

THE MOBILITIES OF GASEOUS IONS IN H_2S - H_2 MIXTURES

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Introduction.—In recent articles one of the writers (L. B. L.) cites an explanation, suggested by Dr. Edward Condon,¹ of the observation that the negative ion mobility is less than the positive ion mobility in vapors like HCl and H_2O . The latter suggests that it is due to the presence in these molecules of the proton near the surface of the molecule which causes a dipole unsymmetrically placed relative to the center of the molecule. On this basis H_2S should show much the same behavior as H_2O , though perhaps in a less degree, since its electronegative component is relatively larger. In a preliminary notice in 1926 one of the writers and Mr. Cravath² reported on the results of some preliminary measurements of the positive and negative mobilities in H_2O and H_2S . At the time the measurements were undertaken certain facts concerning the relative action of impurities on positive and negative ions were not known, and a lowering of the positive ion mobility relative to the negative ion mobility was ascribed to contact potentials. The preliminary results obtained in which, as present results show, the H_2S was not especially pure, were over-corrected for this effect. In order to make certain of the effects observed the preliminary investigation was extended with a new design of ionization chamber³ and under much more carefully controlled conditions by the present writers. It is the purpose of this paper to detail the results of this investigation.

A complete description of the new ionization chamber is to be published elsewhere³ inasmuch as the past experiences of one of the writers have finally led to a fairly successful form of chamber whose construction merits a more complete description than there is space for here. In other respects the methods of measurement are identical with those used before, even the same gauze and plate systems being used as were utilized in other more recent work.⁴

Preparation of H_2S .—The H_2S was prepared as follows. A pound of Baker's analyzed $FeSO_4 \cdot 7H_2O$ was dissolved in distilled water and had H_2S from the generators of the Chemistry Department run into it, the solution being neutralized with NH_4OH as the precipitation proceeded. In one case this H_2S came from a Kipps generator with commercial FeS , and in a later sample it came from a commercial tank of liquid H_2S which has been used as the new general laboratory supply of the Chemistry Department. This precipitate was dried on the filter pump and washed with distilled water. It was then placed in a 2-liter Pyrex flask fastened

to the apparatus. Onto this paste was dropped a solution of concentrated c. p. H_2SO_4 which had been diluted with an equal volume of water. The generator was exhausted to the vapor pressure of water before the H_2SO_4 reached it. This moist gas passed over a water-cooled reflux condenser. Then it went through a trap cooled to -80°C . with frozen alcohol. Next it passed through a tube 1 meter long, 3 cm. diameter and, previously exhausted, filled with CaCl_2 , and then through another filled half with CaCl_2 and half with P_2O_5 . After this it passed through another trap cooled to -80°C . and into a trap cooled in liquid air. Here it condensed as a snow white solid. The mercury of the manometer, however, slowly formed a dark deposit of HgS on the walls. When enough had been condensed out the generator was shut off, any excess of the gas being removed from it by a water aspirator pump, which kept the air of the room less polluted than might have been expected. The small residue of gas in the trap was pumped off at the temperature of liquid air to better than an X-ray vacuum. It was then run into the chamber and studied, either after the pressure had been brought up to 760 mm. with H_2 gas, or alone at the pressure existing.

The Values of the Mobility.—The results may be divided into two groups, the first being the absolute values of the mobilities and certain peculiarities of H_2S , the other being the study of H_2S - H_2 mixtures.

Owing to difficulty in obtaining sufficiently strong ionization a gauze of perforated sheet brass of large mesh has been used in the past. The size of the holes or meshes was such that a considerable interpenetration of fields occurred. In detailing the results obtained the values actually observed will first be given. Then the correction of the values obtained will be given as computed from a calibration of this apparatus with air at various voltages for the crossing of the ions. Of these corrected values two sets will be given, those on the previously accepted standard of a mobility of 1.8 cm./sec. per volt/cm. for negative ions in air, and the other the probably more correct new value of one of the writers,¹¹ to wit, 2.18 cm./sec. per volt/cm. The table below gives the actual results taken under different conditions, together with the number of measurements made.

OBSERVED AVERAGE VALUES OF MOBILITIES IN H_2S IN CM./SEC. PER VOLT/CM.

CONDITIONS UNDER WHICH TAKEN	- IONS	+ IONS	POTENTIAL	NUMBER OF MEASUREMENTS
Old measurements, 1926, old ion chamber	0.638	0.57	37	3
New results at 750 mm.	0.612	0.629	21	2 fillings
				8
Low pressures from 50-260 mm.	0.610	0.589	22	6 fillings
				9
Low pressures 23-90 mm.	0.562	0.555	33	8 fillings
				5
				5 fillings

The previous measurements in 1926 were corrected for contact potentials supposed to be present from air control measurements and were taken as 0.55 for the negative ions and 0.664 for the positive ions. The correction was not warranted as the results were due to another cause, namely, the presence of impurities. The values obtained are, therefore, of little importance.

The new values at atmospheric pressure were as follows:

- IONS	+ IONS
0.588	0.613
0.626	0.626
0.601	0.616
0.626	0.647
0.623	0.688
0.594	0.604
0.550	0.614
0.637	0.630
Av. 0.612	Av. 0.629

These reduced to the absolute scale of a mobility of 2.18 cm./sec. per volt/cm. for negative ions in air with the values 0.688 for the negative and 0.708 for the positive ion. On the previously accepted scale they are 0.572 for the negative and 0.588 for the positive ions. The low-pressure measurements corrected to the new scale are 0.686 and 0.700 for the negative ions and 0.664 and 0.692 for the positive ions.

One observes that the positive ions have a *very slightly higher value* at the higher pressures than the negative ions, the values being on the new scale with all the accuracy that the method warrants 0.69 and 0.71 cm./sec. per volt/cm. This difference is, we believe, real from the trend of the curves, the positive mobility curves universally lying above the negative curves, though the mobilities taken from the extrapolated intercepts in one or two cases indicated the reverse. This difference might be due to traces of the contaminating impurity HCl suspected present. This result, if not due to impurities, seems to support Condon's view, but it is not at all decisive. The old values are to be considered as distinctly less reliable in view of conditions of still greater questionable purity which entered in.

It is seen that at low pressures the values of the mobility constant of the negative ions reduced to the accepted standard are about constant and the reduction to N. T. P. follows the inverse pressure law, the values 0.688, 0.686 and 0.700 lying within the accuracy of the measurements at lower pressures. For the positive ions the low pressure values 0.664 and 0.692 appear to be somewhat less than those at 760 mm. which are 0.708. It appears as if the pressure law did not hold accurately, though the difference is near the limits of accuracy in this case. The reason for this is obscure and if correct is one of the first cases on record. It is possible

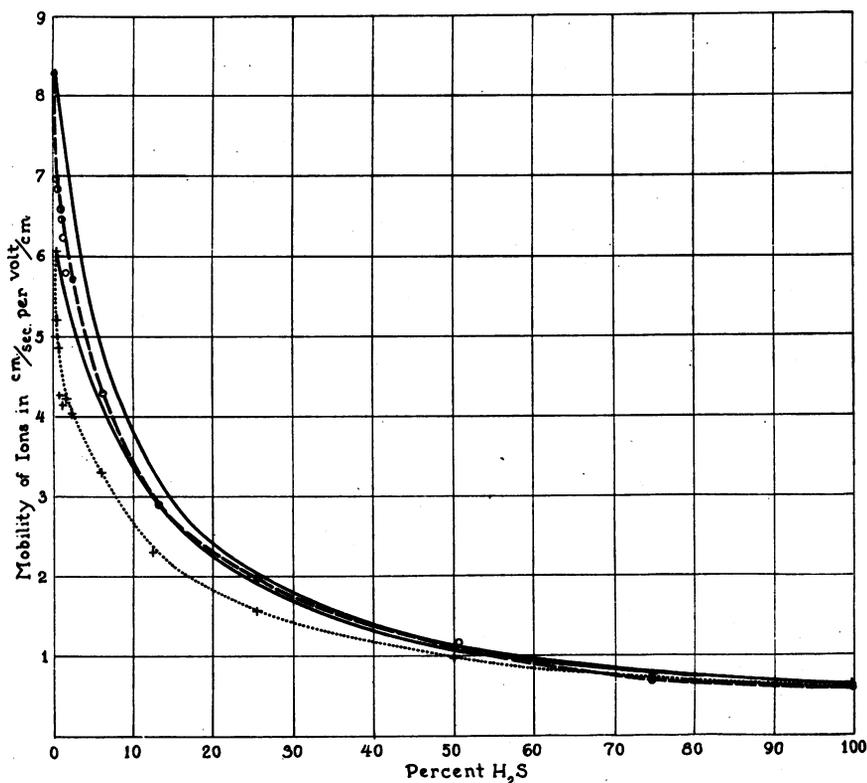
that at the lower pressures the presence of traces of impurity might affect the positive ions more than the negative ions.

In the low pressure work the results of four measurements were not recorded for the negative ions. These low-pressure measurements were made with two ends in view: first to see whether in H_2S the electrons attached readily; and secondly, to see if a prediction made by A. P. Alexeievsky⁵ on the basis of his ion mobility theory would be fulfilled. On the latter theory the van der Waal's forces of cohesion influence the size of the ions, which Alexeievsky considers as larger aggregates or droplets whose mobility can be computed as for oil drops of small size. At low pressures, according to this theory, the size of the cluster should decrease and the mobility reduced to N. T. P. should *increase* for both ions some 10% for the range of pressures studied. This is not the case as is seen above, the reverse effect possibly being observed for the positive ions.

The one low-pressure measurement in the old series of measurement showed that the electrons were not free in H_2S at 30 mm. pressure. The surprise of the writers may be imagined when with the third filling of H_2S in the present measurements, where after a large amount had been collected following a preliminary fractionation, the fraction distilled into the chamber showed *unmistakable signs of some 10% of free electrons at 50 mm. pressure.* This was evidenced by the Wellisch type of curves for the negative ions. On the succeeding day, the H_2S having been condensed out for the night, when the other of the writers made the measurements at 29 mm. pressure with the sample of H_2S distilled over, the free electrons were observed to the extent of some 25%, the break point between the electronic portion of the curve and the ionic portion giving about the proper mobility for the negative ions. An accident then occurred and this gas was lost. New lots of solid H_2S were generated, but gave no such evidence even at 10 mm. pressure. These later samples were doubtless not as good, as they represented the end of the charge of FeS. A new lot of FeS was made up, and the first sample of H_2S from this failed to show this effect on the first filling. This might have been expected as traces of other gases may have been present. Subsequent fillings after removal of an initial fraction, however, showed the effect. At 5 mm. some 3-4% of free electrons were observed, while at 10 and 20 mm. the carriers were *all free electrons*, and at a higher frequency with 38 mm., 20% free electrons were found. The positive mobilities in each case were perfectly normal. The significance of this is that electrons attach to H_2S molecules reluctantly to form ions. That electrons should not attach to H_2S when they attach to H_2O and HCl readily is not at first sight obvious. The fact remains that in pure dry H_2S electrons do not as readily form ions as one might anticipate, the attachment constant lying between that for air and O_2 . The impurity which affected some of the results was possibly HCl coming from

the action of traces of H_2SO_4 carried over to the CaCl_2 tube as a fine spray. As H_2S boils at -85°C . and HCl at -111°C . the initial fractionation, at a low temperature (i.e., 1 mm. vapor pressure of H_2S) probably removed the HCl .

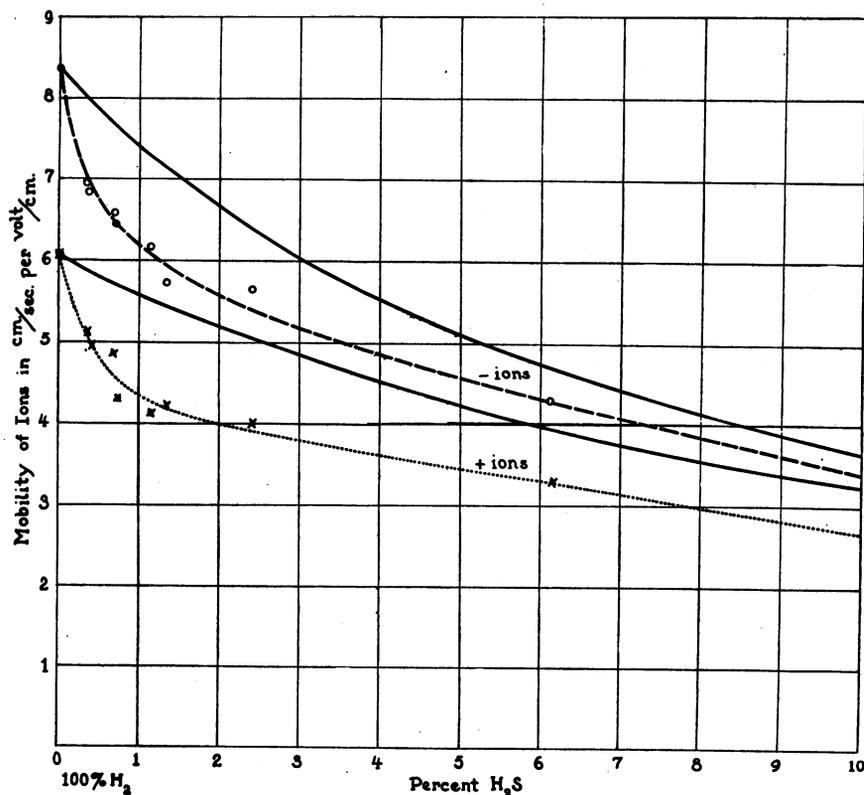
Measurements in H_2S - H_2 Mixtures.—The measurement of the mobilities in the H_2S - H_2 mixtures was carried on as before for other gases,⁴ the results being given in the curves of figures 1 and 2. The absolute values were not used, but the observed values taken at 22.5 volts for the negative



ions and 35 volts for the positive ions were used and values at other potentials were reduced to these by comparison with air. In all but one point this correction meant an *increase* in the values of the mobility, making the points fall *slightly more closely* to the lines representing the *theoretical* curves for mobilities of mixtures with low dielectric constant and no abnormal clustering.

The values for H_2 were in all cases taken from those for a freshly cleaned chamber. This cleaning was accomplished by washing with concentrated HCl , rinsing with distilled water, then with dilute NH_4OH and finally

with distilled water. It was found that prolonged pumping, even at $38^{\circ}\text{C}.$, with the chamber at better than an X-ray vacuum after using H_2S failed to restore the H_2 mobilities to their normal values for a clean chamber. If NH_4OH was admitted and allowed to stand in the chamber for from 10–30 minutes, and was then pumped out, the evil effect of H_2S contamination was removed. However, the values were never as good as for a clean chamber, and in one case with insufficient pumping the high values of the positive mobilities in H_2 due to traces of NH_3 were observed (7.67 cm./sec.



per volt/cm.). The NH_4OH presumably removed the H_2S by making solid $(\text{NH}_4)_2\text{S}$.

The values for the mobilities in H_2S , used in computing the theoretical mixture curve following Blanc's⁶ law, which are represented as the full curves with no points in the figures, were 0.61 for the negative ions and 0.63 for the positive ions. For H_2 gas the values used were 8.36 cm./sec. per volt/cm. for the negative and 6.09 cm./sec. per volt/cm. for the positive, as an average of some nine control measurements made on H_2 in a clean chamber. The H_2 , as before, came from a commercial tank and

was passed over NaOH, CaCl₂, two meter-long tubes of P₂O₅, which were all evacuated to X-ray vacuum before passing in the H₂, and then was passed through two traps cooled in liquid air.

It might be asked why the free electrons reported by one of us⁷ in H₂ were never found. Fortunately, the H₂ described above was sufficiently *impure* to permit negative ions to form, and yet not too impure to yield good values for the negative and positive ions. To see where the impurity came from (one of us suspected it to be a trace of oxygen in the H₂) the H₂ was passed over c. p. copper powder in a pyrex heating tube before entering the drying train. When the heat was on at about 400°C. the H₂ thus heated *gave no trace of negative ions*. All the carriers were free electrons. This gas could be kept two days in the ionization chamber and still showed no appreciable number of negative ions. To such pure gas in one case was added an equal quantity of unheated H₂. The free electrons were still present, but the way in which the curve rose indicated some attachment. This fact that in pure H₂ electrons are permanently free, must cause one to regard with caution any value of the negative mobility in this gas as *the true value*.⁸ If pure enough there are no negative ions. If less pure free electrons complicate the curves and give fictitious mobility values, and if impure one can't be sure of the value in the pure gas.

With the values of the mobilities $K_{\text{H}_2\text{S}}$ and K_{H_2} in the respective gases given, the K_c curves corresponding to a mixture of $c\%$ of H₂S were computed, from the law of Blanc,⁶

$$K_c = \frac{100 K_{\text{H}_2\text{S}} K_{\text{H}_2}}{(100 - c)K_{\text{H}_2\text{S}} + cK_{\text{H}_2}}$$

where c is the concentration of H₂S in per cent and $K_{\text{H}_2\text{S}}$ and K_{H_2} are the mobilities in the respective gases. The experimentally observed points in the figures are indicated by circled points for negative ions and by the dashed curve through them, while the crosses and the dotted curve represent the positive ions.

It is seen that, as in HCl,⁹ both the negative and positive mobilities in H₂ are lowered abnormally by H₂S, the negative being lowered relatively more rapidly than the positive. This differs from the results in ether¹⁰ for positive ions and Cl₂⁸ for negative ions, where only one of the ions was abnormally lowered. In H₂S, as in Cl₂, for negative ions the dielectric constant is not very high and one must look to a clustering effect for an explanation. It is proposed to study SO₂ and H₂ mixtures next in order to contrast them with H₂S, where the H nucleus may play a rôle as Condon suggests.

Summary.—Mobilities in H₂S and in H₂S-H₂ mixtures have been measured. The values on the new absolute scale of mobilities for this gas are 0.69 cm./sec. per volt/cm. for the negative ions and 0.71 cm./sec. per volt/cm.

cm. for the positive ions. Results obtained at low pressures indicate that the inverse pressure law may possibly not hold accurately for the positive ions, while it appears to hold for the negative ions. The small decrease in the mobility constant of positive ions and the constancy of this constant for negative ions is contrary to the expectations of the ion theory of A. P. Alexeievsky. In pure samples of gas, free electrons were observed in H_2S below 50 mm. This places H_2S between air and O_2 in its power of attaching electrons to form ions.

The mobilities in mixtures of H_2S and H_2 gases show that traces of H_2S lower the mobility of both ions well below the values computed from Blanc's law of mixtures. This again indicates a clustering.

In conclusion, the authors wish to express their sincere thanks to Profs. A. J. Dempster, S. C. Lind and Wm. Duane for sending them used emanation tubes as a source of polonium when, by accident, their whole supply was lost, and to Miss L. Lane for her help in taking some of the readings.

¹ Loeb, L. B., *J. Franklin Inst.*, **201**, 286 (1926). Also, *Kinetic Theory of Gases*, McGraw-Hill Book Co., New York, 1927, p. 478.

² Loeb and Cravath, *Phys. Rev.*, **27**, 642 (1927).

³ Loeb and Cravath, *J. Opt. Soc. Amer.*, **1928**.

⁴ Loeb and DuSault, *Proc. Nat. Acad. Sci.*, **13**, 510 (1927); also, Loeb, L. B., *Ibid.*, **12**, 617 and 677 (1926).

⁵ Alexeievsky, A. P., *Phys. Rev.*, **27**, 811 (1927).

⁶ Blanc, A., *J. Physique*, **7**, 825 (1908).

⁷ Loeb, L. B., *Proc. Nat. Acad. Sci.*, **6**, 335 (1920).

⁸ Mayer, Herbert, *Phys. Zeits.*, **28**, 637 (1927).

⁹ Loeb, L. B., *Proc. Nat. Acad. Sci.*, **12**, 42 (1926).

¹⁰ Loeb, L. B., *Ibid.*, **12**, 617 (1926).

¹¹ Loeb, L. B., *J. Franklin Inst.*, **196**, 537 (1923).