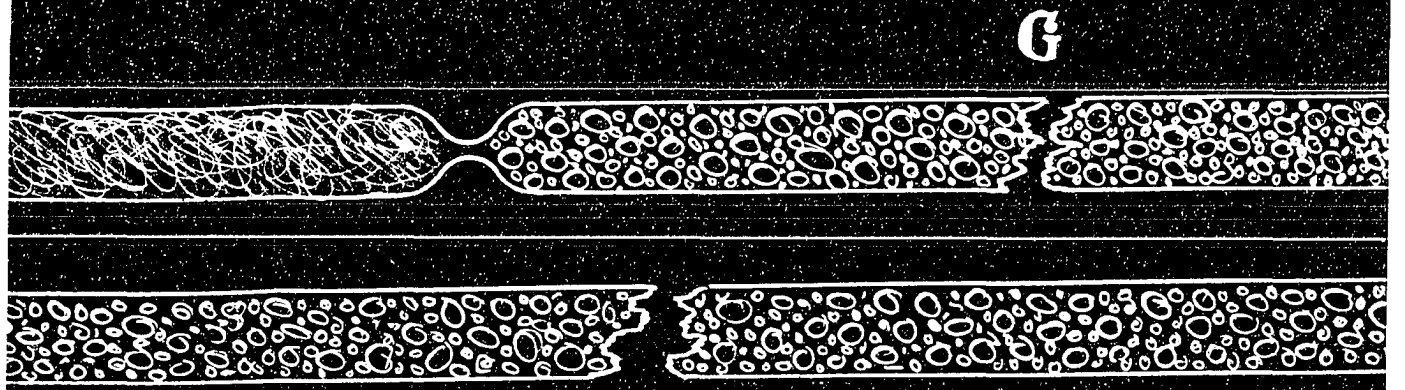
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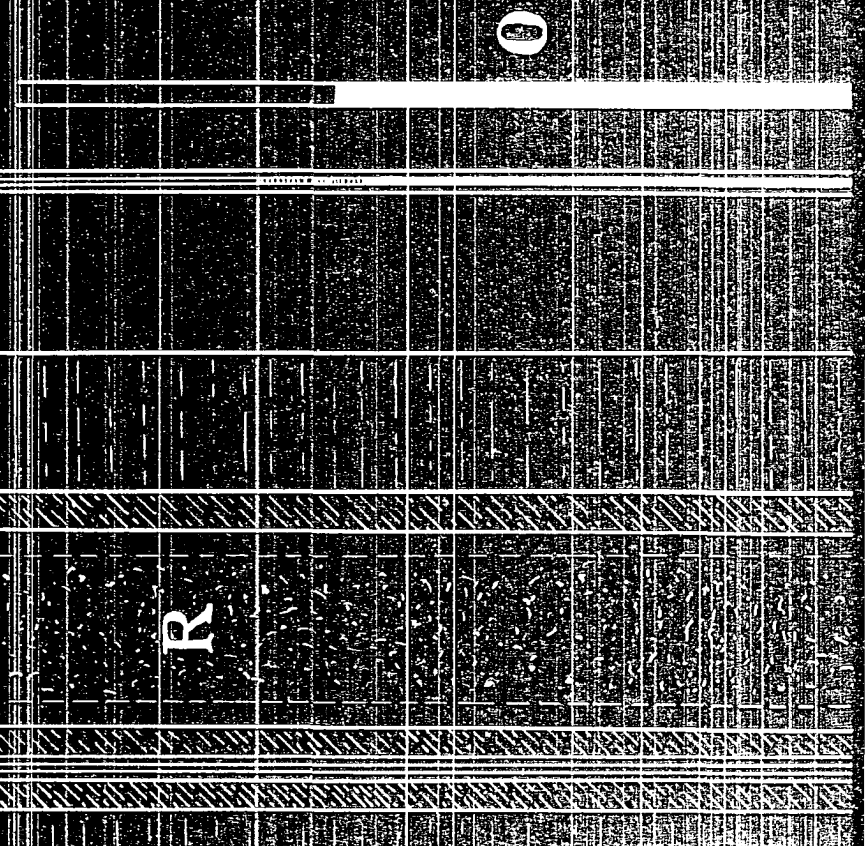
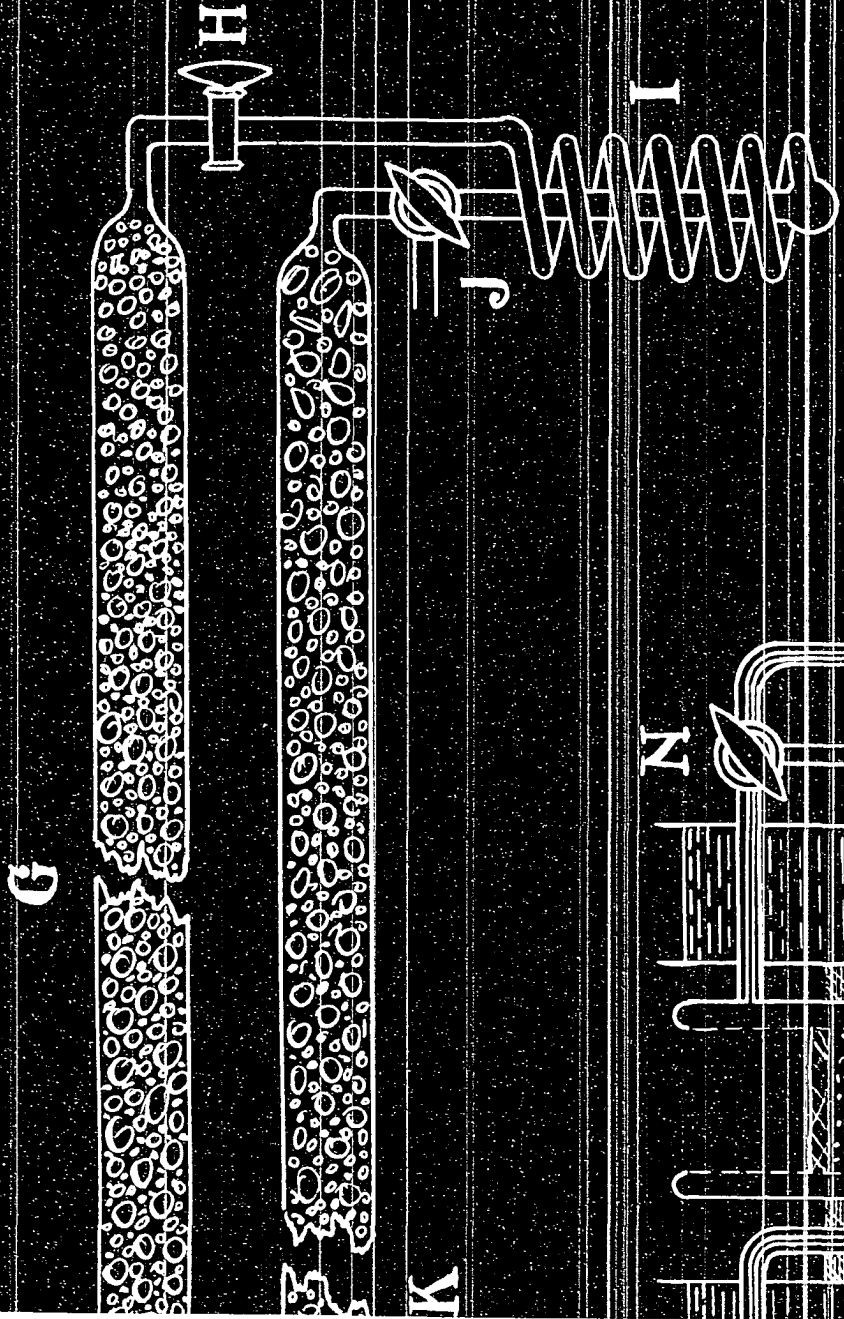
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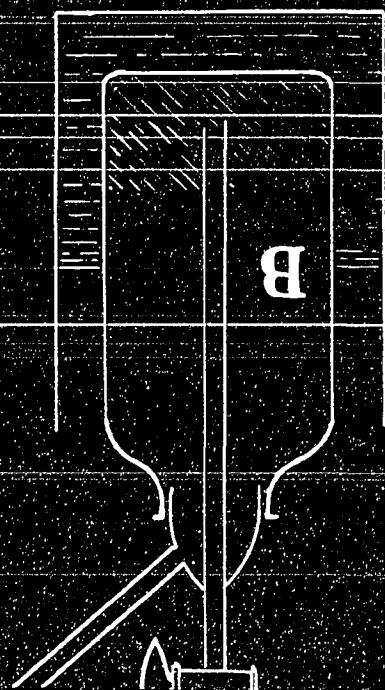
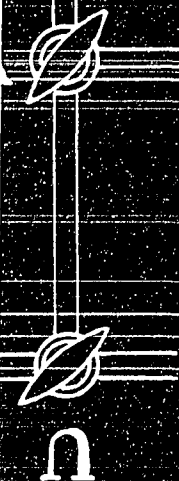
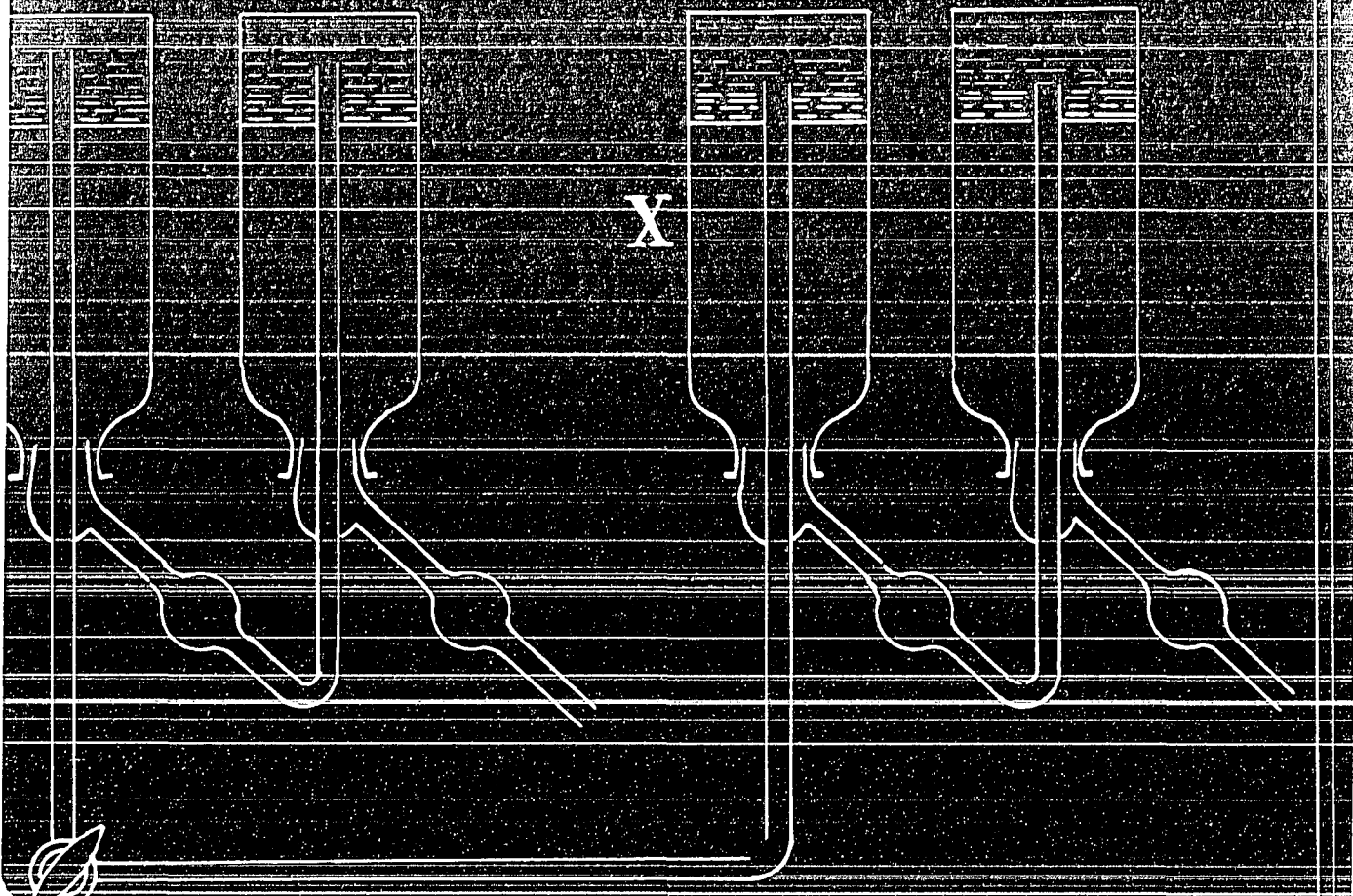
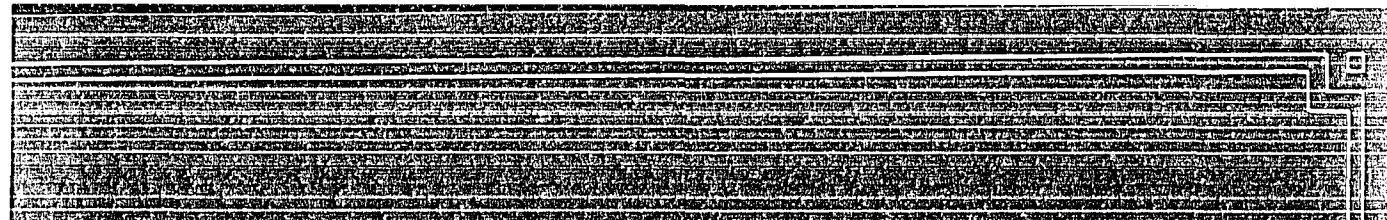
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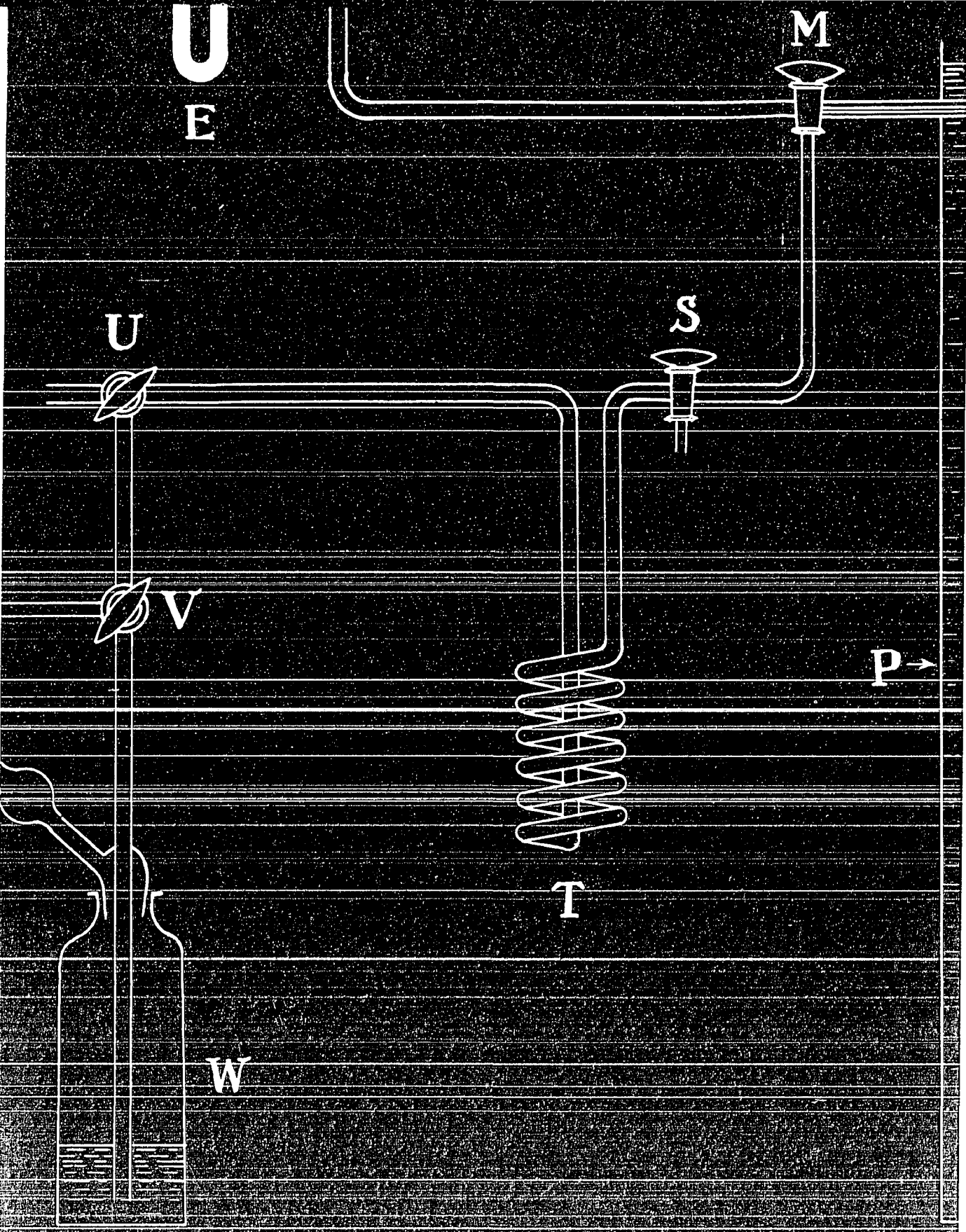
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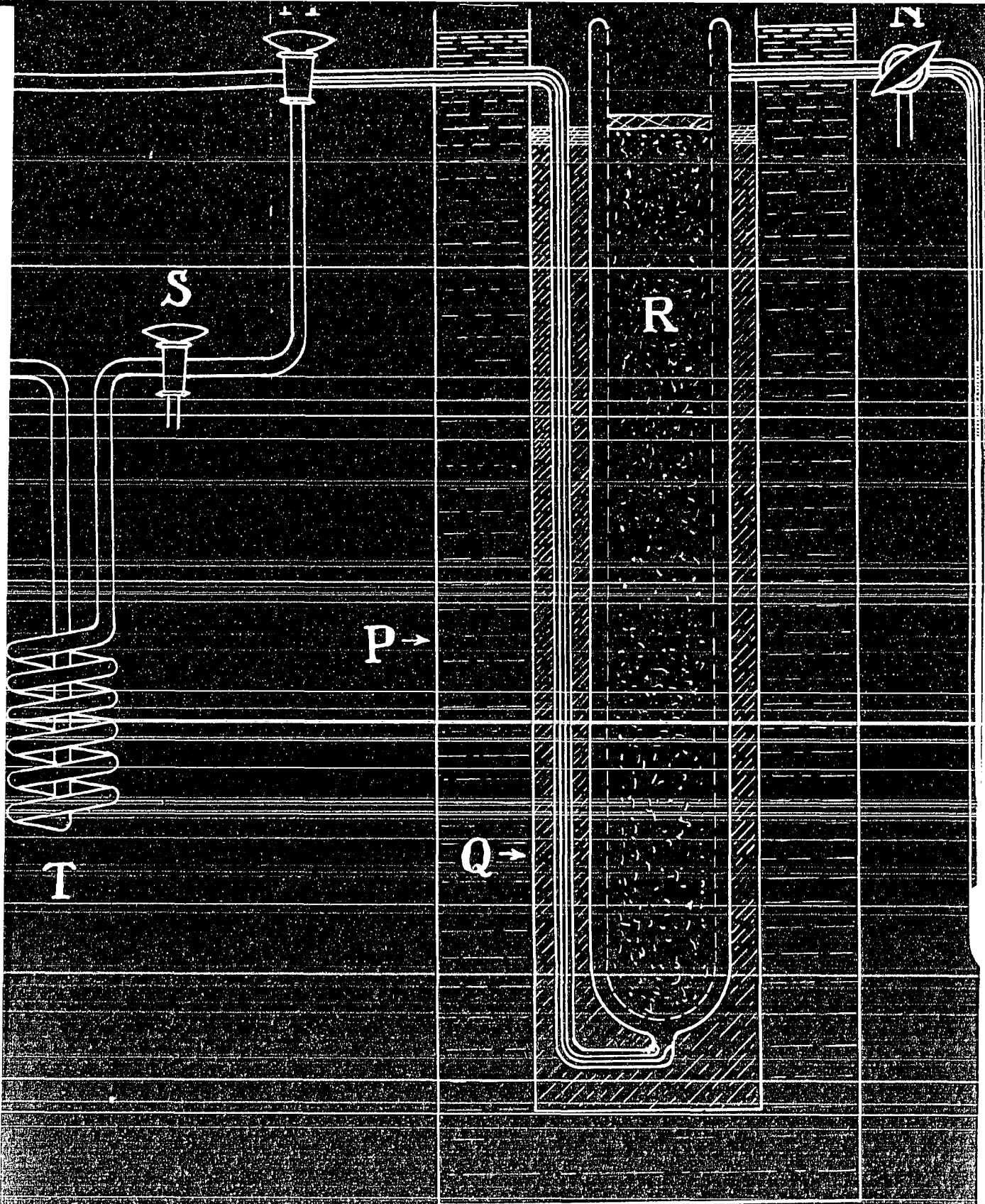
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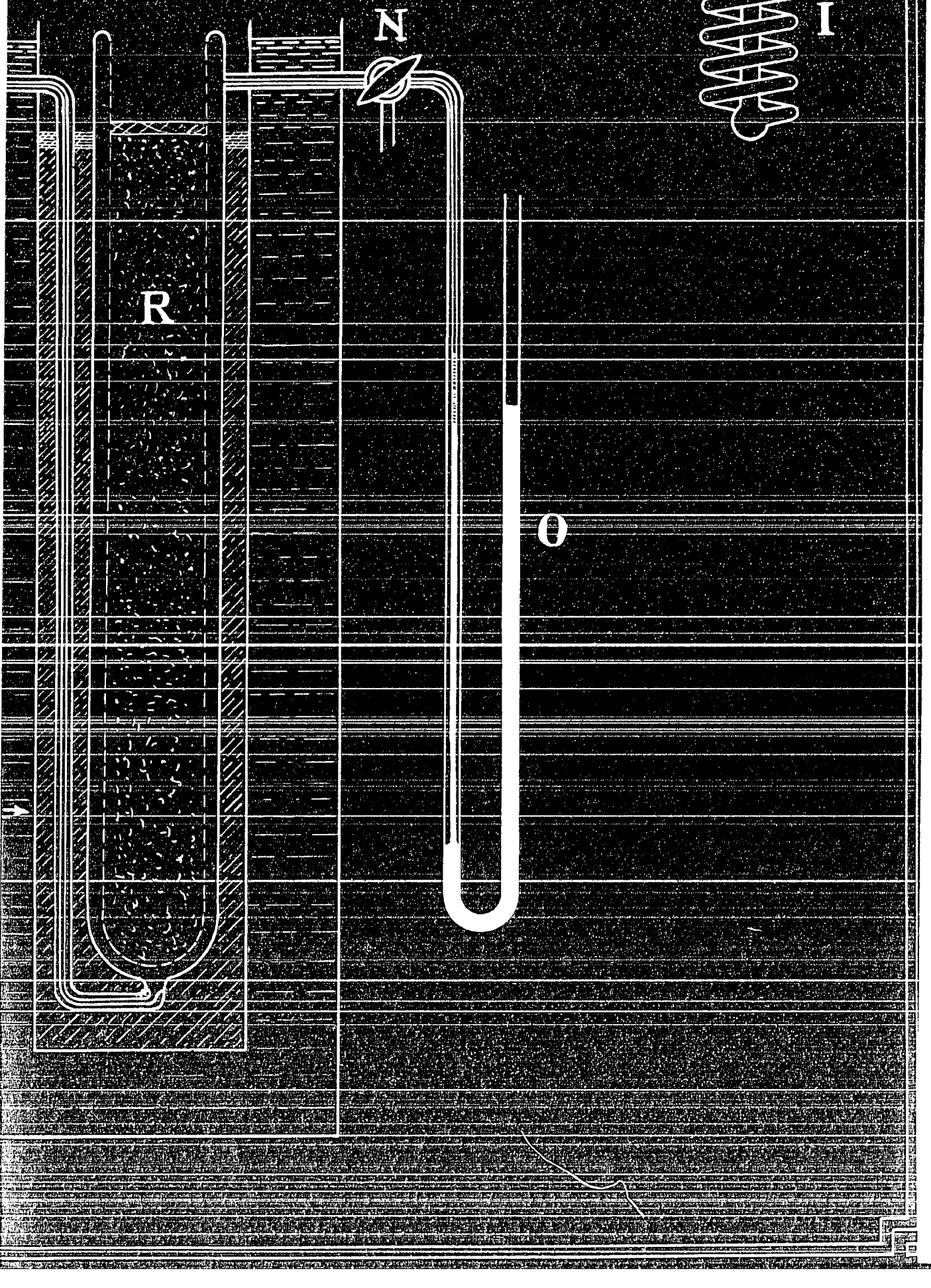
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APPARATUS

The entire apparatus was of soft glass and is shown diagrammatically by the accompanying drawing. A 250 cc. separatory funnel was sealed to the inlet of flask B with two stopcocks between them. The hydrogen bromide was generated in flask B by slowly dropping liquid bromine on red phosphorus in about 150 cc. of water. The tubes C contained moist red phosphorus to remove any free bromine in the hydrogen bromide while the tube D contained glass wool to remove some of the moisture mechanically carried forward. E was a manometer and served as an indicator for keeping a minimum pressure and allowing hydrogen bromide to be slowly generated. The tube F was about 40 cm. in length and was filled with glass wool to prevent the carrying of any liquid spray through the apparatus by the gas. Tubes G and I were filled with granular calcium chloride to dry the gas and were each about 75 cm. in length. H and R indicate spiral glass coils made of ordinary size glass tubing. At the bottom of H was a small bulb of about five cc. capacity to hold the liquid hydrogen bromide.

The discharge chamber K was shaped similar to a Dewar flask with the inside tube centered and with approximately two mm. between the inside walls. The dimensions of the glass tubes used for making the discharge tube were as follows:

	Inside tube	Outside tube
Inside diameter	37.5 mm.	44.19 mm.
Outside diameter	40.5 mm.	46.74 mm.

The volumes of the tubes were 110.5 cc. and 106.7 cc. respectively, determined by filling them with air-free water and weighing, the volume being given by dividing the weight of the contained water by the apparent density. The inlet was a capillary tube sealed near the top. To the outlet was connected a manometer with a three-way stopcock between them. The attached arm of the manometer consisted of a capillary tube while the other was of ordinary size glass tubing. The manometer was filled with mercury with a layer of paraffin oil over the mercury in the capillary arm to protect the mercury.

Before filling the discharge tube with hydrogen bromide, air which had passed through alkaline pyrogallate, potassium hydroxide and sulfuric acid was used to dry the tube. This air could be passed through stopcock N and out through either of the stopcocks L or V. The discharge chamber was placed in a cylinder containing a dilute solution of sodium hydroxide which came to about three centimeters of the top of the discharge chamber. This was covered with a layer of oil 1.5 cm. thick to aid in insulation. On the inside of the discharge tube, aluminum powder was packed to the same height as the

sodium hydroxide solution on the outside. This aluminum powder was covered with paraffin after a copper wire had been pushed into the powder. By connections with a transformer, the aluminum powder served as one electrode and the dilute sodium hydroxide served as the other. In series with the primary side of the transformer was connected an impedance coil with an iron core and across the poles of the secondary side was connected an adjustable spark gap consisting of brass balls two and one-half centimeters in diameter. The 110 volt alternating current lighting circuit served as the source of power.

MANIPULATION

Bromine placed in the separatory funnel A was made to slowly drop into flask B which contained red phosphorus and about 100 cc. of water. This water became saturated with hydrogen bromide and then this solution was warmed slowly by water surrounding flask B which caused hydrogen bromide to vaporize. The coil I which was surrounded by carbon dioxide snow and ether served to liquify the gaseous hydrogen bromide. Any uncondensed gas was neutralized by dilute alkali after it had passed through stopcock J. After approximately six cc. of liquid hydrogen bromide had condensed, cool water was poured around flask B and stopcock H was closed. By

lowering the Dewar flask containing the carbon dioxide snow and ether the liquid hydrogen bromide could be caused to boil and thus dry gas passed through the discharge tube and out through stopcock N. The gas issuing from N was absorbed in dilute alkali. The middle portion of the hydrogen bromide was used for filling the discharge chamber and then the stopcocks M and N were closed and stopcock H opened so that the remainder of the hydrogen bromide was absorbed by the solution in flask B. The discharge chamber was filled at a pressure slightly in excess of the barometric pressure and then maintained at constant temperature by the thermostat P for three-fourths of an hour after which the discharge tube was momentarily opened to the outside through stopcocks M and L. Stopcock N was opened to the manometer and then closed. From the manometer and barometer readings, the pressure of the gas in the tube was determined.

The potential imposed on the walls of the discharge tube during the experiment was determined by the use of the spark gap. The voltage used was calculated by use of the formula $V = 30,000 d + 1500$, where V represents potential difference in volts and d the distance apart in centimeters of the brass balls.

During a run the silent discharge had a heating effect which maintained the inside of the tube about 3^oC. above the

outside and so the thermostat temperature was lowered this amount to maintain the tube at as nearly constant temperature as possible. At the end of a run the pressure of the gas was determined as before starting.

The resulting mixture was analyzed by the following method. The coil T was surrounded by carbon dioxide snow and ether after dry air had been used to dry it. Fifty cc. of standard alkali with two drops of phenolphthalein were placed in the vessels marked X and potassium iodide with water placed in the vessels marked W. Vessels W and X were connected by ground glass joints to the inlet tubes from coil T. To sweep out the discharge tube, air which had passed through alkaline pyrogallate, potassium hydroxide and sulfuric acid was made to enter the tube through stopcock N at the rate of about 12 cc. a minute and thus the resulting mixture was carried through the coil T where the bromine was solidified. The hydrogen bromide was conducted into the standard alkali and there neutralized. Since the temperature of the cooling coil was between -70°C . and -80°C ., the vapor pressure of the bromine was about 0.1 mm. and consequently the phenolphthalein in the standard alkali was not decolorized. After air had passed through the tube for thirty minutes, the bromine was warmed to room temperature and caused to pass into the potassium iodide

solution. At the end of a run, water was poured through stopcock U to wash the inlet tubes to the vessels W and X. The excess alkali was titrated with standard sodium thiosulfate, using starch as an indicator. In some of the determinations, from 0.2 to 0.6 cc. of 0.644 normal KOH was required to neutralize the hydrogen bromide carried into the potassium iodide solution. Knowing the amounts of bromine and of hydrogen bromide at the end of a run and assuming the ideal gas laws, the total volume of these two gases was compared with the volume obtained by calibration of the tube. These results are tabulated with the data.

The water used had been distilled from alkaline permanganate and freed of ammonia and carbon dioxide by partial condensation of the steam. The bromine and potassium iodide used were from Merck and Company, New York, while the phosphorus had been prepared by the Mallinckrodt Chemical Works, St. Louis, Missouri.

DATA

No.	Manometer Reading in Cm. Hg	Barometer Reading in Cm. Hg	Change in Cm. Hg	Cc. KOH to Neutralize KI Solution	Total Cc. KOH Used	Cc. HCl Used	Cc. $\text{Na}_2\text{S}_2\text{O}_3$ Required	Equiv-alent Cc. Normal HBr at End	Equiv-alent Cc. Normal Br_2 at End
	+ 2.80 + 3.00								
1	-12.00 -12.03	73.90 73.96	-0.17	0.30	50.3	17.20	47.00	1.456	2.82
	+ 2.80 + 2.50								
2	-12.00 -11.98	74.37 74.27	+0.22	0.10	50.1	17.30	47.60	1.432	2.856
	+ 2.70 + 2.90								
3	-12.00 -12.00	74.17 74.15	-0.22	0.15	50.75	17.65	47.40	1.438	2.844
	+ 2.70 + 2.75								
4	-12.00 -12.00	73.68 73.55	-0.18	0.4	50.4	17.35	47.50	1.446	2.85
	+ 3.70 + 3.15								
5	-12.05 -12.02	73.85 73.47	+0.20	0.4	50.4	17.02	47.00	1.481	2.82
	+ 2.50 + 2.50								
6	- 6.50 - 6.50	74.42 74.30	-0.12	0.5	50.5	17.42	44.70	1.445	2.682
	+ 2.20 + 2.10								
7	- 6.52 - 6.50	74.03 73.40	-0.51	0.2	50.2	18.80	48.1	1.283	2.886
	+ 2.20 + 3.60								
8	- 6.50 - 6.65	73.32 73.63	-1.24	0.55	50.55	19.6	48.25	1.223	2.895
	+ 2.70 + 3.20								
9	- 6.60 - 6.60	73.75 73.95	-0.30	0.60	50.6	17.60	45.05	1.433	2.703
	+ 2.70 + 3.50								
10	- 6.60 - 6.62	73.83 73.60	-1.10	0.42	50.72	18.05	45.15	1.395	2.709

DATA

No.	Temp. °C.	Hours Time Exposed to Discharge	Volume of Tube		Voltage	% Hydrogen Bromide Decomposed
			From Results	From Calibration		
1	33	3	110.4	110.5	11,000	65.95
2	33	3	110.0	110.5	11,000	66.61
3	33	3	110.2	110.5	15,500	66.42
4	33	3	111.3	110.5	15,500	66.34
5	33	2 $\frac{1}{4}$	111.1	110.5	15,500	65.56
6	33	4	106.0	106.7	15,500	64.99
7	15	4	107.5	106.7	15,500	69.22
8	15	4	106.4	106.3	15,500	70.30
9	33	5	107.0	106.3	15,500	65.35
10	15	4	106.4	106.3	15,500	66.01
	33	5				

The readings of the manometer at the beginning are those which correspond to the beginning barometer reading since the tube was filled at 33°C . under a very slight excess pressure and maintained at this temperature and then the excess pressure released by opening the tube momentarily to the outside through stopcocks M and L. Thus the pressure of the hydrogen bromide gas in the tube was equal to the barometer reading. The plus readings indicate those above the zero of the manometer scale and of the arm attached to the discharge tube, while the minus readings are those which were below the zero of the scale and are of the open manometer arm. The manometer and barometer readings are given for the beginning and the end of the runs and from these the change in pressure was calculated which served as a check on the results.

The cc. of .0644 normal base to neutralize the potassium iodide solution, represents hydrogen bromide carried into the potassium iodide solution and is included with the total amount of base to neutralize the undecomposed hydrogen bromide. The amount of undecomposed hydrogen bromide is obtained by multiplying the total cc. of base used in the analysis by its normality ($= .0644$) and subtracting from this the cc. of acid used multiplied by its normality ($= .1037$), which represents the equivalent of hydrogen bromide in cc. of normal solution. The equivalent cc. of normal bromine at equilibrium is

obtained by multiplying the cc. of sodium thiosulfate used by its normality. The fractional decomposition of the hydrogen bromide is obtained by dividing the equivalent of cc. of normal bromine by the total equivalent cc. of normal bromine and hydrogen bromide.

The volume of the tube as calculated from the results of analysis of the final mixture was determined by using the formula $V = g/m \frac{RT}{P}$ which involves the assumption of ideal gases. V represents the volume in cc.; g , the weight of hydrogen bromide; m , its molecular weight; R , the gas constant in cc. atmospheres; T , the absolute temperature; and P , the pressure in atmospheres. For example, the calculation for run No. 1 would be $V = \frac{4.276 \times 0.080928 \times 82.07 \times 306 \times 76}{80.928 \times 73.90}$. The beginning barometric reading was used in each case.

The calibrated volume of the tube in the runs 8, 9, and 10 differs slightly from the preceding ones due to breaking a connecting arm after which the tube was recalibrated. Two different tubes were used.

The change in pressure in runs number 8 and 10 is large but the results may be considered to show that a larger decomposition occurs at 15° C. than at 35° C. and also that the equilibrium is attained at 33° C. which is the same whether the run is made at 33° C. or cooled to 15° C. and run for a

time and then rerun at 33°C.

The average of runs Nos. 1, 2, 3, 4, 6, and 9 is 65.94% decomposition and this is used in the following discussion.

DISCUSSION

From the data obtained the equilibrium constant for the reaction $\text{HBr} \rightarrow \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Br}_2$ would be calculated as follows,

$$K_p = \frac{p_{\text{H}_2}^{\frac{1}{2}} p_{\text{Br}_2}^{\frac{1}{2}}}{p_{\text{HBr}}} = \frac{(32.97)^{\frac{1}{2}} (32.97)^{\frac{1}{2}}}{34.06} = .9677$$
 where 65.94% is the amount of decomposition of the hydrogen bromide which is taken from the average of the best data obtained.

$\frac{1}{K_p} = 1.033$ is the constant corresponding to the free energy equation (1) $\Delta F^0 = -11,970 + 0.45T \ln T - .000025T^2 - 5.74T$ given by Lewis⁸. Since (2) $\Delta F^0 = -RT \ln K$ we may use these two equations to obtain equation (3), $R \ln K_p = \frac{11,970}{T} - 0.45 \ln T + .000025T + 5.74$, and by substitution of various values of T attempt to find such a temperature that would give the value of $K = 1.033$. It is found that no value of T will give this value of K. Taking the first derivative of the latter equation we obtain (4) $\frac{d(R \ln K_p)}{dT} = \frac{-11,970}{T^2} - \frac{0.45}{T} + .000025$.

8. Lewis and Randall, "Thermodynamics", p. 517, McGraw-Hill Book Co., New York (1923).

Placing this equal to zero and solving, we find that T equals 32,660° A.

The second derivative of equation (3) is positive, which means that for the value T = (32,660° A) is the value at which equation (3) is a minimum. Substituting this value of T in equation (3), we find the minimum value of K = 3.09.

If the heat capacity data, which are from a summary of the best present data obtainable, held at high temperatures then this decomposition of hydrogen bromide attained under the influence of the silent electric discharge could not be analagous to a thermal effect. Lewis⁸ has pointed out that if the above free energy equation is valid the dissociation of hydrogen bromide could not exceed 50% from a temperature effect except insofar as other reactions enter such as the dissociation of hydrogen and bromine into their monatomic forms. Since bromine is known to dissociate appreciably at higher temperatures, it is quite likely that the above free energy equation is not valid at higher temperatures.

Kurt Vogel v. Falckstein⁹ measured the thermal dissociation of hydrogen bromide at 1495° A and find it to be 1.08% dissociated. The formula $\text{Log } K_p = \frac{-5223}{T} + 0.533 \log T - 2.72$

8. Lewis and Randall "Thermodynamics", p. 517, McGraw-Hill Book Co., New York (1923).

9. Kurt Vogel v. Falckstein, Z. für Phys. Chem. 72, 113 (1910).

deduced by Nernst¹⁰ appears to hold well at 1200° A to 1400° A and would indicate that not more than 10% of the hydrogen bromide would be dissociated below 4000° A. In the above

formula $K = \frac{p_{H_2} \cdot p_{Br_2}}{p_{HBr}^2}$. Bodenstein and Geiger¹¹ from elec-

tromotive force measurements have deduced an empirical formula and from it find that 10% of hydrogen bromide would be dissociated at 2311° A.

Hydrogen chloride was subjected to the silent discharge by Moser and Isgarischew¹² and they found 0.6% of it was decomposed in two hours using a voltage of 14,700. Using pure hydrogen and chlorine, they found that only 94% of the possible amount of hydrogen chloride had been formed in two and one-half hours using a voltage of 13,000.

For 0.6% decomposition the equilibrium constant for the

reaction $\frac{1}{2}H_2 = \frac{1}{2}Cl_2 + HCl$ is $K_p = \frac{\left(\frac{99.4}{100.6}\right)}{\left(\frac{0.3}{100.6}\right)^{\frac{1}{2}} \left(\frac{0.3}{100.6}\right)^{\frac{1}{2}}} = 331$.

The corresponding free energy equation given by Lewis¹³ is $\Delta F^0 = -21,870 + 0.45T \ln T - .000025T^2 - 5.31T$ and using a

10. Nernst, Zeit. für Elektrochem. 15, 691 (1909).
11. Bodenstein and Geiger, Z. Physik. Chem. 49, 70 (1904).
12. Moser and Isgarischew, Z. Elektrochem. 16, 643 (1916).
13. Lewis and Randall, "Thermodynamics", McGraw-Hill Book Co., New York, p. 503 (1923).

value of T equal to 2270° A we find $\Delta F_{2270}^{\circ} = -26,158$. Since this is equal to $-RT \ln K_p$ we find K_p to be 328 which corresponds to the K_p obtained above. Since equilibrium was not attained and since the decomposition might be more than 0.6% at equilibrium, the temperature of a thermal equilibrium of this same value would be higher than 2270° A.

Moser and Isgarischew¹⁴ obtained 15.84% decomposition of carbon dioxide into carbon monoxide and oxygen at 20° C. and a final pressure of 804 mm. using the silent electric discharge at 9,800 volts and also at 21° C. with 12,400 volts obtained 18% decomposition. The equilibrium constant for the 15.84% decomposition is

$$K_p = \frac{(P_{CO_2})}{(P_{CO})(P_{O_2})^{\frac{1}{2}}} = \frac{\left(\frac{84.16}{107.92} \times \frac{804}{760}\right)}{\left(\frac{15.84}{107.92} \times \frac{804}{760}\right) \left(\frac{7.92}{107.92} \times \frac{804}{760}\right)^{\frac{1}{2}}} = 19.07,$$

where $CO + \frac{1}{2}O_2 \rightarrow CO_2$ is the reaction. The corresponding free energy equation given by Lewis¹⁵ is $\Delta F_{2520}^{\circ} = -14,805 = -RT \ln K_p$ from which $K_p = 19.24$ which agrees well with the K_p above and thus the 15.84% decomposition corresponds to the thermal equilibrium at 2520° A. For the 18% decomposition, $K_p = 16.38$ and this corresponds to the thermal equilibrium at

14. Moser and Isgarischew, Z. Elektrochem. 16, 613 (1910).
15. Lewis and Randall, "Thermodynamics", p. 575, McGraw-Hill Book Co., New York (1923).

2560° A. Wendt and Farnsworth¹⁶ have also subjected carbon dioxide to the corona discharge and find an equilibrium value which is the same as the thermal equilibrium at 2600° A.

In the Deacon reaction, Moser and Isgarischew¹⁷ found that about 95% of the hydrogen chloride was oxidized in the silent discharge when a mixture of 15 to 20% HCl with oxygen was used. The determination was made between 70 and 80°C. and under these conditions water did not condense. With the assumption of the ideal gas law the equilibrium constant for the reaction $\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{Cl}_2 + \frac{1}{2}\text{H}_2\text{O}$ is calculated as follows:

For a mixture of twenty mols of hydrogen chloride and eighty mols of oxygen in which 95% of the hydrogen chloride is oxidized, there would be present in the resulting mixture one mol hydrogen chloride, 75.25 mols oxygen, 9.5 mols chlorine and 9.5 mols of water or a total of 95.25 mols of gas in the mixture. Since the final pressure was 702 mm. and

$$K_p = \frac{p_{\text{Cl}_2}^{1/2} p_{\text{H}_2\text{O}}^{1/2}}{p_{\text{HCl}} p_{\text{O}_2}^{1/2}}, \text{ the value of } K_p \text{ expressing the partial pressures in atmospheres would be}$$

16. Wendt and Farnsworth, J. Am. Chem. Soc. 47, 2494 (1925).

17. Moser and Isgarischew, Z. Elektrochem. 16, 613 (1908).

$$K_p = \frac{\left(\frac{9.5}{95.25} \times \frac{702}{760}\right)^{\frac{1}{2}} \left(\frac{9.5}{95.25} \times \frac{702}{760}\right)^{\frac{1}{2}}}{\left(\frac{1}{95.25} \times \frac{702}{760}\right) \left(\frac{75.25}{95.25} \times \frac{702}{760}\right)^{\frac{1}{2}}} = 1.0275.$$

Since $\Delta F = -RT \ln K$ and Lewis¹⁸ has given the free energy expression $\Delta F^0 = 6,835 - .02T \ln T - .00085T^2 + .000000185T^3 - 7.27T$ for the reaction $\frac{1}{2}Cl_2 + \frac{1}{2}H_2O(g) \rightarrow HCl + \frac{1}{2}O_2$ then $\frac{1}{K_p} = K$ and $\ln K_p = 6,835 - .02T \ln T - .00085T^2 + .000000185T^3 - 7.27T$. A value of $T = 850^\circ A$ placed in the above expression gives a value of $K_p = 1.0298$ from which it is seen that the effect of the corona discharge on such a mixture of hydrogen chloride and oxygen is equivalent to a thermal effect of $850^\circ A$.

J. H. Davies¹⁹ subjected ammonia gas to the influence of the corona discharge and obtained 2.87% of the gas left with a final pressure of 1,561 mm. and also using nitrogen with hydrogen that 2.86% of the final gas mixture was ammonia where 761.2 mm. was the initial pressure of the nitrogen and hydrogen gas mixture. The equilibrium constant using the latter value for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$ is calculated as follows. Since 21.7 mm. is the pressure of the ammonia formed and the initial pressure is 761.2 mm. then the final pressure must have been $761.2 - 21.7 = 739.5$ mm. The total pressure of

18. Lewis and Randall, "Thermodynamics", p. 504, McGraw-Hill Book Co., New York (1923).

19. J. H. Davies, Z. Physik. Chem. 64, 657 (1910).

the nitrogen and hydrogen which were in stoichometric quantities would be $739.5 - 21.7 = 717.8$ mm. from which the pressure of the nitrogen equals 179.45 mm. and the pressure of the hydrogen equals 538.35 mm. Expressing the partial pressures in atmospheres, the equilibrium constant is

$$K_p = \frac{\left(\frac{21.7}{760}\right)}{\left(\frac{179.45}{760}\right)^{\frac{1}{2}} \left(\frac{538.35}{760}\right)} = .997.$$

The corresponding free energy equation given by Lewis²⁰ is $\Delta F^{\circ} = -RT \ln K_p = -9,500 + 4.96T \ln T + .000575T^2 - .00000085T^3 - 9.61T$ from which a value of $T = 455^{\circ}$ A gives a value of $K_p = 1.00$ and the amount of ammonia formed corresponds to a thermal equilibrium of 455° A. However, if the value of 2.87% of ammonia left using a pressure of 1,561 mm. is used, $K_p = .0563$ and this would correspond to a temperature effect of 592° A.

It has been shown by Warburg²¹ that the yield of ozone greatly increases when oxygen is subjected to the corona discharge at lower temperatures. Lewis and Randall²² have summarized the better data on the reaction $3/2 O_2 \rightarrow O_3$ and have

20. Lewis and Randall, "Thermodynamics", p. 557, McGraw-Hill Book Co., New York (1923).

21. Warburg, Ann. Physik. (4) 9, 781 (1902).

22. Lewis and Randall, "Thermodynamics", p. 476, McGraw-Hill Book Co., New York (1923).

arrived at the equation $-RT \ln K = 34,600 + 2.75 \ln T - .0028T^2 + .00000031T^3 - 22.4T$ from which it may be shown that as T increases K increases. Thus it is seen that a higher temperature tends to increase the yield of ozone and consequently the increased yield of ozone using lower temperatures under the influence of the corona discharge is analagous to a high temperature effect.

It is interesting that of all the equilibria thus far noted, the equilibrium values in the corona discharge are those which correspond to a thermal equilibrium at elevated temperatures. The action may be photochemical in nature resulting from secondary radiation set up in the tube, or it may be the result of ionization caused by the stream of electrons across the gap or a combination of effects. It is known that hydrogen bromide, ammonia and other compounds may be decomposed or synthesized by use of different wave lengths of light and thus if the action of the corona discharge is photochemical, the equilibrium attained would be the result of different radiation frequencies occurring in the discharge tube. However, it is peculiar that all of the equilibria so far attained are those which correspond to thermal equilibria at elevated temperatures and this would indicate that the action may not be photochemical.

Whatever may be the mechanism by which these equilibria are attained in the corona tube, the following condition of affairs would produce the same type of results that have been attained in all these gaseous systems. It may be assumed that some of the molecules become energized and are in such a state that they become reactive or may decompose and that this state corresponds to that which occurs when the substance is heated to an elevated temperature. In this state, the energized molecules react and are immediately cooled to the temperature of the discharge tube and thus equilibrium is reached which corresponds to that of a thermal equilibrium at a temperature much higher than that of the discharge tube. Further evidence in support of the above concept is given since it is known that reactions of dry gases such as, hydrogen and bromine to form hydrogen bromide, and carbon monoxide with oxygen to form carbon dioxide, are slow reactions, and that if such gaseous equilibrium mixtures were suddenly changed from a high temperature or corresponding energy state to a temperature or state where the reaction velocities are extremely slow, such an equilibrium would be attained that would correspond to a high temperature. The previously discussed increase in yield of ozone by lowering the temperature of the discharge tube appears as evidence of the above mechanism.

SUMMARY

The equilibrium of hydrogen, bromine vapor and hydrogen bromide has been determined at 33^oC. under the influence of the corona discharge.

The same equilibrium may be attained if the final temperature of the discharge tube is the same regardless of whether the tube was or was not cooled to a lower temperature during the first interval of a determination.

All of the semi-equilibria in gaseous systems thus far attained by use of the corona discharge correspond to a thermal equilibrium at a temperature much higher than that of the discharge tube.