

2. Observations indicate a strong similarity between the anionic and cationic high molecular weight aliphatic compounds in water.

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## Surface Conditions of Precipitates and Rate of Reaction. IV. Reduction of Mercurous Chloride by Hydroxylamine

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Gurney and Mott<sup>1,2</sup> have proposed the following mechanism for the reduction of silver halides by developing agents<sup>2</sup>: "The molecules of the developer hand over electrons to the metallic silver speck, and raise its potential relative to that of the halide grain. The interstitial silver ions which are present in the halide are then attracted to the silver speck; they will move up to it and adhere to it. Of course, as fast as the silver ions in the grain are used up, new ones are formed. The halogen escapes from the surface of the crystal, and not from the metal-compound interface. Interstitial ions, which may have come from quite distant parts of the crystal, flow through the crystal and join the metal at the interface." A property of silver halide which is essential for the Gurney-Mott theory is that of electric conductivity by ionic migration. The silver halides are known to exhibit relatively large conductivity even at room temperature. Tubandt<sup>3</sup> and co-workers have shown that the conductivity of the silver halides is due principally to the movement of silver ions. Hence, this requirement is fulfilled for the silver halides.

The mercurous halides present an entirely different situation. They are much more molecular in structure than the silver halides, and may be considered to be built up of an aggregation of  $\text{XHgHgX}$  "molecules," so distributed that each Hg atom is surrounded by four X atoms of other molecules, and *vice versa*.<sup>4</sup> Ketzer<sup>5</sup> reported that the specific conductivity of well-dried mercurous chloride is not greater than  $10^{-11}$  ohm<sup>-1</sup>, which

was about the limit of sensitivity of the apparatus he employed. This is to be compared with a conductivity of about  $10^{-8}$  ohm<sup>-1</sup> for the silver halides.<sup>6</sup> It does not appear possible that interstitial mercurous ions ( $\text{Hg}_2^{++}$ ) could form in or travel through the mercurous chloride crystal. It is, therefore, of interest to compare the reduction of this material by the developing agent, hydroxylamine, with that of silver chloride.<sup>7</sup> The experimental results which follow demonstrate that the two processes are formally quite similar.

### Experimental

The general procedure employed in this investigation was the same as that used previously with silver chloride.<sup>7</sup> A stock solution of mercurous nitrate was prepared by dissolving 2.5 mmoles of  $\text{Hg}_2(\text{NO}_3)_2$  in 20 ml. of 1.00 *M* nitric acid. This solution was stored in the dark over pure mercury. No kinetically detectable change occurred within a week, the maximum period any one stock solution was kept. Solutions not stored over mercury showed significant change, due to a poisoning action of the mercuric salts formed.

Mercurous chloride was precipitated by addition from a pipet of 5.0 ml. of 0.20 *M* sodium chloride to 2.0 ml. of stock mercurous nitrate diluted to 15 ml. with water. Thus, an excess of 0.5 mmole of  $\text{Cl}^-$  was present in the standard precipitation. The mercurous solution was mechanically stirred during the addition of sodium chloride solution, and the tip of the pipet was kept below the liquid surface. Reduction was carried out at  $20.00 \pm 0.03^\circ$  in the presence of phosphate buffer.

**Reduction of Mercurous Nitrate by Hydroxylamine.**—Some preliminary experiments were made on the reduction of mercurous nitrate at pH 3.9, using an acetate buffer. The tendency of mercurous nitrate to hydrolyze at this pH, together with the poor stability of colloidal mercury, limited the extent to which quantitative experiments could be carried out in this case. However, the reaction curve was definitely auto-accelerating in form, and the reduction was markedly catalyzed by added colloidal mercury or colloidal silver. Silver nitrate in amounts equivalent to the silver sol used had no noticeable effect upon the reaction rate.

Mercuric chloride is reduced only very slowly if at all by

(1) R. W. Gurney and N. F. Mott, *Proc. Roy. Soc.*, (A)164, 151 (1938).

(2) N. F. Mott, *Reports on Progress in Physics*, 6, 186 (1939); N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," The Clarendon Press, Oxford, 1940.

(3) C. Tubandt, "Handbuch der Exper. Physik," Vol. XII, Part I, p. 384 ff., Leipzig, 1932; C. Tubandt and S. Eggert, *Z. anorg. allgem. Chem.*, 110, 196 (1920).

(4) R. J. Havighurst, *Am. J. Science*, 10, 15 (1925); Ch. Mauguin, *Compt. rend.*, 178, 1913 (1924); M. L. Huggins and P. L. Magill, *This Journal*, 49, 2357 (1927).

(5) R. Ketzer, *Z. Elektrochem.*, 26, 77 (1920).

(6) W. Leffeldt, *Z. Physik*, 85, 717 (1933).

(7) T. H. James, *This Journal*, 62, 536, 1649 (1940).

hydroxylamine in neutral or acid solution.<sup>8</sup> It exerts a marked retarding effect upon the reduction of mercurous nitrate or mercurous chloride in acid solution. Thus, the addition of 0.05 mmole of mercuric chloride to 0.25 mmole of mercurous nitrate decreased the reaction rate by more than sevenfold. A similar addition to a reaction mixture containing precipitated mercurous chloride at pH 6.2 resulted in an even greater decrease in the rate of reduction.

**Reduction of Mercurous Chloride.**—The experiments on mercurous chloride were carried out in the pH range 5.7–6.3. In this region, the mercury remaining at the end of the reaction was in a finely divided state and the volume of gas obtained was, within the limit of experimental error, the theoretical for 100% nitrogen yield. The only oxide of nitrogen which, by itself or mixed with nitrogen, could account for this yield is nitric oxide. The presence of this oxide in the gas evolved could not be positively established, and in any event did not exceed 2% of the total. Thus, the oxidation of hydroxylamine by mercurous chloride and by silver chloride yields predominantly the same reaction products: nitrogen and water. On the other hand, oxidation by mercuric salts, as well as by cupric, ferric and ceric salts, yields predominantly oxides of nitrogen. It is of interest that the latter reactions do not appear to be autocatalytic.

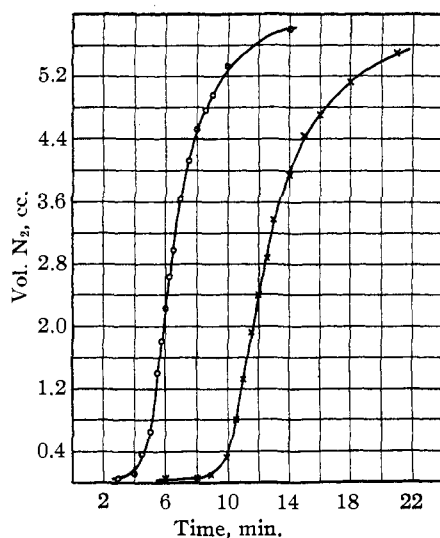


Fig. 1.—Typical reaction curves: O, 25 mmoles  $\text{Hg}_2\text{Cl}_2$ , pH 6.25; —O—O—, 0.50 mmoles excess  $\text{Cl}^-$ ; —X—X—, 1.50 mmoles excess  $\text{Cl}^-$ .

Typical reaction curves for mercurous chloride are given in Fig. 1. The pronounced induction period cannot be due to the presence of the inhibiting mercuric ion. The same induction period was obtained with a precipitate prepared from freshly purified mercurous nitrate solution and from a solution which had stood for several days over mercury. Moreover, the extent of the induction period varied considerably with the method of precipitating the chloride, *e. g.*, the rate of stirring during addition of the chloride solution, and the rate of addition of the solution itself. Colloidal mercury added to the precipitated chlo-

ride only very slightly reduced the induction period. However, the electrolytic mercurous chloride supplied by Eppley for use in calomel half-cells, which contains metallic mercury intimately associated with the chloride, reacted without an induction period. Thus, it appears that the induction period is connected with the formation of mercury catalyst intimately associated with the mercurous chloride.

The specific surface of the mercurous chloride precipitate was determined by dye adsorption. One-fourth millimole of precipitate contained in 30 ml. of solution buffered at pH 6.2 was "titrated" with 0.05% methanol solution of 3,3'-diethyl-9-methylthiacarbocyanine chloride (IVa). The end-point of the titration was taken as the point at which the supernatant liquid showed a definite color of dye after several minutes of stirring with the precipitate. This end-point was quite sharp. The procedure previously employed in determining the specific surface of silver chloride, namely, the addition of excess dye followed by colorimetric determination of the excess, was not satisfactory in the case at hand. There appears to be a considerable tendency for adsorption beyond the monomolecular layer stage.

The dependence of the specific surface upon the age of the precipitate is shown in Fig. 2. The dependence of the rate of reduction of the mercurous chloride upon the age of the precipitate is given in Table I. The precipitates in both cases were aged in the nitric acid solution, and the phosphate buffer was added fifteen minutes before the determination was begun. The time,  $t_1$ , is that required for the evolution of the first 0.30 ml. of nitrogen (5% total reaction) and  $R$  is the slope of the reaction curve at 25% of total reaction. The measured rate at the latter point is at about the maximum. In the lower portion of the table, data are given for half-hour-old precipitates prepared from mercurous nitrate solutions which had been aged in nitric acid and in the absence of metallic mercury for the specified times.

TABLE I  
 $\text{Hg}_2\text{Cl}_2$ , 0.25 mmole;  $\text{NH}_2\text{OH}$ , 2.00 mmole; pH, 5.80; total volume 60 ml.

Age $\text{Hg}_2\text{Cl}_2$ , hours	$t_1$ , min.	$1/t_1$	$R$
0.5	13.3	0.075	0.53
.5	13.9	.072	.52
4.5	15.15	.066	.51
19.0	18.55	.054	.39
66.0	38.6	.026	.19
Age $\text{Hg}_2(\text{NO}_3)_2$			
24	14.0	.071	.48
144	24.5	.041	.39

The comparative curves in Fig. 2 show that the reaction rates do not parallel the specific surface. The decrease in rate due to aging of the mercurous nitrate indicates that formation of mercuric salt<sup>9</sup> may be responsible for a portion of the decrease in rate of reduction of mercurous chloride on aging, but this could not account for the entire decrease. Most of it is due, apparently, to changes occurring in the structure of the precipitate. It appeared from these re-

(8) A. Kurtzacker and F. Wengfeld, *Z. anorg. allgem. Chem.*, **141**, 119 (1924).

(9) T. W. Richards and M. Françon, *J. Phys. Chem.*, **33**, 936 (1929).

sults that no advantage was to be gained in the kinetic experiments by using precipitates aged to give minimum specific surface. Hence, in all further work, precipitates aged about thirty minutes were employed.

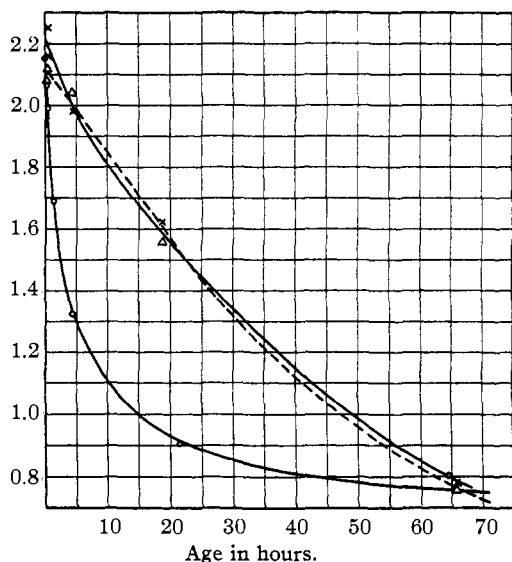


Fig. 2.—Variation of specific surface and reaction rate with age of precipitate: —○—○—, specific surface, ml. 0.05% IVa; —×—×—, reaction rate, 30/*t*; —△—△—, reaction rate, 4*R*.

Data for the variation of reaction rate with hydroxylamine concentration are given in Table II, and as logarithmic plots in Fig. 3. In plotting the points corresponding to the rates at 16% reaction, the hydroxylamine concentrations have been corrected for the amount reacting prior to this point.

TABLE II

VARIATION OF REACTION RATE WITH HYDROXYLAMINE CONCENTRATION

Hg<sub>2</sub>Cl<sub>2</sub>, 0.25 mmole; pH, 6.12; total vol., 60 ml.

NH <sub>2</sub> OH, mmole	<i>t</i> , min.	1/ <i>t</i>	<i>R</i> (16%)
4.00	3.1	0.323	2.00
2.00	6.1	.164	1.36
1.00	11.7	.085	0.90
	13.7	.073	.87
0.488	22.6	.044	.50
	20.7	.048	.54

TABLE III

VARIATION OF REACTION RATE WITH EXCESS CHLORIDE

NH<sub>2</sub>OH, 2.00 mmole; Hg<sub>2</sub>Cl<sub>2</sub>, 0.25 mmole; total vol., 60 ml.

Excess Cl <sup>-</sup> , mmole	<i>t</i> , min.	1/ <i>t</i>	<i>R</i> (25%)	pH
0.50	15.4	0.065	0.48	5.76
.60	22.5	.044	.472	5.76
.70	40.8	.025	.416	5.76
1.00	57.3	.017	.284	5.76
1.20	161.2	.0062	.194	5.76
0.50	4.45	.225	1.55	6.24
1.50	10.0	.100	1.04	6.24
2.50	29.4	.034	0.65	6.24

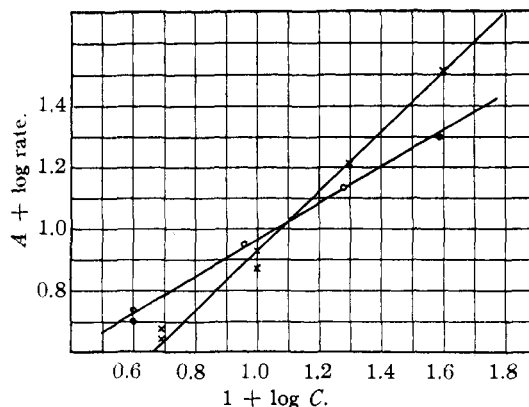


Fig. 3.—Variation of rate with hydroxylamine concentration: —○—○—, *R*, 16%; —×—×—, 1/*t*.

The variation in rate with excess chloride is given in Table III. Sodium chloride in excess of the 1.00 mmole used in the standard precipitation was added to the completed precipitate twenty minutes before use.

**Effect of Dyes and Gelatin on Reduction Rate.**—In these experiments, the dye in aqueous solution was added slowly to the rapidly stirred standard precipitate plus the supernatant liquid, and the stirring was continued for ten minutes before transference to the reaction vessel. Prior to the addition of dye or gelatin, the precipitate was aged for fifteen minutes after the addition of the phosphate buffer, and the pH was about 6.5. The dye, wool violet 4BN, used was the National Aniline product purified according to the method of Kolthoff, von Fischer and

TABLE IV

EFFECT OF CERTAIN DYES ON THE RATE OF REDUCTION

Hg<sub>2</sub>Cl<sub>2</sub>, 0.25 mmole; NH<sub>2</sub>OH, 2.00 mmole; pH 6.2

Micromoles of dye	<i>t</i> , min.	1/ <i>t</i>	<i>R</i> (25%)
Pinacyanol			
0.0000	4.8	0.208	1.32
.0257	5.4	.185	1.11
.0644	7.2	.139	0.88
.1287	8.1	.123	.49
.1673	9.2	.109	.23
.2574	10.6	.094	.14
.3861	18.0	.055	.06
.6435	33.0	.030	.042
1.287	118.0	.0085	.0076
Wool Violet			
0.000	5.2	.192	1.27
.10	8.7	.115	0.32
.50	75.0	.013	.014
Phenosafranine			
0.00	5.2	.192	1.27
0.50	7.1	.141	0.49
1.00	9.9	.101	.36
2.00	11.4	.088	.20
IVa			
0.0000	4.8	.208	1.32
.1326	8.3	.12	0.375
.3977	12.3	.08	.165

Rosenblum<sup>10</sup> and the molecular weight obtained by them, 801, was used in the calculations. The 3,3'-diethyl-9-methylthiacarbocyanine chloride was obtained from L. G. S. Brooker.

TABLE V  
EFFECT OF GELATIN ON RATE OF REDUCTION OF MERCUROUS CHLORIDE; SAME CONDITIONS AS IN TABLE IV, EXCEPT pH 6.25

Gelatin, mg.	$t_i$ , min.	$1/t_i$	$R$ (25%)
0.00	4.5	0.222	1.74
.01	4.9	.204	1.54
.01	4.4	.227	1.70
.02	5.2	.192	1.24
.03	5.7	.175	1.04
.05	7.6	.131	0.34
.10	23.6	.042	.136
1.00	125.0	.008	.012

The results obtained with pinacyanol, wool violet, phenosafranine and IVa are given in Table IV. Data for gelatin are given in Table V. The relative effect of the dyes employed is shown graphically in Figs. 4 and 5.

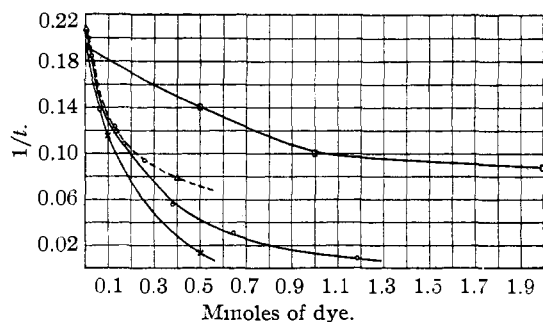


Fig. 4.—Variation of initial rate with amount of added dye: —○—○—, pinacyanol; —×—×—, wool violet; —△—△—, IVa; —□—□—, phenosafranine.

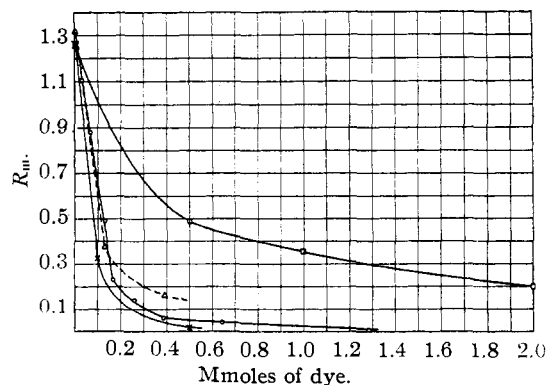


Fig. 5.—Variation of  $R$  with amount of added dye: —○—○—, pinacyanol; —×—×—, wool violet; —△—△—, IVa; —□—□—, phenosafranine.

### Discussion

The action of dyes and gelatin upon the rate of reduction of mercurous chloride differs in one im-

portant respect from the corresponding action on silver chloride. In the latter case, the decrease in the reaction rate is approximately proportional to the amount of surface covered by the added agent. In the former, a much more pronounced decrease in the reaction rate is obtained during coverage of the first few per cent. of the total surface. Thus, approximately 2.5 micromoles of pinacyanol or IVa are required to cover the surface of the thirty-minute-old mercurous chloride precipitate completely. When dye sufficient to cover only 4% of this total is added, the  $1/t$  rate drops to 65% of the original and the  $R$  rate drops to about 50%. When pinacyanol sufficient to cover only 8% of the total surface is added,  $R$  is less than one-sixth of the value for the pure precipitate. Wool violet is just as effective as the pinacyanol in its action on mercurous chloride, in sharp contrast to its effect on the silver chloride. Gelatin is much more effective in its action on mercurous chloride than on silver chloride, and is formally similar to pinacyanol in its effect. Phenosafranine is much less effective than the other agents.

Both the active dyes and the gelatin are strongly adsorbed to mercurous chloride, and their action is definitely a surface effect. Pinacyanol in the largest quantity used in the work with mercurous chloride had only a small retarding effect upon the reduction of mercurous nitrate. Gelatin did not increase the induction period with mercurous nitrate, and produced an increase in the maximum reaction rate, due probably to its protective action on the mercury sol and the accompanying increase in effective catalyst surface. The pronounced effect of relatively small amounts of certain substances upon the rate of reduction of mercurous chloride is good evidence that the reaction starts at certain pre-existing active spots on the crystal surface. The great decrease in  $R$  during the coverage of the first 10% of surface by dye indicates that the number of reaction centers has been sharply decreased by the action of the dye, and the same appears to be true in the case of gelatin. The probable explanation for the difference between mercurous chloride and silver chloride is that in the former case the active spots selectively adsorb the dye and gelatin, whereas, in the latter case such selective adsorption does not occur. This behavior of silver chloride fits in well with the observations of Sheppard, Lambert and Walker on the adsorption of sensitizing

(10) I. M. Kolthoff, W. von Fischer and C. Rosenblum, THIS JOURNAL, 56, 832 (1934).

dyes.<sup>11</sup> The apparent selective action of the active spots in the adsorption of dyes and gelatin by mercurous chloride may have simply a kinetic basis, *i. e.*, the active spots may adsorb at a greater rate than the bulk of the surface. However, a possible participation of other factors is suggested by the discovery of Imre and Hahn<sup>12</sup> that the mercurous halides adsorb much less thallous or lead ions than the considerably more polar silver halides. Their results suggest the participation of active areas in the adsorption of thallous and lead ions by the mercurous halides.

The metal catalysis appears to be even more pronounced in the case of mercurous chloride than in that of silver chloride. The catalysis mechanism probably involves adsorption of mercurous ions by the metallic mercury at the interface,<sup>13</sup> and may be fundamentally the same as the mechanism of reduction of silver chloride.<sup>14</sup> The striking kinetic similarity between the reduction of silver chloride and mercurous chloride suggests the similarity of mechanism. Since the Gurney-Mott mechanism does not apply to the reduction of mercurous chloride, comparison of the reaction kinetics indicates that it does not apply to the reduction of silver chloride either.

The Gurney-Mott mechanism of latent-image formation likewise requires migration of interstitial metal ions, and hence does not apply to the action of light on mercurous chloride. Here, however, the situation is different from that encountered in development. Photographic plates sensitive in the near ultraviolet may be prepared from mercurous chloride and developed in a conventional elon developer.<sup>15</sup> There is evidence that the action of the light results in the formation of metallic mercury.<sup>16</sup> However, the mercurous chloride and bromide are much less sensitive

photographically than the corresponding silver halides. Whereas a concentration-speck theory is definitely required to explain the photographic phenomena exhibited by the silver halides,<sup>17</sup> the mercurous halides have not been sufficiently studied photographically to enable one to pass judgment on this point. The known facts in the latter case could be explained on the basis of absorption of light by impurities and imperfections in the crystal lattice.

Just as in the case of silver chloride, the variation of the  $1/t$  rate with the hydroxylamine concentration is linear. The  $R$  values, however, vary as about the 0.6 power of the hydroxylamine concentration (the power involved in the silver chloride reduction was about 0.8), suggesting that adsorption of hydroxylamine is involved in the catalyzed reaction. The variation of the reaction rate with the excess chloride-ion concentration does not appear to follow any simple rule, and probably involves the adsorption of chloride ions by the active spots on the mercurous chloride crystals. Complex formation may also be involved.<sup>9</sup>

### Summary

The molecular type structure and very low electrical conductivity of mercurous chloride appear to preclude the passage through the crystal of interstitial mercurous ions. It is highly improbable, therefore, that the Gurney-Mott mechanism could operate in the reduction of the compound. However, reduction of mercurous chloride by hydroxylamine is quite similar, formally, to the reduction of silver chloride by this developing agent. A study was made of the effect of the (1) age of the precipitate, (2) adsorbed dyes and gelatin, (3) variation of the hydroxylamine concentration, and (4) variation in concentration of the excess chloride ion upon the rate of reduction of precipitated mercurous chloride.

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(11) S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **7**, 265 (1939).

(12) O. Hahn and L. Imre, *Z. physik. Chem.*, **A144**, 161 (1929); L. Imre, *ibid.*, **A146**, 41 (1930).

(13) H. von Euler and G. Zimmerlund, *Arkiv. Kemi. Min. Geol.*, **8**, no. 14 (1921); R. K. Schofield, *Phil. Mag.*, (7) **1**, 641 (1926); K. Kellermann and E. Lange, *Kolloid Z.*, **81**, 96 (1937).

(14) T. H. James, *THIS JOURNAL*, **62**, 3411 (1940).

(15) G. Athanasiu, *Compt. rend.*, **176**, 1389 (1923).

(16) A. L. Hughes, *Phil. Mag.*, **24**, 380 (1912).

(17) S. E. Sheppard, A. P. H. Trivelli and R. P. Loveland, *J. Frank. Inst.*, **200**, 51 (1925); J. H. Webb, *J. Appl. Phys.*, **11**, 18 (1940).