A PHASE STUDY OF THE SYSTEM AMMONIA–HYDROGEN SULFIDE

By LEOPOLD SCHEFLAN AND C. R. McCROSKY

With the exception of ammonium hydrosulfide, the existence of pure compounds of ammonia and hydrogen sulfide has not been definitely established although a considerable number have been reported by various investigators. The following compounds have been described in the literature: NH_2HS,[1,2,3,4,5,6] $(NH_4)_2S$,[1,6,7,8,9,10] $(NH_4)_2S \cdot (NH_3)_2$,[4] $(NH_4)_2S \cdot (NH_3)_4$,[9] $(NH_4)_2S \cdot NH_4HS$,[2,5] $(NH_4)_2S \cdot (NH_4HS)_2$,[2,5] $(NH_4)_2S \cdot (NH_4HS)_2 \cdot (H_2O)_x$,[2,5] $(NH_4)_2S \cdot (NH_4HS)_{12}$,[2,5] $(NH_4)_2S \cdot (NH_4HS)_{18} \cdot (H_2O)_4$,[2,5] $(NH_4)_2S \cdot (NH_4HS)_{24}$.[2,5,11]

Unfortunately, reports which give methods of preparing these substances with the exception of NH_4HS are vague and sometimes contradictory. In most cases it would appear that the methods which the older investigators used could not have yielded compounds in a pure state.

Scheffer[12] investigated the dissociation equilibrium of the system ammonia–hydrogen sulfide, determining the critical constants of ammonia and hydrogen sulfide, and the three phase line of the compound NH_4HS at which solid, liquid and vapor are in equilibrium with one another.

With the object of obtaining more definite knowledge concerning the nature of the compounds formed between ammonia and hydrogen sulfide, it seemed worth while to make a study of the vapor pressure and the freezing points of mixtures of these substances.

Experimental Procedure

The method of Foote and Brinkley[13] was used in preparing dry ammonia. The pure gas was passed into a flask partly filled with ammonium thiocyanate, which deliquesces and acts as an absorbent. By cooling the flask with ice during the process of absorption, it is possible to get a solution which contains about 45% of ammonia.

[1] Bineau, Ann. chim. phys., **67**, 225–251 (1839); **68**, 416–441 (1839).

[2] Bloxam, J. Chem. Soc., **67**, 277–309 (1895).

[3] Naumann, Ber., **43**, 313–321 (1910).

[4] Troost, Compt. rend., **88**, 1267 (1879).

[5] Bloxam, Chem. News, **68**, 97–98 (1893).

[6] Thomas and Riding, J. Chem. Soc., **123**, 1181–1189 (1923).

[7] Bineau, Ann. chim. phys., **70**, 251–272 (1839); **32**, 227–232 (1839).

[8] Bineau, Berz. J., [2] **20**, 137–138 (1839).

[9] Maumené, Compt. rend., **89**, 506–507 (1879).

[10] Deville, ibid., **88**, 1239–1240 (1879).

[11] Fritsche, J. prakt. Chem., **24**, 460–467 (1841); **32**, 313–317 (1844).

[12] Scheffer, Z. physik. Chem., **71**, 671–704 (1910); **76**, 161–173 (1911).

[13] Foote and Brinkley, THIS JOURNAL, **43**, 1178–1179 (1921).

This flask was sealed to the apparatus as shown in Fig. 1. The gas liberated from A is further dried by passing it over sodium. This metal reacts with gaseous ammonia at elevated temperature but not appreciably at room temperature. Samples of the gas were drawn out after this treatment and analyzed, and found to be free from moisture, non-condensable gases and solid impurities. It was also solidified with liquid air and the melting points were determined. In each case the melting point agreed within less than 1° with that reported in the literature for pure ammonia.

Hydrogen sulfide was prepared by the action of dilute sulfuric acid on pure sodium sulfide and dried over calcium chloride and phosphorus pentoxide. It also proved to be advisable to condense it in a bath of carbon dioxide and ether. By this procedure the hydrogen sulfide could be stored and any moisture frozen out. Samples of the purified gas were found to be free from moisture and solid impurities. When dissolved in sodium hydroxide solution and analyzed, it was found to contain no chloride, nitrite or nitrate ions. Samples of the gas were solidified with liquid air and the melting points were found to agree within less than 1° with the temperature reported for pure hydrogen sulfide.
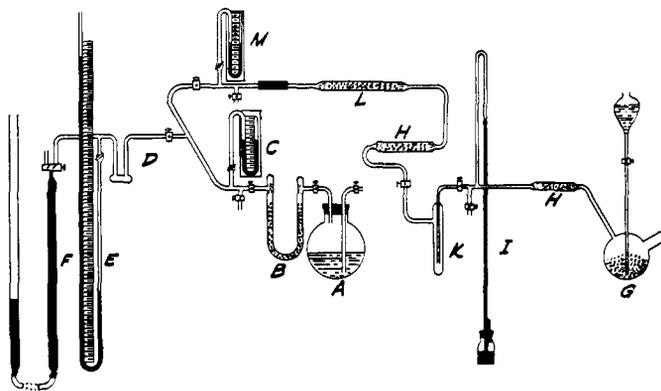

Fig. 1.—Vapor pressure apparatus.

The essential features of the apparatus used in the first part of the work are shown in Fig. 1. The ammonia branch begins with the flask (A) containing the ammonia-ammonium thiocyanate solution. The ammonia is passed over sodium (B) for drying. A manometer (C) and an outlet are included. The hydrogen sulfide branch begins with the flask (G) containing sodium sulfide. A separatory funnel containing dilute sulfuric acid is sealed through this flask. The glass tubing coming from the generator leads to a safety outlet, a manometer (I), calcium chloride tubes (H), a condensing tube (K) from which the hydrogen sulfide can be boiled off whenever necessary, and a phosphoric anhydride tube (L). The two branches meet near the reaction chamber. The gases are condensed in the reaction chamber (D) cooled from the outside with a suitable bath of liquid air or carbon dioxide and ether, and the pressure read on a manometer. The concentration of the mixture is varied by means of the mercury pump made from an ordinary gas buret. Before collecting a sample each half of the apparatus was thoroughly swept out with its own gas.

Ammonia was first condensed in the reaction chamber, which was surrounded by a freezing mixture of solid carbon dioxide and ether. After shutting off the ammonia stream, hydrogen sulfide was admitted, resulting in the formation of a white solid which melted to a clear liquid when the reaction chamber was surrounded by the ice-water bath. Ammonia was withdrawn from the system a number of times and after equi-

librium had been reached the successive pressures were read. From the data obtained, the vapor pressure diagram for 0° was constructed.

The vapor pressure–temperature curve of the three phase system NH₄HS (solid), solution, and vapor, was determined by two methods. (1) Equilibrium was established at 0° with crystals in contact with the solution. The ice-water bath was then replaced by baths of various temperatures, and the pressures were noted. Temperatures below 0° were obtained with salt–ice–water and ice–alcohol mixtures. The desired low temperature was held for a period of time by careful additions of small amounts of alcohol or ice to the well insulated bath. Temperatures above 0° were obtained by mixing hot and cold water. (2) Mixtures of ammonia and hydrogen sulfide were liquefied in a freezing mixture and then immersed in a bath of the desired temperature. Ammonia was pumped off until crystals appeared, and the constant pressure was recorded.
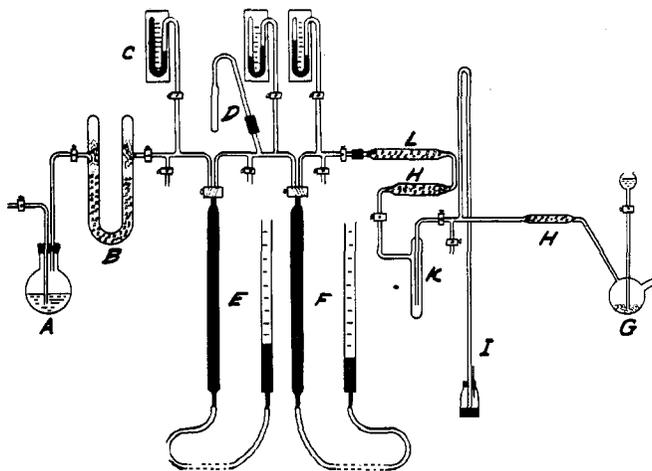

Fig. 2.—Freezing point apparatus.

Figure 2 shows the apparatus used for the determination of the freezing point curve of the system NH₃·H₂S. Ammonia was measured out in known quantities through the gas buret E into the reaction chamber D, which was cooled by the carbon dioxide–ether mixture. After the desired quantity of ammonia had condensed, the quantity of hydrogen sulfide necessary for the particular sample was measured in through the gas buret F from the tube K. In this way the desired mixture was collected in the reaction chamber. Then the sample was frozen and the reaction chamber sealed off. All tubes were approximately the same size: 15 cm. long and 1 cm. inside diameter.

The freezing point of each mixture was determined by using the method employed by Rupert.[14] This method of determining freezing points was checked by determining the freezing points of hydrogen sulfide, water, and acetamide. In each case the freezing point found checked closely with the accepted values for these substances. The thermometers were corrected by comparing them with thermometers calibrated by the Bureau of Standards.

Experimental Results

The Vapor Pressure Diagram of 0°.—In Table I are the data from which the curve in Fig. 3 was drawn. In this curve it is to be noted that

[14] Rupert. THIS JOURNAL, **31**, 851–866 (1909).

there are only two regions of constant pressure at 0°. The crystals which separated out at the first constant pressure region were analyzed and found to have a ratio of NH_3 and H_2S corresponding to the composition of NH_4HS, as shown in Table II.

The analysis was performed in the following manner. As soon as the liquid phase had disappeared from the tube and the pressure had just begun to drop, the reaction chamber was sealed off from the rest of the apparatus. The tube was weighed and chilled in the cooling mixture of carbon dioxide and ether, which greatly decreased the pressure within the tube, and allowed it to be broken under ice cooled water in a closed vessel. In this way, samples with high vapor pressure could be dissolved with negligible

TABLE I

TEMPERATURE OF BATH, 0°   ATMOSPHERIC PRESSURE,   740   MM.   MANOMETER READINGS, MM.

Gas removed, cc.	Left, mm.	Right, mm.	Difference, mm.	Absolute pressure, mm.
0	210.0	815.0	605	1345
40.0	282.0	740.0	460	1200
26.0	320.0	701.0	381	1121
25.5	368.0	657.0	289	1029
25.0	402.5	623.5	221	961
20.5	436.5	591.5	155	895
24.5	465.0	562.0	97	837
45.5	465.0	563.0	98	838
65.4	465.0	562.0	97	837
50.7	465.0	562.0	97	837
36.0	466.0	562.0	96	836
45.8	466.0	562.0	97	837
40.3	466.0	562.0	97	837
40.4	522.0	507.0	− 15	725
30.3	610.0	416.0	−194	546
25.4	708.5	318.5	−390	320
30.2	722.5	253.5	−519	221
20.2	843.0	183.0	−660	80
45.4	843.0	183.0	−660	80
40.1	853.0	183.0	−670	79
35.3	843.0	183.0	−660	80
25.6	843.0	183.0	−660	80

TABLE II

ANALYSIS OF CRYSTALS FROM THE FIRST CONSTANT PRESSURE REGION (840 MM.)

Sample	NH_3, %	H_2S, %
I	34.70	63.75
II	34.53	63.56
III	33.31	63.98
IV	33.10	63.77
V	33.65	64.43
VI	33.43	64.01

Theoretical value for NH_4HS, 33.36

loss. This solution was diluted to a definite volume and aliquot parts were taken for analysis. The remnants of the reaction chamber were carefully collected and weighed. One portion of the solution was run into an excess of acidified standard iodine solution, titrated with sodium thiosulfate solution, and the hydrogen sulfide content calculated.

The ammonia content was determined by titrating another portion with standard sulfuric acid, using methyl orange as an indicator. In every analysis the value obtained for hydrogen sulfide was a little lower than the theoretical value. Undoubtedly the cause for this discrepancy is the escape of small amounts of hydrogen sulfide gas, preceding and during the titration. The odor of hydrogen sulfide was distinctly noticeable in each solution analyzed.

Table III shows the results of the two methods which were used to determine the vapor pressure–temperature curve of the three phase system ammonium hydrosulfide (solid), solution, and vapor. Figure 4 gives this curve as calculated by averaging the results of both methods.

Fig. 3.—Vapor pressure curve system: NH$_3$–H$_2$S at 0°.

The values obtained for the freezing points of the various mixtures are given in Table IV and the curve constructed from the data in this table is given in Fig. 5. Two peaks are noted in this curve, corresponding to the composition of (NH$_4$)$_2$S and NH$_4$HS. Analysis of crystals removed from the region of the first peak shows them to approximate very closely the composition of (NH$_4$)$_2$S, as shown in Table V. Crystals removed at the second peak or higher melting point have a composition closely corresponding to NH$_4$HS as shown in Table VI.
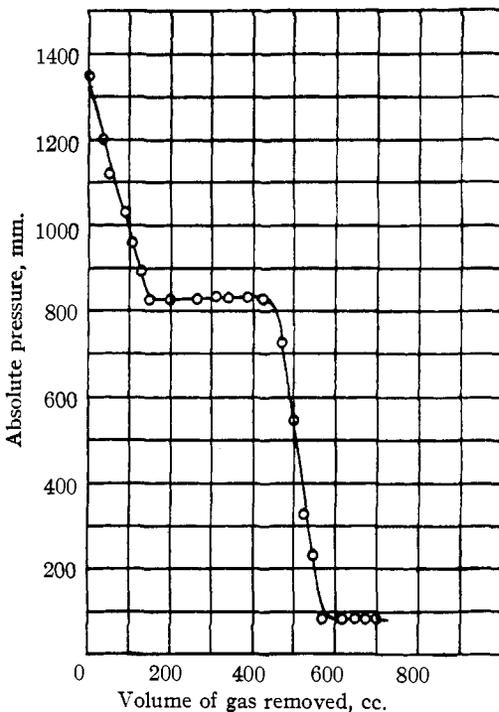
Discussion

The curve drawn in Fig. 3 differs slightly from the one required by the theory as there should be a vertical line between the two horizontal lines.

TABLE III

VAPOR PRESSURES OF THE THREE PHASE SYSTEM NH₄HS (SOLID), LIQUID AND VAPOR

| Temp., °C.	Vapor pressure, mm., determined by Method 1	Method 2	Average
−21	434	437[a]	435.5
−12	547	550	548.5
−10	582	580	581.0
− 7.8	604	605	604.5
− 7.5	633	630	631.5
− 5.9	663	665	664.0
− 5	687	685	686.0
− 4	707	710	708.5
− 2.5	779	781	780.0
0	839	837	838.0
2.5	917	918	917.5
5	1004	1000	1002.0
6	1077	1073	1075.0
7.5	1118	1122	1120.0
9	1200	1203	1201.5
10	1248	1245	1246.5

[a] This particular pressure was determined by Dr. Aden J. King of this Laboratory.
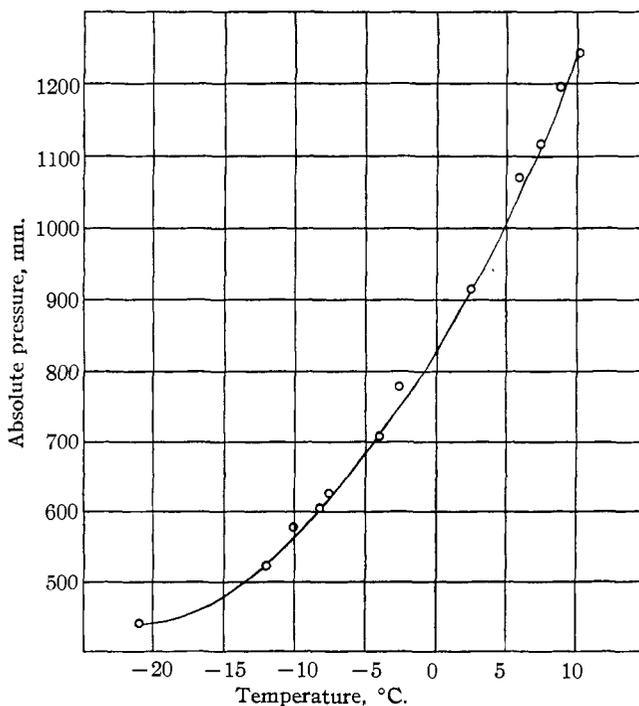
Fig. 4.—Vapor pressure–temperature curve system: ammonium hydrosulfide (solid)–solution–vapor.

TABLE IV
RESULTS OF TWO METHODS

% NH₃ by vol.[a]	% H₂S by vol.[a]	Melting temp., °C.				Average temp., °C.
100.0	0.0	−77	−79	−78	−78	−78.0
97.5	2.5	−85	−84	−82	−83	−83.5
95.0	5.0	−89	−86	−88	−89	−88.0
92.5	7.5	−73	−73	−72	−71	−72.3
90.0	10.0	−59	−60	−61	−60	−60.0
87.5	12.5	−48	−49	−48	−48	−48.3
85.0	15.0	−38	−39	−37	−39	−38.2
82.5	17.5	−31	−30	−29	−30	−30.0
80.0	20.0	−22	−22	−23	−23	−22.5
77.5	22.5	−19	−20	−20	−18	−19.2
75.0	25.0	−17	−18	−18	−19	−18.0
72.5	27.5	11	11	11	12	11.2
70.0	30.0	39	41	40	41	40.2
67.5	32.5	63	62	62	62	62.2
65.0	35.0	78	78	80	80	79.0
62.5	37.5	91	92	92	92	91.8
60.0	40.0	101	100	101	101	100.8
57.5	42.5	105	104	106	106	105.2
55.0	45.0	114	114	115	115	114.5
52.5	47.5	116	117	117	117	116.8
50.0	50.0	118	118	117	119	118.0
47.5	52.5	118	118	117	119	118.0
0.0	100.0	−83	−83	−84	−84	−83.5

[a] These numbers are equivalent to 100 times the mole fraction.

| Moles of NH₃ | 1 | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 | 0.3 | 0.2 | 0.1 | 0.0 |
| Moles of H₂S | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |

Molar concentration.
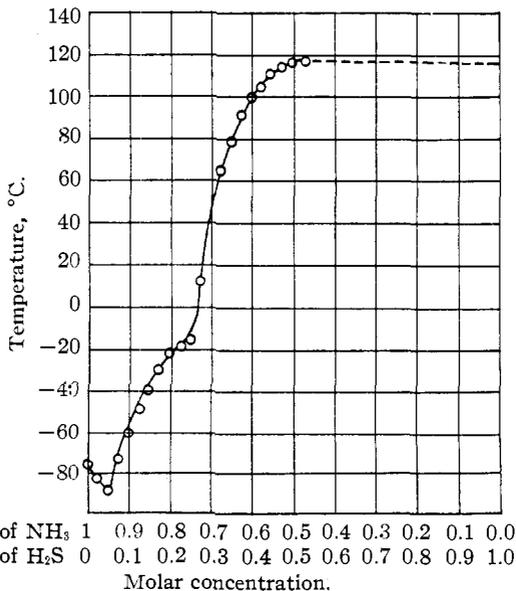
Fig. 5.—Freezing point curve system for NH₃–H₂S.

TABLE V

ANALYSIS OF LOW MELTING POINT CRYSTALS

Sample	NH$_3$, %	H$_2$S. %
I	52.03	47.22
II	51.87	48 11
III	52.24	47.46
IV	51.99	Lost
V	52.47	47.39
Theoretical value for (NH$_4$)$_2$S 50.06		49.94

TABLE VI

ANALYSIS OF HIGH MELTING CRYSTALS

Sample	NH$_3$, %	H$_2$S, %
I	34.71	63.87
II	34.92	64.10
III	35.02	64.23
IV	34.29	63.98
V	34.66	64.26
Theoretical value for NH$_4$HS, 33.36		66.64

When the liquid phase disappeared and more and more ammonium hydrogen sulfide crystallized, the time necessary for the establishment of the equilibrium increased greatly.

On pumping off ammonia at a definite rate, once the liquid phase had disappeared, another region of constant pressure was reached. This is noted in the second flat portion of the curve at a pressure of 80 mm. This, therefore, is taken as the dissociation pressure of ammonium hydrogen sulfide at 0°.

During the two periods of constant pressure the gas was removed at various rates. This change of the velocity had no effect on the pressure.

The latter part of the curve agrees with the results of two other investigators. Walker and Lumsden[15] worked on the dissociation pressure of ammonium hydrogen sulfide at temperatures higher than 0°, determining the vapor pressure–temperature curve for this salt. By interpolating their curve to 0°, a value of a little more than 80 mm. is obtained, in close agreement with our value.

The vapor pressure–temperature curve of the three phase system NH$_4$HS (solid), liquid, and vapor was found to be convex to the temperature axis. This is in agreement with the general rule.

Table III shows that the freezing points of various mixtures having the same composition agree nearly always within 2°. In this type of work such agreement is close enough to indicate the existence of compounds and eutectics.

The melting point of NH$_4$HS, which was found to be 118°, agrees with the temperature as given by earlier investigators. E. Briner[16] found that

15 J. Walker and J. S. Lumsden, *J. Chem. Soc.*, 71, 428–440 (1897).

16 E. Briner, *Compt. rend.*, 142, 1216–1218 (1906).

the melting point of NH_4HS in a closed vessel was 120°, while F. E. C. Scheffer[13] obtained the value of 118°.

The literature contains conflicting statements regarding the existence and stability of ammonium sulfide, $(NH_4)_2S$. Bineau[1,7] obtained it by mixing two volumes of ammonia with one volume of hydrogen sulfide at a temperature of $-18°$. He said that it was stable only at low temperatures and that it easily dissociated into NH_3 and NH_4HS. St.-Claire Deville[10] found that it was not decomposed at a temperature of 90°. Bloxam[5] repeated Bineau's work, but failed to prepare $(NH_4)_2S$ by Bineau's method. Instead of getting ammonium sulfide, he always obtained mica-like crystals of the composition $(NH_4)_2S \cdot (NH_4HS)_n$ or an oily liquid of the composition $(NH_4)_2S \cdot (NH_3)_2$. He states that by carefully regulating the volumes of the gases and their rates of flow he succeeded in obtaining micaceous crystals of ammonium sulfide. From this description, however, it seems very probable that his crystals were always more or less contaminated with ammonium hydrosulfide. Thomas and Riding[6] were unable to obtain ammonium sulfide by Bloxam's method. The following is quoted from their article: "Anhydrous ammonium hydrosulfide is best prepared by alternately passing ammonia and hydrogen sulfide into dry ether. Attempts to convert the hydrosulfide into the monosulfide by prolonged action of saturated solutions of ammonia in ether failed, but in the presence of a small quantity of alcohol a yellow oil having the composition $(NH_4)_2S \cdot (NH_3)_2$ separated out, together with a few transparent crystals, believed to be anhydrous ammonium sulfide. Similar crystals were obtained when the oil was kept in an iron vessel. The ratio NH_3/H_2S was determined for these crystals, the results lying between 1.92 and 2.11."

Our own results indicate that ammonium sulfide must be unstable under ordinary conditions. It has a high dissociation pressure and must decompose very rapidly. This is in agreement with the results of Thomas and Riding. However, their report does not indicate in any way that they succeeded in isolating this compound at room temperature. They weighed and analyzed a rapidly decomposing substance of unknown purity. Therefore their results seem to be questionable.

Summary

1. The vapor pressure curve of the system NH_3–H_2S has been determined at a temperature of 0°.

2. Two regions of constant pressure were obtained: one at a pressure of 80 mm., the other at a pressure of 837 mm. The first pressure represents the dissociation pressure of NH_4HS at 0° while 837 mm. is the pressure at which the solid compound is in equilibrium with solution and vapor at the same temperature.

3. The dissociation pressure of NH_4HS checks with the pressure which

can be predicted from the dissociation pressure–temperature curve of NH_4-HS as determined by Walker and Lumsden.

4. The temperature–concentration phase diagram of the system NH_3-H_2S was determined.

5. The diagram indicates the existence of two compounds NH_4HS and $(NH_4)_2S$ and a eutectic mixture of 95% NH_3 and 5% H_2S.

6. Solid crystalline $(NH_4)_2S$ does not exist above $-18°$. On heating, at this temperature, it decomposes into solid crystalline NH_4HS and melt.

7. The melting point of NH_4HS agrees with the temperature as given by earlier investigators.   ·

8. The vapor pressure curve in this work shows that probably only one compound, ammonium hydrosulfide, is stable above $0°$.

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INTERFERENCE OPTICAL LEVER FOR PRESSURE GAGES, GALVANOMETERS, ETC.

BY W. E. ROSEVEARE

It is possible, with a very simple optical system, to measure deflections with an average error corresponding to about 0.001 mm. for a meter optical arm. The optical system is shown in Fig. 1. The usual galvanometer lamp was replaced by a very narrow slit S and two slit apertures S″ were placed in front of the projection lens P. The projected image of the slit, viewed through an eyepiece or microscope, consisted of a number of straight interference bands with nearly all the light in the three center bands. The source of light L was a 100-watt frosted light bulb placed in a lamp house with a 1-cm. hole in the side to illuminate the slit. The collimator of an old spectroscope was used for the narrow slit and lens. The slit must be one that equally illuminates the two slit apertures when the former is made very narrow. Some spectroscope slits were found to be shaped like A and B of Fig. 1. They were unsuitable and were ground to the shape C or D on a fine oil stone. Projection lenses with a focal length of 15–17 cm. were found most convenient for use with a two or three meter optical lever. The slit apertures were 3 mm. wide and 3 mm. apart and about 20 cm. from the mirror M. A filar micrometer eyepiece was used for measuring deflections up to 1 cm., while a comparator was used for measuring deflections up to 10 cm. The cross hair was always set in the center of the most intense interference band. The mirror must be of good quality plate glass and should be $^3/_8$-inch size. Some