

to use narrower slits and thus a more nearly monochromatic source and at the same time work more rapidly. Figure 2 shows values of δ plotted against λ .

These results show very clearly the type of anomalous dispersion occurring near a K absorption limit. It is of the form predicted by the theories of Kronig and of Kallmann and Mark. It is doubtful that a quantitative agreement exists. For one thing the fluorescent absorption coefficient of calcium is not accurately known in this region. If the dispersion theory were quantitatively reliable perhaps the absorption coefficient could be derived from the dispersion curve. However, it must be noted that in the range of from six to seven Ångstrom units δ more than doubles in value. This is much more than can be explained by either theory.

¹ Stenstrom, also Hjalmar; see Siegbahn, *Spectroscopy of X-Rays*, p. 21, 1925.

² Compton, *X-Rays and Electrons*, p. 205, 1926.

³ Drude, *Theory of Optics*, p. 382.

⁴ Lorentz, *Theory of Electrons*, 2d ed., p. 150.

⁵ Hjalmar and Siegbahn, *Nature*, **115**, 85 (1925).

⁶ von Nardroff, *Phys. Rev.*, **24**, 143 (1924).

⁷ Hatley, *Phys. Rev.*, **24**, 486 (1924).

⁸ Edwards, *Phys. Rev.*, **30**, 91 (1927).

⁹ Kronig, *J. Optical Soc.*, **12**, 547 (1926).

¹⁰ Kallmann and Mark, *Ann. Physik*, **82**, 585 (1927).

¹¹ Doan, *Phil. Mag.*, **4**, 100 (1927).

MOBILITIES OF GASEOUS IONS IN SO₂ AND SO₂-H₂ MIXTURES

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Introduction.—In order to throw possible light on the nature of gaseous ions one of the writers began the study of mobilities of ions in mixtures of various gases of diverse chemical nature.^{1,2,3} This study constitutes a continuation of the work extending it to SO₂-H₂ mixtures. Despite the fact that mobilities have already been measured in pure SO₂ the results obtained in the pure gas alone merit some discussion.^{4,5} While theoretically an easy gas to work with and assumedly easy to prepare in pure form, it was found to be the most difficult gas yet encountered. The results are therefore not entirely satisfactory, but inasmuch as the work must be temporarily discontinued, it seemed best to report the results obtained to date.

Effect of Fine Gauzes in Mobility Measurement.—Before undertaking measurements the writers briefly investigated the question of the nature

of the gauze to be used in the Franck modification of the Rutherford Alternating Current method. One of the writers⁶ had previously investigated the effect on mobilities due to the interpenetration of the auxiliary and alternating fields through perforated sheet brass gauzes. In the past, such gauzes had been used by the writers in their mixture work, but these necessitated corrections for the ratios of the auxiliary and alternating fields used, which were bothersome. According to recent articles of Schilling⁷ and Herbert Mayer,⁸ fine mesh gauzes having fine wires do not produce the changes in mobility with changing values of the above ratio observed by the writer. A number of gauzes of this type were prepared,

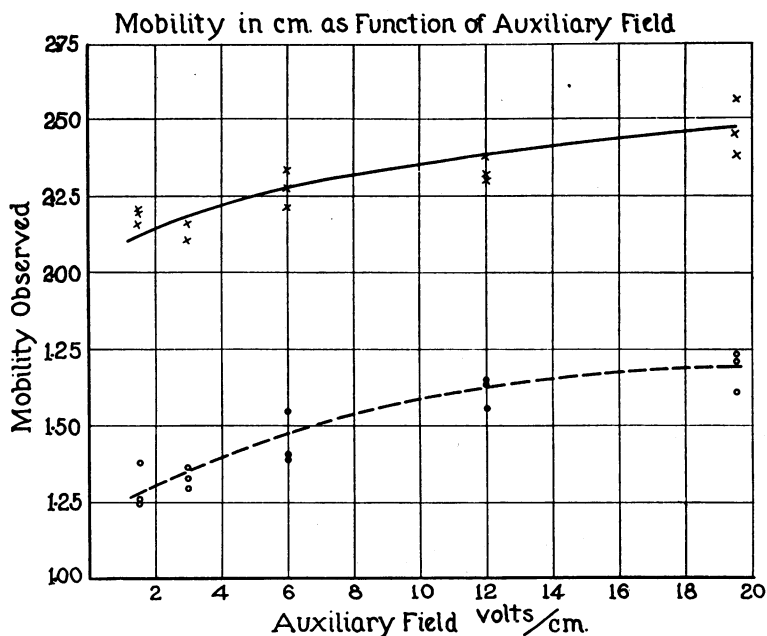


FIGURE 1

and one having meshes 0.33 mm. on a side and wires about 0.1 mm. in diameter was chosen. Such gauzes can be prepared by taking 80-mesh phosphor bronze screening and etching out the wire with HNO_3 . The gauzes so prepared are as fine as any gauzes previously used. By proper mounting they can be made plane and have a very high transmitting power for ions, at the same time having small meshes.

The mobilities were measured in H_2 and in pure dry air in the carefully cleaned ionization chamber used before,¹¹ employing different values of the auxiliary field. Above auxiliary fields of 12 volts per cm. the positive and negative mobilities in air (and also in H_2) were high and

relatively constant up to 20 volts per cm. and presumably higher. Below 12 volts per cm., auxiliary field strength, the mobilities dropped more rapidly. The alternating fields lay in the neighborhood of 30 volts for the negative ions and 40 volts for the positive ions. The values obtained are shown graphically in the curves of figure 1 for air, several different specimens of air being used causing the spread of results. Analogous results were obtained in H_2 . The shape of the curves indicates a more rapid rise of the mobilities of both ions as the field strengths are first increased than later. It is probable that beyond 20 volts auxiliary field strength to 80 volts the change would be relatively slight and possibly masked by the smaller irregularities introduced by the incompletely controllable purity of the air used.

Thus, contrary to the assertions of the authors mentioned,^{7,8} such fine gauzes also show the variable mobility previously described by one of the writers.⁶ The mobility curves obtained at different fields show the same behavior as previously described and the only difference is that the effects occur at lower auxiliary field and, therefore, higher ratios of alternating to auxiliary field with the finer mesh gauzes.

Thus Schilling's apparent constancy was due to a limited range of variation of auxiliary field on the flatter portion of the curve. His high absolute values for positive and negative ions in air are then to be ascribed to the high auxiliary fields used. This is borne out by the fact that the writers observed mobilities just as high as those of Schilling at the fields used by him, on air that he would designate as impure. This is precisely what had been anticipated by one of the writers elsewhere.¹² The conclusion to be drawn from this is that the method is incapable of giving absolute mobilities of ions, and the values obtained must be reduced to an absolute scale through comparison with a more accurate method, or else by calibration with a gas whose absolute mobilities are known.

The measurements to be described were carried out with the gauze discussed above using an auxiliary field of 12 volts/cm. By comparison with air the true values on the new absolute scale can then be obtained by multiplying the observed values by 0.96, and the values on the old recognized scale by multiplying by 0.79.

Preparation of the SO_2 .—The SO_2 was obtained from two sources. In the first case, a sample of the best commercial Na_2SO_3 to be obtained from the Chemistry Department was placed in an evacuated flask and C. P. Concentrated H_2SO_4 was dropped onto it. The SO_2 generated passed through a trap cooled to $-70^\circ C.$ in frozen alcohol, through two previously exhausted tubes of P_2O_5 each a meter long, through another double cooling trap at $-70^\circ C.$ and into a reservoir where it was frozen out with liquid air. In the second case, owing to the peculiar results

first obtained, the SO_2 , on the advice of the Chemistry Department, was taken from a commercial bomb containing liquid SO_2 , the first half of which had already been boiled off. After freezing, the bulb where the SO_2 collected was pumped to the best vacuum obtainable with a mercury vapor pump. In the case of the first sample this was fractionated in use, while the second lot was purified by boiling off half of the 50 cm.³ condensed out in the trap in filling. As far as the writers could foresee, this gas should have been quite pure. There was a trace of Hg vapor in the apparatus due to the mercury gauges. The only other source of possible contamination was the rubber stopcock grease (Lubriseal) used on the stopcocks, which could not be prevented in this system from coming in contact with the SO_2 to a slight extent. After considerable use, on evacuation and washing once with dry H_2 , the ionization chamber on opening had no odor of SO_2 and only a very faint suggestion of an aromatic substance. Occasionally in measurement the last traces of SO_2 were removed with NH_3 gas, but this did not notably change the control mobilities in H_2 if care was taken to pump out the NH_3 .

Results in SO_2 Alone.—The measurements in SO_2 gave the following values in cm./sec. per volt/cm. at atmospheric pressure under the conditions used:

	POSITIVE IONS	NEGATIVE IONS	WHEN MEASURED
1	0.346	0.332	First measurement
2	0.347	0.330	Fifth measurement
3	0.352	0.337	End of the first lot of SO_2
4	0.354	0.307	Beginning of second lot of SO_2
Average	0.350	0.329	
5	0.504	0.462	Central section of first lot of SO_2

The values numbered 1 and 2 were taken near the beginning, 3 was taken near the end of the first charge of SO_2 but after number 5 below had been taken, and 4 was found on the new charge of SO_2 from the commercial bomb. The fifth measurement gave rather surprising values of 0.504 cm./sec. for positive ions and 0.462 cm./sec. for negative ions. These high values were not accidental and had to do with a particular state of purity attained in the center of the first charge of SO_2 , which also characterized itself in other ways.

Absolute Values.— SO_2 in samples 1, 2, 3 and 4 corrected for the auxiliary field, gave mobilities of 0.276 and 0.260 cm./sec. on the old accepted scale and 0.336 and 0.316 cm./sec. on the new absolute scale, for positive and negative ions, respectively. The values on the probably pure sample indicated under 5, reduced to the old accepted scale, are 0.398 and 0.365 cm./sec. and 0.484 and 0.443 cm./sec. on the new absolute scale for positive and negative ions, respectively. The only other values in SO_2 were those of Wellisch⁴ and Yen.⁵ Both made measurements at low pressure 60–

200 mm., using the same method as the one above. Their results have little significance as absolute values, as the fields and gauze were not defined. Their values are 0.415 and 0.414 for Wellisch and 0.412 and 0.414 cm./sec. per vol. cm. for Yen for positive and negative ions, respectively. These are distinctly higher than the values of the writers in the cases 1, 2, 3 and 4 above and lower than the values in case 5 above. Yen⁵ definitely asserted that the negative mobility was greater than the positive. This is in direct contradiction to the results above. In only one case in some forty measurements was the negative mobility observed greater, the results in all cases being such as to leave no doubt.

Results at Lower Pressures.—The present measurements were carried down to lower pressures with the results shown below. The table contains the mobilities as observed directly reduced to 760 mm. with no correction for the auxiliary field.

PRESSURE IN MM.	POSITIVE IONS	NEGATIVE IONS	NUMBER OF MEASUREMENTS
10	0.399	0.385	3
21	0.377	0.364	1
51	0.372	0.398	1
149	0.372	0.347	2
316	0.372	0.339	2
760	0.350	0.329	4

It is seen that there appears to be a real increase in the reduced mobility as the pressure decreases. This appears to be in agreement with a prediction of A. P. Alexeievsky.⁹ It explains the higher values of the mobilities observed by Wellisch and Yen compared to the values observed by the writers as the former worked at low pressures. This, if correct, is an interesting deviation from the inverse pressure law. The measurements in mixtures seem to indicate that the probable explanation of this increase is no real deviation from the inverse pressure law, as Alexeievsky's theory would have it, but is due to the fact that the smaller samples of SO₂ distilled over at lower temperatures have a higher average purity corresponding to the exceptional sample measured in measurement 5 of the set at atmospheric pressure. In all but case number 5 at atmospheric pressure the results indicating the purer specimens of SO₂ came for small amounts of SO₂, distilled over, say up to 30 mm. pressure in the chamber. Although some forty or more measurements were made in this study of SO₂, no control over this variable purity could be obtained, except that the pure samples occurred in the central fractions only and for distillates obtained at the lower temperatures. This type of difficulty is unique for, so far in their experience, the writers experienced no such difficulty which could not be explained or controlled.³ It is possible as stated that the SO₂ reacted with the rubber stopcock grease to give a volatile poison. The possibility of SO₂ as an active impurity was not considered although as

later learned this gas is often present in appreciable amounts according to chemists. According to Zohn similar difficulties were encountered in his work on the dielectric constant of SO_2 . It is hoped at a later date to revert to this problem and discover the nature of the difficulty.

Free Electrons.—The negative carriers in SO_2 down to 1 cm. were always negative ions of mobility less than the positive ions. To test this still further pure hydrogen showing free electrons at 760 mm. was mixed with 1 cm. of SO_2 . The mixture was then pumped down to 3.8 cm. and tested for free electrons. None were observed. Thus a partial pressure of 0.05 cm. of SO_2 in 3.8 cm. of H_2 removes all free electrons. This leads one to conclude that electrons attach to SO_2 to form negative ions nearly as readily as they do to Cl_2 .

Results in $\text{SO}_2\text{-H}_2$ Mixtures.—The H_2 used in these measurements was similar to that used in previous work. It could be purified to give free electrons at 760 mm. pressure at will by heating a copper tube through

% SO_2	POSITIVE IONS	NEGATIVE IONS	NUMBER OF MEASUREMENTS
0.00	6.55	8.90	5
0.01	12.2	6.10	1
0.079	14.4	6.58	4+ and 5-
0.25	11.9	7.03	2 (1 high)
	4.94		
0.49	16.5	6.58	5 (1 high)
	5.64		
1.15	20.3	5.50	3 (1 high)
	4.80		
2.62	22.7	3.99	5 (2 high)
	3.76		
4.92	2.99	3.13	3
10.2	2.09	2.02	1
25.3	1.12	1.06	1
35.0	0.866	0.802	1
50.6	0.602	0.586	1
75.7	0.434	0.378	1
92.0	0.361	0.355	1
100.0	0.350	0.329	5 (1 high)
	0.505		

which it passed. It was used in this work without the heating to get negative ions to work with.³ The mobilities obtained with an auxiliary field of 12 volts per cm. were 6.55 cm./sec. for positive ions and 8.73 cm./sec. for negative ions. The values of the mobilities in SO_2 used in these computations were 0.350 cm./sec. and 0.504 cm./sec. for the positive ions and 0.329 for the negative ions. These were the mobilities directly observed and were comparable to those in the mixtures. The reason for the use of the faster mobility of the positive ion in computation will be seen when the results are given. The values for the mobilities are given

below. These are average values, the number of measurements used being indicated. They are uncorrected for the auxiliary field, being, however, reduced in each case to 760 mm. pressure. The values averaged lay on the whole fairly close together and no such extremes as shown above were averaged.

To study these better they are plotted in the curves of figures 2 and 3, the reciprocals of the mobility being plotted as ordinates against the percentage composition of the mixture as abscissae. The light dashed curves and circled points represent the positive ions and the light full lines and

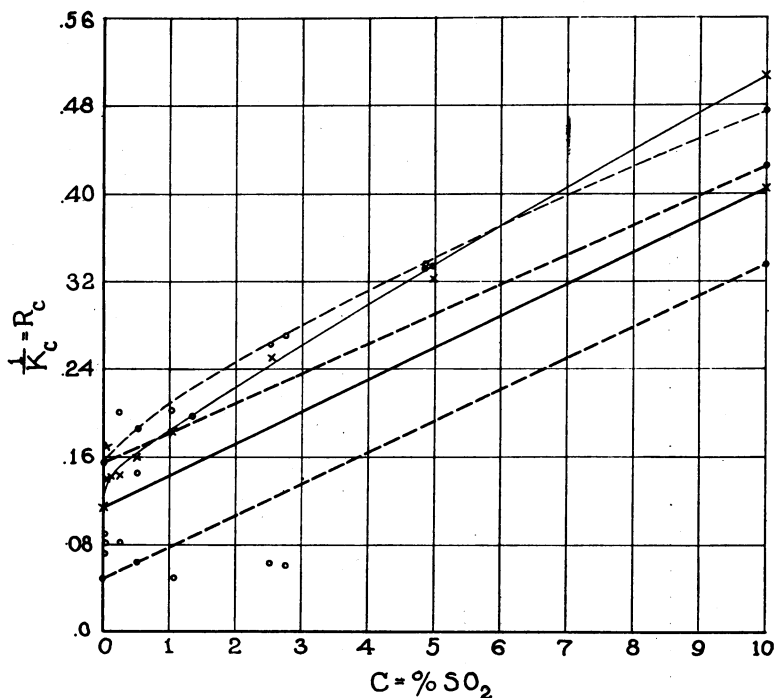


FIGURE 2

crosses the negative ions. Figure 2 goes from 0 to 10%, while figure 3 extends from 0 to 100% of SO₂. There are for figure 2 two sets of positive ion data due to the peculiar effect of the purer samples of SO₂ on the mobility of the positive ion in SO₂-H₂ mixtures in small amounts. The straight lines represent the computed curves from the mobilities in pure gases to be expected if Blanc's¹⁰ law of mixtures holds. The two heavy dashed straight lines in figure 2 for positive ions apply to the computed curves for positive ions for the pure samples and for the normal samples.

If one represents the reciprocal of the mobility in a gas *a* by $\frac{1}{K_a} = R_a$,

and that for a gas *b* as $\frac{1}{K_b} = R_b$, and if in a binary mixture there is a mol fraction *c* of the gas *a* and $1 - c$ of the gas *b* present, the reciprocal of the mobility in the mixture $R_c = \frac{1}{K_c}$ will be obtained by merely adding the quantities R_a and R_b multiplied by the mol fractions of the respective gases present. Thus $R_c = cR_a + (1 - c) R_b$, which represents the

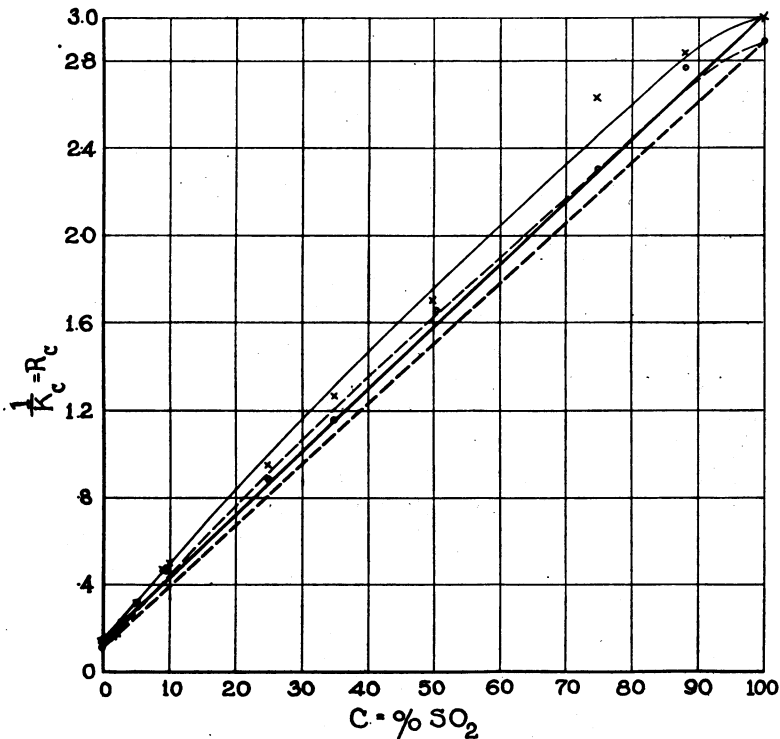


FIGURE 3

straight lines plotted using the observed end values. If the mobilities be substituted the law becomes

$$\frac{1}{K_c} = \frac{c}{K_a} + \frac{1 - c}{K_b}, \text{ whence}$$

$K_c = \frac{K_a K_b}{(1 - c) K_a + cK_b}$, which is the form of Blanc's law used in discussing previous work.^{2,3}

Looking at the curves of figure 3, it is seen that these depart from the straight line law in a sense indicating that either a labile clustering or concentration effect is taking place. These deviations are quite like those

observed in NH_3 and represent a possible dielectric effect. In looking at figure 2, it is seen that SO_2 behaves like NH_3 in its action on the negative ion and also for the positive ions in the less pure samples. In the samples which have so far been specified as the purer samples, the positive ion has its mobility *increased to high values by traces of SO_2* and even by amounts of SO_2 as great as 2.5%. The only possible interpretation of this is that in certain samples of the SO_2 free from some impurity SO_2 replaces the heavier molecule or molecules associated with the positive ion in H_2 , making a more mobile ion. The highest mobilities observed with certainty for positive ions in these low percentage mixtures of SO_2 (they were not observed at higher percentages) were 22 cm./sec. per volt/cm. *This is higher than any negative ion mobility ever observed in H_2 .* Negative ion mobilities as high as 13 have been observed in high auxiliary fields in fairly pure dry H_2 . The effect of NH_3 in increasing the positive mobility in H_2 was, on one occasion in these measurements, found to give a mobility as high as 14. Thus SO_2 is unique in the magnitude of its effect on the positive ion mobility in H_2 . The interpretation of this is quite simple. It is certain that the negative ion in H_2 is formed by attachment of the electron to some molecule of impurity. If it were a stopcock grease or other bulky molecule present, this would even, in the absence of further clustering, give rise to a slower ion. Again in H_2 the ionization of H_2 by the alpha particles will lead to the formation of either H_2^+ or H^+ . It is very doubtful if the positive charge will remain as long as 0.002 second attached to the hydrogen. The traces (from a chemical viewpoint) of impurities will quickly acquire the charge because of the lower ionizing potential. It may also be that the H^+ or H_2^+ will rapidly pick up some heavier molecule of impurity. In any case the positive ion will also be bulky, and apparently more so than the negative, for its mobility is less. Addition of pure SO_2 introduces molecules which have a stronger affinity for the positive ion than the impurity present before and the mobility is that due to a lighter complex. That the mobility should exceed that of the negative ion is not strange, as the latter is also formed about an impurity. Whether the charges are attached to single molecules of impurity or SO_2 in these cases it is impossible to say. The high values observed in SO_2 compared to the negative mobilities make it less likely that one is dealing with single molecular carriers than in the case of NH_3 , where the mobility about equalled the negative. The sensitivity of SO_2 to some unknown impurity, however, shows that there are substances present that are even more effective than SO_2 . This was also found before in the case of ether and NH_3 , the ether being more active on the positive ions than NH_3 .

The results, therefore, add one more striking bit of evidence indicating that besides general dielectric lowering effects, concentration effects or

statistical loose clustering, there are very much more stable complexes formed by the action of charges of one sign or the other on specific molecules. How large these are is still a question of doubt, but that such complexes must form cannot be questioned. Such combinations appear more or less like the complex ions encountered in chemistry, e.g., NH_4^+ , $\text{Cu}(\text{CN})_2^-$, etc., than like clusters in their specific character.

Summary.—The work is an extension of the investigations of ion mobilities in mixed gases to SO_2 - H_2 mixtures. It is shown that the fine-meshed gauzes such as used by Schilling and H. Mayer show the effect of varying the auxiliary field on the mobility just as other gauzes do, differing only in the point where the effects become appreciable. This confirms previous work of one of the writers and leads one to suspect that Schilling's high mobilities are due rather to the high auxiliary fields used than to the exceptional purity. Difficulty was encountered in obtaining a purity as shown by these measurements which was satisfactory. Two sets of values of mobilities were observed at atmospheric pressure in SO_2 . The absolute values on the new absolute scale for the supposedly less pure sample were 0.34 cm./sec. and 0.32 cm./sec., respectively, for positive and negative ions. For the other sample the values 0.48 cm./sec. and 0.44 cm./sec. on this same scale were observed. The mobilities reduced to 760 mm. appeared to increase with decreasing pressure a slight amount. The effect is probably ascribable to the higher purity obtained at lower pressures. Negative electrons could not be detected down to 0.05 cm. pressure of SO_2 in 3.8 cm. of pure H_2 . The negative mobility is unquestionably less than the positive and appears so invariably in these measurements. The effect of SO_2 at higher concentrations in SO_2 - H_2 mixtures is similar to the effect of NH_3 in NH_3 - H_2 mixtures. At low concentrations the supposedly purer samples of SO_2 gave positive mobilities in H_2 of 22 cm./sec. per volt/cm. which exceed materially the negative mobilities observed. This must be ascribed to the formation of a relatively simple and mobile positive ion in SO_2 mixed with H_2 . The negative ion as in NH_3 is unaffected except to have its mobility slightly reduced.

¹ Loeb and Ashley, *Proc. Nat. Acad. Sci.*, **10**, 351 (1924).

² Loeb, L. B., *Ibid.*, **12**, 35 and 42 (1926); **12**, 617, 677 (1926).

³ Loeb and DuSault, *Ibid.*, **13**, 510 (1927); **14**, 193 (1928).

⁴ Wellisch, E. M., *Phil. Trans. Roy. Soc. London*, **A209**, 249 (1909); *Phil. Mag.*, **34**, 59 (1917).

⁵ Yen, K. L., *Proc. Nat. Acad. Sci.*, **4**, 106 (1918).

⁶ Loeb, L. B., *J. Franklin Inst.*, **196**, 537 and 771 (1923).

⁷ Schilling, H., *Ann. Phys.*, **83**, 23 (1927).

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

⁹ Alexeievsky, A. P., *Phys. Rev.*, **27**, 811 (1926).

¹⁰ Blanc, A., *J. Physique*, **7**, 825 (1908).

¹¹ Loeb and Cravath, *J. Opt. Soc. Amer.*, **16**, 191 (1928).

¹² Loeb, L. B., *Ann. Phys.*, **84**, 691 (1927).