ruthenium was reduced to the bivalent state (see Table III and Fig. 1). It may therefore be concluded that the dark blue compounds which form after a small excess of titanous sulfate has been added are compounds of bivalent ruthenium, not of univalent ruthenium as supposed by these authors and by Remy and Wagner.

A bromide salt of ruthenium was prepared by digesting the chloride with bromine and hydrobromic acid and evaporating the solution with potassium bromide. An analysis of this salt showed that it conforms to the formula $K_2RuBr_5(H_2O)$ or K_2RuBr_5OH. Titrations of hydrochloric acid solutions of this salt with thiosulfate after treating it with potassium iodide, and with titanous sulfate by the electrometric method, showed that the ruthenium in the salt was in the quadrivalent state (see Tables IV and V). These results indicate that the true formula of the salt is K_2RuBr_5OH, thus confirming the recent views of Howe.

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[CONTRIBUTION FROM THE METALLURGICAL LABORATORIES OF HARVARD UNIVERSITY]

THE CRYSTAL STRUCTURE OF THE SYSTEM CADMIUM-MERCURY

BY ROBERT FRANKLIN MEHL[1]

The system cadmium-mercury is interesting for a number of reasons. Its composition-temperature diagram (Fig. 1) is the only known example of Roozeboom's Type IV.[2] Various compositions among the mercury-rich alloys have been used in the construction of standard cells. Numerous measurements on electrode potential, and on vapor pressure, of the liquid and partly liquid alloys have led a number of investigators to postulate the existence of intermetallic compounds.[3] These, however, do not appear on the constitution diagram proposed by Bijl[4] (Fig. 1) and repeatedly confirmed.[5] Recently T. W. Richards and C. E. Teeter, Jr.,[6] measured the heats of dilution of these alloys in mercury at room temperature and found no critical points suggestive of a compound.

A few measurements of the crystal structure of the system have been

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[1] National Research Fellow.

[2] Roozeboom, Z. physik. Chem., 30, 385 (1899).

[3] (a) Hildebrand, Foster and Beebe, THIS JOURNAL, 42, 545 (1920); (b) Richards and Forbes, Carnegie Institution Publication, No. 56 (1906); (c) Z. physik. Chem., 58, 738 (1906); (d) Hildebrand, Trans. Am. Electrochem. Soc., 22, 319, 335 (1913).

[4] Bijl, Z. physik. Chem., 41, 641 (1902).

[5] (a) Puschin, Z. anorg. Chem., 36, 201 (1903); (b) Jänecke, Z. physik. Chem., 60, 409 (1907); (c) Schulze, ibid., 105, 177 (1923); (d) Tammann and Mansuri, Z. anorg. Chem., 132, 69 (1923).

[6] Unpublished research.

reported by Cl. v. Simson,[7] but apparently the study was only qualitative, for no analysis of structure was made.[8]

Although the structure of cadmium is well known,[9] the data for mercury are conflicting. L. W. McKeehan and P. P. Cioffi[10] studied its structure at the temperature of boiling liquid air and obtained diffraction spectra indicative of a simple rhombohedral structure, whereas N. Alsen and G. Aminoff[11] obtained diffraction data for mercury imbedded in solid carbon dioxide quite different, and concluded that at this temperature mercury is hexagonal. R. W. G. Wyckoff has briefly discussed these differences[12] and has suggested that the complete disagreement might be explained by the occurrence of a transition point.
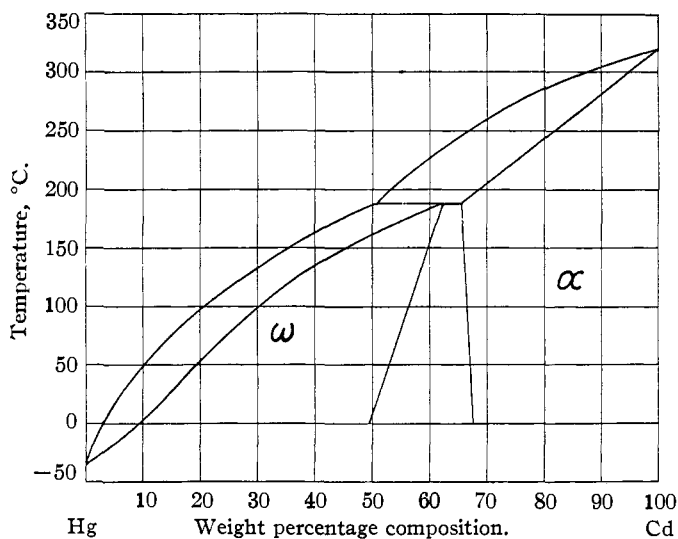

Fig. 1.

If we assume that the diagram of Bijl (Fig. 1) actually represents the mercury-cadmium equilibrium, the problem of the crystal structure of mercury can be attacked in an indirect way. Cadmium is the only metal, so far as known, which forms extensive solid solutions with mercury. Both the ω- and the α-solid solution are terminal solid solutions, formed

[7] Von Simson, Z. physik. Chem., 109, 183 (1924).

[8] It is erroneously stated in this publication that the axial ratio of the pure, triangular close-packed cadmium is 1.39, whereas the true ratio is 1.89 (see the following reference).

[9] (a) Hull, Phys. Rev., 17, 571 (1921); and others, (b) see International Critical Tables, Vol. I, p. 340.

[10] McKeehan and Cioffi, Phys. Rev., 19, 444 (1922).

[11] Alsen and Aminoff, Geol. Fören. Förh., 44, 197 (1922).

[12] Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1924, p. 242.

presumably by simple substitution and exhibiting the space lattice of the solvent metal alone, possibly somewhat altered in dimension.[13] A determination of the structure of the ω-solid solution should, therefore, give the lattice type for mercury.

In order, therefore, to present additional evidence on the constitution of the cadmium-mercury system with especial reference to intermetallic compounds, and indirectly to determine the crystal structure of mercury (*with the assumption of the validity of the constitution diagram proposed by Bijl,*) the present study was undertaken.

Materials and Method

The alloys were made up determinately and not analyzed.[14] The cadmium bore a manufacturer's analysis of 99.961% cadmium, 0.015% zinc, 0.023% lead and 0.001% iron. The mercury was "Redistilled Mercury," which was passed through a nitric acid tower a dozen times and twice distilled in partial vacuum with a stream of dry air. The alloys were melted in Pyrex tubes under paraffin and quenched from the liquid state, the ω-solid solutions in liquid air and the α-solid solutions in ice water. No loss of mercury or cadmium was observed during the preparation and the synthetic compositions given in Table I are, therefore, to be taken as representative of the final compositions.

It became apparent soon after the beginning of the work that drastic deformation followed by prolonged annealing was necessary, especially for the ω-solid solution, to develop a structure crystalline enough to give sufficient diffraction lines for an analysis of structure. Each alloy bar (0.75cm. square) was therefore hammered on an anvil into a nail shaped piece, 0.30 cm. in diameter at the top, tapering to a point at the bottom. These pieces were annealed in a high temperature thermostat[15] and were subsequently treated as noted in Table I.

The powder method of analysis was used, with the "X-Ray Diffraction Apparatus" supplied by the General Electric Company. Early attempts to obtain spectra from wires were unsuccessful because of the high opacity of the alloys. Later experiments on alloy foil were abandoned when it was found an easy matter to obtain filings of the alloys sufficiently fine to pass a 200-mesh sieve. The powdered alloy mixed with finely ground

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[13] This is generally true of terminal solid solutions, with the exception of iron-carbon and manganese-carbon; see G. L. Clark, "Applied X-Rays," McGraw-Hill Book Company, New York, 1927, p. 204.

[14] Most of the alloys were stock alloys from another investigation (T. W. Richards and C. E. Teeter, Jr., unpublished research). The author wishes to thank Dr. C. E. Teeter, Jr., for his kindness in making them available for this work.

[15] Similar to that designed by J. H. Haughton and D. Hanson, *J. Inst. Metals*, No. 2, **18**, 173 (1917), except that the low temperature bulb was eliminated entirely. A constancy in temperature of 2 or 3 degrees up to 650 degrees was attainable.

TABLE I

TREATMENT OF ALLOYS

A = annealed; CD = cold drawn into wire; H = hammered; FSM = filed, sieved and mixed with flour.

Composition (weight % cadmium)	Treatment
23.0	H; A 48 hrs. 60°; FSM; A 72 hrs. 60–70°
27.3	H; A 36 hrs. 70°; CD; FSM; A 72 hrs. 70°
33.8	H; FSM; A 96 hrs. 100–104°
40.0	H; A 48 hrs. 120°; CD; A 72 hrs. 120°; FSM; A 72 hrs. 120°
47.1	H; A 72 hrs. 140°; CD; FSM; A 12 hrs. 140°
50.0	H; A 48 hrs. 150°; CD; FSM; A 12 hrs. 140°
60.1	H; A 48 hrs. 170°; FSM; A 72 hrs. 170°
73.0	H; A 48 hrs. 210°; FSM; A 48 hrs. 210°
80.0	H; A 48 hrs. 230°; CD; A 18 hrs. 225°; FSM; A 72 hrs. 220°
90.0	H; A 72 hrs. 260°; FSM; A 72 hrs. 260°
100.0	FSM

flour as a diluent,[16] and packed into thin-walled glass (Pyrex) tubes of inside diameter 0.5 mm. (approximately), gave the most satisfactory films. Half the length of each tube was devoted to the alloy powder, and the other half to a 1:1.7 mixture of twice recrystallized sodium chloride and flour.

Each film thus had the standard sodium chloride spectrum alongside the alloy spectrum. A film calibration was calculated from the measured positions of the sodium chloride lines[17] and applied to the lines measured for the alloy. All of the measurements given in Table II are so corrected. The time of exposure was usually twenty-four hours, with 17–18 milliamperes passing through the X-ray tube.

Experimental Results

The measurements obtained from the films are given in Table II. The spectra obtained for the ω-solid solution were much less sharp than those for the α-solid solution, and also less complete, as shown by Table II. Film 35 was probably the best in the ω-field. Film 36 was very poor, showing only scattered spots, with no fully developed lines. Film 40 was poor, with all lines diffused and striated except the one at 0.941° Å., which was sharp. Film 45 was poor.

It is clear from the data in Table II that the spectra for all compositions in the ω-field are identical, not only in type but, within the error of measurement, in dimension also. Although the corresponding lines on the different films often appear to differ slightly in position, there is no progressive variation in position with alloy composition. In order to arrive at a series of values for the spectral lines best representative of the alloys

[16] The table of dilutions proposed by W. P. Davey, Gen. Elec. Rev., **28**, 589 (1925), was used in calculating the proportions of alloy powder and flour.

[17] Davey, Gen. Elec. Rev., **29**, 121 (1926).

TABLE II

COMPOSITIONS IN WEIGHT PER CENT. OF CADMIUM

Composition of alloy	23.0		27.3	33.8	40.0		47.1	50.0		60.1		73.0		80.0	90.0		100.0
Film number	34	35	44	40	36	45	47	43	30	37	20	19	38	42	22	46	48
	2.80	2.79	2.81	2.81	2.82	2.80	2.78	2.77	2.77	2.85	2.83	2.81	2.83	2.81	2.81	2.81	2.82
	2.33	2.32	2.33	2.32	2.34	2.33	2.32	2.33	2.33	2.59	2.58	2.59	2.59	2.59	2.60	2.57	2.59
	1.977	1.970	1.97	1.99	2.01	1.98	1.961	1.96	1.96	2.35	2.34	2.33	2.35	2.34	2.36	(2.277?)	2.33
	1.498	1.498	1.502	1.512	...	1.501	1.483	1.492	1.494	1.915	1.904	1.895	1.910	1.894	1.91	1.90	1.892
	...	1.441	1.436	1.433	...	1.444	1.437	...	...	1.526	1.529	1.520	1.523	1.513	1.51	1.519	1.514
	...	1.389	...	...	...	1.384	...	...	...	1.480	1.486	1.485	1.481	1.482	1.485	1.490	1.485
	1.280	1.280	1.282	1.271	1.27	1.275	1.276	1.278	1.285	...	...	...	...	...	(1.400?)	...	(1.398?)
	...	1.241	...	...	...	...	...	...	1.235	1.316	1.316	1.314	1.316	...	1.313	1.316	1.308
	1.194	1.197	...	...	...	...	...	...	1.190	1.254	1.261	1.256	1.254	1.254	1.258	1.258	1.254
	1.162	1.162	1.159	1.153	1.158	...	1.164	1.160	1.160	...	...	...	(1.173?)	...	...	1.176	1.173
	1.020	1.020	1.028	...	...	...	...	...	...	1.060	1.068	1.058	1.058	1.060	1.057	1.062	1.059
	...	1.000	...	...	...	...	(1.000?)	...	...	1.028	...	1.026	...	1.027	1.026	...	1.024
	0.941	0.941	...	0.941	...	...	0.941	0.939	0.937	0.956	0.955	0.957	0.958	0.954	0.957	0.963	0.956
	...	.935	0.931	...	...	...	...	...	...	...	...	.862	.861	.861	.863	.862	.863
	...	.839	...	...	...	...	.850	.841	.844	...	...	.819	.821	.820	.820	.820	.821
	...	...	...	...	...	...	...	...	.773	...	...	...	...	.719	...	...	...
	...	...	...	...	...	...	...	...	...	...	...	...	...	.708	...	.709	...

investigated in the ω-field, the most sharply defined lines from the best films were averaged. These are given in Table III.

TABLE III

THE ω-SOLID SOLUTION

d Average from best films	Miller indices	d Theoretical spacings	Estimated intensities	Number of coöperating planes
2.785	100(2)	2.78	50	2
2.327	111	2.33	75	4
1.966	110(2)	1.965	12	2
1.495	131	1.500	42	8
1.438	001(2)	1.438	2	1
1.389	100(4)	1.390	3	2
1.281	101(2)	1.278	8	4
1.239	120(2)	1.239	trace	2
1.194	331	1.191	trace	4
1.161	111(2)	1.161	3	4
1.020	151	1.019	trace	8
1.000	201(2)	.994	trace	4
0.941	110(4)	.939	trace	2
...	121	.934	1	8
(.844)	113	...	trace	4

The interplanar spacings observed correspond very closely to those required by either the face-centered tetragonal lattice of axial ratio 0.520 or the body-centered tetragonal lattice of axial ratio 0.740. These two lattices are equivalent and alternative.[18] Table III also gives the theoretical spacings as measured from the graph of Hull and Davey[19] for the face-centered tetragonal lattice of axial ratio 0.520. The intensities are averages taken from estimations on films numbers 42, 47, 44, 34, 30 and 35. The dimensions for the unit face-centered tetragonal prism are $a_0 = 5.570$ Å., $c_0 = 2.896$ Å., or for the unit body-centered tetragonal prism are $a_0 = 3.932$ Å., $c_0 = 2.910$ Å. The two values for c_0 should be equal. The difference originates in the error in the establishment of the correct axial ratios and in the absolute values of the lines chosen to give a_0.

The assumption of simple substitution in the ω-solid solution may be tested by a comparison of the calculated and the observed densities. Table IV gives the densities for a series of compositions calculated on the basis of a face-centered tetragonal lattice of axial ratio 0.520, which has four atoms in the unit cell. These densities are compared with densities obtained from the density-composition curve determined by Maey.[20]

[18] An inspection of tetragonal symmetry shows that any face-centered tetragonal lattice is equivalent to a body-centered tetragonal lattice of axial ratio $\sqrt{2}$ times the axial ratio of the former.

[19] Hull and Davey, *Phys. Rev.*, **17**, 569 (1921).

[20] Maey, *Z. physik. Chem.*, **50**, 200 (1905).

and the agreement is found to be very good, indicating that the assumption of simple substitution is valid.

TABLE IV

DENSITY OF CADMIUM-MERCURY ALLOYS

Composition by weight, % cadmium	Calcd. density	Observed density (Maey)
0.0	14.72	(14.6–14.7)
23.0	12.48	12.43
30.0	11.93	11.96
40.0	11.21	11.25
50.0	10.58	10.72

The density for pure mercury calculated on the assumption of a face-centered tetragonal lattice of axial ratio 0.520 is 14.72. It is interesting that an extrapolation on Maey's curve to the mercury axis indicates a density of solid mercury at room temperature between 14.6 and 14.7. The atomic volume calculated from a density of 14.72 is 13.63, as compared with 13.01 for pure cadmium. These atomic volumes are close, in conformity with the extensive solid solution formation observed. The density calculated from the data of McKeehan and Cioffi[21] for a temperature of —115° is 13.97, and the corresponding atomic volume is 14.36. If no solid-solid transitions are assumed, the effect of rising temperature should be to decrease the density and to increase the atomic volume. At room temperature, therefore, the density calculated from the data of McKeehan and Cioffi is much lower than that obtained by an extrapolation of Maey's density curve, and the atomic volume is much further from the atomic volume of cadmium than that calculated from the structure data on the ω-solid solution, a condition not favorable to the formation of extensive solid solution.

It seems possible, therefore, that the crystal structure of pure mercury at its melting point is the same as that observed for the mercury-rich cadmium-mercury solid solutions. If an actual determination of the crystal structure of mercury at its melting point should show a different lattice, the composition-temperature diagram of the system as proposed by Bijl would have to be modified. At present the weight of evidence seems to be against such a modification.

The 60.1% cadmium alloy comes in the heterogeneous field, α + ω, but shows only the lattice of the α-solid solution. The 73% cadmium alloy is in the α-field near the limit of solid solubility. No change in the lattice type or in the lattice dimensions are evident from the spectral lines given in Table I. A change in dimension would be manifested by a progressive change in the positions of the spectral lines with change in composition. No such displacement may be found in the measurements

[21] Ref. 10, p. 445.

given in Table II.   The average positions of the various spectral lines calculated from films 19, 38, 42, 22 and 46 give a spectrum which agrees very closely with that obtained from film 48 for pure cadmium, both of which fit closely to Hull and Davey's graph for the triangular, close-packed lattice of axial ratio 1.89.   The side of the unit triangle is 2.980 Å., as found by Hull.[9a]   The density calculated for the 73% cadmium alloy is 9.72 as compared with the value 9.70 derived from Maey's data, indicating simple substitution in the α-solid solution.

There is no indication in the present work of the existence of any inter-metallic compounds at room temperature.   The composition range from 0 to 23% cadmium, however, has not been investigated, though if the structure of mercury at its melting point should prove to be similar to that observed for the ω-solid solution, the possibility for compound formation in this composition range would be very small.   Nor does the present work afford any basis for the frequent postulation of intermetallic compounds in the liquid alloys, which if present in the liquid state should also be manifested in the solid state, since temperature rise usually has the effect of dissociation. So far as the author is aware there is 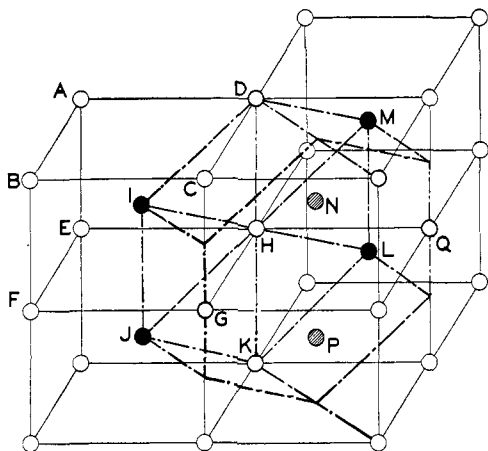no evidence of any intermetallic compound existent in the liquid state which is not also existent in the solid state.[22]

Fig. 2.

Although the similar atomic volumes of mercury and cadmium doubt-less favor the extensive solid solution formation observed, it is difficult to see why two lattices so different as the face-centered tetragonal and the close-packed triangular should show such an extensive isomorphism. The tetragonal lattices pictured in the usual way, with lines drawn parallel to the tetragonal coördinates, do not suggest the presence of any hexagonal arrangement of atoms.   It should be distinctly emphasized, however, that these lines are purely artificial, and that important orientations exist in many lattices which they are insufficient to depict and in fact frequently mask.

It may be shown, however, that in the ω-solid solution there is actually an hexagonal arrangement closely approximating the unit hexagonal

[22] Cf. the work of Bornemann, *et al.*, on the electrical conductivity of liquid alloys, *Metallurgie*, **7**, 396, 655, 730, 755 (1910); **9**, 473 (1912); *Ferrum*, **11**, 276, 289, 330 (1913).

prism in the α-solid solution.   Fig. 2 represents six unit cells of the body-centered tetragonal lattice exhibited by the ω-solid solution.   Cell ABCD-EFGH is such a unit cell.   Let us consider, however, atoms DIJKLM, which lie in a plane and form a hexagon.   Geometrically it may be shown that for the lattice of the ω-solid solution DI = DM = JK = KL = 3.139 Å., and that IJ = ML = 2.910 Å.; angle IDM = angle JKL = 125°46', and angle DML = angle MLK = angle KJI = angle JID = 117°7'.   This hexagon is therefore nearly equilateral.   It may also be shown that it is the basal hexagon of an hexagonal prism, half of which is indicated in Fig. 2 by dotted lines.   Fig. 3 represents the fully developed prism. The similarity between this and the ordinary close-packed hexagonal prism is striking, and would be complete if DIJKLM were a perfect hexagon and if atoms G, N, Q and P were displaced to the left in their plane so that atom P were brought into the center of the triangular prism of which JKH is a basal plane.   The same is true of the other atoms in the GNQP plane.   This deformed hexagonal prism is repeated throughout the lattice and serves completely to define it, that is, it is a unit cell.   The density for the 40% cadmium alloy calculated from it agrees with that

Fig. 3.

given in Table IV.   The basal hexagon will be equilateral when the axial ratio for the body-centered tetragonal lattice is 0.816.
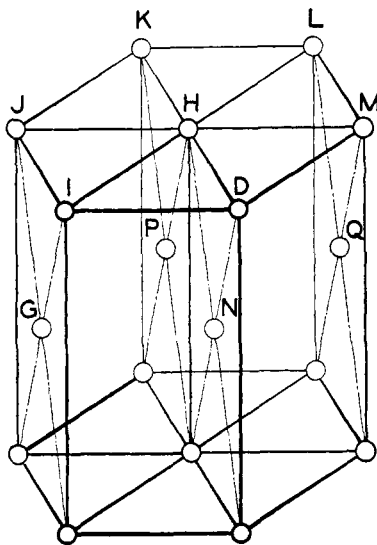
The dimensions of the unit cell are a_0 = 3.139 Å., a_0' = 2.910 Å., c_0 = 5.561 Å., whereas the dimensions of the unit hexagonal cadmium prism are a_0 = 2.980 Å. and c_0 = 5.632 Å.   The α- and the ω-solid solutions are therefore very similar both in lattice dimensions and in atomic volume, thus satisfying two of the conditions necessary for solid solutions formation.

The author wishes to acknowledge his indebtedness to Professor Albert Sauveur, whose kindness made available the apparatus used in this work.

Summary

The crystal structure of the system cadmium-mercury has been investigated by a study of the diffraction of X-rays.   It has been shown that there are at least two, and probably only two, types of lattice in the system, a face-centered tetragonal lattice of axial ratio 0.520 (or a body-centered lattice of axial ratio 0.740) found in alloys of from 23 to 50%

cadmium by weight, and a triangular close-packed lattice of axial ratio 1.89, found in alloys of from 60 to 100% cadmium by weight.

The conflicting data on the crystal structure of mercury are discussed and it is suggested that the present work indirectly indicates a face-centered (or body-centered) tetragonal structure. It is pointed out that the frequent assumption of intermetallic compounds in this system receives no support from the present crystal structure data.

The isomorphism of cadmium and the face-centered tetragonal component (which may be mercury) is favored by similar atomic volumes and also by the presence in the face-centered tetragonal lattice of an atom arrangement closely approximating the unit hexagonal prism of cadmium both in lattice type and in the unit cell dimensions.

A NEW METHOD FOR THE STUDY OF CATAPHORETIC PROTEIN MOBILITY[1]

BY HAROLD A. ABRAMSON

It has previously been shown[2] that the cataphoretic migration of inert particles suspended in gelatin gels represents the movements of the micellae of the gelatin. That is, there seemed to be a rapid formation of a sheath of the gel about the particle which changed its sign at the iso-electric point of the protein. The study of the migration of the particle, therefore, afforded a simple means of studying the cataphoresis of the gelatin micellae themselves. This has led to the study of the influence of proteins on the migration of quartz particles in sols of low concentration. A concentration of 1×10^{-7} already lowers ζ, the electrokinetic potential, appreciably. Between concentrations of about 1.10^{-5} and 1.10^{-4} g. per liter the maximum effect of the protein is reached and the particles behave like gelatin. Egg albumin shows a similar influence.

A suspension of quartz particles in a dilute solution of the proteins mentioned (within limits of dilution) gives the absolute electrophoretic migration of the protein micellae. The complete data and theory of these phenomena will be presented elsewhere.[3] Svedberg and Tiselius[4] have used a rather elaborate method to determine the mobility of egg albumin. It seemed that a comparison of their method with ours was of interest.

[1] The researches here reported were made in part during a tenure of a Medical Fellowship of the National Research Council.

[2] Freundlich and Abramson, *Z. physik. Chem.*, **128**, 25 (1927).

[3] *Z. physik. Chem.*, in press.

[4] Svedberg and Tiselius, THIS JOURNAL, **48**, 2272 (1926).