



THE DETERMINATION OF THE  
DENSITY, BOILING POINT AND  
CONCENTRATION OF  $\text{HBr}$  SOLUTIONS  
AT THREE DIFFERENT PRESSURES

THESIS FOR THE DEGREE OF M. S.

Elmer Huston Leslie  
1934



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Hydrobromic acid

Chemistry

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## Introduction

Hulett and Bonner<sup>1</sup>; and Faulk and Hollingsworth<sup>2</sup> have shown by precise measurements that the composition of a solution of HCl and water which boils at a constant temperature is sufficiently accurate to permit the use of this material directly for the preparation of standard solutions for use in volumetric analysis. This investigation was undertaken to determine the boiling points, compositions and densities of HBr solutions distilling at pressures of 750, 760 and 770 mm. of mercury respectively. Experiments in this laboratory by Ewing and Shaddock<sup>3</sup> have shown that the composition of HBr distillate at 760 mm. pressure is constant. Work with this material by other workers has shown a variety of results. Leger<sup>5</sup> reports the boiling point of HBr at 760 mm. pressure as 127° and the composition of the distillate 48% HBr. Carriere and Cerveau<sup>4</sup> give a boiling point of 126° and a composition of 47.5% HBr for the distillate at 760 mm. pressure. A. Bineau<sup>6</sup> thought the constant boiling acid was the pentahydrate having a composition of 47.43% HBr. Roscoe<sup>7</sup> disproved this by distillation of the HBr solution at two widely separated pressures. At 760 mm. pressure the acid boiled at 126° and showed a composition of 47.86% HBr. At 1947 mm. pressure the same sample of acid boiled at 153°C and had a composition of 46.3% HBr. A review of this range of values lends its support to the advisability of a re-determination of some



of the constants concerned by precise methods.

## Experimental Work

### Preparation of Materials

Water; Conductivity water was used throughout this investigation.

Hydrobromic acid; The best commercial grade of Baker's Analyzed acid containing 34 per-cent of HBr was used . It was purified by fractional distillation. Five distillations of the acid were made. These were carried out in an apparatus similar to that used in the determination of the boiling point. The glassware coming in contact with the HBr solution with the exception of the thermometer was pyrex. No other material except air came in contact with the acid. The 1000 ml. distilling flask with a ground glass stopper and sealed to a condenser was charged with about 800 ml. of the HBr solution and after the system was sealed its pressure was adjusted to 760 mm.of mercury. The distillation was carried out at this pressure which was constant to within  $\pm .2$  to  $.3$  mm.of mercury. When the boiling point of the acid had reached  $124^{\circ}$  a second receiver was supplied. The HBr solution distilling off at  $124^{\circ}$  to  $124.4^{\circ}$  (uncorrected) was collected. As the temperature began to rise toward the end the distillation was stopped, the system recharged with more acid and the procedure repeated. When the acid had been completely worked over the first fraction to

distill off was charged back into the flask and worked over again. This being completed the residue was discarded, the flask rinsed and the procedure repeated using the fraction of distillate from 124° to 124.4°. End portions, the first to distill off and the residue left in the flask were discarded. The distillate with a boiling point of 124.4° was retained and a third, fourth and fifth distillation was carried out in a like manner. This gave a distillate of HBr clear as water. The final portion having a boiling point of 124.4° was considered sufficiently pure for this investigation. It was stored in a carefully cleaned brown glass stoppered bottle, which had previously contained HBr solution, until needed.

Silver nitrate; A commercially pure grade of Baker's analyzed silver nitrate was used. It showed no turbidity when a portion was dissolved in a small volume of water. A five per-cent solution, by weight, containing three ml. of concentrated nitric acid per 1000g. was prepared, allowed to stand overnight in a covered container then filtered through a carefully prepared asbestos gooch crucible.

Nitric acid; A commercially pure grade was used. This acid showed no turbidity when treated with silver nitrate.

Asbestos; Asbestos fiber of good quality was digested in 20% hydrochloric acid for two hours on a steam bath, then filtered and washed until free from chlorides.



It was suspended in water until needed.

Thermometer; An anschutz thermometer was used. It was graduated to read  $.2^{\circ}$  and had a range from  $85^{\circ}$  to  $160^{\circ}$  .

Barometer; The barometer was of standard weather bureau type.

Distillation apparatus; The distillation flask, condenser, receiver and manometer were similar to those used by Foulk and Hollingsworth<sup>2</sup> in their investigation of hydrochloric acid solutions. One end of a 2.9 cm pyrex glass tube was constricted slightly about 2 cm. from the end. The lower end of a heavy wall pyrex test tube was heated, tapered and drawn slightly so that it fitted the constriction in the 2.9 cm tube. This junction was then ground to a perfect fit. A short piece of glass rod having an eye in the end was sealed to the lower end of the ground glass stopper. A hook was fashioned in another piece of glass rod placed through this eye and sealed together thus giving a flexible joint. The lower end of this glass link was so shaped that it would slip under and around the bulb of an anschutz thermometer suspending it freely in the tube. A 500 ml. round bottom flask was sealed on the base of the 2.9 cm. tube. 9 cm. from the flask a distilling arm was sealed on the neck. This arm was in turn sealed to the pyrex core of a condenser, leading to the receiver containing small sample bottles

for the collection of samples of the distillate.

The condenser and flask were painted black with the exception of the neck of the flask above the distilling arm. The bulb of the flask was also covered with a paste made of sheet asbestos and water. This dried well and formed an efficient insulation which aided in maintaining an even temperature and preventing bumping during distillation.

An ebulator made from a piece of pyrex tubing, and pyrex glass beads were also used as insurance against bumping.

The neck of the flask above the distilling arm was wrapped with asbestos rope. A short open space being left for the reading of the thermometer which was suspended so that its bulb hung about 4 cm. below the distilling arm.

The pressure regulator consisted of a bottomless glass bottle sinkered with a sufficient quantity of lead to cause it to sink to the bottom of a 20.5 by 46 cm. glass battery jar filled with water. The neck of this bottle was fitted with a one hole rubber stopper and a stopcock. The bottle was suspended by a wire over a pulley above. The opposite end of the wire was loaded with movable weights so that by adding more or taking off some the bottle could be raised or lowered thus exerting the desired effect on the pressure of the system to which it was attached.



A small amount of friction was necessary for the proper functioning of this device. The stopcock was connected by means of rubber tubing to a T tube one end of which connected to a manometer, the other end to the receiver for the distillate.

Pycnometer for density determination; The pycnometer was of the vacuum type made by sealing a marked capillary tube to the bulb of a 50 ml. pyrex distilling flask and sealing on at the other end of this capillary a stock having a ground junction to fit a filling device and a cap to prevent evaporation.

#### Procedure.

Five small weighing bottles and a 150 ml. beaker were placed on the movable base in the receiver which was then sealed, its lid being held in place by two small clamps. About 400 ml. of the pure HBr solution was placed in the distilling flask which was heated with a burner. The barometer reading was corrected and the pressure in the system regulated by the control to 750; 760; or 770 mm of mercury on the HBr solution. As soon as the distillation was well under way the pressure did not vary more than  $\pm .2$  to  $.3$  mm. of mercury. The pressure was watched carefully and the boiling point was noted each time a sample was collected.

When the 150 ml. container was nearly filled with the distillate, two or three or more samples of from

3 to 4 ml. each were collected. Then the flame was removed, the pressure was released, the stoppers placed in the weighing bottles, weighings made and the samples analyzed.

Part of the work was done by this procedure, then it was found expedient to vary the method slightly so the density might be determined from the same distillation. One 100 ml. beaker and one 150 ml. beaker were placed in the receiver 125 to 150 ml. of the HBr was distilled off then a 100 ml. sample was distilled and collected in the second container. Two portions of this sample were transferred to weighing bottles for analysis and the pycnometer was filled with a portion of the remainder, brought to constant temperature by allowing it to set overnight in a thermostat at 25.05° C. The content of the pycnometer was then adjusted to the mark by means of a capillary tube. Excess HBr solution above the capillary was wiped away and the stopper cap inserted. The outside of the pycnometer was dried, the pycnometer placed in a dessicator for 10 minutes then weighed. Barometric pressure and temperature were recorded for use later in calculation of the density.

In filling the pycnometer was evacuated by a water pump, a charge of the acid allowed to flow in, nearly enough to fill the pycnometer. The pycnometer was



again evacuated until bubbles ceased to come from the HBr solution, then HBr solution was let in slowly until the bulb was filled. The small bubble remaining at the top of the flask was removed by warming the pycnometer in the hands until expansion of the contents expelled it. On cooling to 25.05°C in the thermostat the pycnometer was completely filled with air free HBr solution.

Analysis; The samples of HBr weighing 4 to 5 g each were diluted to 800 mL in tall form liter beakers. Slightly less than the theoretical amount of 5% solution of silver nitrate was added slowly with stirring this operation being carried on in the filtered light of a photographic dark room. The samples were covered and allowed to set for twelve hours then a slight excess of silver nitrate solution was added and finally 5 mL of concentrated nitric acid. Complete precipitation and rapid settling followed this treatment. After standing twelve hours the silver bromide was filtered onto platinum gooch crucibles which had been previously treated by washing with dilute silver nitrate then with water until entirely free from silver nitrate dried at 110° overnight then at red heat to constant weight. The Ag Br was washed with about 1 liter of conductivity water dried overnight at 110° then finally heated just to the fusing of the Ag Br. They were then cooled

in a dessicator and weighed. Treatment was continued to constant weight within  $\pm .0002$  g. All weighings were reduced to vacuo and a correction of  $.54 \times 10^6$  g of Ag Br added for each liter of solution plus wash water used. The factor used for conversion of this weight to the equivalent of HBr was .43091.

TABLE I.  
(Pressure 770 mm.)

Series A	Wt. H Br (Soln) In Vacuum	Wt. Ag Br In Vacuum	Wt. % H Br	Normality
1a distillate	4.89641	5.42599	47.752	8.7318
2b distillate	4.49090	4.97662	47.752	8.7318
3c distillate	5.84827	6.48033	47.748	8.7310
4d distillate	7.38405	8.18395	47.759	8.7331
5e distillate	6.94783	7.69790	47.743	8.7301
6f residue	5.02200	5.56958	47.789	8.7386
<u>Series B</u>				
1a distillate	3.95754	4.38403	47.735	8.7290
2a distillate	3.95467	4.37992	47.724	8.7267
<u>Series C</u>				
1a distillate	4.94206	5.47020	47.696	8.7216
2a distillate	4.76914	5.28080	47.714	8.7248



TABLE II.  
(Pressure 760 mm.)

Series A	Wt. H Br (Soln) In Vacuum	Wt. Ag Br In Vacuum	Wt. % H Br	Normality
1a distillate	4.80890	5.33569	47.811	8.7435
2b distillate	5.16276	5.72665	47.797	8.7409
3c distillate	3.93997	4.37203	47.816	8.7444
4d distillate	4.61754	5.12008	47.782	8.7382
5e distillate	4.74864	5.26276	47.756	8.7334
6f residue	4.40458	4.88890	47.829	8.7468
<u>Series B</u>				
1a distillate	4.55844	5.04670	47.707	8.7245
2a distillate	4.51941	5.00061	47.679	8.7193
<u>Series C</u>				
1a distillate	4.3715	4.84608	47.769	8.7358
2a distillate	4.6414	5.14553	47.771	8.7362

TABLE III.  
(Pressure 750 mm.)

<u>Series A</u>	<u>Wt. H Br (Soln) In Vacuum</u>	<u>Wt. Ag Br In Vacuum</u>	<u>Wt. % H Br</u>	<u>Normality</u>
1a distillate	5.0709	5.6226	47.779	8.7408
2a distillate	4.5175	5.0089	47.778	8.7406
<u>Series B</u>				
1a distillate	4.1924	4.6509	47.804	8.7453
2a distillate	4.2707	4.73631	47.789	8.7426
<u>Series C</u>				
1a distillate	4.7141	5.22331	47.746	8.7348
2a distillate	5.5449	5.03531	47.741	8.7339

TABLE IV.

Ser- ies	Wt. Pycn. HOH in Air	Wt. Pycn. in Vacuum	Wt. Pycn. + soln. in air	Wt. in vacuum Pycn.+soln.	Wt. of HOH corrected	Wt. of solution corrected	Vol. of Pycn.	Density g/cm <sup>3</sup>
(770 mm. of Hg)								
A.	78.6442	24.63114	103.7460	103.80650	53.34374	79.17536	53.50098	1.47989
B.	78.6442	24.63114	103.7337	103.79466	53.34374	79.16352	53.50098	1.47966
C.	78.6442	24.63114	103.7248	103.78529	53.34374	79.15415	53.50098	1.47949
(760 mm. of Hg)								
B.	78.6442	24.63114	103.7240	103.78397	53.34374	79.15283	53.50098	1.47947
C.	78.6442	24.63114	103.7614	103.82233	53.34374	79.19119	53.50098	1.48018
(750 mm. of Hg)								
A.	78.6442	24.63114	103.7828	103.8438	53.34374	79.21266	53.50098	1.48058
B.	78.6442	24.63114	103.7907	103.85207	53.50098	79.22093	53.50098	1.48074
C.	78.6442	24.63114	103.7405	103.80073	53.50098	79.16959	53.50098	1.47978

TABLE V.

<u>Series</u>	<u>Correction</u>	<u>Observed Boiling Point</u>	<u>Corrected Boiling Point</u>	<u>Pressure</u>
A.	.2°	5 - 124.4°	124.6°	760 mm.
B.	.2°	12 - 124.4°	124.6°	760 mm.
C.	.2°	9 - 124.4°	124.6°	760 mm.
A.	.2°	8 - 124.8°	125.0°	770 mm.
B.	.2°	8 - 124.8°	125.0°	770 mm.
C.	.2°	11 - 124.8°	125.0°	770 mm.
D.	.2°	9 - 124.8°	125.0°	770 mm.
A.	.2°	17 - 124.0°	124.2°	750 mm.
B.	.2°	10 - 124.0°	124.2°	750 mm.
C.	.2°	13 - 124.0°	124.2°	750 mm.

\* Number of observations made.



TABLE VI.

Summary of Data

<u>Series</u>	<u>Pressure</u>	<u>Boiling Pt.</u>	<u>% H Br</u>	<u>Density</u>
A B C	770	125°	47.727	1,47968
A B C	760	124.6°	47.785	1,47983
A B C	750	124.2°	47.771	1,48037

## Interpretation of Data

Capital letters in the tabulation indicate the distillation, small letters indicate the separate fractions of the distillate, Arabic numerals, unless otherwise stated, indicate the individual samples of distillate analyzed.

In the calculation of the average for the densities, those densities of the distillate at each pressure were added and an average made.

In the calculation of the average of the H Br content, any unusually high or low value was thrown out, then the accepted results from the individual samples of each distillation were added and an average taken. The final average H Br content was calculated from these averages of each separate distillation. Series B, Table II, was thrown out in this consideration.

## Discussion

The distillation rate was regulated so that 50 to 60 drops or 2.5 to 3 ml. distilled over per minute. It was found difficult to avoid bumping when a rate of distillation slower than 40 drops or 2 ml. per minute was attempted.

A small window for observation of the quantity of H Br solution present was provided on one side of the distilling flask.

The thermometer was read with a magnifier by holding a light back of the flask neck. Estimation of the

temperature to  $.05^{\circ}$  could be made with a high degree of accuracy. No variation could be detected in the boiling point after an equilibrium condition had been attained. A very slight vibratory movement of the manometer was noticed but the pressure once regulated remained constant to within  $\pm .2$  to  $.3$  mm. of mercury.

The calibration of the thermometer was rechecked by reading it in boiling redistilled water at a pressure of 760 mm. of mercury. It was found necessary to apply a correction of  $\pm .2^{\circ}$  to the thermometer used at  $100^{\circ}$ . A constant pressure was easily maintained, but this factor varied less with a low rate of distillation. All weights were reduced to vacuum conditions before calculations were made.

#### Summary

When investigated by precise methods it was found that H Br distillate at 750 mm. pressure boils at  $124.2^{\circ}$  C, contains 47.771% H Br and has a density of 1.48037; that H Br distillate at 760 mm. pressure has a boiling point of  $124.6^{\circ}$ , contains 47.785% H Br and has a density of 1.47983, and that H Br distillate at 770 mm. pressure boils at  $125.0^{\circ}$  C, contains 47.727% H Br and has a density of 1.47968. The constant boiling mixtures have a weight normality of:

5.9035 at 750 mm. of mercury

5.9063 at 760 mm. of mercury

5.8993 at 770 mm. of mercury

a volume normality of:

8.7397 at 750 mm. of mercury

8.7386 at 760 mm. of mercury

8.7286 at 770 mm. of mercury.

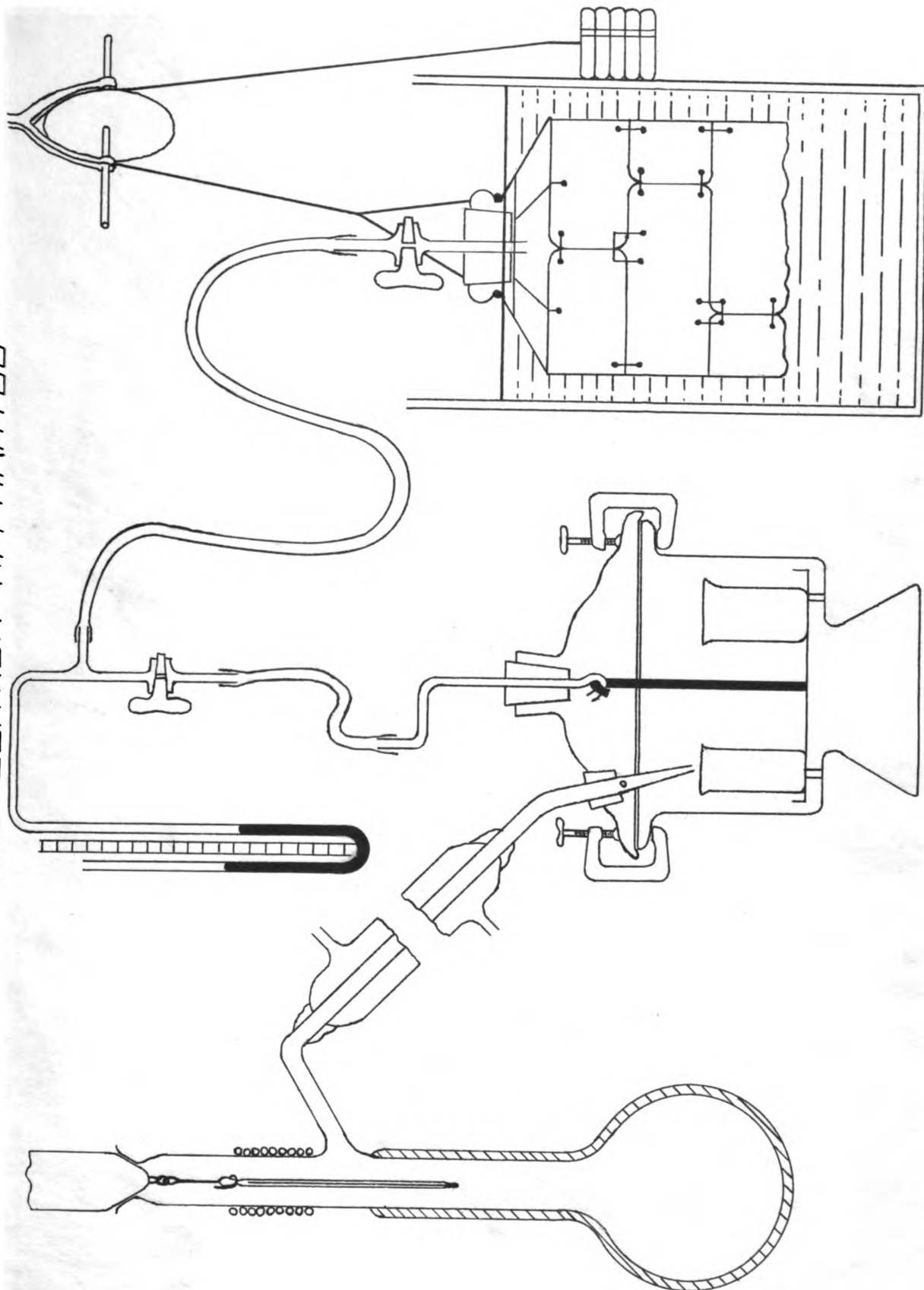
The composition of H Br distillate at 760 mm. of mercury agrees closely with that reported by Ewing and Shadduck <sup>3</sup>.

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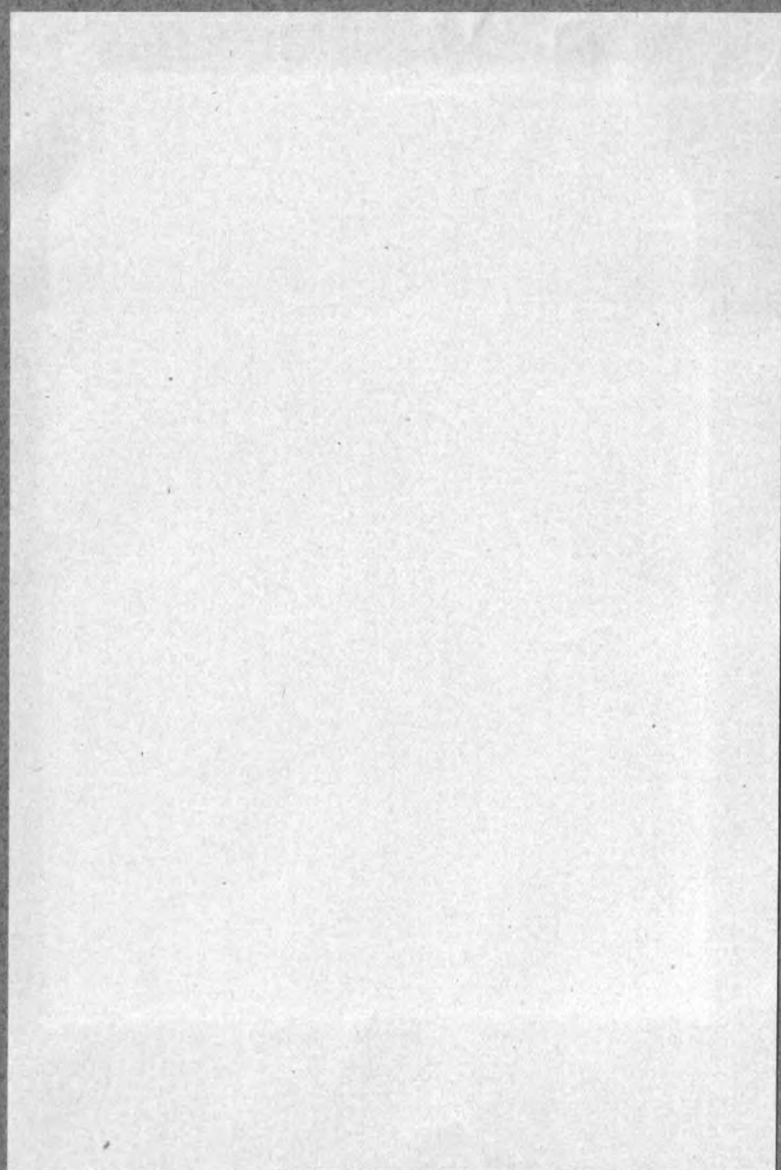
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