

may then be converted into  $\text{Pr}_2\text{O}_3\cdot\text{SO}_3$  and  $\text{La}_2(\text{SO}_4)_3\text{-Pr}_2(\text{SO}_4)_3$  and a considerable separation effected by solution of the latter in water.

7. x-Ray diffraction photographs of some mixtures of oxides and of anhydrous sulfates, obtained by the Hull-Debye-Scherrer powder method, confirmed the conclusions drawn from the decomposition experiments, as to the formation of solid solutions.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

### CHEMICAL EFFECTS PRODUCED BY RADON ON THE SYSTEM: HYDROGEN-SULFUR-HYDROGEN SULFIDE<sup>1,2</sup>

BY E. C. TRUESDALE AND S. C. LIND

RECEIVED SEPTEMBER 14, 1931

PUBLISHED FEBRUARY 5, 1932

In connection with some recent work on the possible activation of hydrogen by alpha particle ionization<sup>3</sup> it was decided to investigate the synthesis of hydrogen sulfide by alpha particle ionization and to extend the work of Wourtz<sup>4</sup> on the decomposition of hydrogen sulfide by radon. In a series of carefully conducted experiments Wourtz found that the decomposition of hydrogen sulfide by alpha particle ionization was less efficient the higher the temperature. Since, in general, the efficiency of chemical reaction by alpha particle ionization is either independent of or increases with increasing temperature, it was thought that further investigation of this apparent exception would be of value. It seemed that the apparent decrease in the efficiency of the decomposition reaction at higher temperature might be due to a synthesis of hydrogen sulfide, both thermally and by ionization, which was itself more efficient as the temperature was increased.

It was therefore planned to conduct experiments on the synthesis and on the decomposition of hydrogen sulfide by alpha particle ionization to determine (1) the effect of increase of temperature, and therefore of sulfur vapor pressure, on the efficiency of the reactions, (2) the effect on this efficiency of varying the intensity of ionization and the amount of radon decomposed, and (3) if possible, something concerning the mechanism of the reactions which follow the initial act of ionization. It was felt that the

<sup>1</sup> Presented at the Buffalo Meeting of the American Chemical Society, September, 1931.

<sup>2</sup> This paper represents part of a thesis submitted by Edward C. Truesdale to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

<sup>3</sup> E. C. Truesdale, *J. Phys. Chem.*, **34**, 2472 (1930).

<sup>4</sup> E. E. Wourtz, *Le Radium*, **11**, 289-298, 332-347 (1919). See also S. C. Lind, "Chemical Effects of Alpha Particles and Electrons," 2d ed., The Chemical Catalog Co., New York, 1928.

experimental method best suited to the properties of the system being investigated was that of mixing the radon with the reactants in small sealed bulbs of known volume, and of determining the extent of the reaction by chemical analysis at the end of the experiment.

### Experimental Procedure

The Pyrex reaction bulbs were from 30 to 50 cc. in volume (about 4 cm. in diameter) and were provided at each end with a capillary tube about 10 cm. long. One of these capillaries was enlarged where it joined the bulb so that by making a clean break at this point the tiny bulb of radon and the sulfur could be introduced, after which the tube could be sealed on again without appreciably altering the volume of the bulb. Suitable constrictions at the ends of these tubes facilitated eventual sealing off and provided the readily breakable tips needed in the method of chemical analysis. The volume of each bulb was determined from time to time by filling it with mercury and weighing the latter; in spite of repeated use the volume of a bulb rarely changed by more than a few thousandths of a cubic centimeter. Since accurate knowledge of the volume of a bulb was especially important in the experiments on the decomposition of hydrogen sulfide, the volume was determined in each case at the end of the experiment.

After introducing the fragile bulb containing the radon and the 10 to 25 mg. pellet of sulfur into the reaction bulb and replacing the capillary tube, one end of the bulb was sealed onto the apparatus for filling it with the desired gas, the other end being similarly connected to a vacuum pump. The bulb was alternately filled with the gas and evacuated ten or twelve times, and (in the case of hydrogen) the gas was then allowed to flow through the bulb for several minutes before making final adjustment of pressure and sealing off the bulb. By careful shaking the tiny bulb of radon was then broken, thus allowing the radon to mix with the gas in the reaction bulb. In the experiments on the synthesis of hydrogen sulfide the bulb was then kept at room temperature for about five hours to allow the radon to come into equilibrium with its active deposit before starting the reaction, while in the experiments on the decomposition of hydrogen sulfide the reaction began as soon as the bulb of radon was broken, thus necessitating a correction for the fact that radioactive equilibrium had not been established.

The hydrogen used was purified in the manner described in a previous paper,<sup>5</sup> the same electrolytic source being used, while the sulfur was some of that previously purified by repeated distillation. The hydrogen sulfide was prepared in an all-glass apparatus by dropping fairly concentrated (1:1) phosphoric acid into 1 *M* sodium sulfide solution, and was purified by bubbling through a suspension of freshly precipitated ferrous sulfide, by passing over anhydrous calcium chloride and phosphorus pentoxide, and finally by double distillation from a trap cooled in liquid air into an evacuated 2-liter bulb. This storage bulb was connected to a mercury manometer, and by suitable stopcocks to the reaction bulb and vacuum line. The freshly-boiled mercury in the manometer did not react with this pure hydrogen sulfide over a period of several months, the surface of the mercury remaining perfectly bright as long as air was excluded. This fact is in accord with the work of Lilienfeld and White<sup>5</sup> and of Roberts<sup>6</sup> on the reaction of hydrogen sulfide with silver and with mercury, respectively. The sodium thiosulfate used in the titrations was recrystallized, the solution being standardized against resublimed iodine in the usual manner. The iodine solution was compared with the thiosulfate. The solutions were standardized frequently to correspond with the termination of an experiment. For the work on the synthesis of hydrogen sulfide

<sup>5</sup> Lilienfeld and White, *THIS JOURNAL*, 52, 885 (1930).

<sup>6</sup> A. L. Roberts, *ibid.*, 53, 1810 (1931).

these solutions were approximately 0.01 *N*, while for that on the decomposition they were 0.1 *N*.

The experiments at elevated temperatures were carried out by placing the bulbs in a small electrically-heated oven provided with thermostatic control, the temperatures being constant to  $\pm 1^\circ$ . The temperatures chosen for the experiments on the synthesis of hydrogen sulfide were 37, 138, 185, 200, 234 and 270°. The first experiments were carried out at 200° in order to provide a sufficiently large vapor pressure of sulfur, without at the same time obtaining an appreciable thermal synthesis. The next series of experiments was conducted at 234°, because this temperature interval provided an approximately three-fold increase in the vapor pressure of sulfur, and because this was the lowest temperature at which the kinetics of the thermal synthesis of hydrogen sulfide had been measured in the classical experiments of Bodenstein,<sup>7</sup> and it was hoped that his results might be duplicated. It may be stated here that while the present experiments gave results of the same order of magnitude for the rate of thermal synthesis, lack of complete agreement is no doubt due to the fact that the different kinds of glass used affected the velocity of the surface reaction differently. The next experiments were conducted at 37° in order to establish the extent to which solid sulfur was entering into the ionized reaction. The marked decrease in the efficiency of the reaction thus obtained suggested that the vapor pressure of sulfur might be the most important variable factor in the reaction, and the experiments at the remaining temperatures were carried out to establish this point. The experiments on the decomposition of hydrogen sulfide were made last, at the four temperatures 37, 200, 234 and 270°. The vapor pressures of sulfur, taken from the recent work of Menzies and West,<sup>8</sup> are  $1 \times 10^{-4}$ , (*ca.*), 0.1, 1.1, 2.1, 7.6 and 23.0 mm. of mercury at the respective temperatures of 37, 138, 185, 200, 234 and 270°.

The following technique was observed in determining the amount of hydrogen sulfide in the bulbs. One stem of a bulb, fitted with a stopper, was placed in a 100-cc. flask provided with a side arm and containing the iodine solution, and the tip of the stem was then broken by pressing it against the bottom of the flask. By varying the air pressure in the flask the iodine solution was alternately forced into the bulb and removed several times, accompanied by shaking of the bulb, to insure complete absorption of the hydrogen sulfide. After breaking the other tip of the bulb the iodine solution was removed as completely as possible and the bulb was washed with a small portion of the thiosulfate solution and finally several times with distilled water. The excess iodine was then titrated with thiosulfate, the presence of colloidal sulfur in no way interfering with the determination of the end-point. While the titration of the hydrogen sulfide involved considerable transferring of the standard solutions, care was taken to make such a transfer quantitative, and blanks on the method were very satisfactory.

In general, each experiment on the synthesis of hydrogen sulfide was accompanied by one or more blank experiments in which no radon was used, in order to determine the correction to be applied for thermal synthesis. In the experiments on the decomposition of hydrogen sulfide several blank runs showed that no thermal decomposition of hydrogen sulfide occurred at 270°, the highest temperature employed, though there was a slight and constant decomposition produced by sealing off the reaction bulb from the filling system, for which correction was made.

### Calculation of Results

The details of the method of calculating the results of these experiments cannot be given here for lack of space, though such details are avail-

<sup>7</sup> M. Bodenstein, *Z. physik. Chem.*, **29**, 315 (1899).

<sup>8</sup> A. W. C. Menzies and W. A. West, *J. Phys. Chem.*, **33**, 1880 (1929).

able for anyone interested. The efficiency of the alpha particle in promoting chemical reaction is measured by determining the value of the ratio,  $M/N$ , of the  $M$  molecules reacting to the  $N$  ion pairs produced on the initial reactant molecules.  $M$  was obtained from the results of the titration of hydrogen sulfide, while  $N$  was calculated according to the method of Mund,<sup>9</sup> in conjunction with the general principles adopted by Lind.<sup>4</sup> The values of certain radioactive and physical constants are referred to here since they are different from those formerly used in such work.

**Definition of Terms.**—The radioactive constants adopted are those given by Meyer and Schweidler<sup>10</sup> as being the best values, and involve slight changes from the values formerly employed. The values of  $\rho$  needed for the Mund factor  $F$  were taken from a table prepared by Glockler, as yet unpublished, but differing only slightly from earlier values given by him.<sup>11</sup> Values of the specific ionization,  $k$ , and the stopping power,  $s$ , have not been determined experimentally for sulfur and for hydrogen sulfide, so that the best values obtainable on theoretical grounds were used. Discussion of these values would require too much space here, and while the values adopted differ slightly from those which would be obtained by using the method of Kleeman<sup>12</sup> for obtaining  $k$ , and of Glasson<sup>13</sup> for obtaining  $s$ , it is believed that they are very close to those which might be obtained experimentally. By combining the results of the present experiments on the synthesis of hydrogen sulfide at three different temperatures it was possible to show that the values adopted for sulfur on the assumption that the molecule was  $S_8$  gave the most consistent results. Values of the specific ionization,  $k$ , were for hydrogen, 1.00, for sulfur, 1.1, for hydrogen sulfide, 1.18; values of the stopping power,  $s$ , were for hydrogen, 0.24, for sulfur, 7.0, and for hydrogen sulfide, 1.1. For a given composition of the reacting system, average values of  $s$  were obtained by multiplying the value of this constant for each component by its partial pressure in the mixture, and adding the partial values thus obtained. In obtaining an average value of  $k$  a similar procedure was employed, except that only the pressures of the initial reactants were considered.

In calculating the  $M/N$  values it was necessary to employ an average pressure for each gas, and it was desired to obtain a weighted average pressure which, if maintained during an entire experiment, would yield the same total ionization as was actually produced in a gas whose composition was constantly changing. This was done by calculating an over-

<sup>9</sup> W. Mund, *Ann. Soc. Sci. Bruxelles*, **44**, 336 (1925); *J. Phys. Chem.*, **30**, 890 (1926).

<sup>10</sup> St. Meyer and E. Schweidler, *Radioaktivität*, 2d. ed., B/G Teubner, Berlin, 1927, pp. 411-439 and Table IV, Appendix.

<sup>11</sup> G. Glockler, *J. Phys. Chem.*, **31**, 1322 (1927).

<sup>12</sup> R. D. Kleeman, *Proc. Roy. Soc. (London)*, **A79**, 220 (1907).

<sup>13</sup> J. L. Glasson, *Phil. Mag.*, [6] **43**, 477 (1922).

all value of the velocity constant,  $k\mu/\lambda$ ,<sup>14</sup> and from this values of the pressure of each component were obtained for the times when one-fourth, one-half, and three-fourths of the total decomposition of radon had been completed. There was thus obtained an average composition of the gas mixture during each of these periods, and by averaging these with the initial and final compositions the desired weighted average was found. Such a calculation, carried out for a typical experiment on the decomposition of hydrogen sulfide, showed that the weighted average pressure of this gas was 99% of the arithmetical mean pressure. Such a weighted value was used in all experiments on the decomposition of hydrogen sulfide and in the experiments on its synthesis at 270°; in the remaining cases of synthesis where the extent of reaction was small, the arithmetical mean pressure was employed.

**Non-Equilibrium Decomposition of Radon.**—In calculating the number of ion pairs produced by radon it is usually assumed that the radon is in equilibrium with its decomposition products through radium C, and that therefore one obtains three times the number of alpha particles coming from radon alone. In the experiments on the decomposition of hydrogen sulfide and in certain of those on its synthesis it was impossible to attain this equilibrium before chemical reaction set in, and it was therefore necessary to find the number of alpha particles which were actually given off during the first four hours and eighteen minutes, the time  $T$ , after the radon bulb was broken. The result is as follows. Instead of obtaining decomposition of 0.03192 of the initial radon and of equal amounts of radium A and radium C during the time  $T$ , the amounts decomposed (expressed as a fraction of the initial number of radon atoms) were as follows

$$\begin{array}{rcl} \text{No. } \alpha\text{-particles from Rn in time } T & = & 0.03192 E_0 N_0 \\ \text{No. } \alpha\text{-particles from RaA in time } T & = & 0.03138 E_0 N_0 \\ \text{No. } \alpha\text{-particles from RaC in time } T & = & 0.02324 E_0 N_0 \\ \hline \text{Total } \alpha\text{-particles in time } T & = & 0.08654 E_0 N_0 \end{array}$$

Dividing this total by 3 we obtain  $0.028845 E_0 N_0$ , a number which may be called the effective three-fold emission during the first four hours and eighteen minutes, and which is to be used in place of the equilibrium value  $0.03192 E_0 N_0$  in calculating the ionization during this time.

### The Synthesis of Hydrogen Sulfide

**Experimental Results.**—The results of the experiments on the synthesis of hydrogen sulfide are included in the following tables. In Tables I and II are to be found the experimental data and in Tables III and IV the derived values necessary to obtain the  $M/N$  values given in the fifth column of Table IV. Since the thermal synthesis of hydrogen sulfide is primarily a surface reaction at all the temperatures employed except

<sup>14</sup> Lind, Ref. 4, p. 116.

at 270°, and since the amount of thermal reaction varies slightly from one bulb to another due to slight differences in surface activity, average values for the amount of thermal synthesis were used at each temperature below 270°, while at the latter temperature it was assumed that the reaction had become primarily a homogeneous one, in accordance with the work of Norrish and Rideal,<sup>15</sup> and the thermal correction to be made in each case was calculated on the basis of simple volume and pressure relationships. In Table II the amount of thermal synthesis is indicated in terms of a volume of 0.01 *N* iodine. The total synthesis, thermal plus ionization, may be found by adding the proper volume from Table II to the corresponding volume in the last column of Table III.

Due to some peculiarity of the oven which was used, the excess sulfur present in the reaction bulb collected as a small patch of liquid on the upper

TABLE I  
EXPERIMENTAL DATA ON SYNTHESIS OF HYDROGEN SULFIDE

Expt.	Reaction temp., °C.	Expt. time, hrs.	Bulb vol., cc.	Init. P <sub>H<sub>2</sub></sub> , mm.	Init. temp., °C.	Init. Rn, mc.	N/100 I <sub>2</sub> , corr., cc.
1	200	186.27	48.85	685.5	25	57.7	7.16
2	200	206.59	34.45	696.5	25	54.9	6.68
3	200	204.42	41.52	699.5	25	56.0	6.87
4	200	203.92	48.75	702.5	23	130.2	13.11
5	200	209.51	51.87	693.0	27	105.7	11.10
6	234	160.25	33.19	729.1	22	62.0	8.42
7	234	156.25	30.60	731.6	22	63.6	7.88
8	234	156.25	31.36	729.1	22	57.3	7.18
9	37	211.00	41.52	729.0	23	56.2 <sup>a</sup>	0.13
10	37	211.75	48.75	727.5	23	43.6 <sup>a</sup>	.26
11	270	120.00	34.36	712.2	26	73.9	16.90
12	270	130.50	33.19	717.2	26	70.6	16.66
13	138	144.00	48.78	710.2	25	66.5 <sup>a</sup>	1.02
14	138	122.00	48.62	710.2	25	72.2 <sup>a</sup>	1.03
15	185	93.00	34.36	707.3	25	89.4 <sup>a,b</sup>	6.84
16	185	141.50	34.30	706.4	25	71.4 <sup>a,b</sup>	6.76

<sup>a</sup> Correction made for attainment of radioactive equilibrium during first four hours eighteen minutes. <sup>b</sup> Reaction bulbs cooled to room temperature for three hours while repairing thermostat during the experiment. Radon decomposed during this three hours not counted.

TABLE II  
CORRECTIONS FOR THERMAL SYNTHESIS OF H<sub>2</sub>S

Expt.	Temp., °C.	N/100 iodine, cc.	Expt.	Temp., °C.	N/100 iodine, cc.
1, 2, 3, 4, 5	200	0.39	12	270	19.18
6, 7, 8	234	1.68	13, 14	138	0.12
9, 10	37	0.00	15	185	.16
11	270	19.87	16	185	.29

<sup>15</sup> R. Norrish and E. Rideal, *J. Chem. Soc.*, **123**, 696. 1689, 3203 (1923).

TABLE III  
CALCULATED DATA FOR SYNTHESIS OF HYDROGEN SULFIDE

Expt.	Total vol. H <sub>2</sub> S, cc.	Av. $P_{H_2}$ , mm.	Av. $P_{H_2S}$ , mm.	$P$ sulfur, mm.	H <sub>2</sub> S formed, %
1	0.85	678.3	7.2	2.1	2.10
2	.79	687.0	8.9	2.1	2.74
3	.81	691.4	8.1	2.1	2.32
4	1.51	689.7	12.8	2.1	3.64
5	1.29	682.6	10.4	2.1	2.99
6	1.13	708.0	21.1	7.6	3.84
7	1.07	710.0	21.6	7.6	3.93
8	0.99	709.0	20.1	7.6	3.56
9	.01	729.0	0.0	$1 \times 10^{-4}$	0.04
10	.03	727.5	.0	$1 \times 10^{-4}$	.07
11	4.12	655.7	56.5	23.0	14.0
12	4.01	660.2	57.0	23.0	14.0
13	0.13	709.1	1.1	0.1	0.31
14	.13	709.1	1.1	.1	.31
15	.78	697.8	9.5	1.1	2.68
16	.79	696.8	9.6	1.1	2.70

TABLE IV  
CALCULATED RESULTS OF SYNTHESIS OF HYDROGEN SULFIDE

Expt.	$\frac{+M_{H_2S}}{\times 10^{-13}}$	$\frac{N_{H_2+S}}{\times 10^{-13}}$	Rn decomp., mc.	$\frac{+M_{H_2S}}{N_{H_2+S}}$	Reaction temp., °C.
1	2.17	1.97	43.5	1.10	200
2	2.02	1.79	43.3	1.13	200
3	2.08	1.93	44.0	1.08	200
4	3.97	4.80	102.3	0.83	200
5	3.36	3.95	84.0	.85	200
6	2.55	2.26	43.5	1.13	234
7	2.39	2.14	44.1	1.12	234
8	2.18	1.91	37.4	1.14	234
9	0.04	1.83	44.6	0.02	37
10	.08	1.50	34.7	.05	37
11	5.12	3.44	44.1	1.49	270
12	5.05	3.42	44.2	1.48	270
13	0.31	1.86	43.9	0.17	138
14	.31	1.78	43.3	.17	138
15	2.07	1.87	46.3	1.11	185
16	2.05	1.88	46.7	1.09	185

surface of the bulb, and since approximately the same excess of sulfur was present in all of the experiments, the area of this patch was always very nearly the same. Consideration of the possibility of loss of ionization through trapping or dissolving of radon and its active deposit in this liquid sulfur showed that under the conditions of the experiments such loss would be entirely negligible.

**Discussion of Results.**—In all but two cases the same amount of radon was decomposed in each experiment, in order to obtain suitable data for

determining the temperature coefficient of the  $M/N$  values. Neglecting Experiments 4 and 5, the average  $M/N$  at each temperature was plotted against the temperature as shown in the lower curve of Fig. 1. The peculiar irregularity of this curve suggests that it is not the temperature which should be plotted against  $M/N$  values, but rather the vapor pressure of sulfur, and by plotting the vapor pressure of sulfur at each temperature against the  $M/N$  values the upper curve in Fig. 1 is obtained. The shape of this curve is readily explained by a consideration of the processes involved in the reaction. At a negligible pressure of sulfur nearly all the ionization produced by the alpha particles must fall on the hydrogen, and

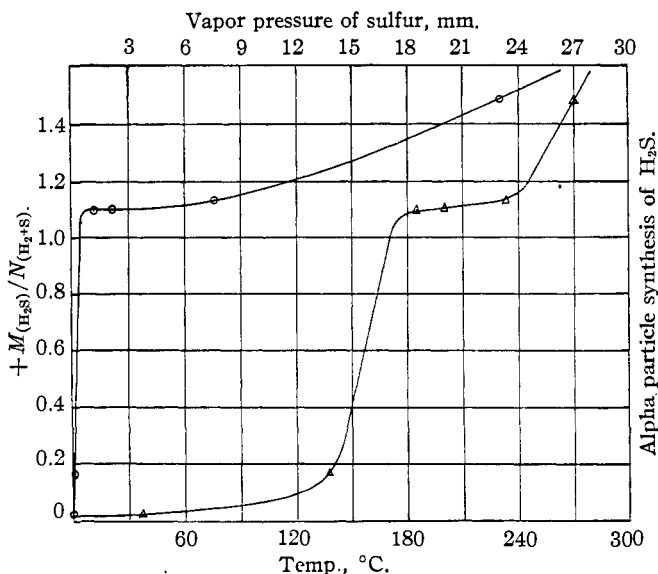


Fig. 1.—○,  $M/N$  as a function of vapor pressure of sulfur; △,  $M/N$  as a function of temperature.

in the absence of an appreciable number of sulfur molecules the chief event that can occur is the recombination of hydrogen ions and electrons, with little resultant chemical reaction. As the vapor pressure of sulfur increases with higher temperature, more sulfur molecules will be available to partake in whatever series of reactions is responsible for the formation of hydrogen sulfide. Over quite a range of pressure we should expect a marked increase in the efficiency of the chemical reaction up to the point where there is a sufficient concentration of sulfur molecules to utilize the ionization energy with maximum efficiency. Also there should at all times be a gradual increase in yield with increase in sulfur vapor pressure since more and more ionization will fall directly on the sulfur in addition to the constant amount falling on the hydrogen. Moreover, as the tem-



perature rises above, say,  $234^\circ$ , the efficiency of the chemical part of the reaction should increase just as it does in the thermal synthesis of hydrogen sulfide, and one would expect a marked increase in  $M/N$  values on this account. That this is exactly the case may be seen from the upper curve of Fig. 1. Under the experimental conditions it appears that a vapor pressure of 1 mm. of sulfur is sufficient to utilize the ionization falling on the hydrogen with maximum efficiency.

In the experiments at  $200^\circ$  three very different amounts of radon were decomposed, and the result of this variation may best be seen by plotting

Synthesis of  $H_2S$  by alpha particles, mc.  
of radon decomposed.  
20 40 60 80 100

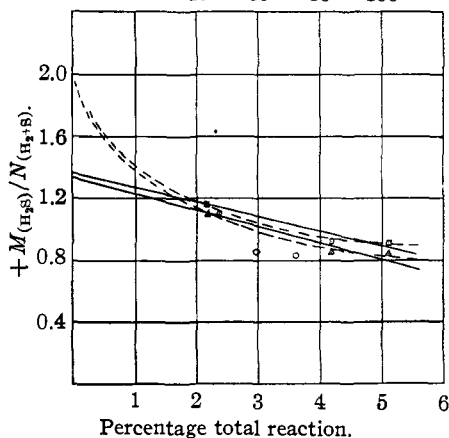


Fig. 2.— $\Delta$ ,  $M/N$  as a function of radon decomposed;  $\square$ , same as  $\Delta$  but with  $M/N$  corrected for back reaction;  $\odot$ ,  $M/N$  as a function of extent of reaction, no curve through these points.

would be preferred. One would immediately suspect that the decrease in  $M/N$  values with increase in the extent of reaction is due to the back reaction produced by ionization falling on the ever-increasing amount of hydrogen sulfide. However, if one calculates the extent of this back reaction, using an average pressure of hydrogen sulfide, it is found to be insufficient to account for all of the observed decrease in the  $M/N$  values. The upper curves of each kind in Fig. 2 are for  $M/N$  values which have been corrected for back reaction due to the ionization of hydrogen sulfide.

A second possible explanation of the decrease in  $M/N$  values with increased extent of reaction would be that the efficiency of the synthesis of hydrogen sulfide is dependent on the intensity of ionization. The chief basis for such an assumption lies in the fact that the vapor pressure of

the  $M/N$  values against the amount of radon decomposed or, since the duration of all these experiments was the same, against the percentage of the total possible hydrogen sulfide which had been formed. The latter method gave irregular results, so that the curves in Fig. 2 were drawn through points obtained by the former method, the three values corresponding to the smallest amount of decomposition having been averaged. Extrapolation to an initial  $M/N$  value is inaccurate, but this value cannot be less than 1.3 nor more than 2.0. The points lie on the straight line to within the limit of accuracy of the experiments; however, if the curve is to be similar to that obtained later in the decomposition of hydrogen sulfide, the broken curve

sulfur is so low at 200°. Thus, by whatever mechanism the reaction proceeds, the presence of a small concentration of sulfur vapor would result in a certain efficiency of synthesis at one intensity of ionization, but this concentration of sulfur might be insufficient to play an equally efficient role if the intensity of ionization were greatly increased, since relatively more hydrogen ions would then recombine with electrons. Consideration of the nature of radioactive transformation shows that since the duration of each experiment was very nearly the same, the intensity of ionization would be proportional to the amount of radon decomposed (and also to the initial amount of radon). The relation between  $M/N$  and ionization intensity might be expressed in the following form

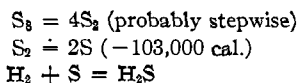
$$M/N = (M/N)_0 - kE$$

where  $(M/N)_0$  is the initial  $M/N$  value for the pure reactants and may be assumed to be independent of ionization intensity, and  $E$  is the amount of radon decomposed. By combining Experiments 3 and 4,  $k$  is found to be equal to 0.0043, and  $(M/N)_0$  becomes 1.27, slightly less than the value obtained earlier by straight line extrapolation in Fig. 2. Assuming the values of these constants, calculated values of  $M/N$  were obtained for Experiments 1, 2 and 5 which differed from the experimental values by less than 4%. On the basis of the above equation the dependence of  $M/N$  upon ionization intensity might be attributed to an abnormal back reaction, whereby the decomposition of hydrogen sulfide would be proportional not only to its own concentration (the normal case) but also to the intensity of ionization. The latter relation might be explained on the basis of exchange ionization, with the ionization flowing onto the hydrogen sulfide molecules from the hydrogen ions. An increase in the intensity of ionization would favor the latter process at the expense of reaction with negative sulfur ions. Other equations may be made to fit the data, however, and other explanations advanced, so that for the present we must be content to state that back reaction, calculated in the normal way, is not sufficient to account for the observed decrease of  $M/N$  values with increased extent of reaction.

It was desirable to know how much of the synthesis of hydrogen sulfide was due to processes occurring in the gas phase and how much was due to reaction on the surface of the excess sulfur. Accordingly, in the two experiments at 37°, sulfur was carefully distilled *in vacuo* onto the surface of each bulb, so that in one case 6 sq. cm. (the area normally covered in the other experiments) and in the other case 74.5 sq. cm. of surface were covered. The ratio of surfaces covered is thus roughly 1:12, in Experiments 9 and 10. By reference to Table IV it is seen that the  $M/N$  values were 0.021 and 0.053, respectively, showing that the extent of sulfur surface does affect the reaction. It is difficult to account for this effect on the assumption that sulfur was removed from the gas phase in the ionized

reaction faster than it could be supplied by evaporation from the wall, since the experiments lasted 211 hours and the total amount of reaction was so small. The alternative is to assume that the reaction occurred partly in the gas phase and partly on the wall, the first rate being constant in the two cases, and that of the second being in proportion to the area of sulfur exposed. Thus, if the gas phase reaction gave an  $M/N$  of 0.018 in each case, the  $M/N$  for the surface reaction would be 0.003 in one case and  $12 \times 0.003$  or 0.036 in the other case, thus giving the observed  $M/N$  values of 0.021 and 0.053. We may thus conclude that the amount of surface reaction occurring in all experiments on the synthesis of hydrogen sulfide at elevated temperatures was negligible in comparison with that occurring in the gas phase.

**Mechanism of the Synthesis of Hydrogen Sulfide.**—In attempting to picture a mechanism for the synthesis of hydrogen sulfide in the presence of radon, one may assume such reaction to be entirely ionic, or to be in the nature of a chemical reaction following the formation or recombination of the ions. In the latter case it would be logical to assume that, at least in part, the same mechanism was effective as is known to govern the purely thermal reaction. From the work of Norrish and Rideal<sup>15</sup> it appears that the thermal reaction  $H_2 + S = H_2S$  begins as a surface reaction and that the homogeneous reaction rate only becomes equal to the former at about  $285^\circ$ . Hence in the present experiments, except at  $270^\circ$ , the thermal synthesis which is occurring will not be directly related to the synthesis by ionization which is occurring only in the vapor phase. The consensus of opinion of those who have studied the thermal synthesis of hydrogen sulfide seems to be that the homogeneous reaction mechanism is probably as follows



It is assumed that the slow reaction whose velocity is measured is the dissociation of  $S_2$ , thus accounting for the agreement between the apparent activation energy of the third step and the dissociation energy of  $S_2$  (103,000/2 or 51,000 cal.). Thus the final equation for the reaction is

$$\frac{+d(H_2S)}{dt} = k(H_2)(S) = k_1k_2(H_2)\sqrt[3]{S_8}$$

One might then assume that the function of ionization in promoting this reaction is to increase the concentration of sulfur atoms and also, by increasing the energy of the reactants, to increase the rate at which they react. But it is not sufficient to limit the reaction to this one mechanism. It is certain that atomic hydrogen is produced under such intense ionization, and it has been shown by Bonhoeffer<sup>16</sup> that sulfur can react with atomic

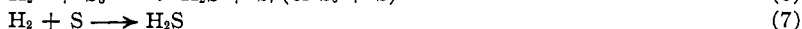
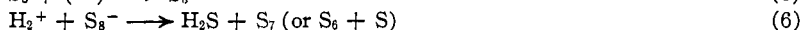
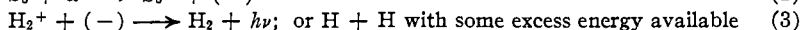
<sup>16</sup> K. F. Bonhoeffer, *Z. physik. Chem.*, 113, 199 (1924).

hydrogen at room temperature to produce hydrogen sulfide. Thus an equation expressing the rate of synthesis by ionization would in its simplest form be of the type

$$\frac{+d(\text{H}_2\text{S})}{dt} = k_1(\text{H}_2) (\text{S}) + k_2(\text{H}) (\text{S}_x)$$

neglecting any purely thermal reaction.

In an attempt to set up a kinetic equation which would express the rate of formation of hydrogen sulfide as a function of the concentration of the more important constituents of the system, including that of radon and of hydrogen and sulfur atoms, a list was made of all the reactions which might occur, and from this group of more than thirty possible reactions the ten or twelve most probable ones were selected. Thus far it has not been possible to secure such an equation in useful form; moreover, the present data are not well suited for insertion into such an equation except in its integrated form, and further data will be needed. We may, however, consider the various mechanisms (the ionic and the atomic, chiefly) proposed as they would be related to changes in the experimental conditions. This may best be done by considering the effect produced on the efficiency of the reaction ( $M/N$  value) by altering the conditions of the experiment. The chief reactions to be considered are the following



Reaction 6 represents the synthesis of hydrogen sulfide by a purely ionic mechanism, in which clustering might or might not occur, while reactions (7) and (8) represent synthesis due to chemical reactions which depend on ionization for their supply of atomic reactants.

**Effect of Increase of Temperature.**—The primary effect of increasing the temperature is to increase the vapor pressure of sulfur, hence in general it is the latter which must be considered. Increase in temperature should have little effect on the efficiency of the reaction if it proceeds by a strictly ionic mechanism, and below 234° it should have no marked effect on any of the steps involved in a *chemical* reaction which follows neutralization of the ions. The fact that a pronounced increase in  $M/N$  values does appear above 234° would indicate that a simple ionic or clustering mechanism either is not involved at lower temperatures, or that above this temperature it is augmented by secondary chemical reactions which are temperature sensitive.

**Effect of Increase of Sulfur Vapor Pressure.**—Increase in the vapor pressure of sulfur will, of course, cause an increase in the ionization falling on the sulfur, this increase being duly taken into account in calculating  $N$ . In addition, an increase in the concentration of sulfur would make more efficient the trapping of electrons by sulfur, thus preventing their direct recombination with hydrogen ions. This fact would certainly increase the efficiency of formation of hydrogen sulfide according to a clustering or ionic mechanism. According to an atomic (chemical) mechanism the only adverse effect of increasing the concentration of sulfur would be a decrease in the number of hydrogen atoms formed; however, the number of sulfur atoms formed would increase approximately as the square of the sulfur concentration, and since the reaction between hydrogen molecules and sulfur atoms is one of the chief chemical steps to be considered there would still be a marked increase in the efficiency of the reaction with increase in concentration of sulfur. The assumption is, of course, made that the vapor pressure of sulfur is so small that any of the reactions considered would be sensitive to small actual, but large relative changes of this pressure.

**Effect of Intensity of Ionization.**—The relation of the efficiency of hydrogen sulfide formation to the intensity of ionization has already been discussed, and the decrease in the value of  $M/N$  with increase in ionization intensity was attributed to an unfavorable shift in the competition between hydrogen ions and sulfur molecules for the electrons, assuming an ionic mechanism. Such a shift in the competition would tend to increase the number of hydrogen atoms being formed, but with only a small constant number of sulfur molecules available, a larger fraction of these hydrogen atoms would have to recombine without producing chemical reaction. Further consideration shows that any of the more probable mechanisms must suffer a decrease in efficiency as long as the concentration of sulfur remains critically small. The lack of suitable information concerning collision diameters, electron speeds, efficiency of ion recombination, etc., precludes any attempt to verify the above suggestions by calculating concentration changes which would be produced if the intensity of ionization were altered.

In conclusion, it may be said that while there is no basis for insisting upon any one mechanism for the synthesis of hydrogen sulfide in the presence of radon, a consideration of the complex situation existing in such a system indicates that both an ionic (clustering) mechanism and a chemical (atomic) mechanism may and probably do occur simultaneously. Since the  $M/N$  value showed a marked increase at  $270^\circ$  over that at  $234^\circ$ , one might conclude that as the temperature is increased that reaction which is similar to the homogeneous thermal reaction becomes more important. Certainly one cannot assume that the size of the ion cluster increases with temperature; however, it is also possible that the added

thermal energy enables more of the cluster to react chemically at the instant of neutralization.

### The Decomposition of Hydrogen Sulfide

Two experiments were conducted at 37°, decomposing in each case about 75 millicuries of radon, in order to obtain data to supplement the results reported by Wourtzcel. Two experiments each were carried out at 200, 234 and 270° and at each temperature the attempt was made to decompose about 20 mc. of radon in one case and about 75 mc. in the other, thus providing data for a study of the temperature coefficient and of the relation of  $M/N$  to the extent of reaction.

The calculations were carried out in the same manner as were those on the synthesis of hydrogen sulfide. The experimental data needed for the calculation of the  $M/N$  values are given in Table V. It should be recalled that in all these experiments correction had to be made for the non-equilibrium decomposition of radon during the first four hours and eighteen minutes. The  $M/N$  values obtained in these experiments are given in Table VI. Interpretation of these results must be postponed until we have considered the results obtained by Wourtzcel.

TABLE V  
EXPERIMENTAL DATA ON DECOMPOSITION OF HYDROGEN SULFIDE

Expt.	Bulb vol., cc.	Init. $P_{H_2S}$ , mm.	Init. temp., °C.	Init. radon, mc.	React. temp., °C.	Expt. time, hrs.	$N/10$ iodine, cc.
1	41.49	705.8	28.5	83.2	37	257.50	21.08
2	51.82	705.8	28.5	85.9	37	258.00	27.78
3	34.38	737.9	32.0	92.0	200	231.25	17.65
4	31.40	733.9	32.0	54.8	200	69.75	20.49
5	48.71	729.7	29.0	50.0	234	69.30	33.80
6	48.82	729.7	29.0	75.0	234	240.31	29.38
7	48.73	727.3	24.0	95.3	270	192.67	29.08
8	52.16	729.3	24.0	40.0	270	103.50	36.70

TABLE VI  
CALCULATED RESULTS ON DECOMPOSITION OF HYDROGEN SULFIDE

Expt.	$H_2S$ decomp., cc.	Av. $P_{H_2S}$ , mm.	Av. $P_{H_2}$ , mm.	$H_2S$ decomp., %	Mc. Rn decomp.	$M_{H_2S} \times 10^{-19}$	$N_{H_2S} \times 10^{-19}$	$-M_{H_2S}/N_{H_2S}$
1	11.17	585.9	120.9	32.0	71.1	30.20	11.46	2.63
2	12.35	598.9	106.9	28.4	73.6	33.41	13.50	2.48
3	10.00	607.0	130.9	33.5	75.6	27.06	12.05	2.25
4	4.09	670.2	63.7	15.1	22.3	11.09	4.10	2.70
5	4.40	684.8	44.9	10.4	20.2	11.91	4.88	2.44
6	9.46	641.7	88.0	22.4	62.6	25.59	13.39	1.91
7	10.29	633.6	93.7	24.0	72.7	27.76	17.44	1.59
8	4.89	683.6	45.7	10.6	21.6	13.23	6.09	2.17

**Experiments of Wourtzcel.**—Wourtzcel<sup>4</sup> studied the decomposition of hydrogen sulfide when mixed with radon in small bulbs of about 40 cc.

capacity (4.3 cm. diameter). Using a rather elaborate apparatus, he followed the course of the reaction by freezing out the hydrogen sulfide and radon from time to time and measuring the pressure of the residual hydrogen, estimating his error in such measurements at about 1%. At the end of each interval the residual hydrogen was pumped off, so that each experiment was begun with pure hydrogen sulfide and, since the extent of reaction was small, the gas was at all times practically pure. In this respect his experiments differed from the present ones, where significant pressures of hydrogen were produced. Wourtzal used smaller initial quantities of radon and the duration of each experiment was much shorter than in the present work. One would thus expect Wourtzal's  $M/N$  values to be higher than those obtained in the present experiments, and the former may be regarded as approximately the upper limit for the  $M/N$  ratio. Wourtzal expressed all his results in terms of the number of molecules of hydrogen sulfide decomposed per ion pair when the gas was at "infinite pressure," *i. e.*, at a pressure sufficiently great to utilize the complete path of an (average) alpha particle. His actual pressures varied from 1.5 to 12 atmospheres, being about 2 atmospheres in most of his experiments. Since a number of the radioactive constants and ionization factors have been revised since his experiments were performed, his results have been recalculated by the same method as that employed in obtaining  $M/N$  values in the present experiments. The first five columns of Table VII are taken directly from Wourtzal's data, and the values in the last three columns are those obtained in the process of recalculation. The gas was assumed to be pure hydrogen sulfide at all times, the corresponding values of  $k$  and  $s$  being used. The factor necessary to account for the recoil atom effect was found to be 1.02 at a pressure of 1 atmosphere in bulbs of the size employed by Wourtzal. At 1.5 atmospheres this factor was 1.015; at 2 atmospheres, 1.01; at 4 atmospheres, 1.005; at higher pressures the recoil atom effect was neglected. In Table VII  $T$  is the time in hours,  $p$  is the average pressure of an experiment in atmospheres,  $v$  is cc. of hydrogen sulfide decomposed (N. T. P.). The sets of Experiments I and II were run simultaneously, a single charge of radon being divided between the two bulbs; one bulb was kept at room temperature while the temperature of the other was occasionally elevated in order to obtain a temperature coefficient for the reaction.

It should be noted that Wourtzal calculated his results in terms of a reaction constant,  $KQ_0/\lambda$ , and then determined his value of  $M/N$  from the average value of this constant in each series. It thus appeared that the decomposition of hydrogen sulfide by alpha particle ionization was less efficient at the higher temperatures. However, when each separate experiment is used to obtain a value of  $M/N$ , as in the present recalculation, it is found that the very values needed to establish this temperature coefficient

TABLE VII  
 RECALCULATION OF WOURTZEL'S RESULTS  
 Expt. I: vol. bulb, 43.49 cc.; initial radon, 58.23 mc.

No.	$t$ , °C.	$T$	$p$	$v$	H <sub>2</sub> S decomp., %	Mc. Rn. decomp.	$-M_{\text{H}_2\text{S}}/N_{\text{H}_2\text{S}}$
1	18	15.00	2.055	4.200	4.69	6.23	3.59
2	18	24.15	1.940	5.315	6.30	8.67	3.40
3	18	24.45	1.828	4.213	5.30	7.30	3.36
4	18	16.55	1.733	3.286	4.35	4.03	(4.83)
5	18	104.15	1.593	8.296	11.92	17.31	3.02
6	18	39.00	1.474	1.650	2.57	3.69	3.01
7	18	79.35	1.430	2.013	3.23	4.86	(2.89)

Expt. II: vol. bulb, 41.00 cc.; initial radon, 54.77 mc.

1	18	15.45	2.172	4.000	4.50	6.03	3.36
2	18	24.45	2.054	5.195	6.20	8.21	3.36
3	18	24.55	1.923	4.176	5.30	6.85	3.38
4	220	16.45	1.819	2.273	3.0	3.93	(3.36)
5	18	104.15	1.706	8.200	11.72	16.19	3.09
6	220	59.15	1.590	1.218	1.86	4.88	(1.60)
7	95	79.85	1.556	1.730	2.70	3.92	(2.91)

Expt. III: vol. bulb, 41.00 cc.; initial radon, 56.4 mc.

1	18	24.35	1.928	5.300	6.72	9.47	3.11
2	18	25.60	1.816	4.362	5.86	8.25	3.08
3	18	22.80	4.009	4.634	2.82	6.12	3.11
4	18	25.60	3.900	4.358	2.73	5.72	3.15
5	18	22.90	6.468	3.676	1.38	4.28	3.23
6	18	24.00	6.356	3.460	1.33	3.74	3.49
7	18	18.30	9.107	2.774	0.74	2.94	3.41
8	18	22.50	11.92	1.552	.32	2.04	2.69
9	18	54.80	11.88	3.307	.68	4.67	2.50

are not in good agreement with others at the same temperature. These values are the ones marked in parentheses in Table VII. One or two general conclusions may be drawn from his results before proceeding to a comparison with the results obtained in the present experiments. In the set of Experiments I, Table VII, there seems to be a trend toward lower  $M/N$  values as the reaction proceeds. The set of Experiments III is intended to show the effect of change of pressure on the  $M/N$  values; there seems to be a slight increase in  $M/N$  as the pressure increases (excepting the last two values), but equally high  $M/N$  values were obtained in Experiments I and II at only 2 atmospheres pressure, so that within the limits of error of the experiments it may be said that increase of pressure (at high pressure) has no effect on the efficiency of the reaction.

One additional point remains to be considered before proceeding to detailed analysis of the results. The temperatures employed by Wourtzell were 18, 95 and 220°, while in the present experiments the temperatures



were 37, 200, 234 and 270°. The lower temperatures may be considered equivalent, since there are no thermal effects involved in the system at room temperature. The remaining temperatures in the present work were, of course, chosen to correspond to those used in the synthesis of hydrogen sulfide. However, since Wourtzell's  $M/N$  values at the higher temperatures seem to be less trustworthy, and since the present results are in logical agreement with one another, the choice of different temperatures is not a serious matter.

### Discussion of Combined Results

**Effect of Extent of Decomposition on  $M/N$  Values.**—Comparable  $M/N$  values may be obtained only from systems having approximately the same composition, and one must then express  $M/N$  values as a function of the amount of radon decomposed (since all experiments began with pure hydrogen sulfide), or if it is necessary to consider the thermal reaction also, as a function of the composition of the system. In Table VIII Wourtzell's most consistent  $M/N$  values at 18°, together with the two values obtained in the present experiments at 37°, are arranged in the order of increasing amount of radon decomposed and also of increasing per cent. decomposition of hydrogen sulfide. These values were averaged as indicated in the table, and the average values when plotted gave the smooth curve numbered I in Figs. 3 and 4. It is at once evident that the initial  $M/N$  value should be between 3.75 and 4.0, and that as the composition of the gas changes the *synthesis* of hydrogen sulfide becomes more and more important, resulting in a progressive lowering of the effective  $M/N$  for decomposition.

TABLE VIII  
 $M_{H_2S}/N_{H_2S}$  AS FUNCTION OF EXTENT OF REACTION

Wourtzell, experiments at 18°							
Expt.	Press., atm.	Radon decomp.	Av. Rn decomp.	H <sub>2</sub> S decomp., %	Av. % decomp.	$M_{H_2S}/N_{H_2S}$	Av. $M_{H_2S}/N_{H_2S}$
II-1	2.172	6.03	6.13	4.50	4.60	3.36	3.47
I-1	2.055	6.23		4.69		3.59	
I-3	1.828	7.30	7.07	5.30	5.30	3.36	3.37
II-3	1.923	6.85		5.30		3.38	
II-2	2.054	8.21	8.78	6.20	6.40	3.36	3.29
I-2	1.940	8.67		6.30		3.40	
III-1	1.928	9.47		6.72		3.11	
II-5	1.706	16.19	16.75	11.72	11.82	3.09	3.06
I-5	1.593	17.31		11.92		3.02	
Lind and Truesdale, experiments at 37°, by titration							
1	0.78	71.1	72.3	32.0	30.2	2.64	2.55
2	.80	73.6		28.4		2.48	

TABLE IX  
TEMPERATURE COEFFICIENT OF HYDROGEN SULFIDE DECOMPOSITION

°C.	Actual values $M_{\text{H}_2\text{S}}/N_{\text{H}_2\text{S}}$ from graph, $t$ , °C.			Ratio $M_{\text{H}_2\text{S}}/N_{\text{H}_2\text{S}}$ at $t$ , °C. to $M_{\text{H}_2\text{S}}/N_{\text{H}_2\text{S}}$ at room temp.		
	5% $\text{H}_2\text{S}$ decomp.	10% $\text{H}_2\text{S}$ decomp.	25% $\text{H}_2\text{S}$ decomp.	5% $\text{H}_2\text{S}$ decomp.	10% $\text{H}_2\text{S}$ decomp.	25% $\text{H}_2\text{S}$ decomp.
37	3.40	3.12	2.66	1.0	1.0	1.0
200	3.22	2.91	2.42	0.95	0.93	0.91
234	2.85	2.47	1.83	.84	.79	.68
270	2.58	2.20	1.56	.76	.71	.59

**Effect of Temperature Increase on  $M/N$  Values.**—The same procedure was then followed with the results obtained in the present experiments at 200, 234 and 270° (one of Wouurtzel's values at 220° seemed to coincide well with the newer values at 200°), the Curves II, III and IV being obtained at these respective temperatures, in Figs. 3 and 4. Although

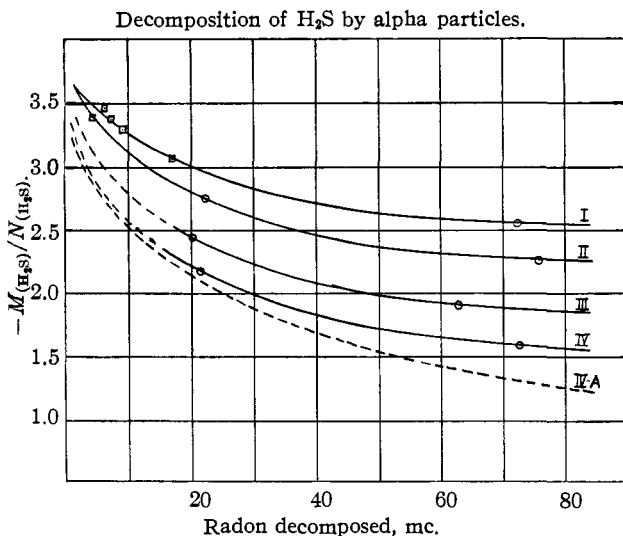


Fig. 3.— $M/N$  as a function of radon decomposed:  $\square$ , recalculated values of Wouurtzel;  $\circ$ , present values.

there are hardly sufficient points on each curve to make it accurate, one may safely be guided by analogy to the curve obtained at room temperature. It seems logical to suppose that the initial  $M/N$  value is about the same at all these temperatures. By plotting the results in this way the effect of increasing the temperature becomes evident at once, as interpreted by reference to the results already obtained in the synthesis of hydrogen sulfide. At 200° the thermal synthesis of hydrogen sulfide is just barely measurable, and in extended experiments of several days' duration would cut down the net decomposition of hydrogen sulfide slightly. At 234° this thermal synthesis would be more than twice as great as at

200°, while at 270° we must consider that synthesis of hydrogen sulfide is occurring thermally both on the wall and in the gas phase. The fact that Curve IV does not then lie lower down than is the case may be explained both by the fact that this experiment was of shorter duration than the others in which comparable amounts of reaction occurred (1,2,3,6), and by an additional factor which will be referred to in the next section. The broken Curve IV-A indicates what one might expect if the duration of the experiment had been of the usual length.

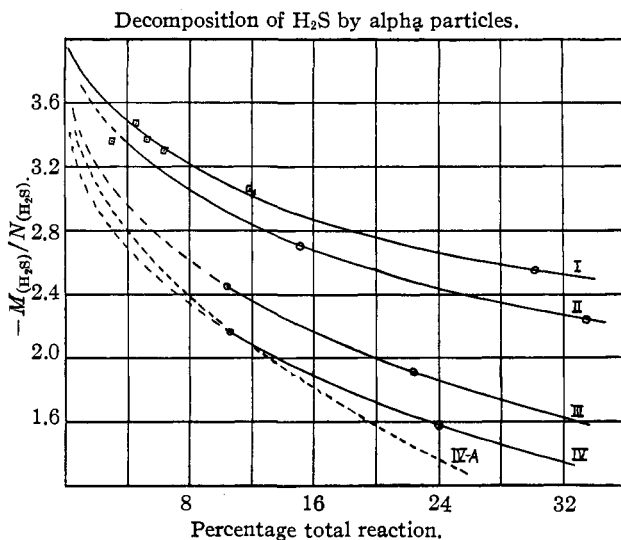


Fig. 4.— $M/N$  as a function of extent of reaction: □, recalculated values of Wourtzell; ○, present values.

We may now obtain a temperature coefficient for the  $M/N$  values. Wourtzell originally reported that the value of the  $M/N$  ratio was 0.90 at 95° and 0.70 at 220° of the value obtained at 18° (2.5 by his method of calculation). Accurate values of the temperature coefficient may be obtained only by comparing  $M/N$  values from gas mixtures of the same composition, and this was done by dividing the  $M/N$  value at a given percentage reaction on each of Curves II, III and IV, Fig. 4, by the  $M/N$  value at the same percentage reaction, from Curve I. These comparisons are indicated in Table IX at 5% (approximately in the range of Wourtzell's experiments) and also at 10 and 25% decomposition. It is seen that these ratios are of the same order of magnitude as those reported by Wourtzell.

**Correction of  $M/N$  Values for Back Reaction.**—If synthesis of hydrogen sulfide is the sole cause of the decrease in  $M/N$  with extent of reaction, then by calculating the amount of this correction we should be able to

obtain a true  $M/N$  value which is independent of both temperature and extent of reaction. Such calculations were made for Experiment 1 at  $37^\circ$ , Experiment 3 at  $200^\circ$  and Experiment 7 at  $270^\circ$ , in the following manner. At  $37^\circ$  there is no thermal synthesis and the only correction is for the synthesis due to ionization of hydrogen and sulfur. Using an average pressure of hydrogen corresponding to that calculated for hydrogen sulfide, and assuming (as an extreme condition) that there is no exchange ionization,  $N$ , the number of ion pairs formed on hydrogen was obtained. Then taking  $M/N$  for synthesis as 0.053 (see Expt. 10, Table IV) since the surface of the bulb was covered with a deposit of sulfur formed by the decomposition of hydrogen sulfide ( $+M_{\text{H}_2\text{S}}$ ), the number of molecules of hydrogen sulfide synthesized, was calculated. This number, added to ( $-M_{\text{H}_2\text{S}}$ ) the number of molecules of hydrogen sulfide decomposed from experiment, gave the number of molecules actually decomposed in the course of the experiment. Similar calculations were made in Experiments 3 and 7, using a theoretical  $M/N$  for synthesis of 2.0 and 3.0, respectively, again to establish the most favorable case. In addition it was necessary to obtain the number of molecules of hydrogen sulfide obtained thermally, ( $+M_t$ ), and the sum of ( $+M_{\text{H}_2\text{S}}$ ), ( $-M_{\text{H}_2\text{S}}$ ) and ( $+M_t$ ) gave the number of molecules of hydrogen sulfide which would have been found to be decomposed had there been no back reaction. For each case this total was divided by the respective  $N$  as originally calculated, giving a new value of  $M/N$  which should have approached the (arbitrary) initial  $M/N$  of 3.75. Errors due to such calculations are chiefly two: (1) if  $M$  is assumed to increase then  $N$  should decrease very slightly due to the change in composition, and (2) the thermal synthesis at  $270^\circ$  could be estimated only approximately.

The results thus obtained at first seemed surprising, but were readily explained. At  $37^\circ$  the back reaction as calculated was about  $1/125$  as large as it should be to account for the drop in  $M/N$  from 3.75 to 2.6. At  $200^\circ$  the calculated back reaction was about one-fourth as great as it should be, while at  $270^\circ$  the calculated back reaction was approximately of the desired magnitude. Thus if we are to maintain the original explanation for low  $M/N$  values, it must be admitted that at  $37^\circ$  the *synthesis* of hydrogen sulfide by ionization in a bulb in which hydrogen sulfide is being decomposed is 125 times as efficient as in a bulb in which synthesis *only* is occurring, that at  $200^\circ$  such synthesis is four times as efficient, and that at  $270^\circ$  the efficiency of the synthesis of hydrogen sulfide is the same whether or not there is a simultaneous decomposition of this gas. The explanation of such a peculiar condition is the following. At  $37^\circ$  sulfur has such a low vapor pressure that it would normally be found almost entirely on the wall of the bulb. In these experiments it can be formed by alpha particle decomposition of hydrogen sulfide faster than it can reach the walls and

come into thermal equilibrium. Hence there will be an excess of sulfur atoms, molecules and larger aggregates in the vapor phase, and this excess is subject to reaction with hydrogen ions and in fact will also receive its share of ionization by alpha particles, thus promoting the synthesis of hydrogen sulfide at a rate very much faster than would be the case if thermal equilibrium were maintained. At  $200^{\circ}$  the vapor pressure of sulfur is at least 1000-fold greater, hence such an effect would be less marked, while at  $270^{\circ}$  the amount of sulfur formed per second would be a negligible fraction of the equilibrium concentration and at this temperature thermal equilibrium would be established much more rapidly.

In support of this argument it may be emphasized that during the decomposition of hydrogen sulfide at  $37^{\circ}$  a "fog" of sulfur particles was always visible in the bulb, sulfur being slowly deposited on the lower surface of the bulb. In addition there must also have been present many smaller, invisible aggregates. A simple calculation shows that the concentration of sulfur present in thermal equilibrium at  $37$ ,  $200$  and  $270^{\circ}$  is  $3.14 \times 10^{12}$ ,  $6.6 \times 10^{16}$  and  $1.5 \times 10^{18}$  molecules per cc. Using the data of Experiment 2, assuming 75 millicuries of radon to be undergoing decomposition and assuming an  $M/N$  value of 4, it is found that there would be produced about  $2.6 \times 10^{13}$  atoms of sulfur *per second* per cc., or assuming eventual formation of  $S_8$  there would be formed  $3.25 \times 10^{12}$  molecules of sulfur per second per cc. Thus at  $37^{\circ}$  there were obtained as many molecules of sulfur per second per cc. as there should be in thermal equilibrium with the sulfur on the wall. Since sulfur continues to be formed at this rate it is easy to see that the concentration in the gas phase soon becomes enormously greater than that required by the condition of thermal equilibrium.

**$M/N$  as a Function of Intensity of Ionization.**—The data on the decomposition of hydrogen sulfide are not suited to a comparison of  $M/N$  values as related to intensity of ionization. The experiments were not planned to test this point, since in a one-component system at a pressure of one atmosphere it seems reasonable to believe that, with any ordinary intensity of ionization, there should always be a sufficient concentration of reactant molecules to partake with maximum efficiency in whatever reactions follow the initial act of ionization.

**Mechanism of the Decomposition of Hydrogen Sulfide.**—It has been shown that as the decomposition of hydrogen sulfide proceeds under the influence of alpha particle ionization, instead of maintaining a two-phase system in approximate thermal equilibrium, we have present a large excess of sulfur vapor and a fairly high concentration of suspended sulfur particles. This condition speeds up both the thermal and ionized back reaction so that, at least below  $270^{\circ}$ , such back reaction cannot be correctly estimated. Moreover, it is not known what role this excess sulfur may

play in influencing the main reaction. It therefore seems doubtful whether one could hope to set up a satisfactory kinetic equation from which information could be obtained concerning the mechanism of the decomposition reaction at temperatures below  $270^{\circ}$ , and at higher temperatures the thermal synthesis of hydrogen sulfide would be so great as to interfere seriously.

The three pieces of evidence upon which a reasonable guess as to the mechanism of the decomposition reaction depends are (1) that the initial  $M/N$  value is nearly 4.0, (2) that this *initial*  $M/N$  is probably independent of temperature and (3) that the value of  $M/N$  is independent of pressure from 0.8 to 12 atmospheres. If we assume that the decomposition of hydrogen sulfide is the result of a reaction between positive ions and electrons, or between positive and negative molecular ions either single or clustered, we should expect the second and third of the above conditions to hold. In order to account for the  $M/N$  value of 4 it would probably be sufficient to assume that ion clustering occurred, for otherwise it would be necessary to assume what amounts to a chain mechanism, which should be dependent on temperature and pressure.

### Summary

**The Synthesis of Hydrogen Sulfide.**—1. The synthesis of hydrogen sulfide by alpha particle ionization has been studied at temperatures from  $37$  to  $270^{\circ}$ , the value of  $(+M_{\text{H}_2\text{S}}/N_{\text{H}_2} + s)$  for this reaction varying from 0.021 to 1.48 in this interval, the chief function of temperature increase being to increase the vapor pressure of sulfur to a point where efficient synthesis can proceed. Above  $234^{\circ}$  there is a pronounced temperature coefficient for the  $M/N$  values due to the increased efficiency of the chemical steps involved in the synthesis.

2. Decrease of  $M/N$  values with increased extent of reaction cannot be accounted for entirely on the basis of normal back reaction, but is related to the intensity of ionization, perhaps through the medium of exchange ionization.

3. The mechanism of the formation of hydrogen sulfide in an ionized system is complex, and seems to be due to a simultaneous reaction between positive hydrogen ions and negative sulfur ions, between sulfur atoms and hydrogen molecules and between hydrogen atoms and sulfur molecules.

**The Decomposition of Hydrogen Sulfide.**—1. The decomposition of hydrogen sulfide has been studied at four temperatures from  $37$  to  $270^{\circ}$ , the maximum value of  $(-M_{\text{H}_2\text{S}}/N_{\text{H}_2\text{S}})$  being nearly 4.

2. The occurrence of a temperature coefficient less than unity for this reaction, first reported by Wourtzell, has been verified. The true  $M/N$  value for this reaction is probably independent of temperature; but a

thermal synthesis together with an abnormally large synthesis of hydrogen sulfide by ionization, gives rise to an effective  $M/N$  which decreases with increasing temperature.

3. The ion cluster mechanism accounts satisfactorily for the observed characteristics of the decomposition reaction (neglecting back reaction), though it is not necessary to insist upon this as the only possible mechanism.

4. The fact that the decomposition of hydrogen sulfide by alpha particle ionization is more efficient than its synthesis is probably due to the fact that the vapor pressure of sulfur is so small at the temperatures employed, thus limiting the efficiency with which the ionization energy may be utilized in the synthesis of hydrogen sulfide.

MINNEAPOLIS, MINNESOTA

---

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

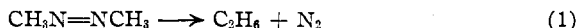
## THE CATALYTIC DECOMPOSITION OF AZOMETHANE, SYM.-DIMETHYLHYDRAZINE, AND MONOMETHYLAMINE: THE THERMAL DECOMPOSITION OF SYM.-DIMETHYLHYDRAZINE

By P. H. EMMETT AND R. W. HARKNESS

RECEIVED SEPTEMBER 19, 1931

PUBLISHED FEBRUARY 5, 1932

A study of the catalytic decomposition of azomethane was undertaken for the two-fold purpose of learning more of the influence of catalysts upon various C-N linkages and of ascertaining whether the first order homogeneous gaseous reaction could be accelerated by the presence of proper catalysts. It soon became apparent, however, that the final products of the catalytic reaction were principally ammonia, hydrogen and carbon, rather than nitrogen and ethane, which Ramsperger<sup>1</sup> has shown are produced by the thermal homogeneous decomposition



Nevertheless, the catalytic studies were continued with a view to elucidating the steps by which compounds such as azomethane decompose over catalytic materials. In the course of the azomethane studies it became desirable to investigate also the catalytic decomposition of dimethylhydrazine and monomethylamine, and the thermal decomposition of dimethylhydrazine.

### Experimental

The catalytic and thermal decompositions were carried out in a static system. The reaction vessel was kept at any constant temperature between 220 and 350° by a surrounding mercury vapor bath, the pressure of

<sup>1</sup> Ramsperger, THIS JOURNAL, 49, 912, 1495 (1927); 51, 2134 (1929).