Anonyme. The Journal of physical chemistry. Published at Cornell university [3puis3 Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1910.

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THE CONDENSATION OF WATER BY ELECTROLYTES[1]

BY F. K. CAMERON AND W. O. ROBINSON

In aqueous solutions the sum of the volumes of the components is seldom the same as the volume of the resulting solution. The case of cane sugar and water is a well-known exception to this generalization, following closely the law of mixtures. But in dealing with dilute solutions it frequently happens that the weight of water, obtained by subtracting the weight of salt from the weight of the solution, is greater than that which could have occupied the same volume as the solution under the same pressure and temperature. Since the assumption of a negative volume for the salt is absurd, it must be concluded that the water has been condensed. That the salt has also been condensed is reasonably certain, as shown by experiments with other substances. Consider, for instance, two mixtures of alcohol and water, one containing a proportionally small amount of alcohol and the other a large amount of alcohol. There is a marked condensation in each case. It is plain that both components of the solution have been contracted.

It is difficult to apportion the total condensation between the solvent and the solute. However, if the solutions be very dilute, the magnitudes of the condensation of the same solvent by different solutes may be determined with sufficient accuracy for purposes of comparison by assuming that the volume of the salt in the solution differs from the volume in the pure anhydrous state by a quantity negligible in comparison with the total condensation of the solution.

This comparative condensation of the solvent by different solutes is believed to have an importance in the study of the properties of water and its relations to solids in contact with it, as for instance, in the extreme cases where on the one hand, finely divided solids, such as clays or silts, are sus-

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[1] Published by permission of the Secretary of Agriculture.

pended in the water, and on the other hand, all the water is distributed over the surface of the solids, as in the case of soil below the optimum water content.[1]

Michel and Kraft,[2] in an attempt to use the determination of specific gravities of simple salt solutions as a method of analysis, stated that the specific gravity of a solution was proportional to the concentration. Kremers[3] showed that the conclusion of Michel and Kraft was not strictly true, for salt solutions showed a marked contraction when mixed with water. That is, the volume of the resulting solution was always less than the sum of the volumes of the salt solution and the water with which it was mixed.

Gerlach[4] showed that there were changes in volume departing from the law of mixtures, where aqueous solutions, containing reacting weights, were mixed. For instance, in the neutralization of solutions of potassium hydroxide with hydrochloric acid there was a large expansion in volume. Tissier[5] developed this idea further and added more experimental data confirming the work of Gerlach. He found that there was a contraction in volume when ammonia solutions were neutralized by an acid, whereas there occurred an expansion if a fixed alkaline hydroxide were used. When solutions of aluminum sulphate and potassium sulphate were mixed there was no change in volume. J. Regnauld[6] attempted to explain why ammonia solutions and solutions of the fixed alkalis showed opposite volume changes when mixed with acids. He considered that the hydrates of the fixed alkalis and acids were true compounds and that when these compounds neutralized one another the water was set free, occupying a greater volume as water molecules than when in combination; ammonia, however, did not form

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[1] Cameron and Gallagher: Bull. No. 50, Bureau of Soils, U. S. Dept. Agriculture (1907).

[2] Ann. Chim. Phys. (3), 41, 471 (1854).

[3] Pogg. Ann., 95, 110; 96, 39 (1855).

[4] Jahresberichte, 44 (1859).

[5] Ibid., 45 (1859).

[6] Ibid., 69 (1865).

true hydrates with water. Ostwald[1] made many measurements on the changes in volume observed when various bases and acids were neutralized, for this purpose calculating the relative affinities of acids for the bases, sodium, potassium, and ammonium.

Valson[2] calculated the specific gravity of salt solutions of certain concentrations by the use of stoichiometrical relations. The difference between the specific gravity of solutions of different metals in combination with the same acid was found to be constant for the same concentration. Thus, knowing the specific gravity of a normal solution of ammonium chloride it was only necessary to add a characteristic number for potassium to obtain the specific gravity of a normal solution of potassium chloride. Valson called these numbers moduli.

From the amount of condensation observed with calcium chloride solutions, Charpy[3] concluded that the dissolved calcium chloride was combined with six molecules of water.

Schneider[4] studied the densities of crystalline hydrates and their aqueous solutions. He calculated that the average density of a water of crystallization was 1.2.

Nicol[5] measured the molecular volumes in solution of a number of salts at concentrations of 1, 2 and 3 mols of salt to 100 mols water. By the molecular volume in solution is meant the volume of water displaced by a gram molecular weight of the solute per liter of solution. For the concentrations above mentioned Nicol found that the molecular volumes of the radicals Cl, SO_4, NO_3, ClO_3 and OH were the same, regardless of the base with which they were combined. The molecular volume of a salt increases with the concentration. Water of crystallization exerts no appreciable effect upon the molecular volume. That is, the molecular volume of the

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[1] Jour. prakt. Chem. (2), 18, 353 (1878).

[2] Comptes rendus, 73, 441 (1874).

[3] Ibid , 109, 299 (1889).

[4] Sitzungsber. Akad. Wiss. Wien, 99, May, 1890. Monatsheft, 11, 1890.

[5] Phil. Mag. [5], 16, 121 (1883): [5], 18, 179 (1885).

SO_4 radical is the same in solutions of $Na_2SO_4.10H_2O$ as in K_2SO_4, or the water of crystallization has the same density as water of solution. As a result of experiments on phosphoric acid and disodium phosphate, the author concludes that the water of constitution is more dense than the water of solution.

According to Mendeléjeff,[1] there is a combination between the solute and the solvent when solution of a solid in a liquid takes place. Were solubility a purely physical effect it is probable that an expansion would take place, for when a solid goes into a liquid state or a liquid goes into a gaseous state, there is an expansion of volume. Since a contraction and not an expansion takes place usually during solubility, it follows that the phenomenon is probably a chemical one. It is true that the volume change is small, but it must be borne in mind that solids and liquids have small coefficients of compressibility. Mendelejeff considered that hydrates were formed in solution.

Traube[2] has collected and examined critically a large amount of data on specific gravities. From the specific gravities he has calculated the molecular volumes in solution. These values decrease with dilution, and for a few salt solutions there are obtained negative values. Traube found that, in general, salts which crystallized with water of crystallization showed a greater contraction than did salts crystallizing without water. He considered that pure water forms a complex molecule and that this is broken down by other molecules or ions to form water of crystallization or hydration which occupies a smaller space.

Thomsen[3] has shown that the heat capacity of electrolytes in water solution diminishes with the dilution, and in dilute solutions it has a negative value. It is obvious that a part of the water, at least, has been so changed that it has not retained its pristine heat capacity.

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[1] Principles of Chemistry, 1, 86 (1891). Longmans, Green & Co.

[2] Zeit. anorg. Chem., 3, 11 (1893).

[3] Thermochem. Unters., 1, 53 (1882).

Tammann[1] has shown that a salt solution has many analogies to the pure solvent under external pressure. Röntgen and Schneider[2] found salt solutions to be less compressible than pure water. They found that certain elements and radicals had a constant effect on the coefficient of compressibility of the salt solution. The recent work of Jones and his associates[3] and the transference experiments of Washburn,[4] and the investigations of Kahlenberg[5] on osmotic pressures, indicate that salts in aqueous solution are combined with water,[6] or that the character of the water has been materially altered by the presence of the solutes.

The data contained in the researches cited above, while sufficing to show that a contraction or condensation of water takes place when an electrolyte is dissolved, are very seldom, however, of such a character as to permit comparisons in any satisfactory way. It has been deemed desirable, therefore, to obtain further experimental data, with this purpose directly in view.

While it is customary to think of condensations in terms of volume changes, this point of view has serious disadvantages for the present purposes, in that the volume changes are relatively small, and small volume changes can not be measured with any high degree of accuracy. On the other hand, condensation in terms of mass changes can be computed from specific gravity determinations, which can be made comparatively readily and with great precision to at least seven significant figures. To this end, condensation of water produced by the introduction and solution of an electrolyte is here defined as the difference in weight of the water in a solution over the weight of pure water occupying the same

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[1] Uber die Beziehung zwischen den inneren Kräften und Eigenschaften der Lösungen. Hamburg and Leipzig (1907).

[2] Wied. Ann., 29, 165 (1886).

[3] Monograph Carnegie Inst. Pub. No. 60 (1907).

[4] Tech. Quart., 21, No. 2, June, 1908.

[5] Jour. Phys. Chem., 10, 141 (1906).

[6] See E. W. Washburn, "Hydrates in Solution, Tech." Quart., 21, No. 4, December (1908).

volume. Let us consider a volume V of solution, with a density D, containing s grams of solute. Then, $VD - s$ is the weight of water in the solution. The volume actually occupied by this water is, $V - v$, where v is the volume of the solute. If D_p be the density of pure water, then condensation, C, is given by the formula

$$C = VD - s - D_p(V - v).$$

If the condensation be determined for a standard volume, V becomes unity; and taking the density of pure water at the temperature of the experiments as unity, the formula is

$$C = D - s - (1 - v).$$

If d be the density of the solute, then, substituting for v, we get

$$C = D - s - \left(1 - \frac{s}{d}\right).$$

Assuming that no material error is introduced by using the value of d obtained from measurements with the dry solid, this formula contains only quantities which can be determined readily with a high degree of precision. In the present investigation, the determinations were made for a liter at 25° C with a number of acids, bases, and certain of their salts, which have a special interest in affecting aqueous suspensions, or the "crumb structure" of agricultural soils.

The picnometers used in this research were of the Sprengel type, of 100 cc capacity. The external opening of the capillaries were very small. Weighings were made against a tare at frequent intervals until the weight had become constant. As the weights of the solutions were all compared to water of equal volume and the differences in density were but slight, no vacuum corrections were necessary. In the calibration of the picnometers it was not difficult to obtain duplicates varying not more than two or three units in the seventh decimal place.

The temperature was carefully regulated at 25° by a thermometer standardized by the Bureau of Standards, and independently by another thermometer standardized by determining the reading for the inversion point of Glauber's salt to anhydrous sodium sulphate (32.38° hydrogen scale), the 25° mark being estimated by breaking off a short thread of mercury and calibrating the bore of the capillary. No difference between the two temperatures could be observed with a Beckmann thermometer reading to 0.01° C.

The bath was regulated to within 0.005° C. The method of procedure was as follows. The picnometers were filled with the solution to be measured at a temperature somewhat lower than 25°. Fine rubber tubes, filled with the solution, were then drawn over the capillaries and the whole immersed in the bath with the ends of the rubber tubes coming out of the water. It was found that the temperature of the solution became constant within half an hour. The rubber tubes were then removed, allowing only the capillaries to come above the surface of the water. The drops were carefully flicked off, the stoppers put on, the whole apparatus was carefully wiped, and the picnometer hung in the balance case.

The water used in this research was distilled from a solution of alkaline permanganate through a block-tin condenser and then redistilled immediately before use. Standing in glass a few days increased sensibly the specific gravity. The air was sucked out of the solutions by connecting the picnometer with the vacuum pump. Kahlbaum's dry chemicals and Baker & Adamson's acids were used without further purification. A solution of the material to be investigated was made up stronger than required and analyzed carefully. From these stock solutions there were prepared by dilution the solutions actually employed in the measurements.

The tables give the observed and calculated data, and are self-explanatory. It must be borne in mind that no claim is made of the rigid validity of the calculations. The formula used, page 6, involves certain assumptions that cannot be proven. For instance, it presupposes that the volume of the salt in solution has not changed from that which it occupied in the solid state; and also that the "combined" water together with the material, should such exist, fills the same space as the material itself.

The examination of the table shows but few generalities.

TABLE I—ACIDS

Acid	Concentration	Density of solution 25°/25°	Density of acid	Volume of acid	H_2O cond. per liter	H_2O cond. per gm. acid	Ratio of mols H_2O condensed to mols acid
H_2SO_4	N/10	1.003420	1.94	2.665	1.181	0.443	2.4
	N/25	1.001410		1.006	0.514	0.485	2.6
	N/50	1.000719		0.533	0.291	0.546	2.9
	N/100	1.000402		0.267	0.179	0.671	3.6
	N/200	1.000210		0.133	0.098	0.73	3.9
HCl	N/10	1.001813	1.46	2.498	0.665	0.266	0.54
	N/25	1.000709		1.000	0.251	0.250	0.50
	N/50	1.000338		0.497	0.107	0.215	0.43
	N/100	1.000151		0.250	0.036	0.144	0.29
	N/200	1.000065		0.125	0.008	0.064	0.13
HNO_3	N/10	1.003366	1.52	4.199	1.183	0.282	0.99
	N/25	1.001330		1.658	0.468	0.281	0.99
	N/50	1.000654		0.829	0.223	0.268	0.94
	N/100	1.000322		0.414	0.104	0.251	0.88
	N/200	1.000145		0.207	0.037	0.18	0.63
H_3PO_4	N/10	1.002701	1.88	1.741	1.070	0.615	3.3
	N/25	1.001100[1]		0.700	0.490	0.700	3.8
	N/50	1.000572		0.349	0.256	0.731	3.9
	N/100	1.000300		0.175	0.148	0.846	4.6
	N/200	1.000151		0.087	0.074	0.851	4.6
CH_3COOH	N/10	1.000860	1.04	5.772	0.633	0.109	0.36
	N/25	1.000350		2.309	0.258	0.112	0.37
	N/50	1.000184		1.154	0.137	0.119	0.40
	N/100	1.000075		0.577	0.052	0.090	0.30
	N/200	1.000050		0.288	0.038	0.131	0.44

There is little parallelism between the chemical nature of the solute (*i. e.*, acids, bases, or salt) and the relative power to condense water. It may be seen that those substances which

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[1] Interpolated.

show large heats of solution or have a tendency to crystallize with water of crystallization show relatively a higher condensing power.

TABLE II—ALKALIS

Alkali	Concentration	Density of solution 25°/25°	Density of base	Vol. of alkali	H_2O cond. per liter	H_2O cond. per gm. alkali	Ratio of mols H_2O condensed to mols alkali
NaOH	N/10	1.004547	2.08	1.924	2.467	0.796	2.7
	N/25	1.001815		0.770	0.985	0.794	2.7
	N/50	1.000900		0.384	0.484	0.780	2.6
	N/100	1.000448		0.197	0.245	0.788	2.6
	N/200	1.000207		0.099	0.107	0.700	2.4
KOH	N/10	1.005155	2.00	2.805	2.350	0.499	2.6
	N/25	1.002076		1.122	0.954	0.507	2.7
	N/50	1.001048		0.561	0.487	0.516	2.7
	N/100	1.000525		0.281	0.245	0.521	2.7
	N/200	1.000265		0.140	0.124	0.527	2.7
NH_4OH	N/10	0.999269	0.600	4.003	0.870	0.362	1.0
	N/25	0.999699		1.602	0.349	0.363	1.0
	N/50	0.999845[1]		0.800	0.165	0.348	1.0
	N/100	0.999902		0.400	0.062	0.28	0.8
	N/200	0.999956		0.200	0.036	0.30	0.8
$Ca(OH)_2$	—	—	(3.30 CaO)	—	—	—	—
	N/25	1.001948		0.356	1.182	1.006	3.1
	N/50	1.000983		0.178	0.602	1.073	3.3
	N/100	1.000484		0.089	0.293	1.046	3.3
	N/200	1.000246		0.045	0.151	1.08	3.4
			(2.08 $Ca(OH)_2$)	0.716	1.178		
				0.356	0.598		
				0.178	0.290		
				0.089	0.150		

It will be noticed that this specific condensing power, in most cases, varies with the concentration, generally increasing with the dilution. Hydrochloric and nitric acids

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[1] Interpolated.

are exceptions, and with these solutes there is an increase of condensation with increase of concentration. For more concentrated solutions the relative amount of water condensed decreases with the concentration, the condensation passing through a maximum value. This maximum occurs, commonly, with solutions of about 1 percent. It is evident, that this contraction is the resultant of two forces at least.

TABLE III—SALTS

Salt	Concentration	Density of solution 25°/25°	Density of salt	Vol. of salt	H_2O cond. per liter	H_2O cond. per gm. salt	Ratio of mols H_2O to mol salt
$CaSO_4$	N/50	1.001317	2.95	0.533	0.288	0.184	0.69
	N/100	1.000666		0.265	0.150	0.194	0.72
	N/200	1.000326		0.133	0.070	0.183	0.69
$CaCl_2$	N/10	1.004609	2.22	2.477	1.584	0.286	1.7
	N/25	1.001879		0.996	0.675	0.307	1.9
	N/50	1.000944		0.498	0.342	0.311	1.9
	N/100	1.000501		0.249	0.200	0.363	2.2
	N/200	1.000277		0.125	0.127	0.462	2.8
Na_2HPO_4	N/10	1.004615	2.22	2.133	2.012	0.425	3.4
	N/25	1.001861		0.853	0.820	0.433	3.5
	N/50	1.000937		0.426	0.417	0.440	3.5
	N/100	1.000464		0.213	0.204	0.432	3.5
	N/200	1.000225		0.107	0.095	0.401	3.2
Na_2CO_3	N/10	1.005528	2.48	2.138	2.361	0.444	2.6
	N/25	1.002225		0.856	0.959	0.454	2.7
	N/50	1.001124		0.428	0.495	0.466	2.8
	N/100	1.000551		0.214	0.234	0.441	2.6
	N/200	1.000275		0.107	0.117	0.441	2.6

It might be thought at first sight that the maximum point was due to the condensation of the solute becoming appreciable in comparison with the condensation of the solvent, but this is impossible, considering their relative masses, and it must be admitted that a satisfactory explanation of the observed phenomena is not yet at hand.

Investigation of the properties of aqueous solutions have in the past been made mainly from the point of view that the variation in properties of the solutions were due directly to the properties of the solute. This point of view has appeared to be wanting in certain investigations, as in the study of flocculation of suspended solids, crumbing of soils, movements of film water, surface tensions, etc., and it has been thought possible to get further light on these phenomena by considering them as due to changes in the water itself, which changes were induced by the presence of electrolytes. Although the data given above do not encourage greatly the idea that this point of view will prove profitable, the paucity of experimental data suitable for comparison does not justify a positive statement, and further work in this direction will be presented as opportunity offers.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

THE PHOTOGRAPHIC PLATE. I

BY WILDER D. BANCROFT

THE EMULSION. PART I

While investigating the electrochemical action of light, it became necessary for me to work out a theory of solarization and incidentally to study the peculiarities of the photographic plate. These latter are for the most part more chemical than electrolytic in nature and it therefore seems wisest to publish the photographic studies as a separate series under the title of "The Photographic Plate." So far as these things can be planned in advance I hope to treat the subject under the general headings: the emulsion; the latent image; the developer; the developed image; fog; intensifiers and reducers; photochromy.

We will begin by a quotation from Eder:[1]

"If silver bromide is formed in a suitable way in an aqueous solution of gelatine, we have first what appears to be an almost clear, slightly opalescent liquid which later becomes milky and which contains the silver bromide particles in so fine a state of suspension that the liquid will pass through filter paper or even through several thicknesses of wash-leather without any of the silver bromide being held back. This mixture of finely divided, suspended silver bromide in gelatine is called a silver bromide gelatine emulsion. The photographic properties, the light-sensitiveness, the fineness of the grain, and the transparency of the emulsion depend on the molecular division of the silver bromide and therefore on the method of preparation.

"If one mixes silver nitrate and potassium bromide solutions in presence of gelatine or other similar substances, such as albumen, starch, Agar-Agar, gum arabic, etc., the precipitation of silver bromide takes place slowly. At first there is no precipitation of silver bromide. The liquid is only

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 22, 23 (1902).

slightly opalescent and is quite transparent in thin films.[1] If the temperature is kept so low while the solutions are being mixed, that the gelatine is just liquid (about 30° C), the emulsion remains apparently unchanged for quite a while. After a quarter to a half of an hour, it becomes gradually less transparent and there is a gradual milky clouding owing to the particles of silver bromide becoming ever larger.

"From the very slight clouding in some mixtures of silver nitrate, potassium bromide and gelatine, one might easily think that the silver salt does not react at once with the bromide but that both co-exist for a while as solutions. The gradual clouding looks as though the reaction between silver and bromine had been retarded and was taking place slowly. This assumption was actually made by J. Gaedicke but was disproved by E. Cohen,[2] who determined the specific electrical conductivity of such mixtures and showed that, even in presence of gelatine, silver nitrate and potassium bromide react at once according to the equation

$$AgNO_3 + KBr = KNO_3 + AgBr.$$

"Although quite transparent and only slightly opalescent, when freshly mixed at low temperature, a silver bromide gelatine emulsion contains the theoretical amount of silver bromide, which is present in colloidal solution."

The question as to the other conditions for preparing an emulsion is described by Eder in a later chapter.[3]

"When potassium bromide and silver nitrate are mixed in presence of gelatine, it is customary to have the first salt present in excess. In contact with gelatine, free silver nitrate is much too easily decomposed and when such an emulsion is cooked there is a decomposition which causes fog when the plate is developed. An absolute equivalence of the silver salt and the bromide is theoretically possible; but it is not

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[1] This observation was first made by Monckhoven, Phot. Mittheilungen, 10, 74 (1879), and later by Gaedicke, Phot. Wochenbl., 1890, 413.

[2] Eder's Jahrbuch der Photographie, 9, 103 (1895).

[3] Ibid., 5th Ed., 3, I, 49 (1902).

feasible practically and the bromide is therefore added in excess. . . . What should be the actual ratio of potassium bromide to silver nitrate? As a result of many experiments Eder is in favor of the ratio of five parts of silver nitrate to four parts of potassium bromide (equal to 3.3 parts of ammonium bromide). This means a considerable excess of soluble bromide. This is the same ratio which he recommended as the best in 1880, as the result of experiments made together with Captain Toth. Bennett, and also Wilson, recommended the use of eleven parts silver nitrate to seven parts ammonium bromide; Abney's ratio was 15 : 11 and Burton's 42 : 25.

"From this it appears that Eder used more of the soluble bromide than was then customary. He had the following reasons for this. In the first place when an excess of potassium bromide is used, there is not so much danger of fog in case the emulsion is cooked for a long time or is treated with ammonia. In the second place, ripening by cooking can be carried farther than when there is only a slight excess of bromide. In the third place a very finely divided, extremely satisfactory silver bromide is obtained by dissolving this salt hot in potassium bromide and then causing it to separate either by cooling the solution or by diluting it with a gelatine solution. In the fourth place bad results are less likely to happen when weighings are made carelessly on insensitive balances.

"A long time after Eder's results were published, Abney[1] confirmed the statement that an excess of potassium bromide has a beneficial effect. He showed that a ratio of twenty parts silver nitrate to fifteen parts potassium bromide gave a much more sensitive emulsion (by the boiling method) than the ratio of 20 : 12. The ratio of 20 : 15 is however almost identical with Eder's ratio of 20 : 16. Abney's explanation is that silver bromide is soluble in potassium bromide and crystallizes, on cooling, in yellowish crystals which yield a green, highly sensitive, silver bromide when washed.

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[1] Phot. News, 1881, 198.

"According to Newberry the ratio of 32.5 grams silver nitrate to 28.5 grams potassium bromide is the best when the emulsion is ripened by boiling. With less potassium bromide there is less sensitiveness and a flat emulsion.[1] Debenham[2] takes twice as much potassium bromide as silver nitrate; but that is undoubtedly going too far. When an emulsion contains too large an excess of potassium bromide, it is apt to be flat or even fogged after ripening by cooking."

While it is easier to get a suitable emulsion by precipitating silver bromide in presence of gelatine, it is possible to make an emulsion by shaking the coarse, compact precipitate from an aqueous solution with a warm gelatine solution.[3] This whole question has been discussed at length by Lüppo-Cramer[4] in a paper from which I quote.

"While colloidal solutions change into so-called gels under the influence of electrolytes, there are also many cases known in which the reverse process takes place[5] and the gel is changed back into the liquid hydrosol under the influence of certain substances which do not necessarily act chemically on the gel. This process has already been called peptonization by Graham because it resembles the change of albumen into peptone.

"Graham studied the peptonization of silicic acid, stannic acid, etc., and found that a very small amount of alkali sufficed to liquefy large masses of the gelatinized substances. Thus one part of caustic soda in ten thousand of water was sufficient to liquefy two hundred parts of silicic acid (calculated as dry) in sixty minutes at 100°. Gelatinous stannic acid is also easily liquefied by a small amount even at room temperature. After the alkali has liquefied the gelatinous colloid, it can be separated from it by diffusion into water in a dialyzer. The dissolving of this colloid under these

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[1] Newberry: Eder's Jahrbuch der Photographie, **2**, 469 (1888).
[2] Eder's Jahrbuch der Photographie, **11**, 401 (1897).
[3] Eder's Handbuch der Photographie, 5th Ed., **3**, I, 28 (1902).
[4] Phot. Correspondenz, **44**, 572 (1907).
[5] Cf. Zsigmondy: Zur Erkenntniss der Kolloide, 165 (1905).

circumstances can be considered as analogous to the dissolving of insoluble organic colloids in the case of animal digestion, with the difference that the dissolving liquid is here alkaline and not acid. Liquid silicic acid can be considered as the peptone of gelatinous silicic acid and we may speak of the liquefaction of the latter by a trace of alkali as a peptonization of the jelly. The comparison with albumen is even more close in the cases of the pure jellies of aluminum, iron and titanium oxides as prepared by dialysis because these jellies are peptonized by small amounts of hydrochloric acid.

"Peptonization has also been known for a long time with silver. The colloidal silver obtained by Carey Lea through reduction with ferrous citrate shows clearly however that a definite state of the silver coagulated from the hydrosol is necessary or the silver cannot be peptonized. It is by no means an indifferent matter what electrolyte is used to precipitate the silver from its hydrosol. The sulphates, nitrates and citrates of the alkali metals and of ammonium precipitate a so-called solid hydrosol which can be peptonized, while strong acids, for instance, precipitate at once a gray silver which cannot be converted back into the hydrosol. Just as with silicic acid and other substances, which appear as colloids, so with silver we must distinguish between the ordinary gray silver which is not colloidal and the colloidal hydrosol and gel.[1]

"Lottermoser,[2] to whom we owe our better knowledge of colloidal silver salts, has recently stated[3] that the gel of silver iodide can be converted into the hydrosol, in other words can be peptonized, by treatment with potassium iodide. Lottermoser started with a zero concentration of the solution and always used equal amounts of pure silver iodide gel and of solution. With increasing concentration

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[1] Lottermoser: Anorganische Kolloide, 40 (1901).

[2] Jour. prakt. Chem. (2), 68, 341 (1903); 72, 39 (1905); 73, 374 (1906).

[3] Die Kolloid-Chemie auf der 79ten Versammlung deutscher Naturforscher. Supplementheft zur Zeitschrift für Chemie und Industrie der Kolloide, 4.

of potassium iodide in the solution, at first continually increasing amounts of silver iodide changed into the hydrosol. With an entirely definite concentration however the formation of hydrosol reached a maximum and then decreased to zero as the concentration of the potassium iodide was increased still further. The conditions affecting peptonization have not by any means been entirely cleared up by Lottermoser but he was able to formulate the following general rule. If one adds to an amorphous substance an ion—or a closely allied ion—at a higher concentration than the substance itself can generate in the solution, the substance will be converted back into a hydrosol. The essential condition for the success of this reaction is that the substance shall be in such a state that it is capable of swelling or of a decrease in the molecular complex by peptonization or addition of the ion; in other words it must be in a definite physical state.

"In the course of my experiments on the coloring of silver halides with colloidal silver, I have repeatedly made observations while preparing the halide salts, which are made intelligible by these investigations of Lottermoser. If one precipitates the silver halides from a fairly concentrated solution in presence of an excess of halogen ions, the silver halide precipitates at first without the supernatant liquid appearing cloudy. When the precipitate is washed and the solution becomes more dilute with respect to halogen ions, the wash water clouds and a colloidal solution of silver halide is formed. Silver iodide forms the largest amount of hydrosol and silver chloride the least while silver bromide occupies an intermediate position. If one precipitates the silver halides without an excess of halogen ions being present, there is either no hydrosol formation at all or it takes place to a very limited extent. There is also no formation of hydrosol if precipitation occurs in presence of a very large excess of halogen ions.

"These phenomena occur in an especially interesting form in presence of gelatine. Ten cc of a 10 percent silver nitrate were added to 7.1 cc of a 10 percent potassium bromide solution diluted with 10 cc of water, and the precipitated silver bromide was washed. Then 50 cc of a 10 percent solution of gelatine at 50° and 2 cc of a 10 percent potassium bromide solution were added to the precipitate. After five to ten minutes shaking, the greenish-yellow, coarse, silver bromide was broken up into a completely homogeneous, very fine-grained creamy solution which was nearly pure white in color and which could be filtered through thick flannel without leaving any residue. If the small amount of bromide is omitted in this experiment, the silver bromide remains suspended in larger particles, and there is no surprisingly fine division and no color change. An actual colloidal silver bromide, a silver bromide hydrosol, appears not to be formed under these circumstances, or only to a very limited extent. Under the microscope (oil immersion and about a thousand diameters) there appears a silver bromide grain which corresponds approximately to that of a silver bromide emulsion such as is used for transparencies. An emulsion, made in this way by peptonizing a coarse silver bromide, behaves photographically like a fine-grained emulsion for transparencies. It should be noted especially that such plates can be developed entirely without fog with a metol-soda developer.

"Under similar conditions (equivalent quantity of potassium iodide instead of bromide) silver iodide behaved like silver bromide except that the breaking-down usually took more time, twenty to thirty minutes. On the other hand, silver chloride, formed by precipitation in this way from an aqueous solution, showed no tendency to emulsify in gelatine under the influence of chlorine ions. On the other hand the photo-bromide[1] and the photo-iodide, obtained by coloring

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[1] I have previously stated that, in contrast to silver chloride, silver bromide, when once precipitated, cannot be colored by colloidal silver, Phot. Correspondenz, 44, 290 (1907). Later experiments have shown that silver bromide can be colored very easily provided an excess of bromide is avoided during the precipitation. With silver chloride and with silver iodide a similar precaution is not necessary. As yet there is no explanation for these phenomena which were the cause of the investigations described in the previous chapter. The three silver halides react with colloidal silver to form the photohalides when heated and also when allowed to stand for a long time at ordinary temperature.

silver bromide and silver iodide with colloidal silver, break down in gelatine to fine emulsions under the peptonizing action of the corresponding halogen ions. Under the microscope we see a fairly regularly distributed grain of about the same general size as in the silver bromide emulsions obtained in the analogous way just described. Somewhat longer time was necessary for the peptonizing of the photohalides, at least half an hour for the photobromide at a temperature of 40°–50°, and from one and a half to two hours for the photoiodide. Since the photo-salts of silver bromide and silver iodide cannot be obtained by direct emulsification in the way described by me for silver chloride,[1] this new way of peptonizing offers a convenient method for obtaining these substances in a finely-divided, completely homogeneous form.

"The enormous effect of the gelatine in the peptonizing of silver bromide shows up especially clearly if one uses still larger amounts of bromide, for instance ten times the amount suggested. Under these conditions there is only a faint opalescence in the supernatant liquid when the silver bromide is precipitated without gelatine, while the duplicate experiment with gelatine yields a creamy emulsion after a very few minutes. With silver iodide the phenomena are more complex. The behavior of the silver bromide in these experiments shows clearly that gelatine aids the peptonization, or even makes it possible, because it is a strong, protecting colloid and modifies the pectizing effect of the bromine ions.

"It is impossible to convert a flocculent and photographically useless silver bromide into a fine gelatine emulsion by mechanical means but it can be done by the method just described, making use of the peptonizing action of halogen ions. This method was not entirely unknown before. Thus Eder[2] writes: 'If we precipitate silver bromide from a cold aqueous solution containing no gelatine or other similar substance,

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[1] Phot. Correspondenz, 44, 484 (1907).

[2] Eder's Handbuch der Photographie, 5th Ed., 3, I, 28 (1902).

we get a coarse, compact precipitate which can easily be washed on a filter. If we pour this precipitate into a warm solution of gelatine and shake, the silver bromide disintegrates and forms a fine emulsion. Under these circumstances the silver bromide behaves differently, depending upon whether it has been precipitated in presence of an excess of bromide or of silver salt. This difference is noticeable no matter how carefully the silver bromide is washed.' It is probable that in these experiments the small amount of bromide, which remains absorbed when the silver bromide is precipitated in presence of an excess of bromine ions, plays the part of a peptonizing agent. While dextrine, gum arabic and albumen have a much less effect than gelatine on the peptonization of silver bromide, collodion is remarkably effective. The silver bromide precipitated from 1 gram of silver nitrate was washed and then shaken with 50 cc of alcohol. After the alcohol had been poured off, 50 cc of a 4 percent collodion and 5 cc of a 10 percent alcoholic ammonium bromide solution was added to the silver bromide. Almost instantaneously there was formed a homogeneous, creamy solution of a pure white color, just like that obtained by treating with gelatine. Neither collodion alone nor a bromide solution alone will produce this result. Even 25 cc of the ammonium bromide solution was sufficient to peptonize the silver bromide alcogel.

"The extraordinary influence of the bromine ions as a peptonizing agent is of course of the greatest importance for the theory of the ripening of photographic emulsion; further study along this line is much needed. The fine division of the coarse silver bromide, precipitated in the absence of a binder, which takes place in gelatine under the influence of a bromide, still occurs even when ammonia is added to the solution in the usual amount, so that theoretically an excess of bromide may act against the actual ripening even in an ammoniacal emulsion and thus retard the coarsening of the grain. As a matter of fact, a highly-sensitive Schleussner emulsion, ready for pouring, was not peptonized by a subsequent treatment with a potassium bromide solution and the grain remained unchanged. In connection with this it is of great importance that only actual hydrogels can be peptonized, as mentioned by Lottermoser in the rule which has already been quoted. Heating is enough to convert silver bromide or silver iodide into a form which cannot be peptonized. If these precipitates are heated for only five minutes under water, they change into a more pulverulent, less voluminous form and cannot then be peptonized by bromine ions in presence of gelatine. Silver iodide behaves quite differently in respect to coloring by means of colloidal silver, depending on whether it has been freshly precipitated or has been boiled for fifteen minutes under water. That which has been boiled can scarcely be colored, while that which has not been boiled is colored an intense reddish violet under exactly the same conditions. The same visible change of the flocculent into the pulverulent silver iodide and the same change in the power to take up colloidal silver can be brought about by a short heating or, as I have found, by simply letting the silver iodide stand for a day or two at ordinary temperature. Also, after standing for a day or two at ordinary temperature, both silver bromide and silver iodide lost the characteristic of being converted into a fine emulsion by the corresponding halogen ion in the presence of gelatine. It is therefore quite intelligible that a ripened emulsion does not have its molecular complexes broken down by peptonization, though of course it is not claimed that the influence tending to check the growth of the grain may not be a factor in some stage of the ripening. Some experiments of A. Müller[1] bring out some interesting facts with reference to this. Müller found great differences in the peptonization of an aluminum oxide gel, according as the precipitate was freshly prepared or had stood for, say, three hours. The amount of electrolyte necessary to etch such a gel depends primarily on the physical structure of the gel. Müller calls attention to the fact that this conclusion is entirely in line

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[1] Die Kolloid-Chemie auf der 79ten Naturforscherversammlung. Supplementheft der Zeitschrift für Chemie und Industrie der Kolloide, 6.

with the fundamental work of van Bemmelen on the structure of the hydrogels and the changes thereof."

In an appendix to this paper, Lüppo-Cramer[1] says: "In the preceding paper I showed that the peptonization of the silver iodide and silver bromide gels by the corresponding halogen ions takes place in quite a striking way in presence of gelatine. Starting from the coarsely flocculent silver bromide obtained by precipitation in the absence of a binder, we can obtain very fine-grained, homogeneous, though by no means colloidal, emulsions.

"Further experiments have shown that the same results can be obtained more rapidly with ammonia than with bromine ions. The reaction was carried on in precisely the same way as the preceding one, merely substituting 2 cc of ammonia (sp. gr. 0.91) for the bromide. The disintegration of the flocculent silver bromide in the gelatine took place immediately and the resulting, completely homogeneous, creamy emulsion showed under the microscope (oil immersion) only very small particles which looked like fine splinters. Ammonia does not disintegrate the silver bromide in collodion while an emulsion is very easily obtained under the influence of a bromide.

"The etching of the silver bromide, to which the emulsification is to be ascribed, takes place also under the influence of small amounts of sulphocyanates, while thiosulphate, sulphite, and thiocarbamide have no effect even though they are all substances which dissolve silver bromide. The alkali carbonates also have no peptonizing action.

"The state of the silver bromide was of fundamental importance for the emulsification in gelatine by means of bromine ions and the same thing is true for the emulsification by means of ammonia. The silver bromide gel loses its peptonizable properties completely just by standing. Samples, which had stood for one, three, six, ten and twelve hours in the dark at ordinary temperatures showed a gradual decrease

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[1] Phot. Correspondenz, 44, 578 (1907).

in the tendency to form an emulsion. After twelve hours standing, no emulsion could be formed at all.

"If the silver bromide is formed from silver nitrate instead of from ammoniacal silver oxide, it differs in shape and color from that precipitated from a neutral solution and it cannot be peptonized in presence of gelatine. Even when not precipitated in presence of ammonia, it only requires a few minutes shaking of the silver bromide with a very dilute solution of ammonia to bring the silver bromide into such a state that ammonia does not cause an emulsification in presence of gelatine. Bromides cannot peptonize a silver bromide precipitated from an ammoniacal silver oxide solution.

"Freshly precipitated silver iodide is quickly converted into an emulsion by the action of ammonia in presence of gelatine; but this does not take place after the silver iodide precipitate has stood for a day or two. An excess of silver nitrate at the time of precipitation has no appreciable effect on the peptonizing action of ammonia on either silver bromide or silver iodide. The same thing is true in case the silver nitrate is added after the precipitation and is then nearly all washed out of the precipitate.

"To show the bearing of these reactions on the manufacture of photographic emulsions I may add that silver bromide precipitated at about 50° differs slightly in appearance from that precipitated at 18°; but it can be completely emulsified in gelatine by means of ammonia."

Before we consider the other properties of a photographic emulsion, we have to answer the question as to the amount of silver bromide usually to be found on a photographic plate. This has been determined for some plates by Tappen and Rekaschow[1] whose paper I quote.

"In connection with other investigations it interested us to determine the ratio between silver and gelatine in the modern, highly sensitive emulsions. Since these data may be of value to some one, we publish our experimental results.

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[1] Phot. Correspondenz, 45, 362 (1908).

"In the literature there are only brief notices on the silver halide and gelatine content of photographic plates.[1] Hurter and Driffield give the amount of silver bromide as 26-49 percent.

"It seemed to us doubtful whether the highly sensitive plates contain either so little or so much silver halide as these limits would imply. When the silver halide is present in very small quantities the film must of course be made very thick if the negative is to be sufficiently intense. We had observed that the amount of emulsion on the plates does not vary very much. For different types of plates we found 0.425-0.625 gram emulsion per square decimeter. A very considerable decrease in the concentration of silver halide in the emulsion would not be compensated by a corresponding increase in the amount of the emulsion on the plates and the plates would consequently give weak negatives. For this reason it seemed to us improbable that the low concentration of silver halide, mentioned by Hurter and Driffield, could occur on modern plates.

"On the other hand, we had noticed in many experiments that emulsions very rich in silver halide decompose extraordinarily easily on long digestion hot in such a way that there is no longer a uniform grain, while emulsions with less silver bromide segregate much less easily. Since the modern, highly sensitive plates are certainly prepared by a long digestion of the emulsion, to a certain extent at higher temperatures, we believed it probable that a very high concentration of silver halide would be considered undesirable from a commercial point of view. It is self-evident that the manufacturer would use as little silver salt as he could, on account of the cost of the latter.

"Our suspicions were confirmed by our analyses. In seven different plates we found a content of silver halide which varied between 40.2 and 46.0 percent. Only one plate, of Austrian manufacture, had 36.4 percent. This one was evidently poured by hand and had only 0.346 gram emul-

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[1] Cf. Eder's Handbuch der Photographie, 5th Ed., 3, I, 76 (1902).

sion per square decimeter. It differed from the plates of other makers in every respect.

"The analyses were carried out in exactly the same way with all the plates. From each make about 200 cm² of the emulsion was shaved off carefully and then weighed after drying in air. The sample was then dried for two hours at 105° to determine the water content, and was next heated in 100 cc of water and 100 cc of nitric acid (1 : 4) at 70°–80° until all the silver halide had settled. The precipitate was filtered in a Gooch crucible, washed with water and alcohol, and then dried at 140° to constant weight. In Tables I and II are to be found the collected data.

TABLE I

Type of plate	Surface in cm²	Emulsion in grams	Water in grams	Silver halide in grams
French make	229.6	1.0043	0.0783	0.4261
English make I	230.3	0.9777	0.0812	0.3715
English make I	231.2	1.0186	0.0881	0.3902
English make I	178.0	0.8490	0.0808	0.3199
English make I	174.9	0.9398	0.0770	0.3729
German make I	232.5	1.1247	0.0983	0.4157
German make II	211.7	0.9155	0.0800	0.3358
Austrian make I	195.3	1.2248	0.0984	0.4893
Austrian make II	231.8	1.1870	0.0816	0.4743
Austrian make III	229.1	0.7934	0.0761	0.2610

TABLE II

Type of plate	Emulsion per 100 cm² in grams	Percent water in air-dried emulsion	Percent silver halide in anhydrous emulsion	Percent gelatine in anhydrous emulsion
French make	0.4373	7.80	46.00	54.00
English make I	0.4246	8.30	41.44	58.56
English make I	0.4406	8.65	41.93	58.07
English make I	0.4770	9.52	41.64	58.36
English make II	0.5373	8.19	43.22	56.78
German make II	0.4838	8.74	40.50	59.50
German make II	0.4325	8.74	40.19	59.81
Austrian make I	0.6272	8.03	43.44	56.56
Austrian make II	0.5121	6.87	42.91	57.09
Austrian make III	0.3463	9.59	36.38	63.62

"It may seem risky to draw conclusions from so few plates in regard to the numberless plates on the market. We have however taken the best-known of the rapid emulsions and those having the widest sale and it is therefore perhaps justifiable to assume that in general the silver halide content of modern, highly sensitive plates lies between the limits given."

If we omit the last Austrian plate, the amount of silver bromide per square decimeter varies between 0.16 gram and 0.25 gram, the average of the nine analyses being about 0.19 gram. In round numbers we may consider that there is about 0.1 gram silver per square decimeter in the fast European plates. If we take the percentage of silver halide in the dried emulsion as a shade over 42 percent and the average water content of the original emulsion as 8.5 percent, we get the following average composition of these emulsions: silver bromide 38.5 percent; dry gelatine 53.0 percent; water 8.5 percent.

A freshly-prepared emulsion, especially if precipitated cold, has a very fine grain and is relatively quite transparent in thin films. It is only slightly light-sensitive and when ripened increases in sensitiveness[1] one hundred- or even one thousand-fold. There are different methods of ripening the emulsion, as the emulsion may be acid, neutral or alkaline during the ripening process, and it may be ripened hot or cold.

In the chapter on the ripening of silver bromide gelatine, Eder says:[2]

"The ripening of a silver bromide gelatine cold takes place in the jelly-like solidified emulsion and in the liquid emulsion. This latter case occurs when the amount of gelatine is so small that the solution does not set at ordinary temperature. When emulsified in gum arabic, silver bromide ripens somewhat even when cold. In the dry state the light-sensitiveness of silver bromide gelatine plates increases

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 24 (1902).

[2] Ibid., 5th Ed., 3, I, 54 (1902).

for a long time towards a certain limit just by standing at ordinary temperature.

"Quite dilute solutions of gelatine, with 0.5 percent gelatine for instance, do not solidify on cooling. If potassium bromide and silver nitrate solutions, containing this amount of gelatine, are mixed there is formed an emulsion which often contains coarsely flocculent silver bromide as well. If there is some alcohol present, a finer emulsion is obtained. In neutral or acid solution, such an emulsion ripens very slowly at 10°–20°; quite rapidly however in presence of ammonia or ammonium carbonate.

"A silver bromide gelatine, which has set to a jelly, increases gradually in sensitiveness by standing at ordinary temperature. This was first observed by Monckhoven.[1] Abney first emphasized the fact that a heated and already highly sensitive silver bromide gelatine showed an increase of sensitiveness after standing cold for a day. This change was more marked on the second and the third day.[2] In a neutral or acid emulsion the ripening in the cold is very slight[3] and does not more than double the sensitiveness. In presence of ammonia, ammonium carbonate or soda, the jelly ripens much more, as was pointed out by Eder in 1880.

"Emulsions, prepared from ammoniacal silver oxide and digested hot until quite sensitive, contain a great deal of ammonia and ripen a good deal if allowed to stand, unwashed, as a jelly in flat dishes for a couple of days, or longer at lower temperatures.[4] These statements apply to freshly-mixed, unwashed emulsions; but washed emulsions ripen quite markedly in the course of a few days if allowed to stand as a jelly even in water. The sensitiveness often doubles.

"Freshly prepared silver bromide dry plates increase

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[1] Phot. Archiv., 1880, 197.

[2] Phot. News, 1880, 567.

[3] If a washed emulsion is left for three to eight days in a cool place and if it is kept from fouling by sprinkling with alcohol containing carbolic acid, the sensitiveness increases but slightly, though the increase in the intensity (density of the negative) is quite marked.

[4] Cf. Cowan: Phot. News, 1882, 753.

markedly in sensitiveness on standing for perhaps six months. Max Wolf[1] has shown in commercial dry plates an occasional trebling or quadrupling of the sensitiveness. It soon reaches a maximum (after five to seven months for instance) and remains constant there for quite a while.

"Schwarz[2] has shown an increase in the sensitiveness of dry plates as a result of standing for two years. The increase was from nineteen to twenty-six degrees Warnerke, in other words a four- to five-fold increase of sensitiveness. The plates fogged at the edges, however, when developed.

"If an emulsion is melted a second time and then allowed to solidify, it is found that the sensitiveness is increased. Henderson[3] divided a washed emulsion into two parts. One part was kept melted while the second part was repeatedly just melted and then just allowed to solidify. He showed that this second portion was more sensitive than the first. This is made use of in manufacturing emulsions when it is desired to increase the sensitiveness of an emulsion, which is not sensitive but which gives no fog, after the emulsion has been mixed and washed. Many manufacturers always make only one emulsion which is first washed, then melted and allowed to solidify again. It is either used the next day or is kept in a refrigerator for several weeks. A trace of soda or ammonia increases the ripening very much.

"If we heat for a long time a gelatine emulsion of normal concentration,[4] containing emulsified silver bromide, an excess of soluble bromide, and the nitrate from the metathetical reaction, there is formed a finely divided, granular silver bromide which however yields a very fine emulsion. Thin layers are yellowish green, with a touch of olive-green,

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[1] Eder's Jahrbuch der Photographie, 6, 258 (1892).

[2] Ibid., 13, 509 (1899).

[3] Phot. Wochenblatt, 1883, 304.

[4] By emulsions of 'normal concentration' are meant those in which all the gelatine and salts, and all the water are mixed at the start; thus about 30 grams $AgNO_3$, 24 grams KBr, 30–50 grams gelatine, and about 600 grams water. This excludes the emulsions in which only a fraction of the total gelatine is emulsified while the rest is added after the digestion is finished.

in reflected light and blue-violet to red-violet in transmitted light. This silver bromide is extraordinarily light-sensitive and is therefore known as 'highly-sensitive' or 'ripened' silver bromide."

"If silver nitrate is mixed with gelatine, water and an excess of potassium bromide, and the mixture is allowed to stand for several days at 30°–40° in a water bath, the sensitiveness increases two-fold to ten-fold. This was the basis of Bennett's process (1878) for making sensitive emulsions. The process was soon superseded on account of the time involved and because the gelatine was attacked badly. In this and similar ripening processes, the grain of the silver bromide increases in five days from 0.0008–0.003 mm."[1]

"At 60° the emulsion is changed partly into the more sensitive form after a quarter of an hour, and pretty completely at the end of one to three hours. It is then nearly opaque to red light and is better ripened after four hours heating at 60° than it would have been after four days at 40°. In boiling water (100°) the molecular change of the silver bromide takes place very rapidly. It is often ended after only ten minutes boiling and is almost always complete after one-half an hour to an hour and a half. The sensitiveness is then about the same as would be obtained by digesting for six days at 35°–40°.[2] In general Eder found that half an hour's heating of silver bromide gelatine at 100° had the same effect as heating for one to two hours at 70°–80°. According to Graeter, heating for fifteen minutes in a Papin's digester at 140° (pressure of four atmospheres) produced the same result as heating for one hour at 100°.

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[1] Cf. Eder Phot. Correspondenz, 17, 30 (1880).

[2] To two Englishmen belongs the priority of the discovery that a silver bromide gelatine emulsion changes into the highly sensitive modification more rapidly at high temperatures than at 30°–40°. It is well known that Wortley found that digesting a gelatine emulsion for a few hours at 60° made it as sensitive as it would become by standing for many days at a lower temperature, Brit. Jour. Phot., 23, 307 (1876). It is less widely known that Mansfield, at a meeting of the Irish Photographic Society on August 13, 1879, recommended that the emulsion be boiled for ten minutes instead of being kept for a longer time in lukewarm water.

"In the Photographic Almanac for 1877 Johnston recommended the addition of ammonia to the emulsion. In 1879 Monckhoven[1] pointed out that heating an emulsion for a few hours with ammonia gave it the same sensitiveness which it would have obtained if the neutral solution had been heated for several days. Since ammonia gives good results only under certain conditions and bad results (fog) under other conditions, Monckhoven later gave up ammonia. The conditions under which ammonia works well were determined by Eder[2] in 1880. Only after that was ammonia used with much success.

"Ammonia, ammonium carbonate, and sodium carbonate accelerate the ripening of silver bromide gelatine cold, as was pointed out by Eder in 1880 and confirmed by Burton and others. These substances increase also the intensity of the negative and make the emulsion creamier. A subsequent addition of the substances to an emulsion which has been heated makes it distinctly more intense on development and more sensitive to light.

"One can add 1–2 percent of ammonia (sp. gr. 0.91) to the liquid, unwashed emulsion. With this normal addition of ammonia the increase in the size of the grain is moderate and such as always takes place when silver bromide is modified. It does not interfere in any way with the delicacy of the image. With more ammonia, there is often formed a grain which is much too coarse and which is visible to the eye in the print. A 5 percent ammonia attacks the gelatine when heated, interferes with the solidification and often causes fog. When the emulsion is digested for a long time (twelve to twenty-four hours) with ammonia, the silver bromide is partly decomposed and causes fog.

"At higher temperatures than 50° an unwashed emulsion containing 1–2 percent of ammonia often fogs. Some gelatines will stand half an hour's heating at 70° and a bromide iodide emulsion stands up much better than a straight bromide

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[1] Phot. Correspondenz, 16, 197 (1879).

[2] Sitzungsber. Akad. Wiss. Wien, 81, II, 687 (1880).

emulsion. Many sorts of gelatine give fog if heated for half an hour with ammonia, and therefore Eder recommends usually not to exceed a temperature of 40°–50°, and not to heat for longer than an hour. Rapid emulsions are prepared at 50°–60°.

"Sometimes an emulsion is cooked and cooled to 30°–40°, when a trace of ammonia is added to make the liquid alkaline (1 drop to 100 cc emulsion for instance). On standing cold before washing, such an emulsion ripens a good deal even in one day. Another method of preparing an emulsion is to boil a slightly acid emulsion for perhaps half an hour, then cool to 40°, add 1–3 percent of ammonia and hold it at that temperature for half an hour.

"In an emulsion which has been prepared with ammonia and then washed thoroughly, there is no more ammonia, which is confirmed by Rammelsberg's observation[1] that silver bromide can be freed completely from ammonia by washing.

"The use of caustic ammonia as a means of increasing the intensity introduces the following disadvantages. The intensity is often too great so that the negatives are too hard for portraits. When made with poor gelatine the emulsion fogs and comes loose from the plate in the fixing-bath. In spite of this, the advantages, especially in respect to sensitiveness, are so great that most manufacturers make use of ammonia in preparing emulsions.

"Ammonium carbonate is less energetic than ammonia. Eder[2] called attention to its good properties in April, 1880. A little later Forrest[3] described a method in which he boiled a silver bromide gelatine together with ammonium carbonate for ten to twenty minutes. Eder obtained good results by heating a neutral or slightly acid silver bromide gelatine, cooling to 40°–50°, and adding 2–5 percent of an ammonium carbonate solution (1 : 10). The emulsion was then held at 40°–50° for one to two hours or was allowed to stand cold

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[1] Gmelin's Handbuch der Chemie, 6th Ed., 3, 961.

[2] Sitzungsber. Akad. Wiss. Wien, 81, II, 687 (1880).

[3] Phot. Archiv., 1881, 38.

for forty-eight hours. In this way the negative becomes stronger without becoming harsh, and there is no danger of fog. At the same time the emulsion becomes creamier and less transparent. It is not so sensitive, however, as one made with ammonia."

One paragraph by Chapman Jones[1] contains some statements to which I may need to refer later, so I quote it.

"In 1878 Mr. Charles Bennett prepared a very sensitive gelatine emulsion, and by its means produced some instantaneous negatives that astonished those who saw them. Bennett's improvement consisted of keeping the emulsion at a temperature of about 90° F for six or seven days. This tedious procedure was shown to be unnecessary by Mr. G. Mansfield in the following year. He heated his emulsion by means of boiling water, and got sensitiveness in minutes instead of days. The highly sensitive condition of silver bromide is obtained only when the heating takes place in the presence of gelatine, and apparently only when the soluble bromide is in excess, so that some remains after it has changed the silver entirely into bromide. The emulsion, when first prepared, appears orange-colored if looked through; but after cooking it transmits grey light. The change of color indicates that its absorptive action upon light is different, and as a matter of fact the 'boiling' of the emulsion confers a slightly increased sensitiveness towards the less refrangible light."

Instead of washing a silver bromide emulsion to remove the potassium nitrate and the excess of potassium bromide, the silver bromide may be extracted in a centrifugal machine and may later be taken up again in a fresh lot of gelatine. An interesting account of some of the characteristics of this process is given in a paper by Baekeland,[2] from which I quote.

"Many years ago, the centrifugal machine was recommended for the separation of bromide of silver from gelatine emulsions. The machine ordinarily used for this purpose

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[1] Science and Practice of Photography, 407 (1904).

[2] Int. Kongress angew. Chemie, Berlin, 4, 411 (1903).

consists mainly of a silver-lined bronze drum about 40 cm wide, having solid unperforated walls and suspended in the centre by a hollow stud protruding from the bottom. When a silver bromide gelatine emulsion is run into this vessel, which revolves at high speed, the particles of bromide of silver, on account of their higher density, are pressed nearer the walls, where they aggregate in a consistent mass, while the gelatine solution containing any soluble salts leaves the vessel near the centre through the circular opening in the cover. The whole operation is very similar to what occurs in a centrifugal cream separator.

"Makers of silver bromide emulsion have a very divided opinion as to the practical advantages of the centrifugal method and I know more than one of them who claim that they never have been able to obtain good results with it. On the other hand, speaking from personal experience, I can state that a properly made centrifugal bromide of silver will give emulsions at least as good as those obtained by any other method and this with a regularity and a simplicity far exceeding those of the washing method. As to the regularity and ease of this process, I could give no better illustration than by mentioning that a few years ago there were manufactured under my direction about 100 kilometers of bromide paper about 63 cm wide and which had to be of the same quality as it was intended for a single order and to be used for one single purpose under the same conditions.

"In order to utilize a centrifugal machine successfully, many factors must be taken into consideration. Aside from the obvious necessity of having a mechanically-perfect operating machine, the speed of which should always be the same, I might mention the following requirements:

"The centrifugal machine should always be operated at the same temperature. This can be obtained by placing the machine in a room where the temperature can be kept as constant as possible during all seasons. It is better to adopt for standard temperature one which is relatively high, as, by doing so, it is easier to obtain regularity in manufacturing.

During colder days it is always less difficult to increase the temperature artificially than to cool the room in summer time. For the United States a working temperature of 30°–35° has proven to be very practical. This temperature is not objected to by the employees, especially if the centrifugal room is isolated from all the others and if they are not required to stay in it during all the time of the operation.

"If the room is not always heated to the same temperature, great variations in the quality of the separated bromide of silver will occur, as the ripening of the emulsion will be activated or lowered according to the temperature.

"The flow of the initial emulsion has to be regulated in such a way as always to deliver the liquid with the same speed so that a given amount of emulsion will invariably take exactly the same time to run through the centrifugal machine.

"Any variations in the flow will produce a more or less ripened bromide of silver which will separate more or less easily and will modify profoundly the ultimate character of the final product. The proper way is to prepare the initial emulsion in small batches at short intervals and to run these through the machine in periods not exceeding thirty minutes; thus it is possible to avoid that the latter portions of silver bromide of a single batch should become much riper than the first ones.

"When the bromide of silver is once separated from the liquid and thereby pressed against the walls of the drum, no further appreciable changes of the photochemical qualities will occur, probably because it is no longer surrounded by salt or ammonia solution which, under ordinary conditions, has a ripening influence on this silver compound.

"It is not desirable to run the emulsion through the centrifugal machine slower than is strictly necessary for easily separating all the bromide of silver except such small fractions as cannot well be separated by centrifugal force, be it that these particles are extraordinarily small or that a certain amount of bromide of silver remains in a colloidal state in the gelatine medium, or is actually dissolved by the alkaline salts or ammonia contained in the liquid. Practice alone will establish these rules for each particular kind of emulsion. If bromide of silver separated from an emulsion by centrifugal force be deposited against the walls of the centrifugal drum, it will be pressed tighter and tighter against it and after enough time has elapsed it will become so hard as to acquire physical properties which will make it rather difficult to disaggregate it again, and renders it unfit to be reincorporated in a gelatine solution. My personal experience has also shown me that the photochemical properties of such hard, pressed bromide of silver become modified to such an extent as to render it valueless for photographic purposes. This is one of the reasons why the amount of bromide of silver separated in one 'run' should be limited to what experience has indicated to be a maximum for each kind of emulsion. In practice I allow an amount of emulsion corresponding to about 5 kilos of nitrate of silver to be run through in one continuous operation after which the centrifugal drum is emptied."

"Bromide of silver separated in the centrifugal machine from a gelatine solution always contains a more or less large amount of organic gelatinous matter. This can be brought to a minimum by treating the firstly separated silver bromide with hot water, grinding it in a mortar and running it again through the centrifugal machine. By repeating this operation several times, almost all organic matter can be eliminated.

"For practical purposes it is not necessary nor desirable to carry on the purification of bromide of silver beyond certain limits. It has, on the contrary, been my experience that bromide of silver centrifuged once will give a more satisfactory emulsion than if it was thus treated several times.

"After some practice with the centrifugal machine, it becomes possible to judge the future qualities of the silver emulsion according to the way the separated bromide of silver feels in the drum. A soft deposit which yields easily to the finger with a greasy feeling is an indication for a dense and rather 'slow' bromide of silver; a hard and dry deposit indicates opposite qualities.

"I found it a commendable practice to submit the deposit of bromide of silver to a superficial washing so as to free it from any excess of adhering gelatine solution. This removes most organic matters, ammonia or dissolved salts. After the machine is finally stopped, any remaining water is carefully poured off and afterwards drained by keeping the vessel upside down for a few seconds, after which the lid of the centrifugal machine can be removed.

"A practical way for detaching the deposit of bromide of silver is to use a strong and broad horn spatula. A certain amount of silver bromide sticks to the walls, but can be removed by rubbing it gently by means of a pure piece of Para rubber, care being taken to moisten the adhering mass at the same time with some lukewarm water. Proceeding carefully there will be almost no loss of bromide of silver.

"The amount of water used for detaching the silver bromide must be deducted from the total quantity of water which will be added afterwards with the gelatine, for the final making up of the emulsion.

"I found it practical to keep the so-separated bromide of silver in properly covered earthenware jars for a considerable length of time. Each vessel bore a label giving full description of the date of preparation of the bromide of silver, also indications as to amount, quality, etc. I was thus able to keep an assortment of different grades of bromide of silver ready for instant use. By mixing this bromide with the required amount of gelatine solution I could prepare in a very short time almost any kind of an emulsion. Anybody who has ever made bromide emulsions will readily see what an enormous simplification has thus been accomplished in the delicate preparation of bromide of silver and its emulsions.

"I made several observations as to the limit of time a so-prepared bromide of silver can be kept without notable deterioration. In some experiments I kept a batch of bromide of silver for over two years and was able to use it at the end of this time. The only change was a slight increase in sensitiveness and some loss in 'density.'

"For bromide of silver as used for bromide paper, there is very little change in the ready-made bromide of silver, even after three and four months. I would advise to avoid keeping this product in rooms which are too hot or in which there are objectionable gaseous emanations. A cool cellar or better, an ice-box is the proper storage place for this delicate product. It is necessary that the silver bromide mass should be kept moist and under no circumstances should it be allowed to become dry; under the latter condition it seems to undergo allotropic modifications by which its photochemical properties undergo objectionable changes.

"It is furthermore of the utmost importance to remove the last traces of ammonia or soluble salts by a final washing as described above. If the ammonia or soluble salts are present, the bromide of silver has a tendency to keep on 'ripening' until it becomes valueless for photographic purposes. This is probably due to the slight solvent action which ammonia or soluble salts exercise on silver bromide, thereby facilitating physical changes in the size and general nature of the particles of silver bromide.

"Reincorporating the centrifugal bromide of silver in gelatine solution is not always an easy operation and has to be done with great care. I can recommend the following method.

"First, dissolve all of the gelatine in a minimum amount of water and keep the remainder of the water as hot as the hand can bear it. Put the bromide of silver in a large porcelain mortar which in winter time should have been previously heated by putting in it some warm water, so as to avoid a chilling effect on the material. If the silver bromide has been kept in stock, under water, pour off this water and take note of the amount of it, so as to replace it afterwards with an equivalent of water when making up the final emulsion.

"Now pour some of the hot water on the mass of bromide of silver and break the lumps of this material by gently pounding some with a pestle. After a while, the material will begin to disaggregate to allow a gentle rotating motion of the pestle, holding the top of the handle of the same between the thumb, forefinger and middle finger, and describing in this way a loose gyratory motion with the lower part of the pestle. Strong grinding should be avoided because the silver bromide particles would thereby undergo changes which are liable to produce 'foggy' emulsions. After a few minutes the feeling of coarse lumps in the bottom of the mortar will disappear. As soon as this point is reached let the liquid stand motionless for about thirty seconds, and afterwards carefully pour off the milky liquid in the hot gelatine solution; while stirring the latter, take great care that only the well-suspended silver bromide particles are poured off, while the heavier and coarser grains remain in the mortar. Add again hot water and repeat the same manipulation several times until all the silver bromide has thus been divided, suspended in water, and poured into the gelatine solution. It is needless to say that during all this time, the gelatine mixture should be stirred continuously so as to facilitate complete incorporation of its constituents.

"It will almost always happen that a small amount of 'sandy' bromide of silver will remain in the bottom of the mortar and refuses to suspend itself in water. This coarse material should be considered as harmful to a good emulsion, and therefore must be absolutely left out. As the quantity of this coarse bromide is very small in a well-conducted operation, the loss resulting therefrom is too small to be mentioned.

"After what I have said about it, it stands to reason that different kinds of bromide of silver, 'quick' or 'slow,' can be compounded in various proportions so as to produce any desirable mixture. As to the amount of gelatine and water, this can vary in very wide proportions, according to the particular purposes for which the emulsion is intended, and this matter depends entirely on specific formulae adopted by each manufacturer.

"Using the above method, extraordinarily large quantities of bromide of silver emulsion can be prepared at the same time.

"Emulsions of centrifugal bromide of silver have a great advantage by the fact that they always have the same chemical composition, which is not usually the case with washed emulsions which may retain variable proportions of uneliminated soluble salts or ammonia, together with undefined products of partial destruction of gelatine. It has been my experience that papers, plates, or films coated with centrifugal emulsions show generally better keeping qualities than those coated with washed emulsions.

"All things being the same, the setting power of a centrifugal emulsion will be greater than that of a washed one, because the gelatine of the former is all added fresh and has not any opportunity to undergo chemical changes during the 'ripening' and washing process.

"By the centrifugal method as described above, the manufacturer is entirely independent of the quality of water as used in the washing process. Everybody knows that in the washing process the water will have considerable influence on the emulsion; the final result may depend on the chemical composition, bacteriological and mechanical conditions, and also by the temperature of the water used for washing. All these facts, especially in summer time, may contribute to produce irregularities in manufacturing and cause financial losses."

Eder[1] points out that there is a connection between the color of a silver bromide emulsion and the degree of ripening.

"While ripening, silver bromide undergoes a change of color. When looked at by reflected light, the yellowish-white color of the unripe emulsion changes to an olive-green shade (conversion of the 'white' modification to the 'green.')

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 65 (1902).

Monckhoven[1] was the first to call attention to this color change.

"Some conclusions as to the sensitiveness of a silver bromide emulsion can be based on the color. For each silver bromide emulsion the color by reflected light becomes more greenish and the color by transmitted light becomes more violet or blue, the longer the emulsion is ripened.[2]

"These colors are quite different, however, with emulsions prepared by different methods. An emulsion prepared with ammoniacal silver oxide at 40° always appears somewhat blue by transmitted light even when it is not sensitive. An emulsion prepared by heating without ammonia may be more sensitive and yet appear reddish violet by transmitted light. This does not change the fact that films from the same emulsion become more transparent to blue light and at the same time more sensitive as the digestion is prolonged. By transmitted light, thin layers of an unripe emulsion appear yellowish-red to blood red by transmitted light. As the ripening proceeds and the sensitiveness increases, the color by transmitted light passes through reddish-violet and gray violet to grayish blue or greenish blue.

"The progressive change in color by transmitted light is accompanied by a coarsening of the grain of the emulsion, while the covering power (opacity) of the solution becomes correspondingly less.

"As a general thing, unripe emulsions (with a red color) develop without fog, but are only slightly sensitive and give harsh negatives which are lacking in half tones. An emulsion with a grayish blue color is usually ripened normally while one with a greenish blue color is over-ripe and fogs when developed. The coarse-grained transparent films are very sensitive but give flat negatives lacking in contrast."

Though ripening an emulsion makes it more sensitive, this process cannot be carried beyond a certain point either

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[1] Phot. Correspondenz, 16, 149 (1879).

[2] Additions of silver iodide and silver chloride change the color and it may then be difficult to draw any conclusion as to the sensitiveness.

because the grain of the silver bromide may become so coarse that the plate is no longer satisfactory or because, as is usually the case, the unexposed plate fogs when placed in the developer. I quote from Eder[1] in regard to both these points.

"Through further heating and other treatment to favor the agglomeration of the particles, the finely-divided silver bromide becomes quite coarse in grain. It is still very sensitive, but the coarseness of the grain makes the film useless for photographic purposes. It would be a mistake, however, to suppose that a coarse-grained silver bromide is necessarily more sensitive than a finely-divided silver bromide."

"The coarsely flocculent silver bromide [precipitated in absence of gelatine] is of no value photographically because it does not give uniform films and because it is extremely insensitive. Eder and Toth heated such a coarsely flocculent silver bromide in glycerine at 100° for more than half an hour. After adding gelatine, a sample was developed with ferrous oxalate but proved to be much less sensitive than the most insensitive of the unripened finely-divided emulsions."

"If the digestion of a silver bromide gelatine is continued for a very long time (8–14 days or more), the finely-divided granular silver bromide usually undergoes another considerable increase in the size of the grain. Lumps are formed 0.02–0.04 mm in diameter. These are visible to the naked eye. They consist for the most part of decomposed silver bromide which blackens in the developer even though not exposed to light. Under these circumstances the plates are said to show 'fog.' A decrease in the amount of gelatine, absence of an excess of potassium bromide, and raising the temperature above 60° are favorable to the formation of these lumps; presence of potassium bromide, etc., prevent their formation for quite a while. It is characteristic of the coarser silver bromide particles of the finely-divided granular silver bromide to blacken in the developer more easily than do the

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 56, 29, 57, 87 (1902).

particles of the finely-divided pulverulent silver bromide.[1] The previously mentioned, very coarse lumps of silver bromide are especially readily blackened by a normal developer even though they have never been exposed to light.[2] The chemical reducibility of silver bromide and the decomposition by light are increased and made easier with the increase in the density of the silver bromide. A developed and fixed negative shows a more or less fine grain of metallic silver corresponding closely to the grain of the silver bromide."

"All the ways of obtaining a highly sensitive emulsion lead finally to a fogging emulsion. If a slightly acid silver bromide gelatine is kept at 30°-40°, the sensitiveness increases from day to day. About the seventh day, sometimes earlier and sometimes later, the emulsion begins to decompose. It fogs in the developer or, in other words, blackens also on the unexposed portions. At higher temperatures the emulsion ripens more quickly and the fogging usually takes place after three-quarters of an hour to two hours, sometimes sooner and sometimes later. Different kinds of gelatine do not act alike by any means.

"In a neutral gelatine solution, digestion or heating causes fogging more quickly than in slightly acid solution. A trace of acetic acid, hydrochloric acid or nitric acid suffices to keep the emulsion clear even though heated for quite a while. For this reason many photographers add acid when ripening an emulsion by boiling because otherwise it is painfully easy to go too far and to cause fogging. When the digestion is carried on at a somewhat lower temperature, the change takes place more slowly and it is possible to keep track of it even without acid. Too much acid is harmful and delays the ripening.

"In presence of substances giving an alkaline reaction,

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[1] If such an emulsion is spread on plates, the coarse-grained silver bromide sinks down upon the glass. When the plate is developed the air side of the film remains clear while the glass side fogs quickly.

[2] This observation was made by Eder during his microscopic measurements and comparisons of plates before and after development. Cf. Phot. Correspondenz, 17, 30 (1880).

the emulsion ripens at a lower temperature and it is not safe to raise the temperature too much or the emulsion will fog. At ordinary temperature 1-2 percent of liquid ammonia (sp. gr. 0.91) produces no fog even after eight days. When the emulsion is digested at 30°-40° with ammonia, fog sometimes occurs in an hour, but ordinarily only after three or four hours. There is always fog if the digestion lasts twenty-four hours. At 60°-70° silver bromide gelatine is entirely ruined at the end of six hours, while it spoils almost instantaneously at 100°.

"A trace of caustic alkali produces no fog at ordinary temperature; at 100° it decomposes the silver bromide gelatine so energetically that the latter turns brown and metallic silver precipitates. Large quantities of caustic ammonia, 10 percent for instance, are very dangerous in an emulsion frequently causing fog even at 30°.

"Alkaline carbonates, such as ammonium carbonate and soda, are much milder. A silver bromide gelatine can even be boiled with one-fourth to one-half percent of solid ammonium carbonate for ten or fifteen minutes without any danger from fog. An emulsion will even stand an hour's heating at 30°-40° in presence of 1 percent of soda without fogging. Of course there is fog if the heating is kept up long enough.

"Since a gelatine emulsion behaves quite differently in presence of an alkali from the way it does when it reacts acid, one must pay attention to the acid or the alkaline reaction of the gelatine. An acid gelatine does not act deleteriously on silver bromide even if kept at the boiling point for a short time. An alkaline gelatine easily causes fog. If one does not add an alkali deliberately and consequently does not take account of its secondary decomposing action, there will be trouble in case an alkali is present by accident, as for instance, in those methods in which the emulsion is cooked. The appearance of ammonia is very disadvantageous when the emulsion is heated for several days at 30°-35° (Bennett's process) because one is not looking out for the unforeseen, secondary reactions of the ammonia which cause fog when the digestion is prolonged. In this case one must start with an acid gelatine which will probably not develop ammonia inside of ten days whereas ammonia is given off from an alkaline gelatine after two to four days. An alkaline gelatine is harmless with alkaline potassium bromide if one deliberately adds ammonia at the beginning because then the whole method is one that is adapted to the alkaline solution.

"The following things tend to prevent fog in the emulsion:

"(1) Addition of silver iodide to silver bromide. A bromide-iodide emulsion does not spoil so readily when heated and also withstands the ammoniacal processes better.

"(2) An excess of soluble bromide during the heating. An emulsion which contains no excess of soluble bromide fogs readily. For this reason, care should be taken not to overheat a washed emulsion when melting it again; the temperature should be kept below 50°–60°.

"(3) An excess of a soluble chloride also tends to check fogging during the ripening, but it is by no means so effective as a bromide.

"(4) An addition of acid checks fogging when the emulsion is to be boiled.

"When silver bromide is precipitated from aqueous solution and washed, and afterwards cooked with gelatine, it fogs more readily than if cooked with glycerine or with gum arabic. Glue (gelatine) acts towards silver salts and in general as a reducing agent as Bizio[1] showed some time ago. He found, for instance, that mercuric chloride is reduced by glue and water to mercurous chloride, and that mercuric oxide is reduced to the metal by an alkaline solution of glue.

"During the month-long action of aqueous gelatine on silver bromide in the cold, the day-long digestion at 30°–40°, and the minute-long digestion at 100°, there is a slight reduction to silver subbromide which does not necessarily show as a darkening. We need not wonder, therefore, that alkaline

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[1] Ber. chem. Ges., Berlin, 9, 1438 (1876).

emulsions fog more rapidly than acid ones. A silver bromide collodion fogs also if left for months in contact with tannin, gallic acid, etc.

"In the dry state gelatine appears to have only a negligible, exceedingly slight, reducing action on silver bromide. At any rate a completely dry emulsion does not usually fog inside of several years."

From the very nature of things an emulsion is rarely homogeneous. I quote from Eder[1] in regard to this point.

"Silver bromide gelatine always contains silver bromide in different degrees of ripeness. The silver bromide that is precipitated at first, is formed in presence of a greater excess of ammonium bromide, etc., than is that precipitated towards the end of the run. If we work with ammoniacal silver oxide, the amount of ammonia varies during the precipitation. A part will of course be digested somewhat longer than the rest. The portions on the walls of the flask will be heated sooner than those in the middle, etc.

"The correctness of these speculations can be tested experimentally. Heat a dilute emulsion containing relatively little emulsion for three hours, and separate the precipitate into three portions according to the rate of sedimentation. The coarse-grained silver bromide, which settles first, gives a transparent emulsion if taken up in a neutral gelatine; it shows 14° on the Warnerke sensitometer and fogs slightly. The second portion gives a fine emulsion and 24° W, while the third portion shows 21° W and does not fog at all.[2] Similar results were obtained by J. Plener[3] with his centrifugal machine in the presence of Eder. In a half-ripe emulsion, prepared with ammonia, the finest, pulverulent silver bromide is the least sensitive while the somewhat coarser (denser) silver bromide, which still gives a fine emulsion, is more sensitive. With emulsions which have been ripened for a long time and which are close to the maximum sensitiveness,

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 64 (1902).
[2] Phot. News, 1883, 81.
[3] Phot. Correspondenz, 19, 306 (1882).

the coarse-grained silver bromide fogs badly, while the finer portion is very sensitive and gives clear images.

"If a gelatine emulsion solidifies slowly when poured on glass plates, it often happens that the silver bromide separates. The coarser (sandy) portion of the silver bromide sinks to the glass, while the surface becomes poor in silver bromide. It may then happen that such slowly-solidified plates give thin, monotonous pictures and frill. If the gelatine film is removed, there remains on the glass, a thinner image from the coarse-grained silver bromide. In other cases there is formed at the surface an image which is thin but not fogged. When plates are looked at from the glass side they appear badly fogged, due to the silver set free from the coarse-grained silver bromide.

"Schaum's[1] investigations on the structure of the negative are of importance. He found that the uppermost layer contains less silver bromide grains than the lower layers—probably as a result of sedimentation. When the finished negative was examined microscopically, only a few scattered grains of silver were found near the surface. A little lower there was a layer containing many grains and below this there were one or more layers of silver grains.

"If one silver bromide gelatine plate is exposed from the film side and another from the glass side (making allowance for the absorption of light by the glass) the first picture develops blacker and the grains of silver are on the surface. In the other case the image is weaker and the grains of silver are nearly uniformly distributed through all levels of the film. Abegg[2] explained this phenomenon as due to the decreased diffusion of the bromide set free by light."

Liesegang[3] has made some observations which seem to him to indicate that silver nitrate can co-exist with a soluble halide in an emulsion. "The condition for this is a very simple one. The two solutions must not be mixed thoroughly.

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[1] Eder's Jahrbuch der Photographie, 15, 281 (1901).

[2] Ibid., 15, 9 (1901).

[3] Ibid., 15, 602 (1901).

His attention was first called to this when preparing a silver bromide collodion emulsion. A titration of the first wash water showed an unusual excess of bromide. On the other hand one part of the emulsion, when squeezed, gave a corresponding excess of silver. The aqueous silver nitrate solution which had been added to the bromide collodion, was too concentrated. In consequence, some of the collodion had been precipitated and this had carried down silver nitrate with it. The reaction between this absorbed silver nitrate and the excess of the soluble bromide outside took place very slowly for reasons which will be given later. Exactly the same thing can happen when preparing a silver bromide gelatine emulsion. A too concentrated silver nitrate solution will precipitate a portion of the gelatine. This is the more surprising because saturated silver nitrate solutions dissolve solid gelatine. Even when the mixture is stirred vigorously, the salts remain for quite a time without reacting, since the gelatine particles, precipitated by the silver nitrate, retain this salt tenaciously. The reaction is complete only after solidification and a washing lasting several hours. In order to show this apparent retarding of the reaction it is not even necessary to have a colloidal medium. An almost saturated aqueous silver nitrate solution is allowed to drop from a pipette into a vessel filled with a 25–30 percent aqueous solution of potassium bromide or sodium chloride. The amount of the latter solution was so great that there was enough halide to react with ten times the amount of silver nitrate to be run in. The mixture was allowed to stand for several minutes, the halide poured off from the silver bromide or chloride, and the precipitate was washed twice with water. The second wash water contained quite a good deal of silver nitrate. When the concentrated silver nitrate solution is poured into the halide solution, at once there is formed around each drop a film of silver bromide or silver chloride as the case may be. This protects the silver nitrate in the interior of the drop. The diffusion of the silver nitrate through this wall takes place fairly slowly. If the two solutions are equimolecular, the diffusion through the membrane may even be suspended for a short time. When the silver halide molecules combine to form larger complexes, this destroys the membrane which consisted of very small, coherent silver bromide molecular complexes. When this takes place, there is a further reaction between the silver nitrate and the halide."

This difficulty cited by Liesegang is a special one and can easily be eliminated. More serious is the lack of homogeneity discovered by Homolka[1] whose paper I give in full.

"Much has been written and said during the last twenty years about the so-called 'edge-fog' of silver bromide gelatine dry plates. Different people have advanced different views in regard to the nature and formation of edge-fog, and they have brought forward hypotheses and theories. All may have been right up to a certain point but no completely satisfactory explanation has been given for the very good reason that no one has made any experiments.

"In the following paragraphs I communicate the results of a series of experiments which may perhaps increase our knowledge as to the formation of 'edge-fog.' The experiments in question lasted over a period of about two years, a time which is too brief for the nature of the subject. On the other hand, if plates remain free from fog at the edges for two years, it is safe to assume that they will not show any great amount of fog at the end of the third year. It is also to be remembered that it is not a commercial custom to keep dry plates for several years unless for very special reasons and to establish some definite point. Also, it is well-known that the very best dry plates do not improve when kept two and three years.

"As experimental material I made use of an ammoniacal silver oxide emulsion, containing 3 percent silver iodide and made according to a slightly modified Eder process. The experimental plates were poured with this emulsion without

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[1] Phot. Correspondenz, 42, 550 (1905).

any previous preparation and were dried in an air-bath at 25° C. Plates thus prepared showed a sensitiveness of 12°-14° Scheiner.

"The following points were then established:

"(1) If every trace of soluble bromide (potassium bromide or ammonium bromide) is removed from the emulsion by very careful washing with ice-cold distilled water, plates thus treated always show a strong edge-fog and a perceptible general fog after about six weeks.

"(2) If potassium bromide is added to the completely washed emulsion before pouring, in the amount of 20 cc of a 1 : 100 potassium bromide solution to a liter of emulsion, such plates show deep fog on the edges after two or three months but remain clear over the other portions up to two years.

"(3) If plates made with a completely washed emulsion are dried, bathed in the 1 : 100 potassium bromide solution, and dried again, there is no trace of fog on the edges or of general fog even after two years.

"It has long been known that the presence of alkali bromides in the emulsion keeps the plates free from fog. It now appears that the effect is different if the alkali bromide is added to the liquid emulsion before pouring or if the dried plates are bathed in a potassium bromide solution and dried again.

"The following experiments confirm this surprising fact and give us a simple explanation of it.

"If a dry plate is bathed for two or three minutes in a 1 or 2 percent solution and is then dried in the dark, the plate becomes a dark blackish-brown after a few minutes exposure to daylight.[1] I have found that quite a different effect is obtained if about 2 grams of sodium nitrite is added to a liter of liquid emulsion just before pouring. Plates made from such an emulsion and dried in the usual way also become colored dark brown after exposure to daylight

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[1] Cf. O'Farrel: Brit. Jour. Phot., 34, 423 (1887).

but along the edge a strip, about 10 mm wide, *remains uncolored and clear, even after being exposed for a whole day.* It does not become either more or less gray than would have been the case with an ordinary plate, which had not been treated with sodium nitrite and which had received the same exposure. *From this one must conclude that the edges of the plates contain no sodium nitrite.* Since it is well known that plates dry first at the edges and last at the centre, the only possible explanation of this phenomenon is that as the plates dry and the solidifying gel is still supersaturated with water, there is a migration or diffusion of the readily soluble sodium nitrite from the drying edge to the still gelatinous centre. This migration ceases only when the centre of the plate has lost so much water by evaporation that the gelatine there is nearer the solid, rigid state than the liquid, mobile state. It is different with the plates which were bathed in a nitrate solution. During the few minutes in which the gelatine was in the nitrite bath it took up very little water, so little that a mobile gel was not formed. Therefore no diffusion of the sodium nitrite from the edges to the centre can take place and the plate therefore becomes uniformly dark on exposure to the light without the formation of a clear strip along the edges.

"What holds for sodium nitrite must also hold for other readily soluble salts, especially for the very soluble alkali bromides. The following experiments show that this is actually so.

"(1) A plate was made from a carefully washed emulsion and was dried in the usual way. It was then bathed for two minutes in a 1 : 100 potassium bromide solution, dried, and exposed to candle light for a short time in a dark room. When the plate was developed, it gradually became uniformly dark with no strip along the edge.

"(2) To a liter of a carefully washed, liquid emulsion 2 grams of potassium bromide were added, the emulsion was poured on plates and dried in the ordinary way. A dry plate, prepared in this way, was exposed to candle light for a short time in a dark room and then developed. The result was a very dense fog along the edges while the centre of the plate only became dark after a prolonged development. After what has already been said the explanation of this phenomenon is a very simple one. During the drying of the plates the potassium bromide has diffused from the edges to the centre. When the exposed plate is placed in the developer, the edges blacken first because they contain little or no potassium bromide, while the potassium bromide present in the centre of the plate produces its usual retarding effect.

"This makes a number of long known phenomena and facts quite clear and intelligible. Among them are the following:

"(1) Small dry plates, which are made by cutting up larger sizes of finished dry plates, never show a strip of fog along the cut edges. The fog appears only along the original edges. The reason for this is that the original edges are comparatively free from alkali bromides while the cut edges, which were part of the middle of the larger plate, contain the normal amount of alkali bromide.

"(2) Every photographer is familiar with the fact that in the large majority of commercial plates, the image, and especially the sky, begins to appear first at the edges of the plate. The reason for this is that the edges, being comparatively free of potassium bromide, develop faster than the centre of the plate where the potassium bromide retards the development.

"As has already been said, these experiments were made with an ammoniacal silver oxide emulsion. Similar experiments with a heated emulsion, having a sensitiveness of 10°-11° Scheiner, gave the same results but it should be noted that there is less tendency to form fog along the edges when the emulsion is ripened by heating than when it is made by the ammonia process."

The nature and properties of the gelatine in making the emulsion has a great importance for the theory of ripening. I quote from Eder:[1]

"The gelatine has a decisive effect on the quality of the emulsion, both through its consistency and through its chemical characteristics. Silver bromide will not stand a long heating or a digestion with ammonia in the case of any gelatine whatsoever; certain bad kinds of gelatine decompose the silver bromide and cause fog even after a short digestion.[2]

"Even when two gelatines work clear and well, they may show differences. The important matter is whether the gelatine is 'hard' or 'soft.' A hard gelatine solidifies quickly and gives a solid jelly which usually swells but slowly when immersed in aqueous solutions. A soft gelatine has quite the opposite characteristics.[3]

"A hard gelatine is generally easier and quicker with which to work, especially in summer, because the emulsion solidifies readily on the plates even in hot weather, and also because the films adhere better to the glass and do not come off, when fixed, so readily as when a soft gelatine is used."

"Along with these advantages, the hard gelatine has disadvantages which should be known by people who are

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 31, 36, 39 (1902).

[2] Gelatines, which contain large amounts of reducing constituents, even color an ammoniacal silver oxide solution dark when heated (reduction to silver). H. W. Vogel recommends, as a preliminary test, to dissolve gelatine in ten parts of water and to heat it with a solution, 1 : 10, to which just enough ammonia has been added to redissolve the precipitate. If the gelatine samples are colored yellow to brown thereby, they are unfit to use in preparing an ammoniacal silver bromide emulsion, because the plates will tend to fog and will not keep well, Eder's Jahrbuch der Photographie, 10, 496 (1901). Eder says this test is only a first approximation and is not conclusive as to the suitability of any given gelatine for use in emulsions. When working on a commercial scale, one should order samples from the different makers of gelatine, should make comparative experiments with silver bromide emulsions made from these samples, and should lay in large stocks of the best kinds.

[3] The manufacturers make 'hard gelatine' by selecting the raw material with care and by boiling the gelatine carefully so as to avoid destroying the setting power by too long or too rapid heating. In addition, a 'hard gelatine' often contains some alum, which gives the jelly a finer consistency. Too much alum is harmful. Gelatine, which is made during the colder months is better than that made in hot weather, a fact first pointed out by Eder in 1886.

going to work with it. A hard gelatine fogs readily; with a soft gelatine it is easier for an unskilled person to make a plate which does not fog. This difficulty with the hard gelatine disappears if the gelatine is diluted or if some soft gelatine is added to it.

"The silver bromide plates made with hard gelatine develop rather slowly. The effect of the hard gelatine is purely mechanical, however. Such plates can be developed to any desired degree of intensity if they are previously softened for a quarter of an hour in cold water and either dried again or developed at once.[1] The slow development can however be prevented from the start by adding to the gelatine emulsion some substance, such as sugar, which is soluble in cold water and which opens the pores to the developer.

"These peculiarities have caused many manufacturers not to use hard gelatine exclusively when preparing gelatine emulsions; but rather to have soft gelatine constitute one-third to one-half the mixture. The hard gelatine should always preponderate in the case of emulsions to be ripened with caustic ammonia because the gelatine suffers more in this process than when boiled."

"As a result of the investigations, to which reference has been made, stress should be laid on the following points when selecting a gelatine.

"(1) For methods not involving ammonia, the gelatine should be acid and not alkaline; this is immaterial in the ammonia processes.

"(2) Many gelatines contain reducing substances. If the emulsion is boiled, treated with ammonia, etc., these substances cause a fogging of the emulsion. In such cases the emulsion must not be cooked a long time and one must give up all hope of reaching a high degree of sensitiveness. With a good gelatine one ought to be able to digest an ammoniacal silver oxide emulsion for thirty minutes at 35°-40° without causing fog.

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[1] Abney: Phot. News, 1881, 415.

"(3) Some gelatines tend to give rise to transparent spots or lines. Unknown gelatines should always be tested for this before large quantities of emulsion are prepared. Nothing but a practical test is decisive.

"(4) Gelatine should contain no fat. Many photographers believe that fat causes small depressions in the film and clear points with blurred edges in the negative(?) The presence of fat can be detected by letting an aqueous solution, containing 20–40 grams of gelatine, stand for some time in a warm place; rings of fat then form on the surface.[1]

"(5) A 4 percent gelatine solution should solidify completely at about 20°. Since this point of solidification corresponds to a melting point of about 29°–30°, we see that the easily-performed melting point determination will serve as a partial test for gelatine. It is safe to assume that the point of solidification is about 8°–10° lower than the melting point. The gelatine is better the higher the melting point and the point of solidification, provided that the gelatine is completely soluble in water at 40°–50°.

"(6) The gelatine should be so firm ('hard') that the silver bromide gelatine films prepared from it cling to the glass and do not come loose during the photographic operations of developing and fixing. If the film comes loose with an otherwise good quality of gelatine, this trouble can be eliminated by addition of a small amount of chrome alum."

"So far as one can judge at present, the changes which the gelatine undergoes during the preparation and keeping of the emulsion are of different nature:

"A. Hofmeister's experiments[2] show that prolonged

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[1] The clear, transparent points are really rarely due to the presence of fat. The real cause of them has not been settled definitely; but people usually make a mistake in ascribing them to the presence of fat; because the same troubles occur also with gelatines containing no fat. For this reason it is useless to extract the gelatine with alcohol before using, as recommended by Hearstick, Phot. Wochenbl., 1884, 422. Besides, alcohol would not dissolve neutral fats. It is pretty risky to use ligroine or benzene, as recommended by Mrs. Scola. Ammonia saponifies fat, E. Vogel, Phot. Mittheilungen, 36, 117 (1899).

[2] Chem. Centralbl., 1879, 56, 71.

heating causes gelatine to decompose into two substances: into semiglutine, $C_{55}H_{85}N_{17}O_{22}$, which is insoluble in alcohol and is precipitated by platinum chloride; and into hemicolline, $C_{47}H_{70}N_{14}O_{19}$, which is soluble in alcohol and is not precipitated by platinum chloride. Semiglutine reduces silver nitrate in time without precipitating it, while hemicolline precipitates silver nitrate as a flocculent mass. The loss of setting power which gelatine undergoes on prolonged heating is due to this decomposition, which is not a putrefaction. After gelatine has been heated for several days, the decomposition has proceeded to such an extent that the gelatine remains liquid. Boiling for half an hour to an hour has no disturbing effect.[1] When boiled for two or three hours at 100°, the gelatine loses some of its tendency to set, the melting point and the point of solidification being lowered 3°–5°.

"B. This loss of setting power takes place also after long heating at 30°–50°, but much later than in the preceding case and consequently it is difficult to tell just how much of the effect is due to the splitting of the gelatine and how much to putrefaction accompanied by evolution of gas and formation of large quantities of ammonia.

"C. Boiling even with small amounts of ammonia or of an acid soon deprives the gelatine of its power to set. The same splitting seems to take place, for Eder observed the formation, in considerable amounts, of products soluble in alcohol and not precipitated by platinum chloride. If gelatine is not heated above 40° in water which contains 1–2 percent of ammonia, the decrease in the setting power and the lowering of the temperature of setting is not serious even after three hours heating. When a 4 percent gelatine solution is heated with a 2 percent aqueous ammonia, five minutes digestion at 30°–40° lowers the temperature of setting 0.5°–0.8°. The lowering is about one degree if the digestion is kept up for three hours at this temperature. The temperature of setting

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[1] There is thus no warrant for Goudoever's assumption that the liquefaction of gelatine caused by boiling is due simply to the taking up of one molecule of water by four of gelatine.

is therefore not affected seriously. The gelatine becomes softer, however, and less resistant, which may be unpleasant. If so, the washed gelatine emulsion may be hardened with alum or chrome alum. Gelatine is destroyed however when boiled with fixed alkalis. When the emulsion is boiled with an acid ammonium bromide solution, the gelatine loses the power of solidification much more rapidly than when neutral potassium bromide is used. That this should be so is quite clear from what has been said.

"D. The loss in the setting power of the gelatine after continued heating at 30°–40° is almost always the result of putrefaction. The germs of decay are everywhere in the air so that no artificial ferment is needed. The putrefaction of gelatine at 30°–40° varies with the nature of the gelatine. Gelatine, which is alkaline at the start, begins to give off ammonia fumes in three to four days and the amount of fumes then increase rapidly. Most gelatines with an acid reaction give off ammonia fumes only after ten days or more."

One of the most natural explanations of the process of ripening is that a slight reduction of silver bromide takes place and that the sensitiveness increases because there is consequently less work for the light to do. Lüppo-Cramer[1] considers this explanation entirely unwarranted.

"As we have already seen,[2] the highly sensitive, ripened silver bromide differs from the unripened product in that it requires a much longer exposure to light in case it is to be developed physically either before or after fixing than in case it is developed chemically. There is not this striking difference with the unripened silver bromide. From this I concluded that ripened silver bromide is changed before it loses bromine in some non-chemical way that makes it more easily reduced by the developer.

"If we test the plates on the market, both the ordinary, highly sensitive plates and the chloride or chloride bromide

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[1] Phot. Correspondenz, 41, 164 (1904).
[2] Ibid., 40, 228 (1903).

plates used for transparencies, we find that the highly sensitive plates and also many of those for transparencies fog considerably either on primary or secondary intensification with metol silver intensifier. This fogging stands in no relation however to the degree of fog obtained with the chemical developer.[1] With the commercial, transparency plates an exposure, which is sufficient for chemical development, is rarely enough for physical development, because even these plates have usually ripened somewhat during the process of manufacture or have perhaps changed somewhat through long standing after they were made. We get however exactly the same time of exposure for both kinds of development and a complete absence of fog even with physical development in the case of silver bromide, silver chloride, or chloride bromide plates if we deliberately prevent ripening.[2]

"When development is carried on for five minutes with the metol-silver intensifier, highly sensitive plates almost always give some fog; but with some of the commercial plates this fog may be so slight that the small globular fog grains can only be detected by the microscope. Though the fog formed on these plates by chemical development stood in no relation the 'reduction fog,' it seemed to me not impossible that the ratio of exposure for chemical and physical development stood in some relation to the fog obtained by reduction. Experiments with several types of commercial plates showed however that this is not the case and that many of the emulsions, containing almost no nuclei, required twenty to thirty times as long an exposure if they were to be developed physically. The infinitesimal reduction of the silver bromide has therefore no effect on the ratio of sensitive-

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[1] Cf. Phot. Correspondenz, 40, 177 (1903).

[2] Phot. Correspondenz, 40, 717 (1903). Emulsions, such as are required for the Lippmann process, are exceptionally suited for physical development, after the same exposure that is necessary before chemical development. I might add here that, when in the form of a so-called grainless emulsion, silver chloride is more sensitive than silver bromide prepared in exactly the same way, always assuming that the physical development is made the same in the two cases.

ness for the two kinds of development, so that the presence of fog cannot be the reason why the ordinary, highly sensitive plates require so much longer an exposure when they are to be developed physically.

"Though it already appears clearly from many of my papers that a reduction of silver bromide during ripening does not determine the sensitiveness or the degree of 'chemical' fog, I will nevertheless report now on a series of experiments which confirms my view still further.

"When softened for a short time in cold water, nearly all the kinds of gelatine known to me have washed out of them considerable quantities of soluble organic constituents, which are precipitated in a flocculent form by tannin. These soluble constituents of the gelatine reduce ammoniacal silver oxide considerably more readily than does the washed gelatine itself. In order to see whether the soluble constituents of the gelatine are appreciable factors in the emulsion, eight commercial samples of gelatine from different sources and of different qualities were washed in water three times for ten minutes each and were then tested as to their action on ammoniacal silver solution. For every experiment ten-gram lots of the washed and of the unwashed gelatine were dissolved each in 200 cc of water at 60° and 10 cc were added of an ammoniacal silver oxide solution containing 10 percent silver nitrate. The sixteen samples were left for fifteen hours in the dark[1] at ordinary temperature. In every case the unwashed gelatine gave more reduction and sometimes very much more reduction than the corresponding washed gelatine.

"From each of the eight kinds of gelatine two silver bromide emulsions were made under exactly the same conditions, one from the washed and one from the unwashed gelatine. The ripening was done in ammoniacal solution and was carried to such a point that on the average emulsions were obtained of normal commercial quality with respect to sensitiveness and degree of fog. This series showed that

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[1] The exclusion of daylight is especially necessary because many kinds of gelatine contain considerable amounts of chloride.

washing the gelatine, and thus freeing it from constituents which are known to have a reducing action, had no effect on the sensitiveness of the plates or on the degree of fog. It also showed that the different degree of reducing power in the different kinds of unwashed gelatine stood in no relation to the sensitiveness and the amount of fog in the emulsions prepared from these gelatines. The test given by H. W. Vogel for determining the suitability of any gelatine for the emulsion process seems not to be of value for the modern kinds of gelatine. Eder[1] also mentions that Vogel's test is only a first approximation. Eder[2] assumes however that the reducing substances in the gelatine might cause a fogging and yet he does not endorse the washing of the gelatine as recommended by Vogel.

"The experiments just described of course give no direct proof of the inadequacy of the reduction theory of ripening because the organic substances which reduce ammoniacal silver oxide, do not necessarily reduce silver bromide. In order to learn whether and how far the silver bromide is reduced in the emulsion, the sixteen kinds of plates were developed physically without having been exposed to light. All the plates gave some fog when developed for five minutes in a strongly acid metol-silver intensifier. With six pairs of plates the washed and the unwashed gelatines behaved exactly alike. With the other two pairs the plate made with unwashed gelatine was fogged very much more than the corresponding plate made with the washed gelatine. A number of special experiments showed that the much heavier reduction fog did not correspond in any way to a difference in sensitiveness or degree of fog when the plate was developed chemically.

"This series of experiments therefore confirms the conclusion from the earlier experiments that the process of ripening, with its accompanying increase in sensitiveness and in degree of fog when chemical development is used, is

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 31 (1902).

[2] Ibid., 33.

not in any way a consequence of partial reduction and formation of nuclei. My experiments on the behavior of mercuric iodide and of silver bromide[1] in different binders proved to me that the hypothesis of the sensitizing action of gelatine during the exposure would not stand the test. The confirmation of my previous view that the reduction theory of ripening is incorrect, leads me now to the view that there must be some sort of a combination between the silver bromide and the gelatine in addition to the coarsening of the grain and to the formation of a new modification."

Eder believes that the ripening is due to the formation of an instable modification.[2]

"We may assume that the 'ripening' of a silver bromide emulsion is connected with the change from the pulverulent silver bromide modifications of Stas to the granular modification. According to this view the increasing sensitiveness and the growth of the grain of a silver bromide emulsion during prolonged ripening is due to the formation of larger and more labile molecular complexes. Professor Ostwald does not share this view because all chemical compounds show a tendency to change into the more stable form. Ostwald[3] believes that, during digestion, the silver bromide reacts slowly with the gelatine forming a compound. Though a reaction with the gelatine is a fact, first demonstrated experimentally by Eder, and though the bound gelatine according to Eder undoubtedly acts as a chemical sensitizer, nevertheless Ostwald's view does not account satisfactorily for the fact established by Stas that silver bromide changes to a form that is more sensitive to light, when boiled with pure water. For this reason the other view is probably the better.

"The sensitizing action of the gelatine is not the chief cause of the increase in the sensitiveness of silver bromide during ripening. Thus the unripe silver bromide used in the

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[1] Phot. Correspondenz, 40, 710, 718 (1903).

[2] Eder's Handbuch der Photographie, 5th Ed., 3, I, 53, 77 (1902).

[3] Eder's Jahrbuch der Photographie, 11, 402 (1897).

Lippmann color process, is in contact with gelatine but is nevertheless relatively insensitive to light in comparison with the rapid emulsion prepared by boiling or by treatment with ammonia (Lüppo-Cramer)."

Lüppo-Cramer[1] is inclined to believe in the formation of a special modification of silver bromide.

"We have shown previously that with the same exposure a silver chloride gelatine emulsion and a silver chloride bromide gelatine emulsion give the same image whether developed chemically or physically after being fixed. On the other hand, if a silver bromide collodion plate is to be developed physically after fixing, it requires six times the exposure necessary for ordinary development while a highly sensitive dry plate requires fifteen times the exposure under corresponding conditions. Further experiments have shown that this fundamental difference does not depend on the chemical nature of the halide in the different emulsions, but probably on the entirely different degrees of ripening. An emulsion of pure silver bromide, made under conditions which prevented ripening, gave an image which was the same for the same time of exposure regardless of the method of development.

"This points conclusively to the fact that it is the increased degree of ripening in the ordinary plate which causes the difference in the two latent but developable images. This was confirmed by following up the fact, previously noted, that the same image was obtained from a highly sensitive silver bromide plate and from a silver bromide transparency plate of medium sensitiveness when the two were exposed in a ratio of 1 : 10 depending on their relative sensitiveness, but that the latent images showed marked differences when treated with bromine water.

"To investigate this phenomenon further I tested the latent images left on plates of different types after being fixed. I exposed the two kinds of plates again in a time ratio

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[1] Phot. Correspondenz, 40, 228 (1903).

of 1 : 10 and at first only about three times as long as was necessary for chemical development. One each of the two types of plates was next washed in bromine water and developed after fixing.[1] The transparency plate gave a complete picture with all details, though a bit foggy and somewhat lacking in contrast. On the highly sensitive plate there were only slight traces of an image in the high lights. On the plates treated with bromine no picture could be developed at all.[2] The fog was destroyed on the transparency plate but unchanged on the other.

"In a second experiment in which the times of exposure were doubled while everything else was kept the same, the transparency plate gave a fully-exposed picture while only the high lights came out on the highly sensitive plate. No image was obtained on the transparency plate that had been treated with bromine while distinct traces of an image could be obtained on the correspondingly treated instantaneous plate. The latent image on the less sensitive plate is therefore much more easily destroyed even with reference to photobromide than the latent image on the highly sensitive plate.

"It is important, however, that the less sensitive plate requires a relatively smaller increase in the time of exposure than the instantaneous plate when it is a matter of development after fixing.

"This is not only in accordance with what we know about the entirely unripened emulsion but also with the fact that the collodion emulsion represents a relatively low degree of ripening and only requires a six-fold exposure when it is to be developed physically after fixing instead of chemically.

"From this it appears to follow that the process of ripening gives to different emulsions the power of furnishing a chemically developable, latent image which is not developable if the plate is fixed first and which therefore does

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[1] I omit all the unnecessary details in regard to washing, etc.

[2] This statement applies only to the exposure in question and does not contradict the observation, Phot. Correspondenz, 40, 178 (1903).

not postulate a setting free of halogen. In other words, it seems to follow that ripening gives rise to a special modification of silver bromide which has the peculiarity of being changed by light to a developable latent image without a loss of halogen, while the unripened modification must lose bromine before it can be reduced by the developer."

In a more recent publication Lüppo-Cramer[1] seems to take a slightly different view of the process of ripening.

"If we keep in mind that an infinite series of intermediate stages are possible from the colloidal sol to the gel and to those forms of amorphous substances which no longer show the characteristic state of the specifically colloidal gel, we shall not be surprised that the physical state of the raw materials is of the greatest importance in the extremely complicated photographic processes.

"The alteration, which in colloidal chemistry is called the change of the sol into the gel, has been known for a long time in photography under the title of ripening. Lottermoser[2] was the first to call attention to this fact. He was also the first to prepare in a pure state the colloidal silver halides, which had been used daily for decades by photographers in the form of films in the printing-out processes."

Schaum[3] seems rather to favor the reduction theory of ripening.

"The microscopical investigation of many kinds of emulsions in different stages of ripening showed clearly that, during ripening, there was an increase in the grain of what was, at first, very finely divided amorphous silver bromide. This change is nothing more than the well-known one that finely divided precipitates become gradually coarser in time because smaller particles have greater free energy and consequently greater solubility than larger particles, in consequence of which the latter grow at the expense of the former. This can be deduced theoretically and was recently demon-

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[1] Kolloidchemie und Photographie, 60 (1908).

[2] Anorganische Kolloide, 65.

[3] Eder's Jahrbuch der Photographie, 15, 280 (1901).

strated experimentally by Ostwald[1] in the case of mercuric oxide which is yellow or red depending on its fineness. Many experimenters look upon this increase in the size of the grain as the sole cause of the ripening, and it is clear that an increased sensitiveness to light must follow the increased opacity to light resulting from the coarsening of the grain of the silver bromide. On the other hand one must remember that the decrease in the free energy due to the increase in grain, would cause a decrease in the sensitiveness to light if the change were not also accompanied by an increasing opacity to light. In the same way any spontaneous change to another modification, such as the crystallizing of the silver bromide, must act in the same way; and consequently it is not permissible to use such changes as an explanation of the process of ripening, though this is often done."

"In all samples of emulsions, after only half an hour's ripening, we found, together with the round, amorphous grains of silver bromide, polygonal, mostly three-cornered particles with fan-shaped markings. Large crystals found with them are water-soluble salts which can be removed by long-continued washing whereas the polygonal forms do not disappear under this treatment. Further experiments will be necessary to determine whether we are dealing with a partial crystallization of the silver bromide, in other words with a change which interferes with the increase of sensitiveness.

"It is a question whether the increase in the absorption of light resulting from the increased size of grain is the only cause of ripening or whether the gelatine also causes a reduction, even though slight, of the silver bromide to sub-bromide or silver which later increases the reducing action of the light. Many investigators have assumed the existence of such a reduction when explaining the phenomena of ripening, and such an assumption is a plausible one because other silver salts such as silver nitrate are reduced by gelatine to

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[1] Zeit. phys. Chem., 34, 495 (1900).

(colloidal) silver. Further, the fogging of over-ripe plates shows that reduction does take place even with silver bromide. Heating and adding ammonia increase the rate of ripening and both would be favorable to the reduction of silver bromide as well as to the increase in the size of the grain. We hope to contribute to the settling of these questions by experiments on the change in the absorption of light during ripening and also by experiments on the prevention of ripening."

"If one makes the probable assumption that ripening consists in part in an infinitesimal reduction of silver bromide, it is obvious that the very slight quantity of silver produced by this must increase the precipitation of silver on an exposed grain while with an unexposed grain it may not increase to visibility under the microscope during the normal period of development. It will become visible in case the emulsion is over-ripe and too much sub-halide has therefore been formed during the ripening, in case the time of development is too long, or in case the developer is too strong. Under these circumstances, the plate fogs."

The theory of ripening has been discussed by Lobry de Bruyn[1] in the last part of his paper on the physical state of substances insoluble in water when precipitated in presence of gelatine.

"Another phenomenon, of fundamental importance in photography, is what is known as the ripening of gelatine. When freshly prepared, gelatine containing limpid silver bromide is not sensitive to light, or scarcely so. When heated for some time the emulsion becomes more and more sensitive to light, and this change is accompanied by a more and more striking decrease in transparency. At first limpid, with a bluish violet color, the chilled and solidified mass, if left to itself at ordinary temperatures, assumes the appearance of porcelain after several days or several weeks, without the formation of any particles visible under the microscope. This change is accelerated very much by a rise

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[1] Recueil Trav. Pays-Bas, **19**, 244 (1900).

of temperature, the mass remaining liquid. This is the usual way of working when manufacturing photographic plates.

"The phenomenon of ripening is explained in two different ways. Eder[1] falls back upon the classical investigations of Stas on the halide compounds of silver,[1] and believes that it is primarily a question of different modifications of silver halide, which are more or less sensitive to light. Others, like Luther,[2] believe that we have to deal with a chemical change like that produced by light. Gelatine, being an organic substance, acts as a reducing agent and reduces silver bromide to sub-bromide, the bromine combining with the gelatine. The presence of the sub-bromide increases the action of the light, the increased action of light being greater, the larger the amount of the sub-halide originally present—up to a certain limit.

"Stas has described five or six modifications of silver bromide, differing among themselves in color (yellow or white), in appearance (flocculent, granular, or powdery), and, sometimes, in their solubility in water. Some of the modifications can be changed into some of the others. If one studies the work of Stas, one does not get the impression that these are well-defined modifications, constituting different phases in the sense that Gibbs has given to the word. It seems rather as though one were dealing with continuous transformations of matter in different states of division.[3]

"However this may be, it does not seem to me necessary to postulate several 'modifications,' real or otherwise, in order to explain the phenomena of ripening. Whenever we obtain this phenomenon, whether with melted gelatine at a

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[1] Eder's Handbuch der Photographie, 3, 37 (1890).

[2] Die chemischen Vorgänge in der Photographie, 57 (1899).

[3] We know that a substance is a little more soluble when it is in a state of extremely fine division than when its particles are a little coarser. An extension of the work of Stas, using modern methods, might clear up the question of the modifications of silver chloride, bromide and iodide. For data on the solubility of $AgCl$, $AgBr$ and AgI see Holleman: Zeit. phys. Chem., 12, 125 (1893); also Kohlrausch and Rose: Ibid., 12, 234 (1893).

high temperature or with solidified gelatine at ordinary temperatures, we may just as well picture to ourselves a progressive agglomeration of invisible particles, which are excessively small (at the moment of mixing, free molecules of bromide), into larger and larger particles which gradually produce a more marked clouding, and which finally become visible and measurable, first under the microscope and then without it.[1] Further, in so far as this phenomenon of ripening manifests itself by an increasing opacity, it can be duplicated, though in a somewhat less marked manner, with other insoluble substances precipitated in a gelatinous medium, for instance with silver chromate, with metallic gold, and especially well with sulphur. The phenomena with sulphur are the most closely comparable with the phenomena obtained with silver iodide, bromide and chloride.[2] It would therefore be necessary to postulate the existence of several 'modifications' of each of these substances.

"We shall note, however, that with silver chloride and silver bromide the essential change taking place during ripening is the continuous increase in the sensitiveness to light. This phenomenon runs parallel with a decrease in the transparency; the more opaque the gelatine becomes, the more sensitive it is to light.[3] In order that light may cause a chemical change, it must be retained and absorbed by the

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[1] Eder has measured the particles visible under the microscope and has obtained values of 0.8μ to 3μ.

[2] It is well-known that AgCl, AgBr, and AgI do not behave at all alike when precipitated in a medium of gelatine. If we make comparative experiments with equivalent solutions, we notice that the gelatine containing silver chloride becomes milky and opaque as soon as the solutions are mixed, while the gelatines containing silver bromide and silver iodide remain limpid. If they are then heated in the water-bath, the gelatine containing the silver iodide clouds much more slowly than that containing the silver bromide. The association of molecules into visible particles appears to take place more slowly the higher the molecular weight. This same difference occurs at ordinary temperatures if the three gelatines are solidified immediately after the solutions are mixed. The ripening takes place most rapidly with silver chloride and most slowly with silver iodide.

[3] Eder states also that the largest particles are the most sensitive to light, Eder's Handbuch der Photographie, 3, 40 (1890).

substances to be changed. It is therefore not astonishing but rather it is necessarily so that the transparent, bluish, silver bromide gelatine (which Cohen has shown actually does contain silver bromide) should be insensitive to light or nearly so; the particles are at most of a magnitude one-fiftieth to one-hundredth of a wave length of light.

"It seems to me that one may cite two facts which contradict the view put forward by Luther[1] that the process of ripening is due to a partial reduction of silver bromide to sub-bromide by the organic matter of the gelatine. The first is that silver bromide gelatine emulsions ripen more slowly, the higher the concentration of the gelatine. If this were a question of a chemical phenomenon, the ripening would take place more rapidly. On the other hand, this observation is entirely in harmony with the view that ripening is a physical or a mechanical process. The more concentrated the gelatine, the more it will prevent the molecules of silver bromide from uniting into larger and larger particles.

"The second fact which I have in mind is the behavior of silver bromide when formed in a colloidal, inorganic medium. I have made some observations on silver bromide precipitated in colloidal silicic acid in the following way. I take two flasks, each containing 10 cc of a solution of sodium silicate having a specific gravity of 1.09; I add an amount of nitric acid (sp. gr. about 1.08) sufficient to decompose the silicate almost completely (about 5 cc in my experiments). As quickly as possible, I add 5 cc of a N/10 $AgNO_3$ solution to one flask and 5 cc of a N/10 KBr solution to the other flask; and then mix the contents of the two flasks. There is formed a white, milky liquid which is only slightly transparent and which sets to a jelly in the course of a couple of minutes.

"If one compares the aqueous gelatine (5–10 percent concentration) with the silicic acid hydrogel, always working with salt solutions of the same concentrations, it is quite striking to note that the formation of silver bromide is not

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[1] Luther admits that there is an effect due to the decrease in transparency but he considers this as of secondary importance.

to be detected in the first case, the solidified gelatine remaining transparent, while the silicic acid jelly is as opaque as porcelain. The silver bromide however has not precipitated as visible particles. From this difference in behavior it is clear that gelatine is much more effective than silicic acid in preventing the agglomeration of silver bromide molecules into large and visible particles.

"Now it is easy to show that the silver bromide in the silicic acid is much more sensitive to light than silver bromide in gelatine even when the latter has been made opaque by being heated in the dark for several hours on a water bath. It seems to me difficult to harmonize this fact with the view that the ripening of silver bromide is primarily a chemical phenomenon, for the formation of sub-bromide under the action of the colloidal medium is impossible in the case of silicic acid. It is easier to consider the difference as due to the different size of the silver bromide particles, those formed in the silicic acid being larger than those formed in the gelatine, and consequently absorbing considerably more light.

"From these experiments it appears that different colloids (gels) do not act in the same way towards substances prepared in them. This difference depends without doubt on a difference in physical structure which happens to be quite noticeable if one compares the silicic acid gel with gelatine. As everybody knows, the former is less elastic and more friable than the latter; it loses its water more easily, under pressure for instance. The gelatine is also a reversible gel.

"It is to be noticed that Agar-Agar, which differs from gelatine in its greater setting power, resembles silicic acid in forming a silver bromide gel which is less transparent than that with gelatine, the two colloids being taken for the sake of comparison in a 1 percent solution."

Sheppard and Mees[1] give a rather discouraging outline

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[1] Investigations on the Theory of the Photographic Process, 267.

of what we know in regard to the theory of ripening and then offer a qualitative explanation of their own. The point of view is so characteristic that I quote in full.

"Before attempting to sum up the series of actions in the photographic process, it is necessary to say a few words as to the nature of 'ripening,' and on the preliminary action in exposure to any chemical reaction. Ripening is the name given technically to various treatments which increase the sensitiveness of silver halide emulsions. We may notice the following points.[1]

"The character of the gelatine is of great importance. Such characteristics as the melting point, solidification point (neither sharply defined), viscosity in aqueous solution, absorption for water, reducing power on ammoniacal silver nitrate, have all been more or less investigated,[2] but no systematic inquiry as to their relation to the sensitiveness numerically expressed has yet been made. In addition, experiments have been made with other colloids.[3]

"Ripening may be brought about either in the cold by certain additions to the emulsion, especially ammonia, or by digestion at a moderately high temperature. The addition of various substances to the emulsion has been the subject of many experiments,[4] but with little result of systematic value. Generally silver solvents facilitate ripening. Oxidizing agents retard it, but this has been dealt with under desensitizers, while reducing agents are said to have a favorable influence. But this may be merely due to a destruction of a desensitizer.

"The most noticeable alteration brought about by ripening is the increase in the size of the halide particles, a process identical with the change brought about in fine-

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[1] Cf. Eder's Handbuch der Photographie, 3 (1890).

[2] Lohse: Eder's Handbuch der Photographie, 3, 25 (1890). Abney: Eder's Jahrbuch der Photographie, 1, 299 (1877).

[3] Agar-agar by Rebjkow Eder's Jahrbuch der Photographie, 6, 386 (1892). Silicic acid by L. de Brunn: Chem. Centralbl., 1900, 889.

[4] V. Bellach: Struktur des photographischen Negativs, 17.

grained precipitates. The smaller particles have a greater solubility than the larger; they go into solution, which becomes supersaturated with respect to the larger particles, so that these increase further in size.[1] Little explanation has been given as to how this influences the sensitiveness, but one doubtless consists in the fact already emphasized, that the *grain* is the limiting aggregate in development, while another is probably the alteration in the opacity and reflecting power to light. Hurter and Driffield[2] have shown that the 'speed' or sensitiveness of a plate depends largely on these physical factors.

"A second change postulated as increasing the sensitiveness in ripening is the formation of a small amount of light-reduction product (photo-halide) by the reducing power of gelatine at higher temperatures.[3] But this does not account for the process of ripening in the cold with ammonia, and also (if confirmed) the greater sensitiveness of silicic acid emulsions. Moreover, Schaum and Braun found that gelatine-free halide was susceptible of a certain amount of ripening. However, over-ripened emulsions certainly tend to fog. A definite crystallization of the silver halide occurs on prolonged ripening and some have sought an explanation in this, or generally in a 'modification' of the halide.[4] But the transition of bodies from a labile form (as amorphous halide) to a stable one is always accompanied by a diminution of the free energy, so that from this cause the emulsion would become not more but less sensitive.[5]

"There is no doubt that the principal factor in the increased sensitiveness is the greater absorption for light or opacity. But how is this brought about? Mere increase in the size of the grain for the same mass of material will not

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[1] Cf. Ostwald: Zeit. phys. Chem., 34, 495 (1900).

[2] Phot. Jour., 22 (1898).

[3] Abegg: Arch. wiss. Phot., 1, 15 (1899); Guébhard: Comptes rendus, 126, 40 (1898); Stolze: Eder's Jahrbuch der Photographie, 4, 306 (1890).

[4] Lüppo-Cramer: Wiss. Arb.

[5] Schaum: Arch. wiss. Phot., 2, 9 (1900)

do this. As a hypothesis we wish to put forward a suggestion not hitherto applied to this process. Attention has already been drawn to Quincke's researches on the nature of silver halide emulsions, and we may regard these as a most intimate mixture of gelatine and halide, partly a solution. Certainly the gelatine cannot be completely removed by mechanical means, such as centrifugalizing. Now, the vibrations of light are considered to be of electro-magnetic nature, and the absorption of light as conditioned by resonance, just as the absorption of Hertzian waves, which can be experimentally studied as a resonance phenomenon. Every electro-magnetic resonance, every preformed electro-magnetic period, is conditioned not only by the electric and magnetic properties of the resonator and its surrounding medium, but also necessarily by their spatial distribution.[1] In fact, the vibration period increases with the spatial extension of the resonator, with the closeness of their packing, and with the dielectric constant of the medium. According to Planck,[2] the magnitude of the absorption is proportional to the intensity of the exciting vibrations proper to the resonator, to its logarithmic decrement, and to the cube of the light velocity; and inversely as the frequency. Now, according to the researches of R. Zsigmondy by the ultra-microscopic method,[3] gelatine consists of a homogeneous mass containing aggregates, the proportion being variable, and influenced by the state of the gelatine. In a gelatine emulsion these 'knots' or aggregates would be naturally associated with the halide, giving their form and distribution to the same. They may be considered as forming the resonators, or groups of systems of resonators postulated above, and this offers an explanation of one function of gelatine as a sensitizer and the influence of cooking in ripening. To the formation of these aggregates is probably due the slow increase in viscosity on 'cooking' gelatine noted by Schröder. It is evident that there is a wide field

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[1] Cf. Luther: Zeit. wiss. Photographie, 3, 269 (1905).

[2] Drude's Ann., 1, 92 (1900).

[3] Zeit. Elektrochemie, 8, 686 (1902).

of research for the correlation of the sensitiveness with the properties of gelatine and the alteration of these. The event of a possible preliminary reduction, and even the absorbent capacity of gelatine for free halogen (Vogel's definition of a 'sensitizer' was a substance absorbing free halogen) must be considered as secondary to the physical process indicated above."

That the ripening of an emulsion does not necessarily include a reduction of the silver bromide is shown conclusively by the fact that the silver bromide from a spoiled emulsion can be used provided it is emulsified again in fresh gelatine. Eder[1] says in regard to this:

"It has been noticed that an emulsion which has spoiled and liquefied allows the silver bromide to separate. If the supernatant, clear liquid is decanted and the silver bromide emulsified in fresh gelatine, one often obtains excellent emulsions which are more sensitive than the original one. Burton found that when silver bromide is cooked for a long time with gelatine a green fog appears on development. If the silver bromide is removed and emulsified in fresh gelatine, clear and highly sensitive plates are obtained."

Quincke[2] has published an abstract of his work on emulsions which is so important in its bearing on the state of silver bromide in a gelatine emulsion that I quote in full.

"When a hot, aqueous solution of gelatine is cooled, a gelatine jelly is obtained. As the gelatine solution cools or as the water evaporates, there is formed a very viscous, oily solution A of gelatine containing relatively little water, and a less viscous solution B of gelatine containing relatively more water. The surface between these two gelatine solutions tends to become as small as possible in consequence of the surface tension. The water-poor gelatine solution A forms the walls and the water-rich gelatine solution B the contents of the small, visible or invisible foam-cells of which the gelatine jelly is made up.

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 39 (1902).

[2] Eder's Jahrbuch der Photographie, 19, 3 (1905).

"The halide salts of silver are more soluble in the water-poor gelatine solution A than they are in the water-rich gelatine solution B. Foam flecks, containing gelatine and silver bromide, and suspended in water, move towards those portions of the water which contain bromine, ammonia or alcohol. Flecks of silver bromide containing no gelatine move also but much more slowly. This is proved by a periodic spreading-out of bromine, ammonia or alcohol on the surface of the particles of silver bromide and gelatine or of silver bromide suspended in the liquid. This action is more intense with silver bromide and gelatine particles than with those of silver bromide alone.

"The silver bromide gelatine films deposited on glass plates are stiff jellies with half-solidified or wholly solidified walls of oily, gelatine solution A, which is rich in silver bromide and poor in water, and which separates from a gelatine solution B which is rich in water and poor in silver bromide.

"In the foam walls and especially in the edges of the foam walls there are bubbles, drops and foam flecks of the gelatine solution A, which are commonly called 'grains.' The process of 'ripening' is a long heating of a cloudy solution of silver bromide and gelatine, whereby the small, suspended particles combine to larger flecks of foam, to larger grains. Judging from the behavior of other cloudy solutions, the flocculating is the result of a periodic spreading-out of a foreign liquid C on the liquid surface of the suspended particles. The 'small' grains of the gelatine solution rich in silver bromide are covered by a layer of a foreign liquid C and are combined to larger drops, bubbles, and foam flecks.

"The author has shown by special experiments that the layer of foreign liquid C is a water-rich gelatine film, containing less silver bromide than the oily, water-poor, silver bromide gelatine A of the actual foam walls. The thickness and composition of the gelatine film C depend on the temperature at which the ripening takes place and on the time which it lasts. Fine grains of silver bromide are precipitated from the gelatine film C whenever it takes up water or loses gelatine, in other words when there is too little gelatine within the molecular sphere of action of the silver bromide because the gelatine increases the solubility of the silver bromide.

"We must now account for the slow action of light on the oily silver bromide gelatine of the unripened emulsion and the rapid action of light on silver bromide in the ripened emulsion. On exposure to light the oily silver bromide gelatine solution A precipitates in spherical bubbles or in visible or invisible foam walls. From this silver bromide gelatine, light sets free metallic silver slowly.

"The 'grains' of the ripened silver bromide gelatine plates consist of an oily silver bromide gelatine solution and not of pure silver bromide. In the unripened emulsion the oily, silver bromide gelatine solution is covered with an imperceptibly thin film C of a gelatine rich in water and poor in silver bromide. The thickness of this film is less than the doubled sphere of action of the molecular forces, less than one-fifth of a wave length. While the melted emulsion is ripening, the surface of the oily silver bromide gelatine solution A becomes smaller and the thickness of the gelatine film C greater, this gelatine film C changing thereby into a solution supersaturated with respect to silver bromide. From this supersaturated solution invisible particles of silver bromide precipitate gradually and remain hanging in the film C. When the emulsion is cooled, the oily silver bromide gelatine solution A forming the foam walls, and the gelatine film C solidify or at least become very viscous liquids.

"The ripening of silver bromide gelatine corresponds to the flocculation of cloudy solutions. The methods of, practical photography increase the sensitiveness of ripened silver bromide gelatine, by first creating artificially a large surface of the oily, silver bromide gelatine solution A and a large film of gelatine C, and then decreasing this surface by causing another liquid such as bromine, alcohol or ammonia, to spread out over it, thereby precipitating many (invisible) particles of silver bromide.

"When exposed to light, silver bromide is decomposed into silver and bromine. The latter spreads out over the surface of the oily, solidified silver bromide gelatine solution A. The particles of metallic silver cling on this surface and in the gelatine film C. They form the so-called latent image and are the condensation nuclei on which, by contact action, there are precipitated new particles of silver coming from the silver formed in another solution in case of so-called physical development, or from the particles of silver formed out of the silver bromide of the oily silver bromide gelatine solution during the development of the photographic plate.

"The photographic silver bromide gelatine plates become less sensitive in time if a part of the precipitated silver bromide dissolves again in the very viscous gelatine solution A or if the walls of silver bromide gelatine solution become horny through loss of water.

"The chemical action of light on silver bromide is a resonance phenomenon. The particles of silver bromide decompose more readily the greater the amplitude of the vibrating particles; with equal intensity of light, more readily the smaller the mass of the vibrating particle.

"A number of well-known phenomena are in complete harmony with this view, such as the photochemical induction; the existence of a least exposure which will cause a decomposition of silver bromide or a visible blackening (when developed); the relatively slight effect of a weak light; the difference between continuous and intermittent illumination; and the dependence of the blackening on the period and wave length of the intermittent light."

While plates are ordinarily made by mixing solutions, they can be prepared by adding an aqueous solution of a silver salt to a solidified gelatine containing a soluble halide salt. This process introduces some special peculiarities which are discussed by Lüppo-Cramer.[1]

"If a gelatine solution containing salts is poured out on glass plates and allowed to solidify, interesting reactions

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[1] Phot. Correspondenz, 43, 485 (1906).

with other substances may be obtained in these films, as has been described by R. E. Liesegang[1] in his book on chemical reactions in jellies. These reactions are not only interesting along the lines followed by Liesegang but in addition they are very useful when studying the formation of silver halides.

"When preparing gelatine emulsions, it is necessary that the gelatine solutions should be liquid and therefore that a relatively high temperature should prevail, a circumstance which promotes ripening. The solidified gelatine jelly on the other hand can be silvered just as a wet collodion plate is by bathing, or, more simply still, by dropping silver solution upon the solidified jelly.

"To 200 cc of 10 percent gelatine solutions were added 5 grams KI or the equivalent quantities of 3.5 grams KBr or 1.7 grams NaCl, and plates were made from the solutions. When a 10 percent silver nitrate solution was allowed to drop upon the solidified films, the iodide film clouded the quickest, then the chloride film and lastly the bromide film. The difference is quite striking but, so far as the silver bromide and silver iodide are concerned, the results are quite in harmony with what is known in regard to the behavior of wet collodion plates. That silver chloride ripens faster than silver bromide under the same conditions follows from earlier experiments of my own.[2]

"The results are quite different if ammoniacal silver oxide is substituted for silver nitrate. While only a faint, passing, opalescence is to be detected when silver chloride or silver bromide are formed from a neutral silver solution, the solution with ammonia causes at once an opaque, white clouding which is however much less with silver iodide than with the other two halides. In fact the clouding with silver iodide is incomparably greater when a neutral silver solution is used than when ammonia is present. When silver chloride or silver bromide is prepared in ammoniacal solution, the immediate formation of dense, opaque silver halide, as against

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[1] Chemische Reaktionen in Gallerten.

[2] Phot. Correspondenz, 40, 714 (1903); 41, 165 (1904); 43, 31 (1906).

a faint opalescence in the absence of ammonia, is an argument in favor of the view that the ammonia is a decisive factor at the very moment of formation of the halides. If the silver solution is diluted to one-tenth, the silver halide becomes opaque very rapidly. When the amount of gelatine is increased, the ripening is retarded considerably, as is also the case with the regular emulsion.

"Bathed plates can also be made from the solidified jelly and the results are quite as good as with the corresponding collodion plates. The 10 percent gelatine solutions pour almost as well as the 2 percent collodion solutions. They can be poured in exactly the same way and then allowed to harden. If they are bathed in a 10 percent silver solution, the silver iodide is again incomparably more opaque than the silver bromide. When making the silver iodide plates, it is well to saturate the silver nitrate solution with silver iodide just as is done when making collodion plates. The silver bromide plate is slightly opalescent and looks like a Lippmann emulsion, while the silver iodide has a good deal of covering power and is yellowish, like a collodion plate. From the experiments with bathed plates as well as with drops it appears that ammonia has much more effect in ripening nascent silver bromide than it does when applied to silver bromide after the halide is formed. When the jelly is bathed in an ammoniacal silver oxide solution (10 percent $AgNO_3$) there is formed at once a dense, white, silver bromide film. On the other hand if one bathes the opalescent silver bromide layer, prepared originally without ammonia, of course in a very dilute ammoniacal solution, the grain increases in density very slowly.

"With bathed collodion plates the formation of silver iodide takes place faster than with bathed gelatine plates. This is not surprising when we remember that a collodion solution, suitable for pouring, contains only one-fifth the amount of binder that the corresponding gelatine solution does.

"Bathed gelatine plates, consisting of silver bromide or silver chloride, show only a slight opalescence which is much the same for either halide. As I have previously pointed out,[1] with such films the silver chloride may easily be more sensitive to light than the silver bromide because the former ripens faster at first. If we let the films darken under silver nitrate solution, we notice the phenomenon described recently by me[2] in my experiments on the printing-out process, that silver bromide blackens faster than silver chloride at first but that the latter soon passes it.

"Both with the bathed collodion plates and the corresponding gelatine plates, the addition of one-fifth bromide, for instance, to the iodide has a very surprising effect. The films become much more opaque and much yellower than with pure silver iodide. This occurs even in presence of ammonia.

"With the wet collodion plates it is customary to use much more silver iodide than silver bromide, but the reverse is the case with dry plates. If one takes one part of potassium iodide to five of potassium bromide in making a bathed gelatine plate, the rate of formation of silver halide from a neutral silver solution is no greater than with pure silver bromide, but the silver brom-iodide shows a much yellower color at once. With ammoniacal silver solution the effect of the iodide content is quite extraordinary. There is formed at once an intensely yellow, dense, silver brom-iodide, although the pure silver bromide is white under these circumstances and the pure silver iodide is only slightly opalescent."

There are some other curious things about emulsions containing silver iodide and silver bromide, all of which will have to be straightened out before we get through. I quote from Eder:[3]

"We must always remember that silver iodide is less readily reduced by the developer than silver bromide, while silver chloride is more readily reduced. Silver bromide stands between the other two in respect to ease of reduction.

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[1] Phot. Correspondenz, 40, 714 (1903); 41, 165 (1904); 43, 31 (1906).

[2] Eder's Jahrbuch der Photographie, 20, 646 (1906).

[3] Eder's Handbuch der Photographie, 5th Ed., 3, I, 117-121 (1902).

"The addition of silver iodide to silver bromide gelatine was first recommended by Penny[1] in 1877 and the effect of so doing was more carefully by Abney[2] in 1880. The advantages of silver iodide in the silver bromide gelatine are that it keeps the emulsion clear, makes possible a longer cooking of the emulsion without fogging, etc. Silver iodide behaves quite differently however depending on the way in which it is incorporated into the silver bromide emulsion. This important fact was first recognized by V. Schumann[3] and was confirmed by Eder.[4]

"If a silver iodide gelatine emulsion and a silver bromide one be prepared separately and then are mixed after having been washed, this brom-iodide emulsion is less sensitive in general and especially so towards red and yellow light. Abney[5] and H. W. Vogel[6] consider this very advantageous because one can therefore use a brighter light during development and because such plates can stand a longer exposure[7] than a straight silver bromide plate without solarizing."

Plates, which are rich in silver iodide, not only take longer to fix than a bromide plate, but in an old fixing bath they will often show a faint milky fog which takes several hours soaking to remove though it dissolves very rapidly if a fresh fixing bath is used.[8]

"Emulsions, nowadays, are very seldom prepared by mixing silver iodide gelatine and silver bromide gelatine after they have been washed.

"If we dissolve potassium iodide and bromide, or the corresponding ammonium salts, in water containing gelatine, and then add silver nitrate to this mixture, the formation of silver brom-iodide takes place all at once. Some sort of a

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[1] Yearbook of Photography for 1878.
[2] Phot. News, 1880, 174, 196.
[3] Phot. Wochenbl., 1882, 1883, 1884.
[4] Phot. Correspondenz, 21, 95 (1884).
[5] Phot. News, 1880, 196; 1881, 8, 20.
[6] Phot. Notizen, 1881.
[7] Abney: Brit. Jour. Phot., 1881, 528.
[8] Schumann: Phot. Wochenbl., 1884, 319.

double salt appears to be formed because the behavior of such a silver brom-iodide is different from that of silver iodide and silver bromide prepared separately and then mixed. It is also recommended to dissolve the iodide in the concentrated silver nitrate solution, add gelatine if possible, and then to mix the resulting solution with a potassium bromide gelatine solution. In this way a high sensitiveness is said to be obtained.[1]

"If a brom-iodide emulsion is digested for a sufficient long time, it is more sensitive than a pure bromide emulsion both for lamplight and for daylight.[2]

"At present many good commercial emulsions contain silver brom-iodide, the amount of silver iodide being 1–5 percent of that of the silver bromide. In the early editions Eder recommended the addition of iodide for emulsions which were to be ripened by boiling. Nevertheless, some manufacturers of high standing are in favor of a pure silver bromide emulsion. Their reason is that with such an emulsion one can make handsome portraits with plenty of detail, with a saving of time in development and in fixing. It is still an open question whether a pure silver bromide emulsion or a silver brom-iodide emulsion is better for portraits. In Germany, Austria and France the pure bromide emulsion is more in favor, while in England they make rather more silver brom-iodide emulsions. These latter have only a small content which however makes the plate saffron-yellow. Emulsions containing 10 percent silver iodide are not commercial products because they usually give thin negatives which are hard to develop.

"For landscapes, brom-iodide emulsions, containing 3–4 percent silver iodide, are distinctly preferable to the straight bromide emulsion because there is less danger of halation, and because sharply-defined, thin branches stand out better against the sky."

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[1] Eder's Jahrbuch der Photographie, 5, 452, 454 (1891).

[2] This observation was first published by Schumann: Phot. Archiv., 1882, 121.

"When a silver iodide emulsion is added to a silver bromide emulsion, it acts as a mild restrainer and keeps the plate clear during development. Why is silver bromide reduced more slowly by the developer when silver iodide is present? Why does silver iodide retard the development of a silver bromide emulsion and why do silver bromide and silver iodide retard the development of a silver chloride emulsion? When silver iodide gelatine and silver bromide gelatine are prepared separately and then mixed, no double salt is formed and consequently one must turn to chemical statics [?] for an explanation for the restraining and fog-preventing action of the silver iodide. It is known that silver, for instance, cannot be extracted from a gold or platinum alloy by nitric acid when the concentration of the acid exceeds a certain limit. Dilute hydrochloric acid or sulphuric acid, when mixed with certain indifferent substances such as glycerine, gum-arabic, etc., act much more slowly on an iron, zinc, ultramarine, etc., and therefore the restraining is purely of a physical nature, as was pointed out by Lunge.[1] Without doubt a number of the 'restrainers' in photographic processes come under this category, as Eder pointed out in the earlier editions.

"The interspersed silver iodide is hard to reduce and nearly photographically inert; it retards the reduction of silver bromide by the developer. In fact an increase in the amount of gelatine acts in the same way, though not so energetically. That silver iodide makes the image thinner is undoubtedly due at least in part to the inactinic color which cuts off the light. A yellow dye would replace the silver iodide satisfactorily so far as this latter is concerned but not with respect to the restraining action.

"Sugar, glycerine or dextrine in the developer also act as restrainers but can substitute for silver iodide only in this respect because they help to produce dense negatives.

"If this view is correct, the addition of any other diffi-

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[1] Ber. chem. Ges. Berlin, 9, 1315 (1876).

cultly reducible silver salt to a cooked silver bromide emulsion should prevent fog, should act as a restrainer during development if present in suitable amounts, and should not affect the sensitiveness. As a matter of fact, unripe silver bromide emulsions, which give no fog, act in just this way when added to a highly sensitive emulsion having a slight tendency to fog. The different behavior of brom-iodide emulsion prepared in one operation (greater color-sensitiveness, etc.) is most easily explained on the assumption of a double salt of silver iodide and silver bromide; as a matter of fact, the spectroscopic behavior is entirely changed."

In this paper I have given an outline of what seem to me to be the most important facts in regard to methods of preparation; amount of silver in film; sensitiveness of film to light; methods of ripening; limits to ripening; inhomogeneity of emulsion; reducing action of some gelatines; question of reduction during ripening; theories of ripening; state of silver bromide in film; and behavior of mixed emulsions. In the second paper I expect to discuss: opacity; coarsening of grain; effect of water content; effect of gelatine content; effect of salt content; nature of medium; and increased sensitiveness to different lights. We can then see in how far it is possible to formulate a single hypothesis which shall take account of all the facts.

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ON A DEVICE FOR MEASURING TRANSPARENCY

BY L. H. FRIEDBURG

When viewed in transmitted light, the silver precipitate of a developed photographic plate appears to be denser, blacker, or more opaque in proportion to the amount of silver deposited per square unit of the film. The opacity of a plate is influenced, moreover, by the molecular condition—size of grain and number of grains. We have to do here with finely divided, so-called molecular silver, *i. e.*, silver, the particles of which are separated from each other by foreign particles, as opposed to what is ordinarily termed coherent silver.

In this connection, two mathematical expressions for opacity or its converse, transparency, have been proposed:

(I) According to J. M. Eder.[1]

If for a given blackening, a represents the relation of impinging light i, to transmitted light i', we have:

$$a = \frac{i}{i'} \qquad \text{(I).}$$

as an expression for the opacity of a plate. By analogy with the phenomena observed in the passage of light through transparent bodies of different thickness, a may be put as e^D,

$$a = e^D, \qquad \text{(II).}$$

in which e is the basis of the system of natural logarithms, and D, the density of the developed photographic plate, D being analogous to the thickness of the transparent bodies.

Considered in this sense, the density of a plate, or its degree of blackening, is the logarithm of its opacity towards light.

For practical reasons, Eder decided to use the common

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[1] Sitzungsber. Akad. Wiss. Wien, **108**, II*a*, 1407 (1899); **109**, II*a*, 1103 (1900); **110**, II*a*, 1103 (1901); **111**, II*a*, 888 (1902). See also Eder und Valenta: Beiträge zur Photochemie und Spektralanalyse, 1904.

system of logarithms of Briggs. He recommends that the equation (II) be expressed in the form:

$$a = 10^S$$

in which S is to be considered as a practical measure of the blackening, S being the ordinary logarithm of a. We have then the equation:

$$S = D \log. e = 0.4343 D.$$

(II) According to R. Luther.[1]

If for a plane-parallel layer, i stands for impinging, and i' for transmitted light, we have the following expression for the "transparency" of a plate:

$$\frac{i'}{i}.$$

This transparency is always a real fraction. For a perfectly transparent layer, it is equal to 1, and for an absolutely opaque layer it is O. The transparency of a continuous series of layers is equal to the product of the individual transparencies.

On the other hand, the reciprocal of the above fraction:

$$\frac{i}{i'}$$

is termed "opacity." The numerical value of opacity is always greater than 1, being 1 for absolutely transparent media, and ∞ for absolutely opaque layers. The opacity of a continuous series of layers is equal to the product of the individual opacities.

The decadic logarithm of opacity is called "extinction," by Luther, and it corresponds precisely with the conception of "blackening," according to Eder and Schwarzschild, and with the conception of "density," according to Hurter and Driffield.

In the pursuit of certain photochemical investigations, I found it necessary to determine in an exact manner, differ-

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[1] Zeit. phys. Chem., 33, 252 (1900).

ences in opacity of photographic negatives. Heretofore we have been accustomed to speak of plates, showing "greater" or "lesser" density, and the eye *alone* was allowed to judge such differences. There are apparatus in existence, such as Eder-Scheiner's, which enable us to ascertain the optical density of developed dry-plates by exact measurement, but they are expensive and cumbersome. All I desired was an apparatus offering a unit for measurement, readily accessible, easily manipulated and of fair exactness in results. It is obvious, that a simple apparatus, furnishing "polarized light," will fulfil these requirements. An opaque plate, *not* rotating the plane of polarization, when interposed between two parallel mounted tourmaline plates, which are cut parallel to their optical axes, will reduce the angle of 90°, produced by rotating from maximum brightness to maximum darkness. This reduction will be directly proportional to the density of the silver deposit. The greater the density of the deposit, the greater will be the reduction in rotation. Conversely, the *angle* formed on rotation to darkness, after interposing a denser plate, will be smaller than that which results in the case of a less dense plate.

The density of the deposit is thus measured in angles, inversely proportional to such density.

A goniometer, from which the support for the crystals had been removed, and to which subsequently the two tourmaline plates had been attached, one of them in a fixed position, similar to the polarizer in a polariscope, the second one movable with the rotating disk of the goniometer, both mounted parallel to each other, and in such a manner as to allow the space between them to be widened at will, is all that was used. An ocular and a collimator may be attached, but these are not a necessity.

The plate to be examined was fastened in a clamp, allowing it to stand between, and parallel to the tourmaline plates, and the observations were made with diffused daylight, with lamplight or with monochromatic light.

Measurements made by means of this simple densitometer, or absorptiometer, are fairly exact, after a little practice has been acquired. They are, of course, less exact for slighter densities, when the eye of the observer is frequently in doubt, whether the maximum brightness or the maximum darkness are reached or not. In such cases, the removal of the plate under observation, and a new determination of the angle of rotation needed, so as to reach the two extreme points of the tourmaline *alone*, suffices to establish the confidence of the observer in a following determination of the density of the plate, after renewed insertion.

In order to find out whether the plate inserted between the tourmalines possesses rotating power "*per se*," a single observation in the strongest sunlight or arc-light will decide. I did not find a single plate, which when thus observed, showed rotating power.

It is almost needless to remark, that the same apparatus (if need be, mounted vertically rather than horizontally) can be used for colorimetric experiments, such as we customarily perform in water analyses, etc., always provided that the liquids interposed are contained in proper vessels of equal depth, and that those liquids do not rotate the plane of polarization. In such cases, the densities can be determined in *one* experiment, instead of in many, such as we are obliged to perform, when repeated dilution of the liquid under scrutiny becomes necessary.

New York, October, 1909

NEW BOOKS

Kapillarchemie. *Eine Darstellung der Chemie der Kolloide und verwandter Gebiete. By Herbert Freundlich. 17 × 25 cm; pp. viii + 591. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1909.*— In the preface the author says:

"Colloidal chemistry is a subdivision of the broader science of capillary chemistry. Both subjects are developing rapidly at present. Under these circumstances, it may seem unwise to present the subject from a general point of view instead of contenting oneself with collecting the experimental data and the theoretical ideas. The reason that I have attempted such a thing is that if one starts with a certain general point of view it becomes easier to see what is settled territory, what is new land, and where one can start work with the best prospect of success. This emphasizing the general point of view made it necessary to treat capillary chemistry as fully as possible. In colloidal chemistry we have to deal with very complex structures and it is much more difficult to master the general laws governing the phenomena (adsorption, change of solubility, changes due to frictional electricity, etc.) than is the case in the simpler systems with which capillary chemistry chiefly has to deal. These latter systems therefore form the foundation upon which it will be easier to build up colloidal chemistry."

The author divides his book into two parts, the first being concerned with the properties of surfaces in general and the second devoted to dispersed systems. In the first part the subheads are: surface between gas and liquid; surface between solid and gas; surface between liquid and liquid; surface between solid and liquid; capillary electric phenomena; properties of surface films. In the second part we have discussions of: clouds and foams; smoke and lamellated structures such as opal; colloidal suspensions; colloidal emulsions; systems with solid dispersing media.

The book is full of interesting passages. In speaking of the contact angle, for instance, where liquid, solid and vapor meet, the author says, p. 18:

"It is *a priori* conceivable that a definite contact angle might be a characteristic of such a meeting of three surfaces. Experiment does not confirm this view. In fact it seems more probable that the limiting cases of complete wetting and of no wetting are the well-defined ones and that cases of partial wetting are usually to be considered as instances in which a surface which can be wetted completely is contaminated by substances which are not wetted by the liquid. Under these conditions the contact angle varies enormously in apparent value."

On p. 51 we find Gibbs's theorem in regard to the relation between the change of surface tension and the concentration in the surface film.

On p. 99 it is pointed out that the important factor in the adsorption of a gas by a solid is the change in the surface tension with the change in the pressure. "It is not enough that the adsorbing solid should have a large surface. It is entirely conceivable that a solid might have an enormous surface but that its surface tension might change very slightly with increasing pressure of the gas. Under these circumstances the adsorption would be very slight in spite of the enormous surface."

On p. 135 there is a very clear statement of the conditions under which a crystal gives rise to a plant-like growth in a solution.

"The phenomenon is as follows: If a crystal of a manganese salt for instance, is dropped into a water-glass solution of suitable concentration, trunk-like tubes grow upwards out of the crystal, then side branches shoot out, which later give rise to fine twigs so that the test-tube is filled finally with a plant-like or moss-like structure.

"The explanation of the phenomenon is that the crystal first dissolves in the water-glass solution. So soon as the saturation point is reached, a film of solid magnesium silicate forms round the manganese salt solution which covers the crystal. This membrane is semipermeable, water passing through it but not the silicate. The film is stretched by the water flowing through it until, at a specially weak spot, a jet of manganese salt solution spurts out into the silicate solution. This is immediately coated with a film of manganese silicate and the game goes on again. The direction of the growth is determined by the fact that the film is always thinnest at the top and therefore gives way first there. The unequal thickness is due to the fact that the lightest and therefore the most dilute solution collects in the upper portion of the cell."

On p. 218 we find an account of the experiments of Mylius and Fromm on the electrolytic formation of metal films on the surface of the solution. On p. 261 is an account of the formation of a liquid jet from drops when the water is electrified.

"It might seem remarkable that electricity could have any effect on the change of a single jet of liquid into drops. One would naturally assume that, when a charged body was brought near, the drops would all become electrified in the same way and would therefore repel each other instead of uniting. Now the original breaking of the jet into drops is due to the possibility of forming drops which are not equally large and which do not move equally fast. The result of this is that they collide and bound apart. An electrically charged body does not affect all the drops equally. Depending on the relative distances of the drops from the electrically charged body, on the relative sizes of the drops, etc., there will be slight differences of potential which will determine the combining of the drops. If the electrical excitation is too strong, these slight differences in the charges become negligible and the jet goes to pieces again."

On p. 302 there is a discussion of the conditions for producing a fairly permanent lather.

"A gas and a liquid can always be made to foam by shaking the liquid and the gas together, by bubbling gas through a liquid or by forming gas bubbles when the liquid boils. The foam cells thus formed are usually extraordinarily short-lived. The question whether a liquid can form a foam really depends on the question whether fairly permanent, thin films of the liquid can be formed. The properties of the liquid determine this matter and the properties of the gas are of secondary importance.

"The formation of a thin film of liquid always means an increase in the surface tension above the normal value. This is more easily accomplished if the normal surface tension is small and, as a matter of fact, all the frothing liquids (soap solutions, etc.), have small surface tensions. This is not in itself sufficient to establish foaming because liquids such as benzene, alcohol, etc., give no permanent foam.

"The chief difficulties with these liquids is that *they are not viscous enough* and that they are too volatile, so that the films are easily destroyed. Since marked viscosity, slight volatility and a small surface tension are never combined in a single pure liquid, it follows from this alone—though other reasons will be given later—that pure liquids do not foam. Only solutions foam, and especially aqueous solutions containing substances which lower the surface tension very much."

On p. 378 there is an important paragraph on the chemical inertness of hydrosols.

"A certain chemical inertness of many sols depends in part on the amorphous *or solid state of the suspended particles* and in part, on the adsorption sheath produced by the active third substance. Zsigmondy noticed that mercury often does not amalgamate with the particles of a gold sol. This is perhaps due to the fact that the liquid films separating the two are not easily broken through. Of special interest is McIntosh's statement that the silver in Bredig's silver sol is only slowly attacked by HNO_3 and H_2SO_4 while it dissolves readily if several drops of a permanganate solution are added. The fact that most sols are entirely tasteless is a sign of their inertness."

On p. 490 there is an account of the apparently mysterious phenomenon of drying from the centre outwards.

"Bütschli has *often noticed* with silicic acid gels and pieces of tabaschir filled with chloroform, also with hardened gelatine gels filled with xylene, that the clouding takes place first in the middle of the gel. At first sight this seems quite remarkable since the evaporation takes place from the surface and the outer layers should first lose so much liquid that air bubbles can enter. On the other hand the phenomenon is exactly what one would expect from a liquid under negative pressure. In fact the gel is very like the systems which have been employed for the study of negative pressure. The walls are more easily permeable to water and water vapor than to air. If the liquid evaporates from the surface of the gel, more is sucked out from the interior just as water is sucked up from below when *evaporation takes place through* a plaster membrane. The breaking of the liquid and the first formation of a bubble of vapor take place most easily in one of the cavities in the interior of the gel, because the cell walls there are the least elastic and are strained by negative pressure of the liquid in both directions, whereas a wall at the surface is drawn in only one direction and can therefore yield more.

"This explanation of the phenomenon of clouding is satisfactory in another way. The process is a very uncertain one and its occurrence depends upon a number of minor points, on the rate of drying, etc. This is exactly what one would expect of a phenomenon involving the formation of gas nuclei. The explanation given is that of Bütschli.

"Now one might suppose that the gel would remain opaque if dehydrated further and that the water still present would pass off according to an adsorption isotherm as soon as all the water had evaporated which was held by capillary action in the cavities. This however is not quite so. As more water is removed the gel becomes less opaque, passes through similar stages to those it had passed through when clouding, though in the opposite direction, and finally becomes as clear as glass again."

"The only possible explanation is the one given by Bütschli as the result of a microscopic investigation. The thickness of the cell walls is so much less than a wave length of light that the gel cannot appear opaque even though it does scatter the light somewhat."

These extracts should be more than enough to show the quality of the book. It is distinctly readable. One can open it anywhere and find something that ought to interest him. I do not mean by this that the book should be read a page at a time during odd moments. It is a book which should be read through very carefully and then read again. *Wilder D. Bancroft*

Grosse Männer. *By Wilhelm Ostwald. 17 × 24 cm; pp. ix + 424. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1909.*—Ostwald makes the attempt to classify scientific men of genius and to formulate the laws governing their careers. He divides the men of genius into two general classes, the romanticists and the classicists, the chief difference between them being one of mental reaction velocity. The classicists have a low reaction velocity and the romanticists a high one. The classicists tend to be phlegmatic and melancholic while the romanticists are sanguine and choleric. The difference is thus one of mental temperature.

The difference shows even in youth. As might be expected, the romanticists mature very early. This is very noticeable with Davy and Liebig while it is not so marked with Mayer and Helmholtz, two classicists. The difference shows in the relation between the man of his genius and his neighbors. The romanticist, with his agile mind, reads everything, and is interested in everything and everybody. As a result of his enormous consumption of facts, he soon feels the need of publication. Liebig emphasizes the fact that he had always received great assistance from all with whom he came in contact. This is usually the case with the young romanticist. The eagerness and vivacity of his spirit wins him friends and helpers everywhere. On the other hand, the classicist works more silently and more alone, and does not obtain recognition so easily. Mayer, for instance, never obtained it from his immediate neighbors. Mayer's scientific friends often remarked that he did not look like a great discoverer. When a man of genius looks like one, it is usually safe to assume that he is a romanticist and not a classicist.

The temperament of the romanticist is such that he is enthusiastic himself and arouses enthusiasm in others, one of the necessary conditions of a great teacher. To keep a large laboratory running it is not enough to have plenty of ideas for the students to work on. In addition, a man must keep all the past and future details of each piece of work in his mind, and must be able to answer questions in regard to them off-hand and in a manner which the student can understand. Helmholtz was never able to do this in spite of his marvellous knowledge and his great creative power. Consequently he never founded a school.

"Together with the great advantages which the special gifts of the romanticist ensure him, there comes the very serious danger that he may be satisfied with a solution of a problem which is really no solution at all. Of course, in a sense one may say that no problem is ever completely solved, since later generations will always find occasion to add to or even to transform conclusions which were entirely satisfactory to an earlier generation. The romanticist however runs the danger of stopping before he has done the best which the time requires, a danger which the classicist always strives to avoid.

"If we glance over the history of science, we see that this danger is often a real one to the romanticist. The youthful publications of Davy contain such unripe fruits in large amounts and Liebig produced such in the second period of his scientific life even to a greater extent than during the first purely chemical period. When applying his chemical knowledge to agriculture and physiology, he saw so many important results immediately before him that he did not care very much whether some secondary conclusion, which he made use of, could really stand a severe test. To overcome the inertia of a sluggish world was his chief object and to do that it is necessary to claim more than is quite justified by a calmer consideration of the facts. In cases of this sort one must seem to overshoot the mark if one is going to hit it.

"For this reason the romanticists are the ones who revolutionize science, while the classicists usually do not produce such a change directly, though a thorough-going transformation is often a consequence of their labors. For this reason there is more scope for the activity of an investigator of the romantic type, the younger a science is and the greater changes it presumably has to undergo before it takes its final form. Thus one can hardly see how a man could be a very effective worker in the science of sociology unless he belonged to the romantic type, while a romantic mathematician would seem an utter impossibility if it were not that the nineteenth century furnishes an instance of such a man in the Englishman Sylvester.

"The methods of the romanticist are such that the phenomena of exhaustion are apt to appear early and in a severe form. These phenomena are not necessarily limited to this type because they depend also on many other conditions, such as health, surroundings, recognition, etc. Nevertheless, the high reaction velocity tempts the romanticist to over-exertion and to the rapid exhaustion of his stock of energy. In consequence, collapses, involving temporary or even permanent suspension of work, are more common with the romanticists than with the classicists though these latter do not always escape.

"While the first care of the romanticist is to solve the problem in hand so as to clear the way to the next one, the desire of the classicist is to treat the subject he is studying so thoroughly that neither he nor any of his contemporaries can improve on the result. For this reason he is very reluctant to give his work to the public and Helmholtz says definitely that he rarely sent off a paper without seeing within a day or two one or more points in which he could have improved it. If a zoölogical comparison is permitted, the attitude of the romanticist toward his works is that of the cuckoo to its egg. He is satisfied to have brought it into the world and is quite willing to leave its further development to others. The classicist is more like the traditional bear who licks his young into shape very carefully and thoroughly, and does not let it go out into the world until it has received all the development possible."

Ostwald takes Humphry Davy, Liebig and Gerhardt as three typical romanticists and he gives a sketch of the life of each. He follows the same course with each of his three typical classicists, Faraday, Mayer and Helmholtz. In one point Ostwald is distinctly naive. He says, p. 373, that these six men were not selected because their inclusion under these types could be carried out in an especially convincing way. From the study of their biographies, this difference occurred to him at once as the first generalization and further investigation brought out more clearly the usefulness of this classification. Ostwald does not seem to see that he is admitting frankly the very thing which he is trying to deny. If he recognized the existence of romanticists and classicists from a study of these six men, it follows necessarily that biographies of these men will bring out clearly the distinction between the two types. From a purely scientific point of view the value of the hypothesis should have been tested on other cases than those from which the hypothesis was deduced.

The extracts and paraphrases which I have given are all from a single chapter, the eleventh. Almost equally interesting selections could have been made from any of the other chapters. Nothing could be more striking than the way in which Ostwald brings out the tendency of the romanticist to change in later life to another branch of the science or even to another science. Ostwald attributes this, apparently properly, to mental exhaustion but he rather implies that it is also connected with the romantic temperament. In this I think he gives a false impression, though I may be reading into his words more than he meant to put there. I should prefer to word the matter a little differently. As a result of his temperament the romanticist is more likely to break down than the classicist, consequently more likely to suffer from mental exhaustion, and consequently more likely to change his subject in later life. On the other hand, if the classicist breaks down, I see no reason why he should not change his subject and one instance of this occurs to me. If the romanticist does not break down, I should doubt his changing over to another branch of the same science. It looks to me rather as though Ostwald had done what he says Liebig did, and had exaggerated things in order to overcome the inertia of a sluggish world.

However that may be, the book is an extraordinarily interesting one and is written in Ostwald's best style. It is very much to be hoped that Ostwald will carry out his promise and will give us studies of other great scientific men either from this same or from any other point of view. *Wilder D. Bancroft*

Grundriss der Kolloidchemie. *By Wolfgang Ostwald. 15 × 22 cm; pp. xii + 525. Dresden: Theodor Steinkopff, 1909. Price: linen, 12 marks; bound, 13.50 marks.*—In this book the author has tried to present the phenomena and laws of colloids in a systematized form so far as possible. He first gives a historical sketch of the subject in which he recognizes three periods. The first is from Graham to Barus and Schneider about forty years (1851–1891). The second runs from Barus and Schneider in 1891 to the invention of the ultramicroscope in 1903. The third period extends from 1903 to the present.

The second section of the book has to do with the theory of the colloidal state. Here we meet with a number of new words, such as: dispersed phases, dispersoids, suspensoids, emulsoids, etc. In the suspensoids the two phases are supposed to be liquid and solid whereas we are dealing with two liquid phases in the case of the emulsoids. Colloidal gold is an instance of the first and a gelatine solution is an instance of the second. The distinction is more clearly defined than in A. A. Noyes's colloidal suspensions and colloidal solutions; but the general idea is the same. This section also contains a chapter on surface tensions. The last paragraph of this section, p. 143, is distinctly interesting. It is entitled "The Conception of Colloidal Chemistry."

"The most important conclusion from the discussion in the preceding paragraphs is that we must no longer speak of colloidal substances as opposed to crystalline substances, if by this we mean to imply that the colloidal state is a consequence of the special chemical properties of the substances. Colloidal chemistry is therefore not the chemistry of colloidal substances but rather the chemistry of the colloidal state of substances. In the same way colloidal phenomena are not, strictly speaking, the properties of colloidal substances but rather the peculiarities which almost any substance may show when it occurs in the colloidal state. The difference between the two definitions will perhaps be clearer if we compare colloidal chemistry with thermochemistry. Clearly the latter is not the science of hot and cold substances but rather the science of the phenomena of heat and of the changes caused by heat. In the same way colloidal chemistry is not concerned with a description of the single colloidal substances but with an investigation of the characteristics which the special colloidal systems serve to illustrate. By means of the definition of colloids originally given, we can limit these characteristics to the relations of the surface energies to other energies in so far as they are of especial importance in dispersed heterogeneous systems. Owing to the dominating position of the surface energies, colloidal chemistry appears as a branch of physical chemistry, coördinated with electrochemistry, thermochemistry, photochemistry, radiochemistry, etc. All these are sciences which deal with the relations between the form of energy specified in the name and the other forms of energy. People have tried to take this into account by calling the science of the phenomena of dispersed systems: capillary chemistry (Freundlich); stratochemistry (Drucker); microchemistry (Wilhelm Ostwald); etc. Since philological and other objections can be urged against any of these names, in this book we will stick to the name of colloidal chemistry which has a historical as well as a practical justification."

The third section is given up to the general, physical chemical properties of colloids, the separate chapters being entitled: experimental methods of colloidal chemistry; mechanical properties of colloid systems (including volume and mass relations, Brownian movements, osmosis, diffusion, and viscosity); optical properties of colloidal systems; electrical and magnetic properties of colloidal systems.

The fourth, and last, section deals with the changes of state of colloids. In this section are the special facts in regard to reversible and irreversible changes, to gelatinization, to swelling, to absorption, and to coagulation. The following paragraph, p. 271, shows that the author is not prepared to commit himself definitely on the question whether irreversible changes do or do not occur, though he makes it clear which way he inclines.

"If a colloidal system has undergone a change of state and if the original conditions are then restored (by eliminating a coagulating substance either through dialysis or dilution, for instance, or by bringing the system back to the original temperature), the system goes back into its original state at rates which vary very much with the conditions. In some changes of state such as swelling, gelatinization, coagulation of albuminoids by neutral salts, etc., the change to the original state is fairly rapid, though not faster, as a rule, than the initial change of state. In other cases, with other systems and changes of state, the old state is reached very slowly or not even with a measurable velocity. The first class of changes are called reversible and the second irreversible. Further consideration shows that this distinction is somewhat arbitrary. The question of the reversibility of a change of state depends obviously on the velocity which one assumes as a necessary minimum for the reversal of the change of state. In the majority of cases it is possible to detect very slow changes tending to restore the original state."

The author has done his work very well and has given a consistent, critical presentation of the subject, which was what he undertook to do. He has not erred on the side of claiming more than we actually know and consequently his book will prove very valuable as a statement of our knowledge and of our ignorance. In the discussion of colloidal silver and the action of light upon it, the author has overlooked Gallagher's work which certainly carried our knowledge of the subject considerably beyond the point at which it was left by Stoeckl and Vanino, and by Blake. The sins of omission and commission are surprisingly few when one considers the ground covered in the five hundred pages. No one who is interested in colloids can afford to be without the book, and nowadays, everybody is interested in colloids. *Wilder D. Bancroft*

Explosivstoffe *auf Grund des in der Literatur veröffentlichten Materials bearbeitet. By H. Brunswig. (Handbuch der angewandten physikalischen Chemie. Herausgegeben von Prof. Dr. G. Bredig.) Band X. 16 × 25 cm; pp. 177. Leipzig: Johann Ambrosius Barth, 1909. Price: paper, 8 marks; bound, 9 marks.* —The author first discusses the properties of explosives in general and then takes up the specific properties of explosives, this being approximately a division into theory and practice. In the first part the subheads are: conditions bearing on explosive reactions; rate of explosions; explosion pressures; explosion temperatures; gaseous products; shock; flame. On p. 7 the author gives an interesting example to show that the heat effect is a relatively unimportant factor in determining the effectiveness of an explosive. The combustion of one kilogram of petroleum sets free twelve thousand calories while the explosion of one kilogram of dynamite sets free only thirteen hundred calories. The difference in effect depends on the difference in rate at which the heat is evolved. On p. 19 the author discusses the problem of the action of different detonators. He favors the view that the decisive factor is the explosion wave. On p. 28 is a table of the temperatures at which different explosives go off spontaneously under the conditions of the test. How little we really know about the theory of explosives appears from the attempt, p. 59, to connect the disruptive power with some other property of the explosive. On p. 93 we find the limiting distance for serious damage from great explosions at about five hundred meters, though windows may be rattled even at a distance of eleven kilometers. There is a pretty full account of Dixon's work on explosion waves and of Hoitsema's on reaction velocity.

In the second part of the book the material is classified under the headings:

changes of state of explosives; detonators; sporting and military powders; explosives. One of the interesting items is the chart, p. 157, showing that the number of people engaged in the manufacture of explosives in England has increased from 2000 in 1885 to 4000 in 1905, but that the accident rate has fallen from 4 percent to 1 percent in the same period. *Wilder D. Bancroft*

The Periodic Law and the Hydrogen Spectrum. *By W. F. Kemble and C. R. Underhill. 14 × 23 cm; pp. 16. New York: D. Van Nostrand Company, 1909. Price: Paper, $0.50 net.*—The authors plot atomic volumes as ordinates against atomic weights as abscissus. Then they say that "a glance at these periodically rising and falling broken lines reminds us of a part of the expression $y = \tan x$. . . . . However, the relation appears to be expressed even better by $y = \sqrt{\tan x}$. But $\tan \theta = \sin \theta / \cos \theta$." We are not told what $\tan \theta$ is or why it is substituted for $\tan x$; but the authors next plot "the ratio $\sqrt{\tan \theta}$ in dotted lines, for three complete cycles with both parts of the curve on the same side of the axis and, by a system of 'trial and error,' have found a curve R by means of which the ratio $\sqrt{\tan \theta}$ may be projected, as shown in full lines, with atomic weights as abscissae." In the next paragraph we are told that the illustrations are very accurate and that "the dotted periodic curves are only used in construction, hence ordinates may be considered as atomic volumes, but with values considerably below the observed." If the authors have really worked out anything of value, it seems a pity that they should not have taken the trouble to put their results in such a form as to be intelligible to the chemist.

The second part of the pamphlet is devoted to the hydrogen spectrum. Balmer has worked out the formula

$$\frac{1}{\lambda} = c\left(1 - \frac{4}{m^2}\right).$$

Where $c = 27418.75$, the convergence frequency, and m is to be given the successive values 3, 4, 5, 6, 7, etc. The authors "have discovered that this formula of Balmer's may be resolved into the equation

$$\frac{1}{\lambda} = c\,\frac{m(m+2)}{(m+1)^2} \text{ or } \frac{1}{\lambda} = c\,\frac{(m+1)^2 - 1}{(m+1)^2},$$

wherein c has the same value as before, and m is to be given the successive values 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, etc."

In the last paragraph the authors say:

"Again, there are lines in the hydrogen spectrum which are not accounted for. Can we not, then, assume that the hydrogen atom at least is, in a way, made up of a whole periodic system of its own, in which the strong lines might correspond to Li(0.5), K(1), Rb(1.5), Cs(2), etc., weaker lines corresponding to elements of low atomic volume?" *Wilder D. Bancroft*

THE PHOTOGRAPHIC PLATE. II

BY WILDER D. BANCROFT

THE EMULSION. PART II

Since only those rays can act photochemically which are absorbed, it is not surprising to find that the increase in sensitiveness of a photographic plate, due to the ripening of the emulsion, is accompanied by an increasing opacity of the silver bromide. In the preceding paper, this was mentioned a number of times[1] and the following quotation from Eder[2] emphasizes the connection between the transparent emulsions and the lack of sensitiveness.

"Emulsions with very fine grain and also extreme lack of sensitiveness are known as 'entirely unripened silver bromide emulsions' and are used in Lippmann's process of color photography[3] because it is essential to have an emulsion which will give the most transparent, homogeneous films in consequence of the extreme fineness of the silver bromide particles. . . . The Lippmann color process depends on the formation of stationary light waves formed by passage of light through very fine-grained, transparent films of silver bromide gelatine or the like, and reflection from a mercury surface. To obtain these waves, Otto Wiener[4] has shown that the film must be sufficiently transparent but that it need not be absolutely without grain."

Another passage[5] seems to imply that opacity and sensitiveness do not increase together. "According to Gaedicke,[6] if a freshly mixed emulsion is ripened, there comes a point at which the opalescent liquid changes to a non-transparent milk which has great covering power and which is red

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[1] Jour. Phys. Chem., 14, 64, 67, 68, 71 (1910).

[2] Eder's Handbuch der Photographie, 5th Ed., 3, 1, 25, 27 (1902).

[3] Eder's Jahrbuch der Photographie, 8, 448 (1904); 9, 504 (1905).

[4] Ibid., 10, 59 (1896).

[5] Eder's Handbuch der Photographie, 5th Ed., 3, 1, 66 (1902).

[6] Eder's Jahrbuch der Photographie, 9, 209 (1895).

by transmitted light. In this stage the emulsion is not sensitive but gives a very dense, fine-grained negative. When ripened further, the grain coarsens, the sensitiveness increases, and the covering power of the emulsion decreases."

The discrepancy between this paragraph and the preceding ones is due to the fact that Gaedicke is considering the emulsion as a whole and not the grains of silver bromide embedded in an excess of gelatine. An emulsion can appear quite opaque, even though the two phases are each highly transparent, as, for instance, if one shakes chloroform and water together. As the grain of the silver bromide coarsens on ripening, the spaces between the silver bromide complexes increase,[1] and the covering power of the developed silver decreases. There is nothing in this which is inconsistent with the idea that the increase in sensitiveness is accompanied by an increase in the opacity of the silver bromide complex, which is the only thing that counts. Why the opacity should increase during ripening is one of the problems which we shall have to face when we formulate a theory of ripening.

Mention has been made, repeatedly, that the grain of the silver bromide coarsens during ripening, and the question arises whether this is merely a coincidence or whether the increase in grain and the the increase in sensitiveness are necessarily connected, at least within certain limits. Lüppo-Cramer[2] points out that there are some forms of very coarse silver bromide which are distinctly not especially sensitive to light. This refers to special cases and, in general, it is accepted as an established fact that a coarse silver bromide is more sensitive than a fine one.[3]

The tendency of highly sensitive plates to give thin and flat negatives is discussed by Herzka[4] as follows:

"The sensitiveness of a plate depends primarily on the state or change of the silver bromide. According to Stas

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[1] Cf. Herzka: Eder's Jahrbuch der Photographie, 16, 113 (1902).

[2] Phot. Correspondenz, 38, 158 (1901).

[3] Cf. R. Child Bayley: Phot. Jour., 28, 58 (1904).

[4] Eder's Jahrbuch der Photographie, 16, 113 (1902).

there are six different modifications of silver bromide, the three most important of which I shall call the flocculent, the pulverulent and the granular. For the gelatine process, the last one, the granular modification, is the only one to be considered. Within certain limits an increase in the size of the silver bromide grain is accompanied by an increase in the sensitiveness, so that we are wont to say that the grain is coarser the more sensitive the plate.

"To bring out the connection between the grain of the silver bromide and the general properties of a dry plate, I shall distinguish three types: the fine grain; the medium grain; the coarse grain. The first type, with the small grain, is shown in a photomicrograph, Fig. 17[1] taken of a plate having a sensitiveness of about 10° W. The photograph shows us that the single grains of silver bromide are small but that they lie very close together. If we examine a cross-section under the microscope, we find that there are numerous grains in the lower layers so that there are a great many silver bromide grains superposed one on the next, the total number in any layer decreasing gradually as we get down towards the glass. The film contains no active nuclei and the scattered, larger grains, which show in the photograph appear to be agglomerated grains of silver bromide, which become smaller in the lower layers until, next the glass, we have the single molecules of silver bromide. The practical result of the development of such a silver bromide film after exposure is somewhat as follows. Since the separate grains of silver bromide are small and close together, we get an almost opaque deposit, *i. e.*, great strength in the high lights, while the shadows remain glass-clear. It is obvious that the intermediate steps between light and shade cannot be very numerous and consequently we get a negative with great contrasts, such as is especially suitable for reproducing line drawings. With films of this type, over-exposures do not cause much damage because the numerous underlying silver bromide particles give sufficient covering power

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[1] [The cuts referred to in the text are not reproduced in this article.]

to compensate for what is lost in the uppermost layer through over-exposure.

"In Fig. 18 is shown the second type, what I have called the medium grain. This is a photomicrograph of a silver bromide film having a sensitiveness of about 14° W. In comparison with Fig. 17 the separate grains appear much larger and are also nothing like so close together as in the preceding case. There are also fewer layers of grains as we pass down through the film and the number of grains decreases as we get nearer the glass. A plate of this type will give a negative with good covering power and with much better gradation than was possible with a plate of the first type. For the reasons given in the case of the first type, over-exposures do not affect the result seriously.

"In Fig. 19 we have the third type, the one with the coarse grain; the photomicrograph represents a highly sensitive plate, of about 25° W. Although the film does not contain less silver than the preceding two, there are many fewer grains of silver bromide in the same surface. Each grain is much larger than in the other two cases; but they are scattered round more sporadically and there are not so many of them in the lower layers. When developed, such a plate gives the unsatisfactory result for which we only too often criticize the highly sensitive plate. Since the grains are far apart, we have not the essential condition for sufficient covering power in the negative. In order to get round this difficulty, we necessarily try a longer development, which does not however give the desired result because the shadows become too much developed before the lights are developed to a sufficient intensity. In this case we get a flat, monotonous image, which requires much too long time for printing. Since the lower layers do not count for anything, the slightest over-exposure produces disastrous results, and it is very difficult to obtain any intensity. The plate strikes through, as we say, the image becoming visible on the glass side and fixing to a flat negative with no contrast at all. Most people then believe themselves justified in complaining about 'lack of silver' on the plate although the plate, as has been said, contains as much silver bromide as the plates of the other two types which anybody would call 'silver-rich,' judging by the results obtained with them.

"It is not justifiable to assume that all highly sensitive plates must necessarily show these defects. The elimination of the trouble is a problem for the photochemist and the way of doing it is shown graphically in Fig. 20 which represents a film having the same sensitiveness and the same amount of silver bromide as the one shown in Fig. 19. By a change in the preparation of the emulsion, advantage was taken of the lesson taught by the plates of the first two types. The object was to prepare such a silver bromide grain that, when the ripening was finished, the grains should lie close together and one above another so as to avoid the defects of the third type. The photomicrograph, Fig. 20, shows that the problem has been solved successfully. While the grain is distinctly coarser than in Fig. 17 and Fig. 18, there is everywhere a sufficient number of grains per unit surface and the number in the lower layers of the film is also satisfactory. The result is that this type of plate develops easily and certainly in a reasonable time, giving good intensity and a harmonius gradation. Since the grains in the lower layers are available, an over-exposure does not produce bad effects. The image does not strike through, because the plate acquires intensity in the lower layers, and consequently we have the type of a 'silver-rich' highly sensitive plate.

"In this investigation we have made use of photomicrography to enable us to interpret our observations and practical experiments have confirmed the theoretical conclusions that we had deduced. Thus we see that, in photochemistry as in all other branches, every phenomenon can be defined scientifically and that every success is the outcome of a happy union between theory and practice."

This is, of course, very satisfactory as far as it goes, but Herzka has refrained carefully from telling how he got his result. If the cross-section of the silver bromide grains is approximately the same in the two cases, it is not easy to see how the same amount of silver bromide can give more grains per unit surface both in the outer layer and in the lower layers unless the grains are flattened in the one case and spherical in the other.

Schaum[1] has made some measurements on the size of the grains in a ripened emulsion.

"The change of silver bromide during ripening is shown to consist primarily in a considerable coarsening of the grain. According to our measurements the surface-increase is about seven-fold, the silver bromide remaining chiefly, and perhaps entirely, amorphous. This last is important because the amorphous form has the greater free energy. It alone is able to dissolve dyes, which is of the greatest importance for sensitizing, since crystalline substances cannot be sensitized. The size of the grain of ripened silver bromide varies between about 5 and 9 μ^2, depending on the nature of the emulsion. In our experiments, however, more attention was paid to determining the changes in size rather than to obtaining absolutely accurate data."

"A good many people do not share Schaum's view that a crystallization of silver bromide necessarily means a decrease in sensitiveness. Banks[2] says: 'There is one point which Mr. Driffield has not mentioned in connection with the physical properties of silver in combination with gelatine, and that is that the sensitiveness of the plate depends to a great extent upon a crystalline formation of a bromide during the process of preparation. It is not as generally recognized as it should be that bromide of silver, although insoluble in water, is soluble in gelatine; the crystalline formation which gives the sensitive salt of bromide of silver is formed by the crystallizing out of this salt in the emulsion. It is well known that many of the most insoluble salts are soluble in gelatine, such as sulphate of baryta and sulphate of lime, and the crystalline formation arises from the crystallizing out, as it were, on the

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[1] Eder's Jahrbuch der Photographie, 17, 193 (1903).

[2] Phot. Jour., 22, 159 (1898).

nucleus of a precipitate in the gelatine. It is an important question as to the effect of difference of temperature on the amount of silver bromide dissolved, and also the certain amount of decomposition which takes place during the cooking of a gelatine emulsion; there is no doubt that the gelatine is in a different state at the end of the cooking process than it was at the beginning. If you take a precipitate of silver bromide (precipitated in the manner that Captain Abney, I think, was the first to point out), precipitated in water or with a very minute portion of gelatine, and then emulsifying that, I think you would find—if you divided the precipitate into two portions, and put one portion into an uncooked solution of gelatine, and the other in a cooked solution—that there would not be much difference between the two, and I do not think either of them would be any good."

In view of this quotation it seems inaccurate to say[1] that "Schaum and Bellach were the first to call attention to the important fact that, during ripening, silver bromide changes partially into a distinctly crystalline form." This does not affect the remaining portion of the abstract, which is as follows. "Dr. Lüppo-Cramer not only confirms this observation but extends it by pointing out that in many coarse-grained and highly sensitive plates the whole of the silver bromide appears crystalline if examined with sufficient magnification (1000 diameters). There are no spherical, amorphous grains but only tetrahedra or distinctly hexagonal structures. It seems therefore as though the highest degree of sensitiveness was intimately connected with the crystalline structure. If the first action of the light consisted in a decomposition of the crystalline silver bromide and if the amorphous silver bromide did not undergo this change, we should have an explanation for the latent image of ripened emulsions which would not make necessary either the very improbable action of nuclei as the explanation of the increase in sensitiveness, or the almost equally hypothetical change in the absorption of light."

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[1] Eder's Jahrbuch der Photographie, 18, 335 (1904).

Dyer[1] is said to have published photomicrographs of undeveloped silver bromide gelatine plates which show distinctly a crystalline structure of the silver bromide. The fast plates show especially well-formed and relatively large crystals of silver bromide.

Another aspect of the same matter is brought out by Lüppo-Cramer.[2]

"In a previous paper[3] I had found that, when ripening was prevented, an emulsified silver chloride was not at all less sensitive to light than a similarly prepared silver bromide. The enormous superiority of silver bromide is the result of prolonged ripening, a process which under the usual conditions of an ammoniacal solution can only be carried out to a very limited extent[4] with silver chloride gelatine on account of the readiness with which gelatine reduces silver chloride. In order to ripen silver chloride gelatine without introducing any possibility of reduction, experiments were made on emulsification in a strong hydrochloric acid solution, with an excess of halide salt and a high temperature.

"To a solution of 10 grams gelatine in 160 cc water + 7 grams NaCl + 10 cc concentrated hydrochloric acid (sp. g. 1.19) heated to 80° there was added 10 grams silver nitrate + 100 grams water also previously heated to 80°. The resulting mixture was boiled for fifteen minutes, more gelatine was added, and the emulsion was then worked up in the usual way. In this way there is obtained an emulsion having considerable covering power and a grain which is entirely amorphous and which is distinctly finer than that of the ordinary dry plate. At a magnification of a thousand diameters, the grain can be seen distinctly whereas this is not the case with silver chloride gelatine emulsions made in the ordinary way.

"In comparison with the sensitiveness of fine-grained, silver chloride gelatine plates, the sensitiveness of this ripened

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[1] Eder's Jahrbuch der Photographie, 18, 437 (1904).

[2] Ibid., 20, 59 (1905).

[3] Phot. Correspondenz, 40, 714 (1903); 41, 165 (1904).

[4] Cf. Eder's Handbuch der Photographie, 5th Ed., 3, 718.

silver chloride emulsion is very high, being about three times that of the commercial silver chlor-bromide emulsions. It is however very much less than that of silver bromide gelatine. To compare the two, all other conditions were kept the same and a silver bromide emulsion was made by substituting an equivalent quantity of potassium bromide for the sodium chloride. This silver bromide did not differ noticeably in size of grain from the ripened silver chloride, but was enormously superior in sensitiveness both as regards chemical and physical development. Numerous other experiments were made to carry the ripening of the silver chloride to a higher stage. The amount of halide salt was increased; the gelatine concentration was decreased; ammonia was used with simultaneous excess of salt to prevent the possibility of reduction; the ripening was even carried to the point of producing a crystalline grain. In spite of this the sensitiveness of the silver chloride was always very much less than that of silver bromide prepared in a corresponding way. It is interesting to note that an excess of halide salt causes a crystallization of the grain more readily with silver bromide than with silver chloride, while ammonia changes silver chloride to the crystalline state more readily than it does silver bromide. Silver iodide is extraordinarily readily soluble as a complex salt and we shall see in the following paper that it becomes crystalline especially easily when a large excess of iodide is used, while ammonia seems to have no effect of that sort at all.

"Silver bromide is therefore superior to silver chloride in sensitiveness when the disturbing possibility of reduction during ripening is eliminated and when the two halides have approximately the same size of grain. This appears especially clearly from experiments in which ripened silver chloride plates were converted into silver bromide solution, then washed and dried. Though the size of the grain remained the same, there was a marked increase in sensitiveness. For this experiment it is necessary to take the ripened silver chloride emulsion because in this the grain can be detected

If one takes unripened silver chloride such as Lippmann emulsions or the ones prepared according to my directions,[1] there is a distinct increase of grain while the plate is being converted into bromide and before it is dry once more. This increase in the size of the grain makes it impossible to compare the sensitiveness with that of a silver bromide plate prepared under similar conditions because this fine-grained silver bromide is itself coarsened by the action of the potassium bromide bath and its sensitiveness is consequently increased. It may be mentioned here that many of the contradictory statements in regard to the increase of the sensitiveness of emulsions are due to the fact that people have started with emulsions having a fairly coarse grain. With these, many reagents, such as ammonia, do not give results though they would have easily changed a fine-grained silver salt."

That the crystalline state is not in itself a bar to sensitiveness is shown by Lüppo-Cramer's[2] experiments with mercurous iodide gelatine. "In the unripened state mercurous iodide is only very slightly sensitive, the development being made with metol soda. When the originally amorphous emulsion is cooked, it changes completely into crystalline iodide and the sensitiveness to light may increase five hundred fold."

The conditions for obtaining an emulsion containing crystalline silver bromide are given by Lüppo-Cramer.[3]

"That the grains in the emulsions do not consist of pure silver bromide but of an oily silver bromide gelatine solution (Quincke) and that they therefore have a structure is made probable by the experiments of V. Bellach[4] who found that the size of the grain often decreases as the plate is dried. Thus he observed that, in the course of several day's drying of an emulsion prepared according to Eder's directions there was a contraction from 0.67×10^{-5} mm^2 to 0.57×10^{-5} mm^2.

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[1] Phot. Correspondenz, 40, 717 (1903).
[2] Eder's Jahrbuch der Photographie, 20, 381 (1906).
[3] Photographische Probleme, 50 (1907).
[4] Zeit. wiss. Photographie, 3, 355 (1905).

It must however be remembered that with emulsions having a distinctly crystalline grain it is perhaps not permissible to assume that the silver bromide is shot through with gelatine.

"Numerous commercial silver bromide dry plates, however, show a markedly crystalline structure of the silver bromide while in others the grain is more spherical. Emulsions containing crystalline silver bromide are prepared easily by emulsifying in neutral and very concentrated solution with a large excess of bromide at high temperature (boiling) and in presence of relatively little gelatine; for instance, by mixing at 70° a solution containing 100 cc of 2 percent gelatine and 28 grams KBr with a solution of 20 grams $AgNO_3$ in 100 cc water, and boiling the mixture for fifteen to thirty minutes. The most important factor for the production of a crystalline grain appears to be the absence of ammonia for, in the formula given and in numerous other experiments, the use of ammoniacal silver oxide always prevented the formation of crystals, though by this I do not mean to say that under all possible circumstances this one thing always determine the formation of crystals.

"A further knowledge of the nature of jellies would doubtless be of great importance in interpreting the processes taking place during ripening. Zsigmondy[1] says that the relations in solutions of colloids are much simpler than those of jellies and that only when we know enough about colloids will the theory be able to deal successfully with the finest structures of the jellies which are not accessible to direct observation. We are still very much in the dark as to what is the essential thing in the process of ripening. The conditions for ripening are comparatively simple in the case of colloidal emulsions; but it does not seem possible to bring the coarse-grained emulsions in as part of a single system. Colloidal emulsions can only be brought to a relatively slight increase of sensitiveness (and of size of grain); and it is well-known that the first stages of the emulsion process, the conditions under which the silver bromide is precipitated, are of

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[1] Zsigmondy: Zur Erkenntniss der Kolloide, IV (1905).

greater importance than the subsequent development of the ripening. People have early and often considered the possibility of a reduction of silver bromide by gelatine being the important factor in ripening. I shall have something to say in regard to this a bit later when discussing the formation of fog. When everything is taken into account, it is still a problem to formulate a theory of the ripening process of highly sensitive emulsions in which the sensitiveness is increased to twenty to thirty thousand times that of a Lippmann emulsion. The making of emulsions is still pretty largely an empirical matter."

In a later book Lüppo-Cramer[1] comments in an entirely different way on the experiments of Bellach. "These observations of Bellach are of great importance in determining the nature of the silver bromide grain. If we assume that we are not dealing with pure silver bromide, the composition of the grain becomes so extraordinarily complicated that all our assumptions rest on an entirely unknown foundation. For instance we can no longer assume that the apparently crystalline forms of silver bromide are actually crystals because it is very improbable that the crystals should contain gelatine. In Figs. 4-6[2] are photomicrographs of silver bromide grains. These are the grains of a commercial highly sensitive silver bromide plate and certainly look very like crystals. On the other hand other films of equal sensitiveness show a more spherical grain. Our knowledge of the subject is at present so limited that more experiments are necessary before we can get ahead much. I refer however to the possibility that we are dealing here with structures analogous to the sphero-crystals of Bütschli. I must also mention the fact that, in my numerous microscopic observations of the grain of silver bromide, I have often noticed that in a certain stage of the ripening spherical structures grouped themselves together to what were apparently crystalline tetrahedra."

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[1] Kolloidchemie und Photographie, 69 (1908).

[2] [The cuts referred to in the text are not reproduced in this article.]

It seems to me that Lüppo-Cramer has got the cart before the horse in this matter. His reasoning is that crystals cannot contain gelatine and that the grains of silver bromide do contain gelatine, consequently they cannot be crystalline. The thing to do is to determine whether the grains are crystalline or not. If they prove to be crystalline, we can then decide whether we will drop the premise that crystals cannot contain gelatine or the one that the grains do contain gelatine. It does not seem to me at all impossible that crystalline substances may contain gelatine.

Reference has already been made to the fact that silver bromide changes into what is apparently a crystalline form more readily in presence of an excess of bromide than in presence of ammonia. We also find differences in the way in which different substances affect the coarsening of the silver bromide grain during the process of ripening. Lüppo-Cramer[1] has made a special study of this point and I quote from his paper.

"The process of ripening increases the sensitiveness of emulsions from very different initial values, depending on the conditions of preparation, to values which may be very much greater than the initial ones. It has been proved conclusively that the process of ripening consists in part in a coarsening of the silver bromide grain. Extensive investigations on the grain of silver bromide plates have been made by Kaiserling,[2] Herzka[3] and Schaum[4] among others. Through exhaustive studies, Schaum in particular has recently contributed much to our knowledge of the change in the grain of silver bromide during ripening.

"In all the experiments that have been made previously, people have started with emulsions which were relatively highly sensitive, in which the grain was already fairly large, and in which the further change could be followed by the

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[1] Phot. Correspondenz, 40, 89 (1903).

[2] Phot. Mittheilungen, 34, 7, 29 (1898).

[3] Eder's Jahrbuch der Photographie, 16, 113 (1902).

[4] Vortrag auf der 74ten Naturforscherversammlung zu Karlsbad.

unassisted eye. The increase in the size of the grain can be recognized by the eye for any plate merely by noticing the greater or lesser reflecting power of the surface of the film. The coarser the grain, the duller the film appears provided a sedimentation of the silver bromide has been prevented by the use of sufficient gelatine and by causing the emulsion to solidify sufficiently rapidly.

"It seemed to me desirable to study the effect of chemical reagents upon the increase in the size of the grain without having to have recourse to the microscope. It soon proved that the so-called grainless emulsions, such as are used for the Lippmann color process, furnish an excellent material for just such experiments, as will be proved by the results to be described.

"We can make a suitable grainless emulsion by mixing, at 35°, 300 grams of a 10 percent gelatine solution containing 4.5 grams potassium bromide with 300 grams of a 10 percent gelatine solution containing 6 grams silver nitrate. It is better to work by lamp light though a weak diffused daylight does no harm. When nothing is said to the contrary, 1 cc of a 10 percent solution of the reagents was added to 10 cc of the unwashed, slightly opalescent emulsion.

"If the emulsion is heated for a short time without anything being added, we notice that, if it is then allowed to stand quietly, the opacity increases slowly; but that at the end of an hour, the filament of an incandescent lamp can still be seen distinctly with a reddish yellow color through a film the thickness of the test tube.

"Different groups of reagents act very differently in regard to the coarsening of the grain and the difference is easily detected. In all cases the emulsion was heated for a short time after the solution in question had been added. The following results were obtained when the emulsion was examined after it had stood for ten minutes:

"(1) The coarsening of the grain was prevented by potassium bichromate, potassium ferricyanide, 3 percent hydrogen peroxide, absolute alcohol, silver nitrate.

"(2) The coarsening was not affected by pyrogallol or potassium ferric oxalate.

"(3) The rate of coarsening was increased very slightly by potassium ferrocyanide and by sodium nitrite.

"(4) The rate of coarsening was increased very much by sodium bisulphite and by sulphuric acid.

"(5) The rate of coarsening was increased even more by soda, sodium bisulphite, sodium amino-acetate, and also by ammonium sulphocyanate of which only the merest trace should be added or else the whole of the silver bromide may easily be dissolved.

"(6) Ammonia, ethylene diamine, and potassium bromide produce, in a very few minutes and to about the same degree, an extraordinarily rapid coarsening of the grain, resulting in complete opacity of the emulsions.

"The test tubes were allowed to stand over night and were then examined again. The solutions containing the oxidizing agents, bichromate, hydrogen peroxide and potassium ferricyanide, were entirely unchanged, and were slightly opalescent just as on the preceding day. The solution containing silver nitrate was also unchanged, while that to which alcohol had been added was a little less transparent but much less opaque than the emulsion to which nothing had been added. The emulsions containing potassium ferric oxalate, sodium nitrite, and potassium ferrocyanide showed practically the same opacity as the emulsion to which nothing had been added. The coarsening of the grain by the other substances had proceeded to the point of complete opacity. The emulsions were pure white and in thin films allowed grayish-blue light to pass through. This was most noticeable with the coarsest emulsions, those ripened with ammonia, ethylene diamine, and potassium bromide.

"If we now consider the results and attempt to deduce some law from them, we see that some generalizations are possible but the exceptions make it necessary to be cautious about putting forward hypotheses. Of great importance seems to be the fact that the oxidizing agents, bichromate, hydrogen peroxide, and potassium ferricyanide, completely prevent the coarsening of the grain. Since oxidizing agents are known to prevent the entire process of ripening, *i. e.*, the increase in sensitiveness and even are known to decrease very much an existing sensitiveness, the extraordinary effect of these substances upon the coarsening of the grain is an argument against the very plausible assumption that ripening consists of a reduction, because it is difficult to see what connection there can be between reduction and coarsening of the grain.

"Ammonia, ethylene diamine, potassium bromide, sodium sulphite, sodium amino-acetate and ammonium sulphocyanate all coarsen the grain very much and have the property in common that they dissolve silver bromide to a greater or lesser extent. Since the growth of the grain, judging from analogy, takes place through the coarser particles 'destroying' the smaller ones, it is easy to see that a transitory solvent action of these reagents upon the finer particles would increase the rate at which these were deposited upon the coarser particles.

"The acceleration of the coarsening of the grain by soda, bisulphite, and sulphuric acid cannot be accounted for in the same way because these substances have no solvent action at all upon silver bromide, as is easily shown by the fact that they do not prevent the precipitation of silver bromide. Since the growth of the grain is obviously affected by the greater or lesser viscosity of the colloidal medium, we might account for the effect of these reagents, and especially of sulphuric acid, by postulating that they increase the rate of growth indirectly by decreasing the cohesive action of the glue and by thus permitting the grains to coalesce more readily.

"Hydrochloric acid also accelerates the ripening very much, acetic acid and nitric acid only slightly, while sodium chloride is as effective as hydrochloric acid, obviously because the chlorides and also hydrochloric acid dissolve silver bromide. The nitrates of potassium and sodium, which are formed during the emulsification of silver bromide, have no effect on the coarsening of the grain.

"To test whether bichromate and potassium ferricyanide perhaps check the growth of the grain by preventing the solubility of silver bromide in potassium bromide, I precipitated silver bromide under otherwise exactly similar conditions, once with and once without addition of the oxidizing agent to the bromide solution. I was not able to detect any effect upon the precipitation.

"The action of alcohol in checking the growth of the grain may be explained either as an action upon the gelatine or as due to the fact that all physical-chemical reactions take place more easily in dissociated media. This made it seem desirable to study the growth of the grain in 'grainless' collodion emulsions.

"To 100 cc of a 4 percent collodion I added 10 cc of a 50 percent aqueous alcohol containing 2.25 percent of potassium bromide. To another 100 cc of the collodion solution I added 3 percent of silver nitrate and then mixed the two solutions. The resulting emulsion is even less opalescent than the Lippmann gelatine emulsion.

"The reagents to be used were all diluted with alcohol and were added very slowly to prevent coagulation of the collodion. It turned out that addition of water, ammonia, sulphite or ethylene diamine had no effect on the growth of the grain, while ammonium bromide and still more ammonium sulphocyanate (this latter used only in homeopathic doses) very soon caused a complete opacity.[1]

"This surprising contrast to the gelatine emulsion, that ammonia and ethylene diamine produce no coarsening of the grain in a collodion emulsion, might perhaps be accounted for on the assumption that the double salts of these substances with silver bromide are insoluble in alcohol or perhaps are not formed in alcoholic solution. The result however is in harmony with the fact that the sensitiveness of a collodion emulsion increases but slightly when the emulsion is digested with ammonia. That a collodion emulsion prepared by the

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[1] Check experiments were of course made to prove that the clouding was not due to a precipitation of the salts in the collodion.

ammoniacal silver oxide method has a higher sensitiveness than one emulsified in neutral solution, may be due to the formation of an entirely different grain at the moment of precipitation. It is also impossible to bring a Lippmann emulsion to what we should nowadays call a high degree of sensitiveness by digestion with ammonia.

"It is perhaps not improper to add to this purely preliminary paper an experiment which proves that the coarsening of the grain does not necessarily run parallel with the increase in sensitiveness.

"In my investigation upon the action of hydrogen peroxide upon the photographic plate[1] I attributed to the reaction between the peroxide and the binder the extraordinarily intense action of infinitesimal amounts of hydrogen peroxide upon the ordinary dry plate, an action which does not take place with collodion plates even when these are exposed to stronger solutions for a very long time. Later[2] I found that the less sensitive silver bromide gelatine transparency plates are only blackened by hydrogen peroxide after a much longer exposure. Recently I have found that Lippmann plates show not the slightest formation of fog even when left in a 3 percent hydrogen peroxide solution for several days. By further experiments with a large number of highly sensitive plates from different sources I proved that these plates show the hydrogen peroxide reaction to a degree which is approximately proportional to their sensitiveness. The different behavior of the emulsions toward hydrogen peroxide therefore cannot be a result of the binder and must be due to differences in the silver bromide grains.[3]

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[1] Phot. Correspondenz, 39, 563 (1902).

[2] Ibid., 39, 563 (1902).

[3] Further studies on the nature of the different types of fog . . . showed that over-digested collodion emulsions are affected by hydrogen peroxide in the same way as the highly sensitive dry plates. We may anticipate by saying that with the highly sensitive dry plates we have a latent fog which apparently depends solely on the molecular state of the silver bromide and we also have a fog which can be proved to be due to a slight reduction of the silver bromide. In view of the very important new results in catatype work obtained by Ostwald

"The Lippmann plate[1] which had stood for three days in a 3 percent hydrogen peroxide solution was surprisingly opaque while the grain of the check plate, which had stood in water, had increased perceptibly but was incomparably finer than the other. After the hydrogen peroxide had been washed out thoroughly, the plate was less sensitive to a surprising degree than the check plate, both being completely free from fog. It is possible that a change in the gelatine plays some part in this instance of a coarsening of the grain without an increase in the sensitiveness. On the plate which had stood in hydrogen peroxide, the gelatine film had swelled very much more than on the plate which was only treated with water."

In a later paper[2] Lüppo-Cramer returns to the same subject.

"In a previous paper of this series,[3] I had pointed out that the grainless silver bromide gelatine emulsion is an admirable medium in which to study the effect of chemical reagents on the coarsening of the grain without having to use a microscope. I also found the remarkable fact that all substances which dissolve silver bromide coarsen the grain of a so-called Lippmann emulsion quickly and visibly when the latter is heated in presence of one of them. Instances of this were: ammonia, ethylene diamine, ammonium sulphocyanate, sodium sulphite, sodium amino-acetate, bromides, chlorides, and especially hydrochloric acid.

"To this is now to be added that potassium cyanide and the thiocarbamides coarsen the grain of silver bromide rapidly,

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and Gros, we might assume that the "silver nuclei" present in the highly sensitive emulsion accelerate the decomposition of the hydrogen peroxide catalytically and that this is the explanation of the behavior of the fogged and the unfogged emulsions. On the other hand the reactivity with hydrogen peroxide seems to run more parallel to the "molecular" fog than to the actual reaction fog. More recent experiments of my own show that the "reversal" of the hydrogen peroxide reaction is actually due to an oxidation (added January 17, 1903).

[1] The thickness of the emulsion was that of an ordinary dry plate.

[2] Phot. Correspondenz, 43, 485 (1906).

[3] Ibid., 40, 89 (1903).

while thiosulphate either dissolves the whole of the silver bromide or converts it into silver sulphide if added in small amounts. As I have previously pointed out, soda, sulphuric acid, bisulphite, and nitrite also produce a coarsening of the grain; the effect of sulphuric acid, for instance, is very much less than that of hydrochloric acid. Grainless plates even when dried are quickly changed to complete opacity by bathing in ammonia, hydrochloric acid, bromide or chloride solutions while soda and sulphuric acid do not have any ripening action on the dried film. We have here the same situation as with the colloidal silver gelatine, that the sol. in the dried film is not coarsened in grain by reagents which do affect the liquid emulsion or the emulsion which has only set to a jelly. The difference is that the gelatine does not exert anything like the same protecting influence over the colloidal silver halide compounds as it does over the colloidal silver. The tanning of the gelatine also does not prevent the coarsening of the grain of colloidal silver silver bromide though the change does take place a little more slowly when the plate is bathed in a 10 percent potassium bromide solution, for instance. Even though the film of colloidal silver bromide has been tanned until it is completely insoluble, merely boiling with water will make it absolutely opaque. On the other hand the (untanned) colloidal silver gelatine is not changed in its appearance or in its reactions with electrolytes even though boiled with water for several hours. The sol of the silver chloride[1] is even less stable than that of the silver bromide. This can be seen in the pure aqueous solutions in which the silver chloride hydrosol very soon becomes cloudy and settles, while silver bromide prepared in the same way remains for a long time as a fine, white milk from which a part of the silver bromide settles as a fine yellowish-white mud only in the course of several days. Gelatine also exerts less of a protecting influence over silver chloride hydrosol than over the silver bromide hydrosol. All the substances which ripen silver bromide act more rapidly and more in-

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[1] Cf. Lottermoser: Jour. prakt. Chem. (2), 72, 39 (1905).

tensely upon the grainless silver chloride gelatine. In addition, some electrolytes produce a rapid coarsening of the grain with silver chloride gelatine and have no effect at all on silver bromide gelatine. Instances of this are sodium sulphate and very dilute nitric acid. On the other hand, the pure silver iodide hydrosol is more stable than the silver bromide hydrosol and the grainless silver iodide gelatine does not have the size of the grain changed by sulphuric acid or soda.

"From these investigations it follows that colloidal silver and the colloidal silver halide compounds are protected by gelatine from a number of electrolytes which pectize the pure hydrosol at once; and that this protecting action is greatest with the silver sol and least with the silver chloride sol.

"The coarsening of the grain of the colloidal silver halide gelatine is really due to the change of the hydrosol into the gel, and the gelatine protects to the extent of retarding the action of electrolytes which form complex salts with the silver halides and of checking entirely the action of many other electrolytes which pectize the pure sol rapidly. The hypothesis that this is the significance of the process of ripening was first pointed out by Lottermoser.[1] He noticed that plates prepared in the absence of electrolytes were scarcely sensitive to light at all. The gradual ripening Lottermoser believed to be certainly due to the electrolytes formed when the solutions were mixed. Lottermoser believes that the photographic plate contains the hydrosol of silver bromide. We must remember however that the grain of a highly sensitive dry plate is by no means ultramicroscopic but is of a size which we do not attribute to colloidal substances. In addition, the grain of many plates shows distinct signs of a crystalline structure or at any rate of a change to a crystalline state.

"While the coarsening of the grain in a colloidal emulsion can undoubtedly be interpreted as Lottermoser has done it, it is possible that the total process of ripening, *i. e.*, the in-

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[1] Lottermoser: Anorganische Kolloide, 65.

creased sensitiveness to light which can only be detected photographically is due to the combination of several changes in the silver bromide gelatine. In connection with this I refer to the investigations of Quincke.[1]

"Finally I wish to call attention to a case of the ripening of silver iodide, which finds its explanation in the investigations on the absorbing power of colloids. All colloidal substances, and especially those prepared in presence of organic colloids, are difficult or impossible to prepare in the pure state because they always carry down more or less of the protecting colloid or of the colloid mixed with them. Thus colloidal silver prepared according to Carey Lea by means of dextrine always contains 8–10 percent of organic matter[2] which cannot be removed in any way by washing. Eder[3] found that gelatine is held fast by silver bromide and cannot be removed from it by passing through a centrifugal.

"Not only the organic colloids but the ions held firmly by the hydrosols have a protecting influence and are essential in many cases even if they are not absolutely necessary to the existence of every hydrosol.[4] Thus Köthner and Aeuer[5] have shown that the silver iodide gel has a considerable power of taking up silver nitrate. This cannot be removed by excessively long washing. The amount taken up is about 0.1 percent of the weight of the silver iodide and can be extracted only by digestion for twenty-four hours with ammonia. This adsorption of silver nitrate by silver iodide has been one reason, so these authors claim, that too low a value was formerly obtained for the atomic weight of iodine. Köthner and Aeuer also claim that the amount of silver nitrate in the silver iodide manifests itself in the sensitiveness to light and heat. This is in harmony with well-known photographic facts.[6] The action of silver nitrate on silver iodide can be

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[1] Eder's Jahrbuch für Photographie, 19, 3 (1905).
[2] Lottermoser: Anorganische Kolloide, 41.
[3] Eder's Handbuch der Photographie, 5th Ed., 3, I, 53 (1902).
[4] Lottermoser: Zeit. Elektrochemie, 12, 628 (1906).
[5] Cf. Lottermoser: Jour. prakt. Chem. (2), 73, 376 (1906).
[6] Cf. Eder: Photochemie, 246 (1906).

seen in a striking way with a grainless silver iodide emulsion, and even better with a silver iodide collodion emulsion made by mixing 100 cc of a 4 percent collodion containing 0.2 gram $AgNO_3$ with 100 cc of a 4 percent collodion containing 0.2 gram KI. On adding a little alcoholic silver nitrate solution, it is not long before the emulsion becomes entirely opaque and assumes a pure white color. No such change takes place with a similarly prepared silver bromide or silver chloride emulsion. Silver nitrate also has a marked ripening action on grainless silver iodide gelatine. The greenish yellow opalescent emulsion becomes at once intensely yellow. If it is heated it soon becomes entirely opaque and the grain even coarsens until the plate lets grayish blue light through, whereas a pure silver iodide emulsion scarcely changes at all. The ripening, or grain-coarsening action, of an excess of an iodide is much less than that of an excess of silver nitrate when the emulsion is hot, while the reverse is the case when the emulsion is cold. With the grainless silver bromide gelatine, silver nitrate checks the ripening process as I have already pointed out, and the same effect is produced with silver chloride gelatine.

"Subsequent experiments on the ease with which silver bromide hydrosol is reduced, brought out a fact which is very important in its bearing on the nature of chemical fog, namely that the pure hydrosol is relatively hard to reduce, as might be expected from the low conductivity which is a characteristic of colloidal solutions; but that the hydrosol is readily reduced after it has been precipitated by any electrolyte or after it has ripened spontaneously."

It is not merely an academic question whether the apparent connection between coarseness of grain and sensitiveness to light is a fundamental one or not. Since the size of the silver particles in a developed negative depends to a greater or lesser extent on the size of the particles of the silver bromide in the unexposed plate, we ordinarily get a negative with fine grain from a fine-grained emulsion. This is a matter of great importance to astronomers as appears from the paragraphs which I quote from Wallace.[1]

"It is a matter of importance to those making use of photography as a means of recording scientific data that a definite understanding be arrived at regarding the size of the silver particles which constitute the image. More particularly is this so in the case of astronomical photography, where the original negatives must necessarily undergo considerable enlargement in order that the detailed structure of the object photographed may be rendered readily apparent.

"In many instances this enlargement is carried to such an extent that the individual particles composing the negative image become so obtrusive that detail is entirely masked (for close observation) and can be discerned only when the enlargement is held off at some distance. In such a case there is absolutely no gain but rather the reverse, as it is much easier to study detailed structure of any kind when at the distance of normal vision.

"It is with special reference to this usage that the present work was begun, since there are many plates available for the astronomer or physicist, each of which is supposed to combine in itself (according to the manufacturer) those qualities which make them valuable, *viz.*, speed, fineness of grain, and general uniformity."

"Although a more sensitive emulsion certainly means a coarser grain, yet that coarseness of grain is not synonymous with speed is shown by the researches of Lüppo-Cramer, who instances the use of too strong a solution of nitric acid in the manufacture of the emulsion, or too strong ammonia (or too great a quantity), also an insufficient amount of gelatine; even the shaking up of the sediment during this process of 'cooking' is likewise certain to result in coarseness."

The author did not follow up this last paragraph; but contented himself with measuring the size of the particles of reduced silver in different makes of plates. We may have occasion to refer to this article again when we take up the

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[1] Astrophys. Jour., 20, 113 (1904).

problem of the developed image; but there is nothing more in it that concerns us now.

We have seen that an emulsion can be ripened so that it is many times as sensitive as it was at first; but it is not possible to start with any emulsion we please and ripen it so as to obtain the highest sensitiveness. The early history of the emulsion is a factor and it is now necessary to consider how the properties of an emulsion vary with initial concentrations of water, gelatine and other substances. As to the effect of water and gelatine, I quote from Eder.[1]

"When mixing potassium bromide and gelatine with silver nitrate solution it is by no means a matter of indifference whether the solutions are diluted with much water or only with a little. Attention was called to this point by Monckhoven[2] years ago. The emulsions containing only a little water ripen the fastest. If a concentrated emulsion is boiled for ten minutes, it acquires a greater sensitiveness than one which is twice or three times as dilute and has been boiled for thirty minutes. If the emulsions are too concentrated, they often fog, under the same conditions, if boiled for twenty minutes and they should therefore be made strongly acid with hydrochloric acid or nitric acid. On the other hand, dilute emulsions will stand being heated anywhere from three-quarters of an hour to two hours.

"If the concentrated emulsions are not to precipitate coarse-grained, sandy, or lumpy silver bromide when boiled, they must contain a good deal of gelatine, about 10 percent. A high concentration is not an advantage in a solution containing only a little gelatine because too much silver bromide settles to the bottom.

"If silver bromide is emulsified with the normal amount of water and a liberal quantity of gelatine, equal weights of silver bromide and gelatine for instance, the hot solution ripens pretty slowly. If everything else is kept the same but the amount of gelatine reduced very much, to perhaps one-

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 58 (1902).

[2] Phot. Archiv, 1880, 192.

tenth of the weight of the silver nitrate, for instance, the ripening takes place more rapidly both when the emulsion is boiled and when digested with ammonia. The sensitiveness can usually be increased further. Silver bromide seems to change more easily into the sensitive modification when in non-viscous, gelatine-poor solutions.

"When preparing the emulsion it is very often customary not to add the whole amount of the gelatine at once but only one-half, one-third, or an even smaller fraction (for instance, in the Henderson emulsion), and to add the rest after the digestion is finished. Prepared in this way, the jelly keeps better. Burton carried this practice to an extreme for he added only one eight-hundredth of the gelatine to the water when making the emulsion and let the very dilute emulsion settle after it had been boiled. The silver bromide which separates is then emulsified again in the proper amount of gelatine. Eder found this method not practical because the pictures from such emulsions lack intensity and brilliancy.

"If the amount of water in the mixture is very small and if the quantity of gelatine is also cut down, the combination of these two favorable factors results in the formation of a very sensitive silver bromide; but when the amount of gelatine is insufficient, the concentrated silver and bromide solutions give rise, when mixed, to coarse, granular and even flocculent emulsions having bad photographic properties.

"When only a little gelatine is present, ammoniacal emulsions quickly become very sensitive; but the so-called green fog is apt to form easily when the plate is developed with pyro and ammonia.[1] The film also becomes very transparent, the gradation is defective in the high lights, and the plates fix slowly. Better results are obtained with solutions containing very little gelatine if the mixture contains alcohol."

This matter of the effect of alcohol and of other sub-

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[1] With pyro and potash or pyro and soda this green fog does not occur, and also not when ferrous oxalate or hydroquinone is used.

stances besides gelatine and water is discussed more in detail by Eder in a later chapter from which I quote extracts.[1]

"To a solution of ammonium bromide in water, alcohol may be added before the silver nitrate solution is poured in. This addition is especially to be recommended in the ammoniacal silver oxide process when the emulsion is to be digested at a high temperature and there is danger therefore of too coarse a grain. The presence of 5–20 percent of alcohol in the aqueous gelatine solution causes the formation of a finer silver bromide but retards the ripening in case a good deal of gelatine is present. On the other hand the presence of alcohol is very advantageous in case the solution contains very little gelatine. The addition of alcohol during the emulsification is of great value in Henderson's cold process. According to the author's experiments alcohol prevents silver bromide from dissolving in ammonia and makes the emulsion creamier. As a matter of fact, when there is 70 or even 80 percent of alcohol present, it is possible to increase the sensitiveness in Henderson's cold process to ten times the value that could be obtained without the alcohol.

"In an acid emulsion or when the emulsion is to be boiled, alcohol is of no advantage but acts as a restrainer. * * * Alcoholic solutions of silver bromide gelatine emulsions are difficult to prepare because the ordinary pure gelatine is insoluble in alcohol. Addition of alcohol to aqueous gelatine solutions causes the precipitation of gelatine in lumps. In presence of acids, however, alcohol is able to dissolve gelatine. In this way it is possible to bring a finished silver bromide gelatine into solution in alcohol, to pour it on glass plates just like collodion, and to dry it rapidly. This method simplifies the preparation of plates by the amateur, but it is unsuited for commercial work and costs more than the processes involving an aqueous gelatine emulsion."

"Glycerine, sugar, dextrine, gum arabic and similar substances readily soluble in water are recommended as additions to the finished, washed emulsions, to be added in

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[1] Eder's Handbuch der Photographie, 5th Ed., I, 125–140 (1902).

amounts of 0.5-1.5 gram per 100 cc of emulsion. They accelerate the development of the plates. All these substances give the negatives more intensity, increase the contrasts, and prevent fog during development. Since there is great difference of opinion as to the value of these substances, people should be careful about using them and should remember that they can only be of use in case the plates do not develop fast enough or with sufficient brilliancy."

"Mineral acids act as restrainers during the preparation of the emulsions and still more so when added to the washed emulsion. Thus hydrochloric acid decreases the sensitiveness very much if added to the emulsion just before pouring. Acetic acid decreases the sensitiveness of the plate and the intensity of the negative, but not to the same extent with all emulsions. It has a very bad effect on a melted ammoniacal silver oxide emulsion[1] and does very little damage to an acid emulsion ripened by boiling. In the case of an emulsion ripened by boiling, a small amount of some acid is added to the mixture just before boiling so as to prevent the formation of fog. One to five drops of nitric acid or hydrochloric acid per thousand grams of emulsion do not retard the ripening. Larger amounts, such as ten to thirty drops per thousand grams of emulsion, cause a lack of sensitiveness and of intensity. A subsequent, short digestion with ammonia restricts the intensity again. Hydrobromic acid is more energetic than hydrochloric acid and even destroys the latent image.[2]

"Acetic acid does not have much effect but citric acid does. A good deal of citric acid in the emulsion prevents ripening and gives the emulsion, especially the chlor-bromide emulsion, the property of yielding thin, delicate images which develop with ferrous citrate, etc., to a reddish color which is desired for the positive copying processes."

"Ferric chloride and cupric chloride decrease the sensitive-

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[1] Manufacturers are said to expose the solidified, unwashed, ammoniacal silver oxide emulsion to the vapors of glacial acetic acid before washing it.

[2] Davis: Phot. Jour., 1882, 135.

ness if added to the emulsion while it is being prepared and if present in it during the exposure. They destroy the latent image. If cupric chloride and ferric chloride are added to the emulsion when mixed, they retard the ripening of a boiling emulsion. A small amount of these salts makes a foggy emulsion develop clear. If cupric chloride is added to an emulsion after the boiling, it produces a clear plate, which is only slightly sensitive; but which gives a very dense image."[1]

"If a cooked gelatine emulsion is made permanently alkaline by addition of soda, it becomes more sensitive as was pointed out by the author[2] in April, 1880. Potassium carbonate and ammonium carbonate act similarly. Jastrembski found later that the sensitiveness could be increased fourfold if five grams of soda are added to one liter of emulsion; but so large an amount of soda is bad for the film. So small an amount of soda as 0.1 gram crystallized soda per liter of emulsion makes the plates more sensitive and gives more details in the shadows without damaging the gelatine.[3] Potash, basic phosphates, and other alkaline salts act in the same way.

"Stosch praises the sensitizing action of caustic alkali. He dissolved 1.5–3.0 grams KOH in 100 cc alcohol (87–90°), bathed the plates in this solution for four or five minutes, and dried them. The sensitiveness was increased thereby about fourfold."[4]

"In presence of ammonia, sodium sulphite in the emulsion reduces silver bromide and precipitates metallic silver as a mirror on the walls.[5] It is also said to form green fog.[6] According to other authorities the addition of sodium sulphite to the finished emulsion just before pouring makes the emulsion more sensitive and keeps the plates clear during

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[1] Abney: Photography with Emulsion, 229, 239 (1882).

[2] Phot. Correspondenz, 18, 204 (1881).

[3] Plener: Eder's Jahrbuch der Photographie, 1, 200 (1887).

[4] Phot. Mittheilungen, 18, 271 (1882).

[5] Wellington: Phot. News, 1885, 223.

[6] Henderson: Phot. News, 1885, 224.

development. Silver bromide gelatine plates, which are bathed in sodium sulphite and then dried, blacken more rapidly in the light and also give very dense pictures if exposed in the camera and then developed."[1]

The amount of water in the finished plate has a definite effect on the sensitiveness. I quote from Eder on this point.[2]

"When silver bromide gelatine plates were moistened with water and allowed to swell before exposure, they were not found to be as sensitive on development as air-dried plates.[3] On the contrary the images were weaker, probably because the water prevented the rays of light from penetrating. Wet gelatine plates develop and fix more slowly than dry plates.[4] Since dry plates differ from wet ones especially in regard to the intensity of the developed image, gelatine plates should never be tested before they are dried as otherwise one is likely to draw false conclusions.

"Since the gelatine plate, when wet, is five to six times as thick as when it is dry, the surface of the wet film often projects above the sharp focussing plane. In addition, the surface of the swelled gelatine is much more uneven than that of the dried film. This explains why one often gets thin and blurred pictures with wet gelatine plates. It is to be noticed that silver gelatine bromide plates are less transparent when wet than after they are dried, while the reverse is true for collodion emulsions."

Since wetting a plate makes it less sensitive, it is of course possible that drying it beyond the normal might make

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[1] Redding: Eder's Jahrbuch der Photographie. 13, 455 (1901).

[2] Eder's Handbuch der Photographie, 5th Ed., 3, I, 78 (1902).

[3] Pure bromide plates, acid emulsions which have been treated for a short time for instance, are more sensitive after they have been dried than before. The sensitiveness may nearly double during the drying. On the other hand, the author [Eder] has experimented with mixtures of silver iodide gelatine with silver bromide gelatine which were much more sensitive immediately after solidification than after being dried.

[4] This is usually the case; but some plates develop faster when wet than when dry. This is not uncommon with the highly sensitive, ammoniacal emulsion.

it more sensitive. According to Farmer,[1] this is exactly what happens.

"It is well known that dry plates, as ordinarily used, retain a considerable percentage of water, mainly in molecular combination with the gelatine. I find that the presence of this water in the film at the time of exposure has a large influence on the image, all the chief characteristics, *i. e.*, definition, detail, density, speed, time of development, etc., being affected. Moreover very small differences in the quantity of this moisture materially affect the result, so that negatives vary with the atmospheric conditions, as to temperature and humidity, at the time of working. The dryer the film, the better the definition and the greater the power of rendering fine detail; in lesser degree, the greater the speed and facility of developing density.

"This property of the film can be utilized by desiccating plates for work where definition, detail, brilliancy, or maximum speed are desired, and in exposing plates wet where softness of image or the destruction of small textures and details are sought for. Extra rapid plates or orthochromatic plates, in which the former of these qualities are usually found lacking, gain them when thoroughly desiccated to an extent hitherto only found in wet collodion or other specially prepared films.

"A perfectly flat-topped kettle containing boiling water is a convenient appliance for desiccating plates. They are simply laid on the flat top of the kettle with a piece of bibulous paper between to equalize the heating, and kept there a few minutes at a temperature of 200° (93° C) before being placed in the slides, or a thick copper slab with an asbestos cover can be used. Too great or too prolonged heating will crack the film or induce fog. Desiccated plates have been (with increasing satisfaction) in daily use at the Polytechnic for several months past, and are already widely adopted in the trade and for scientific work."

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[1] Brit. Jour. Photography, 47, 457 (1902).

Some quantitative data are given by Schaum.[1]

"The thickness of the film and the sensitiveness of course depend on the amount of moisture in the emulsion. Plates which were stood in desiccators over water or concentrated sulphuric acid showed the following mean changes in the thickness of the films.

Hours	4	50	90	150
Water.........	+0.0036	0.0059	0.0078	0.0093
Conc. H_2SO_4....	—0.0029	0.0030	0.0036	0.0037

"The weight of course changed in the same sense as the thickness. The sensitiveness (in Scheiner degrees) changed in the following way with varying amount of water in the film."

Hours	0	4	24	30	46
Water.........	12°	11°	11°	12°	12°
Conc. H_2SO_4..	12°	14°	17°	16°	16°

It would not be safe to conclude from the data that addition of water first causes a decrease in the sensitiveness and then an increase, or that the drying action of concentrated sulphuric acid causes the sensitiveness to pass through a maximum; but the experiments do open up an interesting field for research. We need a thorough investigation of this point with special reference to the effect of moisture on plates of different initial sensitiveness.

The general theory of the effect of so-called chemical sensitizers in the emulsion has already been given in the first paper[2] on "The Electrochemistry of Light." Chemical sensitizers are depolarizers. When we come down to details we find that the difficulties in the way of applying this theorem or its converse seem to some people to be insuperable. Lüppo-

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[1] Eder's Jahrbuch der Photographie, 17, 194 (1903).

[2] Bancroft: Jour. Phys. Chem., 12, 230 (1908).

Cramer[1] is one of these and he has treated the subject in a number of articles from some of which I quote.

"A new series of experiments on the action of different reagents upon the latent image or upon silver bromide yielded results which seem likely to make us modify essentially our theory of chemical sensitizers and at the same time our conception of a removal of bromine during the period of exposure.

"It is generally known that oxidizing agents or substances furnishing halogen destroy or at least weaken the latent image. It is also well known that these substances decrease the sensitiveness of the silver bromide in gelatine plates very considerably. Since all these substances act in gelatine plates only because they change the permeability or other properties of the gelatine or because they cannot be removed from the film by washing, experiments to show the effect of these substances on the sensitiveness of dry plates yield no results which can be distinguished sharply from results due to the action of the same substances upon the latent image. With collodion emulsions this difficulty does not occur, for the collodion is entirely indifferent to many of these reagents and they are also not retained in the film to an appreciable extent.

"A. As substances furnishing halogen or oxygen I took ferric chloride, cupric chloride, ammonium persulphate, potassium permanganate, potassium ferricyanide, and chromic acid. I used 1 percent solutions of these reagents. As a chromic acid solution I took a 1 percent potassium bichromate solution and to 200 cc of this I added 10 cc of sulphuric acid, 1 : 5. I always exposed for a normal length of time and allowed the bath to act for one minute upon the carefully washed collodion plate, which was then washed off thoroughly.

"I. Ferric chloride. The latent image is destroyed. If added before exposure, the sensitiveness is reduced to one-sixth or one-eighth.

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[1] Phot. Correspondenz, 38, 218, 422, 427 (1901); 40, 25, 174 (1903); 43, 433 (1906).

"II. Ammonium persulphate. (The solution was not acidified but was used after it had stood for twenty-four hours, which is also necessary if a neutral solution is used for reducing intensity). The persulphate is much less energetic in action than ferric chloride. The latent image is not destroyed completely but the negative looks as though the plate had been exposed for one-tenth the time. If ammonium persulphate is added before the exposure, the sensitiveness is reduced to about one-half.

"III. Surprisingly enough, potassium permanganate acts in exactly the same way whether added before or after the exposure. In both cases, only the merest traces of an image are to be found.

"IV. Potassium bichromate (acidified with sulphuric acid because the neutral bichromate has no appreciable effect whether added before or after the exposure) destroys the latent image completely. Bathing the plate in the solution before the exposure reduces the sensitiveness to about one-fifth.

"V. Cupric chloride and potassium ferricyanide have a good deal more effect on the latent image than on the sensitiveness.

"B. Substances which absorb halogen. If a collodion plate is bathed for one minute in a 1 percent aqueous solution of aqueous hydroquinone and the plate is then washed thoroughly, the sensitiveness is doubled and there is not the slightest formation of fog. Adurol, the halogen-substituted product of hydroquinone, behaves just like the latter; but no increase of sensitiveness is to be noted when the plate is bathed in pyrogallol, metol, gallic acid or iron vitriol. On the other hand it seems as though these substances behave like hydroquinone if the plates are left in the solutions for a longer time. An effect is obtained with pyrogallol by allowing the emulsion to stand in an alcoholic pyrogallol solution for several hours. Exactly the same thing happens with narcotine, in regard to which von Hübl[1] also established that its action as a sensitizer only appears after a long time.

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[1] Die Collodium emulsion, 35, 52.

"These results seem to me to be of considerable importance for our theory of sensitizers. In the sense that H. W. Vogel uses the term chemical sensitizer, we mean a substance which absorbs bromine and which facilitates the splitting-off of bromine during the exposure on account of its predisposing affinity for bromine. Now these investigations show that the increase in sensitiveness caused by the sensitizers occurs when the sensitizer has been in contact with the unexposed silver bromide for a greater or lesser time but has been removed completely from the film. This involves an entirely different view of the state of the silver bromide in the film. Before I go into this matter, I must try to meet several possible objections.

"The old theory of sensitizers would doubtless remain satisfactory if we could prove that traces of the substances which absorb bromine remain in the film in spite of the careful washing. This is actually the case with tannin but this is a special case; for the adhering, mordanting properties of tannin are made use of extensively. Just as the tannin is held fast by the collodion, so potassium ferrocyanide, which used to be employed as a sensitizer, is held fast by the silver bromide itself and not by the collodion. Of course I have tested all the substances used as sensitizers to see whether they adhered to the collodion or to the silver bromide. With respect to hydroquinone, adurol, pyrogallol and narcotine, I found that no trace remained in the film. In testing the behavior of silver nitrate as sensitizer before the exposure if one may so speak, a collodion emulsion was digested for a long time with an acid silver nitrate solution; it was then washed until every trace of silver was removed. After that the collodion was destroyed by boiling with fuming nitric acid. In the filtrate there was not the slightest trace of silver.

"Of course people can maintain that traces of the sensitizer remain in the film in spite of the impossibility of detecting it by analytical methods; but it seems to me that, so long as no proofs are offered, the hypothesis is dictated by the necessities of the theory of sensitizers.

"Some observations from the days of collodion plates with so-called 'preservatives' seem to show that people knew even then that the preservatives could be removed from the film and still exert their sensitizing action. With the wet collodion plate, for instance, there was always the difficulty in the case of long exposures that irregularities in the film might be caused by the silver iodide dissolving in consequence of the evaporation of the concentrated silver solution. As a remedy against this Abney recommended the washing of the silver plate, in other words the removal of the sensitizer. The plate was then to be silvered again (for physical development) after the exposure.

"The following passage from the historical treasure house of our technical literature[1] should be quoted here: 'Fothergill was the first to observe that the preservative could be washed off the silver brom-iodide collodion plate and yet enough be left to produce an effect.' The analogy with the action of the substances supplying halogen or oxygen, for which there are very delicate chemical tests, makes the action of the substances which produce the opposite effect on silver bromide seem less impossible. Ferric chloride, permanganate, chromic acid, and persulphate are all easily detected when present in small amounts. These substances are not kept back by the film. If plates which have been treated with ferric chloride or permanganate are given a sulphite bath, there is no change. This is in line with my previous experiments with bromine, where subsequent treatment with nitrite or sulphite showed that no bromine was left in the plate and yet that there was a great loss of sensitiveness.

"We are therefore justified in considering that these investigations have proved that substances which absorb bromine can change silver bromide so that the sensitiveness to light increases, while substances which supply halogen or oxygen decrease the sensitiveness. This contrast is very marked with the best sensitizer, silver nitrate, and with bromine which is the very type of all substances which can

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[1] Eder's Handbuch der Photographie, 2, 315.

supply halogen. I have previously described the action of these reagents as a physical action and not a chemical one, and our views on the subject are given a definite bias by this contrast. If we consider silver bromide as a compact solid we have absolutely no ground for assuming a chemical action of bromine on silver bromide and especially for the opposite effect of substances like narcotine which certainly do not absorb bromine readily in the ordinary chemical sense.

"The behavior of emulsified silver bromide seems rather to indicate that we must consider the substance as a loose, labile structure in which the silver and the bromine are at least partially in a state similar to the ions in solution. I leave it to professional electrochemists to determine how far this view is justified and I will here call attention to some results which came up in an entirely different connection and which led me to consider the theory of ions in my studies on the latent image. In my 'Investigations on Optical Sensitizers'[1] I proved that when dyes of the eosine series are used to color precipitates of silver bromide, barium sulphate, calcium carbonate, and lead oxalate these precipitates are decolorized by salts which have an ion in common with the dyed, insoluble salts.

"The practical daily use of potassium bromide during development is also intelligible only on the basis of the theory of ions.[2] This effect of the bromide can be shown in a very surprising way if one adds a solution of a bromide to silver bromide precipitated in aqueous solution. While pure silver bromide is reduced at once by the developer even without exposure, no reduction takes place in presence of a bromide solution.

"While I was testing the proofs for a chemical change of silver bromide when exposed to light, one of the main arguments was the theory of sensitizers, which postulates a setting free of bromine during exposure. Now that we know that

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[1] Phot. Archiv, 2, No. 12.

[2] Cf. also Bredig: Eder's Jahrbuch der Photographie, 9, 221 (1895).

the sensitizers can do their work even though they have been removed from the film, it is superfluous to assume that sensitizers act as bromine absorbers during the exposure. The sensitizers act just like the reagents which increase the ripening of silver bromide, like the alkalies and certain alkaloids with which the emulsion is digested and which are afterwards washed out of the emulsion.

"It is hard to say in what way these substances react with silver bromide. From the fact that all substances which promote ripening are able to absorb bromine and that all substances which supply halogen prevent the ripening, it follows that some kind of a dissociation of the silver bromide structure must occur before the exposure and that this dissociation is increased so much by light that the developer is able to cause an actual reduction."

"Investigations along another line led me to the view that between different developers there was an (unsuspected) difference which was considerable in amount and which was of great importance for practical photographic work. I mean the effect which the developing bath has on the light-sensitiveness of the plate. The importance of this lies in its bearing on the sensitiveness of the plate in the dark room before and during development.

"If a dry plate is bathed for one minute in a metol developer of known composition (metol:crystallized sulphite: crystallized soda:water = 1 : 10 : 10 : 200) and is then exposed without loss of time along with a check-plate, it will be found that the sensitiveness of the plate, which has been in the metol bath, has sunk to about one-third. Of course the exposure must take place so rapidly that no development occurs at the beginning of the exposure. If that were to happen, the precipitated silver would interfere with the further action of the light. It makes no apparent difference whether the plate is bathed for a moment or for two minutes.

"In order to find out what it was which was the chief cause of the decrease in the sensitiveness, I began to check the single constituents of the developer.

"(*a*) A solution of metol in water (1 : 100) behaved like the complete developer; but the effect was not so marked, as the sensitiveness decreased to one-half.

"(*b*) Sulphite solution (1 : 10) alone has very little effect on the sensitiveness. The image appears sooner than on the check-plate but the latter soon catches up with and passes it.

"(*c*) Soda solution (1 : 10) alone, curiously enough, has practically no action at all. The image develops a little faster than on the check-plate but the end result is the same in the two cases.

"(*d*) Metol and soda without sulphite destroy the sensitiveness completely while the check-plate was entirely satisfactory. The solution became a good deal colored while the plate was being bathed so that it seems probable that the oxidation products of the developer are the chief cause of the decrease in sensitiveness. This can be illustrated in a striking way with the iron developer. When a fresh oxalate developer was used, the other conditions being as before, the decrease in sensitiveness was only 30–40 percent. When the plate was bathed in an old iron developer, the sensitiveness fell to one-third.

"The effect of metol and iron on the sensitiveness of the plate is not a general phenomenon and we have a striking exception in the case of hydroquinone. No change of sensitiveness was to be detected when using a hydroquinone solution (hydroquinone : sulphite : potash : water = 2 : 10 : 10 : 200); but immediately after the exposure there was so much fog and everything was so affected thereby that I tried to devise a way whereby the light might act immediately after or during the wetting by the developer. I therefore made use of a very small amount of light which should suffice to show a change in sensitiveness in the form of fog on the bathed or the unbathed plate just after it had been laid in the developer. After some experiments I found a clear, massive, ruby glass which was very satisfactory as a source of light at a distance of 25 cm from the plates. This was the more satisfactory because the results became hereby of a good deal of practical importance.

"A number of dry plates were exposed all except a broad edge. For purposes of comparison, one of the latent images thus obtained was brought quite close to the red lamp and removed after one minute. Then a second one of the plates was laid in the developer in the dark and the developing tray together with the plate was placed as near the red light as the dry plate had been and was kept there for one minute. When the plates were developed without further exposure to an effective light, it appeared that the dry plate[1] which had been exposed to the light was so completely fogged that only traces of the image could be detected, while the plate which had been exposed to the red light after being wetted with the metol developer was just as clear after the same period of development as a check-plate which had not been exposed to red light at all.

"The experiments were repeated with the iron developer and the results were the same as in the previously described camera experiments. The old developer produced much more of an effect than the fresh one. With the iron developer it was desirable to reduce to a minimum the absorption of light due to the color of the iron oxalate and I therefore had only the thinnest possible layer of developer over the plate during the exposure to red light.

"When tested by this method, hydroquinone again caused only a very slight decrease in sensitiveness. The fog caused by the red light was a little less when the plate had previously been wetted with hydroquinone developer but the difference was of no practical importance.

"Amidol, *p*-amido phenol, glycine and pyrogallol all behaved almost exactly the same as metol and iron. With all these substances the action of the solutions causes such a decrease in the sensitiveness of silver bromide that the matter is undoubtedly of practical importance. If one takes the

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[1] It made no difference whether the plate was wetted with water or not before it was exposed to the red light.

precaution to keep the plate in the shadows as much as possible or at some distance from the lamp until the developer has been poured over it; one can develop without fear of fog (except when hydroquinone is used) in a light which from the usual point of view is anything but spectroscopically perfect. Thus the ordinary yellow wrapping paper, when formed into a cylinder and placed round a candle or a kerosene lamp gives a light which, according to my present experiments, is a very pleasant one and almost completely non-actinic."

"When discussing the theory of chemical sensitizers in my paper on the latent image,[1] I touched briefly on the printing out process and showed that the small amount of chlorine which is formed during the exposure of precipitated silver chloride is not increased by the addition of silver nitrate and that organic silver compounds are necessary if there is to be a complete reduction to silver. I will now describe some experiments which throw some light on the printing out process even though they were made for the most part with silver salts free from binder.

"In the paper referred to, it was established that the formation of metallic silver, in the amounts which we must assume to account for what happens in the direct copying processes, takes place also with precipitated silver chloride if we add some organic silver salt, such as the citrate, tartrate, etc. In order to obtain some clue as to what occurs when a mixture of silver chloride and silver citrate is exposed to light, each of the substances and mixtures of the two were spread out in shallow dishes and exposed to light under the same conditions.

"(1) Five grams of silver nitrate were dissolved in 25 cc H_2O and precipitated by 2 grams NaCl dissolved in 15 cc H_2O. The silver chloride was washed free of sodium nitrate.

"(2) A similar silver solution had 2 grams of potassium citrate added to it.

"(3) The silver citrate from No. 2 was added to the washed silver chloride from No. 1.

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[1] Phot. Correspondenz, 38, 225 (1901).

"It is really not necessary to state that the three samples in all the following experiments were kept wetted with the same amounts of water and that as uniform an exposure as possible to diffused daylight was obtained by a frequent shaking of the precipitates.

"It is quite noticeable that the pure citrate is only slightly changed by light. At the end of half an hour it is only colored slightly pink while the chloride and still more the mixture with the citrate showed after a three hours' exposure the relative change which had previously been established. The pure silver chloride, after exposure to light, was treated with thiosulphate. There was left behind a very small amount of silver. The mixture of chloride and citrate showed a marked reduction, while the pure citrate yielded only a trace of silver after an exposure lasting two days. If the silver chloride is mixed with the citrate after the exposure, there is no change. When this mixture is dissolved in thiosulphate, the amount of silver left behind is infinitesimal in comparison with the silver left by a mixture of chloride and citrate which had been exposed after being mixed.

"This raises the question as to what reaction takes place when a mixture of chloride and citrate is exposed, since the single salts give no appreciable amounts of silver. If we start from H. W. Vogel's theory of sensitizers, we might make the assumption that the silver chloride is the substance which really furnishes the silver and that the organic silver salt was merely the necessary sensitizer, the substance that had to be added to absorb the chlorine. We should account for silver nitrate not being effective by referring to the nitric acid produced by the reaction. Eder[1] does account for the beneficial action of ammonia fumes as due to the neutralization of the nitric acid. He says that nitric acid is set free from the silver nitrate and that silvered paper gives a slightly acid reaction with water when blackened by light (Devanne and Girard). In presence of nitric acid the reduction of silver compounds take place more slowly and this is the reason why

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[1] Die Copirverfahren mit Silbersalzen, 17 (1897).

silvered paper, which has been exposed to the fumes of ammonia is blackened more rapidly and more intensely by light.

"If the theory of sensitizers in its simple form was able to account for the setting free of chlorine at any rate from silver chloride containing no binder, a substance which absorbs chlorine without setting free nitric acid ought to cause more of a decomposition. Experiments with ammonia showed that this was not the case. Parallel experiments were made with pure silver chloride and with a silver chloride to which 2.5 cc ammonia (sp. g. 0.96) were added. After several hours' exposure the amount of silver formed was no greater in presence of ammonia than without it. Attempts were then made to increase the alleged sensitizing action of silver nitrate and to eliminate the dreaded action of the nitric acid by adding ammonia.

"Five grams of silver nitrate were precipitated by 2 grams of sodium chloride; the precipitate was washed clean and then added to a solution of 5 grams silver nitrate in 100 cc water to which enough ammonia had been added to dissolve the silver oxide. The advantages of this are that the silver chloride is in contact with a solution which prevents entirely the formation of nitric acid, which also absorbs chlorine or hydrochloric acid, and which eliminates any disturbance from the formation of ammonium chloride.

"It turned out however that no considerable amount of silver was set free and a parallel experiment with the previously mentioned mixture of chloride and citrate showed clearly that an amount of silver was set free from this mixture in comparison with which the silver set free in the same time from the ammoniacal silver oxide mixture was negligible.

"Since comparative experiments seemed to me of great importance when applying the theory of sensitizers to the printing out process, I made use of them also with emulsified silver chloride. Five grams of silver nitrate dissolved in 20 cc of water and 1.5 grams NaCl dissolved in 5 cc of water were added separately to solutions containing 5 grams of gelatine in 50 cc of water, and the resulting solutions were mixed. To one such emulsion there was added the amount of ammoniacal silver oxide which is formed from 5 grams of silver nitrate. To another similar emulsion 5 grams of silver nitrate and 2 grams of potassium citrate were added. The ammoniacal emulsion is grayish-white by transmitted light and the one containing citrate is brownish-yellow. If these emulsions are spread on paper or, better still, on glass plates, and are then exposed to light, the change of the color is at first about the same for both; but before long the emulsion containing citrate becomes much the darker. When the plates are fixed, it is easy to see that there has been much more reduction with the citrate emulsion than with the ammoniacal one.

"The theory of sensitizers is therefore not sufficient to account for the action of the substances added to the silver chloride in the printing out process. From the experiments described, it seems rather as though the citrates, etc., did not act merely in a secondary way as chlorine absorbers but rather as though the actual formation of silver came in great part from the organic compounds even though these in themselves are relatively insensitive to light.

"Of course experiments with silver compounds containing no binder do not give an absolutely accurate reproduction of the printing out process, because it is well known that not only is the binder of importance but also the supporting material. Owing to the extraordinarily fine state of the grain in the emulsion, the light has many more points of attack than in the case of precipitated silver chloride and then there is also the action of the binder at any rate in the case of albumen or gelatine. With collodion emulsion, the nitric acid may attack the alcohol. We see that for these reasons the differences resulting from the exposure of the previously mentioned mixtures do not need to be so marked in the case of emulsions as they are in experiments with compounds containing no binder."

"In the preceding section of this series we saw that a number of substances, which are or might be classed as sensitizers, such as ammonia, hydroquinone, the ready mixed developers, and the bromine absorbers, decrease the sensitiveness of silver bromide to light when they are present during the exposure. Even silver nitrate, which can only be used in a strongly acid solution, is less effective as a sensitizer than when added before the exposure. I have carried these important experiments further and must now show that most of the substances, which according to H. W. Vogel are sensitizers and which have been considered as sensitizers owing to their ability to react with halogen, really decrease the sensitiveness a good deal and do not increase it in any case. With collodion plates as well as with gelatine plates, this holds to about the same extent for hydroquinone and metol when the bath consists of a 1 percent solution. With collodion plates pyrogallol increases the sensitiveness a little but with the dry plate no increase in sensitiveness was to be detected. Sodium nitrite in 4 percent solution decreases the sensitiveness considerably, both with dry plates and with the collodion emulsion. Ferrous sulphate in 2 percent solution also decreases the sensitiveness of the dry plate; the subsequent development was made with ferrous oxalate. There is a side complication however due to the formation of fog by which one must not be misled. During the development it is not easy to see that the half of the plate which had been wetted with ferrous sulphate blackens more slowly than the half which had been moistened with water only. The difference in sensitiveness is quite perceptible after the plate has been fixed. A 4 percent sodium sulphite solution had no definite effect one way or the other either on collodion plates or on gelatine plates. Potassium ferrocyanide is known as a sensitizer but a 4 percent solution decreases the sensitiveness of a dry plate very much. Tannin acts in the same way with a collodion plate.

"These results not only do not harmonize with the theory of chemical sensitizers but they are apparently in flat contradiction with what were supposed to be well-authenticated facts.

"The decrease in sensitiveness caused by the sodium nitrite seems to contradict the actual sensitizing of printing out paper by Andresen[1] for the actinometry of sunlight. This process has the authority of Eder[2] back of it and I therefore decided to make a thorough study of the conditions as they applied to the development of the latent image. I will state in advance that one result was the important fact that the theory of chemical sensitizers is not false in itself but that it does not apply at all to the formation of the latent image; because a setting free of halogen is here not only a secondary phenomenon but apparently actually disadvantageous to the process.

"If dry plates and collodion plates are wetted partially with aqueous solutions of silver nitrate, sodium nitrite, sulphite, ammonia, ferrous sulphate, hydroquinone, metol, pyrogallol, potassium ferrocyanide, and tannin, and if the plates are then exposed to daylight, the emulsion plates and especially the dry plates blacken very quickly and very intensely at the places where they have been wetted by the substances in · question.[3] The intensity of the darkening is approximately the same in all these cases. There are slight differences in the color varying from brown to blue; but these are unimportant and need not be described in detail. If the plates are fixed, a pretty heavy covering of silver is left on the portions which had been wetted. Even when the plates have only been exposed for a short time, this silver deposit is incomparably heavier than can be obtained by an exposure of plates containing no solution for periods far exceeding the time for solarization. This is especially true for the collodion plates.

"All these substances therefore act as sensitizers when it comes to the direct blackening of silver bromide by light. They absorb the bromine set free by long exposure and apparently thus prevent the reversal of the process, consequently

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[1] Eder's Jahrbuch der Photographie, 13, 148 (1899).

[2] Ibid., 10, 436 (1896).

[3] It is well known that wetting with water has no effect of this sort.

making it possible for more particles of silver bromide to decompose.

"Since these so-called sensitizers do not increase the sensitiveness as far as the formation of the latent image is concerned but on the contrary decrease it usually to a marked extent, this is another proof that the setting free of bromine after a short exposure to light[1] (first established conclusively by me) is a phenomenon which has no real connection with the reducibility of the silver bromide brought about by the light.

"A setting free of bromine to an appreciable extent combined with a simultaneous appearance of the image, in other words a direct blackening by light, is a phenomenon which we know to occur during solarization. The question now arose whether solarization was perhaps accelerated by the presence of these sensitizers. I selected sodium nitrite as the most suitable sensitizer because it is the only one which owes its action exclusively to the power to absorb bromine. The results might easily be complicated by the tendency of ammonia and sulphite to dissolve silver bromide, by the actual reducing action of the developers on silver bromide, and by the tendency of silver nitrate to cause fog, especially with dry plates.

"One-half of each dry plate was therefore wetted with water and the other half with a 4 percent sodium nitrite solution. The plates were given a solarizing exposure to a sunny winter landscape. After a three-minute exposure with the full opening of a portrait lens, the image was distinctly to be seen on both halves of the plate but was much more intense on the part wetted by the nitrite. When the exposure was continued ten minutes longer, the difference in the intensities of the direct blackening became much greater.

"When these plates were developed, a most unexpected result was obtained. The half of the plate wetted with water gave a good and fairly clear transparency. The half wetted with nitrite became covered with fog during development

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[1] Wissenschaftliche Arbeiten, 12 (1902).

but, after fixing, the negative could still be seen quite distinctly. The picture on this half of the plate looked like what one would get by a long over-exposure which was however insufficient to bring the plate to the so-called neutral state.[1]

"From this experiment one might consider the nitrite as decreasing the sensitiveness. The exposure was therefore increased enormously, up to three and one-half hours, the other conditions remaining the same. Even after this excessive exposure the part of the plate which had been wetted with nitrite was not yet solarized. Instead, it was fogged so completely that it was only with difficulty that one could see that the image was still a negative.[2] The direct blackening was extremely intense.

"According to these experiments the particular setting free of bromine which is helped by the sensitizers does not accelerate either the formation of the latent image or the solarization. It retards the first process and apparently prevents the second entirely. The investigations described in the preceding paper thus receive another confirmation."

"Following the example of H. W. Vogel, people have explained the great sensitiveness of the gelatine dry plate as due to the sensitizing properties of gelatine. Two years ago[3] I called attention to the fact that the sensitiveness of the gelatine emulsion used in the Lippmann color process is negligibly small in comparison with that of a silver bromide collodion emulsion. This in itself disproves the assumption of a 'sensitizing' action by the gelatine. In opposition to this one may say that the considerably larger grain of the collodion emulsion causes a much greater absorption of light than occurs in a slightly opalescent, 'grainless' emulsion

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[1] [The picture was really just beyond the second neutral state. W. D. B.]

[2] Abney had previously noticed (Eder's Handbuch der Photographie, 5th Ed., 3, I, 138 (1902)) that nitrite prevents solarization; but he interpreted the action on the basis of his oxidation theory of solarization which I have disproved (Phot. Correspondenz, 39, 134 (1902)).

[3] Phot. Correspondenz, 38, 158 (1901).

and that one should only compare emulsions showing approximately the same (optical) absorption of light. Without discussing this objection now,[1] we will examine what justification there is for considering gelatine as a sensitizer.

"That gelatine can react with bromine is a well-established fact. When we consider the low reaction velocity of such organic compounds as gelatine, it seemed very improbable that the tendency to react with bromine could be as great as that of substances such as the alkalies, sulphite, nitrite, silver nitrate and the other compounds already mentioned as sensitizers. From the point of view of the chemist it was more natural to assume that these other substances must be better 'sensitizers' than the gelatine. My belief was confirmed by the experimental test. Collodion plates were washed thoroughly with water, were then covered with a film of a 1 percent gelatine solution, and were exposed along with a check-plate. When the plates were developed, the one covered with gelatine developed somewhat more slowly than the other; but when allowance was made for this it was found that the gelatine layer had not increased the sensitiveness in any way. On the other hand there was no increase of sensitiveness such as has been shown to occur with a number of the substances commonly characterized as sensitizers. The effect of the gelatine on the direct blackening was next tested and this also confirmed my assumption. A film of gelatine on a collodion emulsion plate caused only the slightest increase in darkening even with a very long exposure, while a plate wetted with a nitrite solution became very dark in a few minutes. There is therefore absolutely no justification for the hypothesis that gelatine is an extraordinarily effective 'sensitizer' and this hypothesis belongs in the group with the other fundamental errors.

"According to these experiments we have no satisfactory explanation for the enormously greater sensitiveness of the gelatine plate relatively to the collodion plate. This

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[1] For my views in regard to this matter see Phot. Correspondenz, 38, 563 (1901).

fact and also some difference in the behavior of the latent image in the case of emulsions with different binders[1] caused me to make some careful experiments as to the difference between the image obtained on a gelatine plate by physical development after the plate had been fixed and the image obtained by normal development.

"In a previous chapter I have shown that from four to six times as long an exposure is necessary with a collodion plate if physical development after fixing is to give results which are to be comparable in any way with the normal image. The logical conclusion from this is that normal development can take place before any setting free of bromine can be shown. Some years ago I made some experiments for practical purposes on development after fixing, since that process had come up anew. From that time there remained the memory that with physical development I was able to get satisfactory images on dry plates only after exceptionally long exposures. These results agreed with those of other investigators.

"Physical development of a gelatine plate is successful only when everything is kept scrupulously clean and when certain precautions are observed. When fixing, a considerable addition of sulphite is advisable (100 grams anhydrous thiosulphate + 500 cc water + 20 grams anhydrous sulphite). The plate must be washed for a long time, two hours, in running water. The developer must be kept very acid so that the silver precipitates very slowly (2 grams metol + 10 grams citric acid + 100 cc water mixed with one-fourth its volume of a 10 percent silver nitrate solution). The development lasts eight to ten minutes.

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[1] The weakening of the latent image on collodium emulsion by potassium bromide does not occur with gelatine plates (Phot. Correspondenz, 39, 641 (1902)). We might be tempted to explain this as due to the finer grain of the collodion plate since toning with gold, etc., occurs only with fine-grained silver and not with the coarse silver of the ordinary negative. This assumption is contradicted however by my discovery that the latent image on the fine-grained plate used for the Lippmann color process is not affected at all by potassium bromide.

"For development after fixing, the plates were exposed for two, four, eight and sixteen seconds, one minute and four minutes, while with the check-plate for normal development (metol and soda) the exposures were two, four, and eight seconds to plaster busts with black background. With physical development after fixing, the plate which had been exposed for two seconds showed slightest traces of an image only in the high lights. With the negative which was developed normally this same exposure was about right. A fairly close agreement was obtained between a negative exposed for four seconds with normal development and a negative exposed for one minute but developed physically after fixing. We can therefore put the time necessary for exposure when development is to take place after fixing at approximately fifteen times that necessary when the development is to be normal.

"While we do not know at all what the change is which makes chemical development possible, we see that it precedes the setting free of bromine by a much greater amount in the case of the gelatine plate than in that of the collodion plate."

"A good while ago[1] I announced that the sensitiveness of silver bromide collodion plates can be increased considerably by a silver nitrate bath before exposure and that the sensitizing action usually attributed to silver nitrate actually occurs, provided the sensitizer is removed before the exposure. As I have recently shown,[2] the action of the silver salt during the exposure cannot be explained simply as an absorption of bromine set free, because the increase in the sensitiveness is greater if the salt is washed out again before the exposure than if it is present during the exposure. With collodion plates there is a very distinct increase in sensitiveness when the silver nitrate solution is in the plate during the exposure. In this respect silver nitrate differs from sodium nitrite, potassium ferricyanide and the other so-called sensitizers.

"One cannot test the action of silver nitrate on gelatine

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[1] Phot. Correspondenz, 38, 161 (1901).

[2] Ib.d., 39, 701 (1902).

plates using chemical development because the plate becomes completely fogged. Physical development after fixing offered a possibility of testing the action of silver nitrate on gelatine plates. If the gelatine reduces a trace of the silver salt in the time necessary for the process, it was to be assumed that a complete fogging would take place with physical development after fixing. If this does not happen, it should be possible to detect a sensitizing if it exists.

"Ordinary dry plates were bathed for two minutes, in one case in a neutral 1 percent silver nitrate solution and in the other case in an acid solution containing 5 cc HNO_3 (sp. gr. 1.4) to 200 cc of a 1 percent silver nitrate solution. The two plates were exposed along with a check-plate which had been dipped in water. The three plates were washed for a short time, fixed in a thiosulphate bath to which sulphite had been added, and then washed for two hours. The plates were developed physically when it appeared that no serious fogging had been caused by the silver bath but that the sensitiveness had been decreased a good deal by the neutral silver bath and still more by the acid silver bath. We thus have another instance of the inaccuracy of the theory of sensitizers in its application to development if one makes the theory general and makes the mistake of considering as identical the setting free of halogen in a long or a relatively short exposure such as we usually have in a normal camera exposure."

"In the course of other investigations I observed some interesting phenomena which shall be recorded briefly here. Several years ago I reported[1] that the chemical sensitizers decreased the sensitiveness of silver bromide so far as short exposures were concerned. This effect is even more striking with silver chloride gelatine. Its sensitiveness to light is reduced enormously by a solution of metol and sulphite and still more by nitrite solutions, when short exposures to daylight are made and the check-plate is in pure water. The

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[1] Lüppo-Cramer: Wissenschaftliche Arbeiten, 31 (1902); Phot. Correspondenz, 40, 25 (1903).

setting free of chlorine is actually retarded, for the effect of the solutions is quite marked with physical development after fixing. Very striking indeed is the retarding action of the nitrite upon the direct blackening of the silver chloride gelatine, a phenomenon which did not appear with silver bromide. A silver chloride film exposed to light under a 5 percent nitrite solution remains unchanged long after a check-plate under water is colored quite deeply. What is left on the plates after a primary fixing shows that the setting free of chlorine has actually been retarded by nitrite. Precipitated silver chloride also blackens more slowly under a nitrite solution, than under water. The water plays a great part in these reactions. If a silver chloride gelatine plate is bathed in a nitrite solution and then dried, the real sensitizing action appears and the setting free of chlorine is accelerated. The amount of moisture is also of importance for if the silver chloride plates are merely moistened with the nitrite solution, the retarding action does not occur to any great extent.[1] Solutions containing other sensitizers increase the rate of blackening of silver chloride and do not show any retarding effect. The presence of moisture also plays a great part in the decrease of sensitiveness caused by solutions of developers and of other substances which absorb bromine. Silver bromide plates may be dried with pyrocatechuic acid plus bisulphite or with nitrite without a reduction of the silver bromide taking place. These plates have not lost any of their sensitiveness but a mere wetting with the aqueous solutions causes a decrease in the sensitiveness. It must be stated explicitly, however, that water alone does not have this effect for the check-plates were of course always wetted with water."

While I do not care to discuss these experiments of Lüppo-Cramer's in detail until we have made more experiments, there are a few criticisms which might as well be made now as at any other time. Lüppo-Cramer is quite certain that the reducing agents and oxidizing agents were washed com-

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[1] Phot. Correspondenz, 40, 97 (1903).

pletely out of the film and out of the silver bromide but he does not tell us how he knew it. He gives details in the case of silver nitrate in a collodion plate but this is a case where it would be quite impossible for him to tell whether any silver nitrate had been absorbed by the silver bromide or not. Of course he may have taken all possible precautions in the other cases; but it is certainly suspicious that his proof should be worthless in the one case where he gives details.

In the experiments on mixtures of silver chloride and silver citrate Lüppo-Cramer's criticisms are solely destructive. He offers no suggestion at all as to the reason why light sets free much more silver from the mixture than from either salt alone. The argument rests entirely on an experiment with silver chloride in presence of an ammoniacal solution. It is easy to see why ammonia was taken as the best substance; but it was an unfortunate choice nevertheless. Ammonia dissolves silver chloride readily and consequently tends to keep down the concentration of silver as ion. While this difficulty is not so serious as it would be if the solution were not saturated with respect to silver chloride, the test is not as satisfactory as one would like. It certainly loses all value until we have an explanation of the phenomenon that a small amount of a solution of a nitrite solution accelerates the blackening of silver chloride while a larger amount of the same solution pretty nearly eliminates the blackening.

In the experiments on the decrease of sensitiveness when there is a developer in the film, Lüppo-Cramer gives no details as to the length of exposure to daylight. One cannot help wondering whether he may not have given a solarizing exposure without knowing it. We know that his conclusion that sodium nitrite prevents solarization is utterly wrong and that his mistake is due to the fact that all his exposures were too long.[1] Our own experiments with a developer in the film showed that the time necessary to obtain a good negative[2] was reduced to one-twelfth under certain con-

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[1] Bancroft: Jour. Phys. Chem., 13, 462 (1909).

[2] Perley: Jour. Phys. Chem., 13, 643 (1909).

ditions and was not reduced perceptibly under other conditions. In the two cases the lights differed both in quality and intensity and we do not yet know which variation was the more important, though that point will probably be settled before very long. It is clear that the same factors must be taken into account in Lüppo-Cramer's experiments with a red light.

In this paper I have given an outline of our knowledge in respect to the effect on sensitiveness: of opacity; coarsening of the grain; concentration of water and gelatine during the precipitation of silver bromide; and concentration of water in the finished plate. I have also given at length the argument against the theory of chemical sensitizers. In the third paper of the series I shall take up the increased sensitiveness to different wave lengths, the effect of the medium, and the reduction of unexposed silver bromide.

Cornell University

THE MEANING OF CURRENT DENSITY

J. W. TURRENTINE

The question has been raised by Tommasi as to the exact meaning of current density. There is perhaps not much doubt in the minds of most electrochemists that the term, current density, as applied to any particular electrode, means the amount of current flowing through unit surface area of that electrode, or the quotient obtained by dividing the amperage of the current passing by the surface area of the electrode. Ordinarily, one deems this method of specification quite sufficient. In the following paragraphs it is intended to show that the consideration of these two factors alone is not sufficient, except under certain circumstances, to convey an exact idea of current density.

The usual way in which current density is defined is decidedly loose; this makes it impossible to reproduce conditions of electrolysis with accuracy and certainty. The success with which such conditions have been repeated heretofore has been due to a fortunate set of circumstances, tending to regulate and equalize conditions, rather than to any definiteness on the part of the author describing the conditions. It is with the hope that electrochemists may be induced to give in greater detail the size and shape, construction and position of the electrodes when these items tend to influence current density, that these lines are written.

The paths of the electric current through an electrolytic cell, its concentration on certain parts of, and its distribution over, the electrode surface are determined, in agreement with Ohm's and Kirchhoff's laws, by the resistance which it encounters. This resistance is found (1) in the substance of the electrode itself, (2) in the surface of contact between the electrodes and the electrolytic bath, in which region polarization occurs and energy-consuming reactions take place, such as the deposition of a metal, and (3), in the bath itself. The resistance there is due to the friction which the solvent offers to the passage of the migrating and current-bearing ions. The resistance within the electrode may be considered constant for that electrode. In cases where the electrode is of considerable bulk or thickness, as, for example, in the case of the anode used in the electrochemical purification of copper in the multiple system, the resistance within it may easily become entirely negligible.

At the point where the current passes from the metallic portion of its circuit to the liquid portion, the resistance varies with the nature and concentration of the electrolyte, with the sort of reaction which there takes place and with the kind of products which are there produced. The resistance due to the nature of the electrolyte is measured in terms of decomposition voltage and rarely exceeds that which is represented by 2.5 volts.

The concentration of the electrolyte operates to influence resistance at the electrode surface by determining the supply of ions. With a more concentrated solution as the bath, the number of ions in proximity to the electrode is increased and the chances for the impoverishment of ions are lessened. With impoverishment of ions resistance increases.

The influence of the nature of the electrode reactions on resistance is again largely a matter of decomposition voltage. The products of the electrode reactions produce this effect through forming coatings on the electrodes which are more or less impenetrable to the current. The increase in resistance due to the phenomenon usually designated as polarization is caused by gas films which more or less effectually intercept the passage of the current. They separate the electrode from the electrolytic bath. In the "electrolytic forge" this film becomes so thick and its resistance so high that an arc is formed between the solution and the electrode.

The resistance within the electrolytic bath itself varies directly as the distance apart of the electrodes and with the concentration and the temperature of the bath. With a rise in temperature the mobility of the liquid of the bath is enhanced; it therefore presents less friction to the passage of the ions. Where the distance between the poles is great the resistance of the bath may be so increased that that from the other sources mentioned may become relatively insignificant.

The effect which the resistance in the different portions of the circuit, as outlined above, exert on the direction of the flow of current will be seen when we consider the case where the anode is a point and the cathode a plate.

The electric current does not always flow through an electrolytic bath in straight lines; it is able to pass around obstructions, where, by so doing, energy is conserved. Thus the current flows through the substance of, or through the interstices in, a diaphragm of the porous, conducting type, depending on whether the resistance in the circuitous path through the pores of the diaphragm offer a greater resistance than the ohmic resistance of the substance of the diaphragm itself, plus that produced by the necessity of decomposing the electrolyte at the two faces of the diaphragm. But it stands to reason that the current does flow in straight lines when it can do so.

The resistance presented by an electrolytic bath acts like ohmic resistance in that it varies directly with the length and inversely as the cross section of the liquid conductor. The length of the conductor is shortened when the path is straightened. We may then represent the paths of the current from anode to cathode as a number of straight lines drawn from the anode to different points on the cathode face. The shortest line is that drawn perpendicularly to the cathode face at a point directly opposite the anode. It is seen that the current would tend to flow in general along this one line from electrode to electrode and to enter the cathode at that point on its surface, directly opposite the anode. That the current is not confined to this spot, though it may be, and probably is, concentrated there, is a matter of observation and is no doubt due to the increase in resistance at the electrode surface with increase in current density. The augmented resistance may arise either from a more vigorous evolution of gas or from impoverishment of ions. The current would then tend to flow to those regions where these impediments exist to a less extent. This scattering of the current is limited by the resistance of the electrolytic bath; this would become so great in the peripheral regions of the current's path that the electromotive force of the current would be expended in passing through the bath so that on arriving at the electrode surface, the current would find itself, so to speak, so depleted in electromotive force that it would not be able to overcome the counter electromotive of the electrolyte which it must decompose there. How soon this limit would be reached depends on the potential difference back of the current. At the same time, with increased potential difference, the current would be better able to overcome an increased resistance due to gas films or to impoverishment of ions. Thus the equilibrium between the two counteracting forces is not overthrown by changes in electromotive force. Or, different lines drawn from the point to the plate may be regarded as so many split circuits, to the flow of current through which Kirchhoff's law is applicable. The resistance in each circuit is equal to the resistance of the bath plus the decomposition voltage of the electrolyte. With the exclusion of all consideration of the effect of electrode films and ion depletion, by Kirchhoff's law it would be possible to calculate exactly the distribution of the current over the electrode surface.

The concentration of current at one point on the cathode face is greatly heightened when the two plates are brought into close proximity; like-wise, when the two are more widely separated the relative advantage, in point of resistance of the bath, of one line of travel over any other is greatly diminished. As the electrodes are brought closer together, then, the current tends to concentrate in one region, and as they are moved apart, it tends to distribute itself with equal intensity over the face of the electrode.

Passing to a case at the other extreme, where the electrodes are two plates of the same size, and are placed directly opposite to each other, with their faces in parallel planes and with the current admitted equally to all portions of them, then we generally have a practically uniform current density on both. These are the ideal conditions, but they do not often obtain actually in practice. Frequently electrodes are plates of metallic foil and are so thin that they present considerable resistance to the passage of the current through them. With the current admitted only to their upper edge, as is nearly always the case, the path of least resistance through the cell is from the upper portion of the one electrode to the upper portion of the other, instead of through their entire lengths. This tendency is heightened where the anode is a soluble one, by the convection current of the heavier solution of that salt, which is the product of the corrosion, flowing downward over the face of the electrode. With a copper anode in a sulphate or nitrate bath a line of accentuated corrosion just beneath the top surface of the electrolytic bath is very noticeable.

The same considerations would apply in varying degree to cases between these two extreme ones, where the electrodes are of different size and shape. Likewise, varying the relative positions of the electrodes would have its effect on current density.

Usually in reckoning current intensity per unit area, one-quarter to one-third of the back of sheet electrodes is considered included in the active electrodes surface. The back of an electrode may be entirely inactive, depending on the distance such an electrode is placed from the walls of the containing vessel. The limiting case, of course, is that in which the electrode is placed *against* the sides of the containing vessel. All action on the back of the electrode would then be prohibited. How far from the cell walls the electrodes must be so that the distance is not a factor in determining the course of the current is hard to say, nor is it especially desirable to know so long as this distance is specified when current densities are recorded.

What then should be specified in describing current density? Certainly the size of the electrodes, not of one but of both, should be given, and their distance apart, and their distance from the walls of the cell. Also, in cases where conditions of current density are of especial importance, mention should be made of the relative positions of the electrodes, whether parallel and opposite each other, and of the construction and thickness of them. In every case, of course the current strength must be specified.

Wesleyan University,
December, 1909

THE REDUCTION OF ZINC BY MERCURY AND THE ELECTROMOTIVE FORCE OF ZINC AMALGAMS

BY J. L. CRENSHAW

If a mixture of two metals be brought into a solution of their salts, one metal will go into solution while an equivalent amount of the second will be precipitated until the equilibrium condition is reached. The condition of equilibrium is:

$$A - F_1 + \frac{RT}{n_1} ln \frac{P_1}{p_1} + F_2 - \frac{RT}{n_2} ln \frac{P_2}{p_2} = 0$$

the well-known equation derived by Nernst[1] in which P_1 represents the solution tension of the first metal, p_1 the osmotic pressure of its ions in solution, n_1 its valence, F_1 the difference in potential between the metal and the solution; the same letters with the subscript (2) refer to the second metal. A, represents the difference of potential between the two metals, R, the gas constant and T, the absolute temperature. In the case of an amalgam $F_1 = F_2$ and $A = O$ so that the above equation reduces to:

$$\frac{RT}{n_1} ln \frac{P_1}{p_1} = \frac{RT}{n_2} ln \frac{P_2}{p_2} \quad \text{or,} \quad \sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}.$$

Ogg[2] has verified the above equation in the system mercury, silver nitrate and water. In this case the equilibrium concentrations are of sufficient magnitude to be determined analytically. Hulett and Delury[3] found evidence of a definite equilibrium in the system mercury, cadmium sulphate and water. The present work was undertaken for the purpose of investigating the equilibrium conditions in the system mercury, zinc sulphate and water.

If mercury is shaken with a zinc sulphate solution we may expect some mercury to go in solution and some zinc

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[1] Zeit. phys. Chem., 22, 539 (1897).

[2] Ibid., 27, 285 (1898).

[3] Jour. Am. Chem. Soc., 30, 1805 (1908).

to be precipitated into the mercury forming a very dilute amalgam. As in the case of cadmium the concentrations involved in this equilibrium are too small to be determined by chemical means, but since the e. m. f. between two zinc amalgams is proportional to their relative concentrations it was thought that a determination of the potentials of very dilute amalgams would indicate at least the order of magnitude of these equilibrium concentrations. All previous workers have found that the potential of dilute zinc amalgams decreases with the time, indicating a loss of zinc, and the more dilute the amalgam the greater the relative loss. It is well known that oxygen dissolved in the solution above a zinc amalgam removes zinc from the amalgam. The rôle played by the oxygen in this process may be very well explained in the light of the results of the investigations on very dilute amalgams carried out in this laboratory. No reliable observations could therefore be obtained on the e. m. f. of dilute amalgams until means were devised for really removing and excluding oxygen. This is fundamental for all work with dilute amalgams. For this purpose it was very important to have an adequate supply of hydrogen which was unquestionably free from oxygen.

The Preparation of Oxygen-Free Hydrogen.—The hydrogen was generated in a Kipp generator from Kahlbaum's No. II zinc and Baker's analyzed hydrochloric acid. The gas after passing through a tower containing soda lime and calcium chloride was conducted over a platinum spiral consisting of over a meter of tenth mm platinum wire wound on a small porcelain tube. When hydrogen was being used this platinum wire was glowed continuously with an electric current and caused the hydrogen to combine with any residual oxygen. Nernst[1] and his co-workers have shown that in a case of this kind the gaseous mixture very rapidly comes to the equilibrium conditions corresponding to the temperature of the wire. They have also given us the

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[1] Thermodynamics and Chemistry, Nernst, Langmuir: Jour. Am. Chem. Soc., 28, 1357 (1906).

necessary data for calculating the equilibrium constant for the equation $2H_2O \rightleftarrows 2H_2 + O_2$ for any given temperature. The temperature of the spiral was not far from 1000° absolute so that the calculated partial pressure of the oxygen in our hydrogen was of the order of magnitude of 4×10^{-18} mm. Oxygen then was practically out of the gas phase. All hydrogen passed over this glowing spiral immediately before it was used.

Cell.—The form of cell used is shown in Fig. 1. The cell was separated into compartments, by little dams about 1 cm high which prevented the mixing of the amalgams but allowed a thorough mixing of the electrolyte when the cell was rocked. The contact wires were short 10 mm platinum wires sealed into tubes which made well ground joints with the tubes *a*, *b*, *c*, *d* and *e*. The application of a very little marine glue made these joints perfectly tight. A little mercury was introduced into these tubes carrying the contact wires and made contact between the platinum wires and the copper wires which extended out of the cell. A spiral of 1/20 mm platinum wire (*g*) was fixed inside the cell by means of two larger lead wires sealed through the sides.

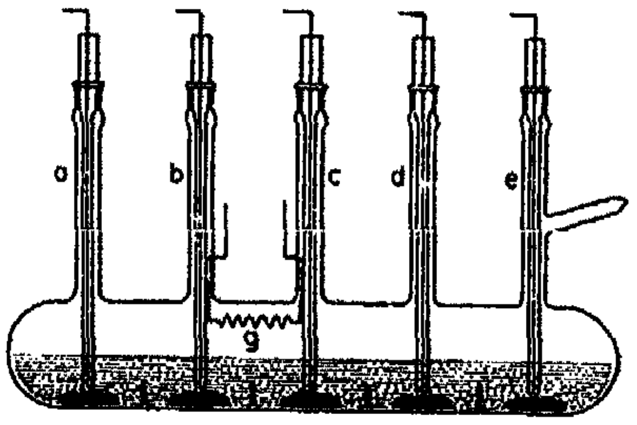

Fig. 1

The side tube was connected by means of a T tube and two stopcocks to the hydrogen generator and a vacuum pump. The cell was first evacuated and then hydrogen was let in, this hydrogen with the residual oxygen was then removed by the vacuum pump and more hydrogen let in. This process was repeated until the air originally in the cell was replaced by hydrogen. The platinum wire (*g*) was then glowed to cause any residual oxygen to combine with hydrogen.

The Electrolyte.—The electrolyte was placed in a separatory funnel, the stem of which was connected, in the same manner as the cell was, with a vacuum pump and the hydrogen generator. The separatory funnel was first evacuated and the solution shaken vigorously in vacuum, hydrogen was then admitted and the solution shaken again to saturate it with hydrogen, this hydrogen with the residual oxygen was removed by evacuation and shaking and fresh hydrogen again let in. This process was repeated six or seven times before the electrolyte was put into the cell. One of the ground glass joints was then opened, after the marine glue had been warmed, and the oxygen free electrolyte was introduced against rapid stream of hydrogen. The other materials which were introduced into the cells were also well washed by the hydrogen which was forced out through the tube through which they were introduced. The spiral (*g*) was continually glowing and took care of any oxygen which might have escaped these precautions.

Purification of Material.—All the mercury used in this work was chemically purified and then distilled by the method devised by Hulett[1]. In this method a continuous stream of air is allowed to bubble through the mercury which is distilled under diminished pressure. The air is very essential to this process as otherwise both zinc and cadmium will distil over if present.

Mylius and Fromm[2] have succeeded in obtaining very pure zinc and their most satisfactory method, with slight modifications, is the one used in this work. The zinc sulphate was first dissolved and then treated with Kahlbaum's best zinc oxide, hydrogen peroxide and electrolytic ozone being used to oxidize any *ous* iron. After digesting two or

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[1] Phys. Rev., 21, 388 (1905).

[2] Zeit. anorg. Chem., 9, 176 (1895).

three days on a water bath all of the iron was considered precipitated. The solution was then filtered, made slightly alkaline with ammonium hydroxide and treated with hydrogen sulphide until a fairly heavy precipitate of zinc sulphide was obtained. This was then digested for two or three days on a water bath with frequent agitation which insured the complete precipitation of the heavy metals. The solution was then filtered and the zinc sulphate crystallized out. This purified zinc sulphate after crystallizing and centrifuging three times was used as the electrolyte from which our electrolytic zinc was obtained. The anode used was a piece of platinum foil of about 6 cm^2 area. This was enclosed in a filter paper anode cup. In order to keep the solution from becoming acid during the electrolysis the anode cup was kept full of a basic sulphate of zinc prepared in the following manner: ammonium hydroxide was added to the solution of the purified zinc sulphate until the precipitate at first formed redissolved. This clear solution was then allowed to drop slowly into boiling water, a steady stream of steam being passed in to prevent bumping. A white crystalline precipitate was obtained that could be readily filtered and washed. The cathode was a tenth mm platinum wire sealed into a small glass tube so that about only one-half mm protruded. The current was regulated by resistance, the density being kept low enough to obtain a compact deposit of zinc. The zinc thus obtained, after being washed and dried, was melted in a hard glass tube with ammonium chloride (specially purified) which took care of the dross and occlusions and left the zinc clean and bright at the bottom. This ingot was carefully scraped with clean steel and then melted in a high vacuum to remove any volatile impurities. It was then transferred to another hard glass tube and distilled in vacuum. The distillation was always stopped before all of the zinc had distilled over. The distilled portion was run into the drawn out end of the tube and kept sealed up until used. In the distillation of zinc it was found necessary to continue the evacuation until the zinc started to distil over otherwise all the gases were not removed and the tube softened before the distillation temperature was reached.

In the purification all cork and rubber stoppers and connections were carefully avoided and when connections were necessary the glass was sealed together. The solutions were always kept in Jena flasks.

Preparing and Handling the Amalgams.—The masses of mercury and zinc necessary for making an amalgam of any given concentration can be very accurately weighed out on the balance, but the difficulty of mixing the two metals without a loss of zinc by oxidation has been a very serious obstacle. This has been overcome by the following very simple device first used by Hulett and Delury.[1] A short piece of glass rod (*a*) Fig. 2 was sealed onto the edge of a small crystallizing dish. The glass tube (*b*) had a platinum wire sealed into its lower end and extending up through the tube. Another platinum wire (*c*) extended across the centre of the dish and was sealed onto the outside of the tube (*b*). The tube was fastened securely to the upright rod, (*a*), by means of insulating tape or a little marine glue and thus formed a very compact piece of apparatus. The mass of zinc to be used in a given amalgam was weighed out on a balance sensitive to 0.01 mg. The mass of mercury required for a given concentration was then calculated and weighed out. All weighings were made by substituting calibrated weights for the tared metal. The vacuum correction was applied to the weights of mercury but since the density of zinc was about the same as that of the weights the vacuum correction for it was disregarded. After weighing, the mercury was put in the apparatus just described (Fig. 2) and made cathode by twelve volts under distilled water. The weighed pieces of zinc were now dropped on the mercury,

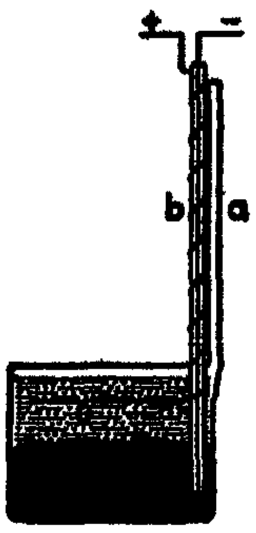

Fig. 2

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[1] Loc. cit.

and dissolved without forming a coat. All the amalgams made up in this way presented a surface as clean and bright as pure mercury and could be preserved for any length of time. Amalgams were thus made up of very exact composition without the slightest chance of a loss of zinc by oxidation. It has been suggested that the mercury distilled by the process which we employed might contain dissolved oxygen.[1] There is no evidence of the solubility of oxygen in mercury, but even if it were found to be soluble there is no question that the e. m. f. applied in the above method of preparing the amalgam would rapidly depolarize any dissolved oxygen. It also reduces any coat of oxide that might have formed on the zinc.

The Standard Electrode.—Previous workers have observed that the e. m. f. between two dilute zinc amalgams of different concentrations increases considerably with the time. It is obvious that this increase did not show the actual loss of zinc but only the relatively greater loss of the more dilute amalgam, since the e. m. f. depends only on the ratio of the two concentrations according to the equation, e. m. f. = $\frac{RT}{nF} ln \frac{C_1}{C_2}$, and if both amalgams lost zinc in proportion to their concentration there would be no change in e. m. f. This fact was pointed out by Hulett and Delury[2] in their work on cadmium amalgams and they made use of a two-phase amalgam as a standard basis of reference for all potential measurements, since the potential of such an amalgam depends only on the temperature. This principle has been made use of in the present work and an amalgam containing about 5 percent of zinc has been used as the basis for all the potential measurements. It is well known that for a given temperature the potential of all zinc amalgams containing something over 2 percent of zinc is constant. Considerable loss of zinc by oxidation or from any other cause could not, therefore affect the concentration or the potential of the standard

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[1] Carnegie Pub., 118, p. 8.

[2] Loc. cit.

electrode, so that any increase in e. m. f. between this standard and a dilute amalgam indicated a loss of zinc from the dilute amalgam *only* and the exact amount of this loss could be easily calculated.

Density and Composition of Zinc Amalgams.—It was desirable to know the concentration of zinc in the liquid portion of this standard electrode at the temperature of the e. m. f. measurements, 25°. The work of Richards and Forbes[1] on the density and composition of zinc amalgams at 20° indicated that the density was a linear function of the composition, but their results extended only over a limited range. We have found that the density, at 25° is a linear function of the composition from pure mercury up to the saturated amalgam. This curve was accurately located so that it was only necessary to know the density of an amalgam to calculate its composition.

The pycnometer used (Fig. 3) was of the same form as that used by Hulett and Delury[2] which was found to have many points of advantage over the ordinary type. One of the capillary tubes had a single mark near the end while the other was marked off into twenty-one equal divisions.

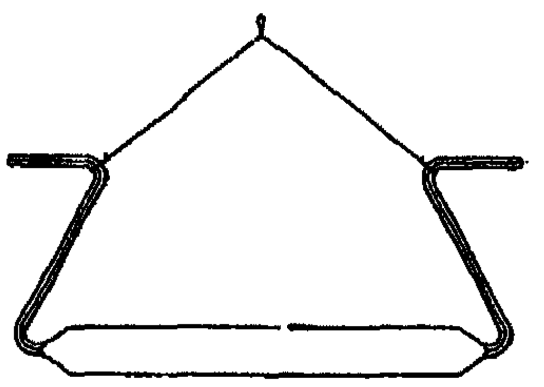

Fig. 3

This graduated end was carefully calibrated so that it was only necessary to adjust the amalgam to the single mark on the other end. Each division on this stem was 0.708 mm. The capillary was filled with varying amounts of

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[1] Zeit. phys. Chem., 58, 693 (1907).

[2] Loc. cit.

mercury and the length of the column and the weight were carefully determined. Three determinations gave as the weight of one division 0.00230, 0.00228 and 0.00231 respectively. If we take 0.00230 as the weight of mercury required to fill one division and the density of mercury at 25° as 13.53396 the volume of one division of the stem is found to be 0.00017 cc.

This pycnometer was weighed frequently during the time it was used. For example it was weighed five times on as many successive days, three of these weighings were exactly the same 15.9621 the other two were 15.9623 so that 15.9622 was considered very near the true weight. The average of five weighings of this pycnometer filled with mercury to the 21st. division at 25° gave 107.24385. This gives 91.26261 as the mass of mercury in the pycnometer and from this the volume at 25° is calculated to be 6.7432 cc. The pycnometer was then filled to the 7th. division of the capillary and found to weigh 107.21124 which gave as the mass of mercury 91.23000 giving 6.7408 as the volume to the 7th. division. The difference of these two volumes 0.0024 cc should be equal to the volume of the fourteen unfilled divisions of the capillary. The volume of one division was found to be 0.00017 so that the volume of fourteen divisions would be 0.00238 showing the two results to be in perfect agreement.

The densities of amalgams of four different concentrations were determined with this pycnometer. The amalgams containing respectively 1, 1½ and 2 grams of zinc in 100 grams of mercury were made by weighing out very accurately the required amounts of zinc and mercury for the different concentrations. The zinc was weighed out first on a balance sensitive to 0.01 mg., the air weight of mercury required was then calculated and weighed out. By means of a fine capillary joined to a piece of rubber tubing the amount of mercury was easily adjusted to one or two tenths of a milligram.

Weight of zinc	1.48624	1.70912	3.12705
Weight of mercury	148.63247	113.94540	156.85811
Vacuum correction	0.00817	0.00626	0.00862
Mass of mercury	148.62430	113.93914	156.84949
Grams of zinc per 100 grams of mercury	0.999998	1.500028	1.993600

The saturated amalgam was made by rotating an excess of zinc with mercury in a 25° thermostat. The separation of the saturated amalgam from the excess of zinc without changing the temperature was effectively accomplished by the use of the piece of apparatus shown in Fig. 4. The mercury with an excess of zinc was placed in (A) through the end (*a*) which was then sealed off. The cock (C) was closed and an aspirator applied to (*b*). After the pressure in B had been reduced to about 3 cm the thickened part at (*b*) was sealed off. This whole apparatus was then slipped into a large glass tube and rotated at 25° ± 0.02 for several weeks then without removing it from the bath the apparatus was held in a vertical position, the end (E) being down, and after standing one hour the cock (C) was slowly turned. The amalgam then passed into (B) through the filter (D), composed of asbestos well packed in. Since zinc floats on the amalgam and the amalgam is drawn off from the bottom there can be little doubt that this method effectively separated the two phases. As soon as sufficient of the amalgam had passed into (B) the apparatus was removed from the bath, the tube (B) cut open and the amalgam brought into the apparatus (Fig. 4) and made cathode by 12 volts under distilled water until used.

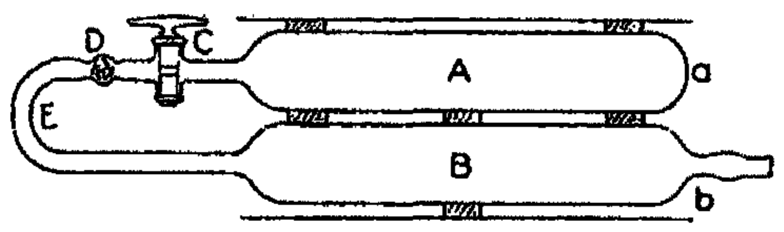

Fig. 4

To insure complete saturation the zinc and mercury were usually heated up to 50° or 100° with frequent agitation before the rotation began so that the equilibrium was approached from the higher temperature.

DENSITIES

	1/100	1.5/100	1.9936/100
Pycnometer + amalgam	106.66306	106.34468	106.04772
Pycnometer	15.97622	15.97622	15.97622
Weight of amalgam	90.68764	90.36846	90.07150
Vacuum correction	0.00498	0.00497	0.00495
Mass of amalgam	90.67286	90.36349	90.06655
	(to 18th)	(to 7th)	(to 3rd)
Volume of pycnometer	6.7427	6.7408	6.7401
Density	13.4490	13.4054	13.3628

DENSITY OF THE SATURATED AMALGAM

From three tubes	A	B	C
Pycnometer + amalgam	105.95668	105.94731	105.95207
Pycnometer	15.97622	15.97622	15.97622
Weight of amalgam	89.98046	89.97109	89.97585
Vacuum correction	0.00495	0.00495	0.00495
Mass of amalgam	89.97551	89.96614	89.97090
Pycnometer division	(to 20th)	(to 17th)	(to 18th)
Volume of pycnometer	6.7430	6.7425	6.7427
Density	13.3435	13.3431	13.3434
Average	—	13.34333	—

Taking the density of pure mercury at 25°, (13.5340) and that of 1, 1½, and 2 percent amalgams the density composition curve was plotted. The following relation is the result of the above determinations and represents very accurately the density of any amalgam. $D_{25°} = 13.5340 - 0.0859\, p$ where p is the number of grams of zinc in 100 grams of mercury. The point on this line which corresponds to the density of the saturated amalgam, 13.34333, indicates a composition of 2.2196 grams of zinc to 100 grams of mercury.

The composition of the saturated amalgam prepared as described above was also determined by analysis. The amalgam was treated with hydrochloric acid[1] (1 vol. conc.

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[1] Kerp and Böttger: Zeit. anorg. Chem., 25, 1 (1900).

acid to 1 vol. of water) which dissolved the zinc with an energetic evolution of hydrogen and never dissolved a weighable amount of mercury unless the acid was allowed to stand in contact with the mercury many times longer than was necessary for the removal of the zinc. It was found necessary to hasten the reaction by means of a platinum spiral which made contact with the amalgam and extended up through the acid. A small glass bead was fused on the wire just above the point reached by the amalgam surface to prevent the mercury from creeping up the wire and destroying its effectiveness. After all of the zinc had been dissolved the acid was removed with a pipette and the mercury washed and dried in a vacuum desiccator over calcium chloride. It was found necessary to use every precaution to prevent a loss of mercury by "spurting" when the desiccator was evacuated. In order to dry the mercury effectively a comparatively high vacuum was necessary and if any particles of water happened to be under the mercury their rapid expansion threw a fine spray of mercury up against the sides of the flask and out of the top if uncovered. As much as twenty milligrams of mercury were often lost in this way. This difficulty was effectively overcome by providing the analysis flasks with loosely fitting stoppers, setting them in shallow dishes and covering them with inverted beakers when they were put in the desiccator. The following are the results of duplicate analysis of amalgams taken from two different tubes I and II.

	I		II	
Flask and amalgam	23.9132	28.1761	35.0044	51.0937
After treatment with acid	23.5386	27.8001	34.3882	50.2204
Mass of zinc	0.3746	0.3760	0.6162	0.8733
Flask	6.6599	10.8565	6.6600	10.8570
Weight of mercury	16.8787	16.9436	27.7282	39.3634
Mass of mercury	16.8778	16.9427	27.7267	39.3613
Grams of zinc in 100	2.2194	2.2192	2.2224	2.2186
Average	2.2193		2.2205	

The average of these two values gives 2.2199 as the number of grams of zinc soluble in 100 grams of mercury at 25°

This value is in good agreement with the value 2.2196 calculated from the density-composition relations. These results are very probably reliable to the third place decimal so that 2.220 has been taken as the correct value.

The Electromotive Force of Zinc Amalgams at 25°

The cell used in the potential measurements has already been described (p. 160).

The electrolyte in some cases was a saturated solution of zinc sulphate with an excess of zinc sulphate crystals covering the amalgams, in other cases a solution which was not quite saturated at 25° was used. The oxygen was very effectively removed from the electrolyte before it was introduced into the cell as has been described (p. 161).

The amalgams up to a dilution of $\frac{1}{10^4}$ (that is one part of zinc to 10,000 parts of mercury) were made as follows. The zinc was cut into small pieces so that there was no especial difficulty in obtaining the correct mass of zinc for just enough of the given amalgam for one of the compartments of the cell.

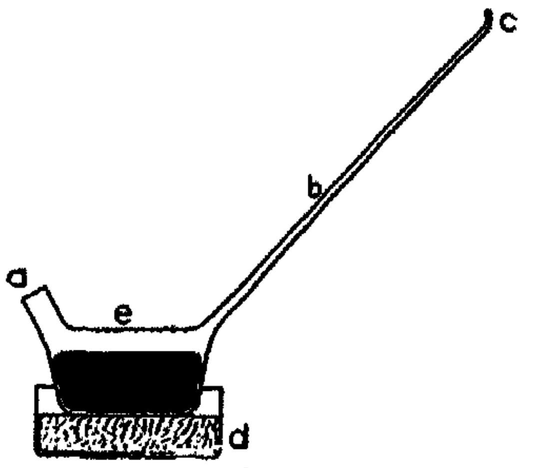

Fig. 5

The mass of this zinc was determined to 0.01 mg. The air weight of mercury was then calculated and this amount of weights was placed on the balance pan together with a tube of the form shown in Fig. 5. The cut is not to scale, the small tube being relatively much longer than is shown. The diameter of the largest part of the tube was about 15 mm.

The end (*a*) was drawn down to about 5 mm and (*b*) to about 0.3 mm internal diameter. The end *c* was closed and bent as shown. Just at the bend a scratch was made with a diamond. On the balance this tube rested on a cork support (*d*). After this tube and the weights were tared the weights were removed and the correct amount of mercury put into the tube, the last bit being adjusted with a capillary. The tube was now removed from the balance and (*a*) was connected by means of two stop-cocks alternately with an aspirator and the hydrogen generator until the air about the mercury had been replaced with hydrogen.

One of the compartments of the cell was now opened and the end (*c*) of the tube slowly introduced and thus washed externally with the stream of hydrogen which was forced in through the side tube and out through the opened tube (Fig. 1). By gently pressing the end of the tube (*b*) on the bottom of the cell, the end C was broken off at the point where it had been scratched and the mercury flowed down gently into the compartment under pressure of hydrogen from the generator.

The pieces of zinc were now held for some seconds in the stream of hydrogen issuing from the cell and then lowered slowly about half way down the tube to wash them with hydrogen; finally they were dropped into the mercury where they soon dissolved. This method could not be used for preparing amalgams more dilute than one part of zinc to ten thousand parts of mercury on account of the difficulty of weighing such a small amount of zinc with the required accuracy.

By comparing the potential of an amalgam made in this way with one of the same concentration made up outside of the cell and then introduced we have found that the method of making up the amalgam in the cell is the more reliable of the two, since it is almost impossible to introduce a very dilute amalgam without some oxidation taking place.

In the case of the more dilute amalgams the electrolyte and the two-phase amalgam were introduced in the manner just described; weighed amounts of mercury were put into the other compartments and after the ground joints were all sealed with marine glue the side tube was sealed off with the hand blowpipe. The wire (g) in the cell was brought to a glow with an electric current intermittently for three or four days, the contents of the cell being agitated continuously during this time. This was effected by an eccentric attached to a water motor which slowly raised and lowered one end of the cell causing the electrolyte to flow back and forth over the dams. The wire was glowed every few seconds instead of continuously because by this means less heat was generated in the cell.

As has been shown (p. 159) the glowing removed any residual oxygen in the gas phase and it seems that any trace of dissolved oxygen in the electrolyte would have been completely removed by the agitation in an atmosphere of pure hydrogen and continually coming into contact with the two phase amalgam. The cell was then put in the 25° bath and zinc from the two-phase amalgam was deposited electrolytically in the mercury. These two methods of making up the amalgams were made to overlap. That is two amalgams containing one part of zinc to ten thousand parts of mercury were made up, one by weighing out the metals directly and introducing them separately into the cell, the other by depositing the zinc electrolytically, and the potentials of the two were in excellent agreement.

Measurement of Electromotive Forces.—The basis of all e. m. f. measurements was Clark cells which had been made at intervals since 1903 and all of which were in good agreement. These cells are reproducible to better than one part in 50,000 their absolute value being 1.42040 at 25° or 1.4330 at 15°. For this work a 100 liter oil bath was used. It was electrically heated and controlled and did not vary from 25° by more than 0.01° at any time. The thermometer used in locating this temperature was checked at the transition point of Glauber's salt, 32.383°.

The instruments used in the e. m. f. measurements were a high resistance Wolff potentiometer, a Broca galvanometer with 1000 ohm coils; a Nernst glower lamp and scale, a regulating resistance and two standard batteries[1] which gave a very steady and constant current. The resistance coils of the potentiometer were carefully calibrated and the whole system thoroughly insulated. Moisture or dust on the hard rubber base of the potentiometer introduced very considerable disturbances so the instrument was kept scrupulously clean and on damp days no measurements were taken.

The cells used for the amalgams had five or six compartments and each amalgam was measured against the constant electrode. The e. m. f. between any two amalgams was given then by the difference between their e. m. f's. as measured against the constant electrode. This method of measurement is the only one as yet employed by which one can be sure as to whether any amalgam is losing zinc. The values obtained by taking the difference between the e. m. f's. of two amalgams against the constant electrode and the value obtained by direct measurement were compared and never differed by more than a microvolt. The reproducibility of the constant electrode is shown by the following measurements. Two amalgams containing respectively 5 parts and 2.5 parts of zinc to 100 parts of mercury were put into two compartments of a cell. At 30° or below, these two amalgams should have the same potential, as solid zinc is present in both amalgams at or below this temperature.

Mar. 19th, 25° e. m. f. between the two was 0.000008 volt.
Mar. 25th, 20° e. m. f. between the two was 0.000006 volt.
Mar. 30th, 15° e. m. f. between the two was 0.000003 volt.
Apr. 19th, 25° e. m. f. between the two was 0.000002 volt.
May 6th, 30° e. m. f. between the two was 0.000000 volt.

Another of the advantages in measuring all potentials against the standard electrode is that the results from any two cells are directly comparable since the e. m. f. of any amalgam concentration cell is independent of the concentra-

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[1] Phys. Rev., 27, 33 (1908).

tion of the electrolyte. It is only necessary to *accurately* control the temperature.

It was found convenient to express the concentrations as fractions the numerator giving the grams of zinc and the denominator the grams of mercury. The concentration of the standard electrode is then $\frac{2.220}{100}$ at 25°.

Cell No. 1 charged with the following amalgams gave:

Days	*a* $\frac{2.220}{100}$	*b* $\frac{2.5}{100}$	*c* $\frac{2}{100}$ *a*—*c*	*d* $\frac{1}{100}$ *a*—*d*	*e* $\frac{1}{1000}$ *a*—*e*
1	—	—	0.000878	0.007780	0.035470
2	—	—	0.000875	0.007782	0.035470
6	—	—	0.000876	0.007781	0.035471

There was no evidence of a loss of zinc in this time even by the $\frac{1}{10^3}$ amalgam. It was impossible to observe this cell longer as one of the contact wires broke and the cell had to be opened.

Cell No. 3 was charged with the following amalgams:

Days	*a* $\frac{2.220}{100}$	*b* $\frac{2.2}{100}$	*c* $\frac{2}{100}$	*d* $\frac{1.8}{100}$	*e* $\frac{1.4}{100}$	*f* $\frac{5}{1000}$
1	—	0.000200	0.000891	0.001845	0.004260	0.015633
2	—	0.000074	0.000875	0.001829	0.004253	0.015620
3	—	0.000047	0.000873	0.001829	0.004260	0.015625
140	—	0.000047	0.000889	0.001830	0.004310	0.015700

Between the 3rd and the 140th day the cell was put at 30° and at 35° then left at laboratory temperature all the summer so that the slight increase in the value of the $\frac{5}{1000}$ amalgam is not surprising.

Cell No. 2 with the following amalgams at 25° gave:

Days	2 phase $\frac{2.220}{100}$	*b* $\frac{2}{10^3}$	*c* $\frac{1}{10^3}$
1	—	0.026768	0.035465
2	—	0.026764	0.035470
15	—	0.026773	0.035479

The $\frac{1}{10^3}$ amalgam remained practically constant at 0.035470 for a week, which was the same value as was observed for an amalgam of the same concentration in cell No. 1.

Cell No. 6 had six compartments. One compartment contained the standard electrode, the next four contained weighed amounts of mercury and into the sixth were put 60.7021 grams of mercury and 0.00607 grams of zinc making a $\frac{1}{10^4}$ amalgam. The cell was then sealed off and put at 25°. The e. m. f. of this $\frac{1}{10^4}$ amalgam against the constant electrode was:

5 hours	0.064937
7 hours	0.064995
10 hours	0.065000
1 day	0.065226

There is some evidence of a drift here but the e. m. f. was practically constant at 0.065000 for some time.

The cell was now taken out of the thermostat and was rocked and the wire glowed for several days to remove any residual oxygen before depositing the mercury in the other compartments to form the more dilute amalgams. The cell was then warmed up to about 35° before it was put back in the 25° bath as it had been found that the two-phase electrode comes to equilibrium more quickly from the higher temperature.

In depositing zinc in the mercury a storage battery of 120 volts was closed over large external resistances which included an accurately calibrated set; after the circuit was closed the fall of potential over 1000 ohms was measured with the potentiometer. The internal resistance was so small that the current was practically the same before and after the cell had been switched into the circuit, so that the time necessary for each deposition was calculated before the cell was switched into the circuit. The time was taken with a stop watch and the fall in potential over 1000 ohms was measured at frequent intervals during the time the current was depositing zinc.

Compartment (*b*) contained 35.0004 grams of mercury and it was desired to deposit 0.00035 grams of zinc from the two-phase electrode.

At	9:15, circuit was closed.		
	9:16,	fall of potential over 1000 ohms was	0.19947 v.
from	9:20, to 9:50	" "	0.19941 v.
At	9:55,	" "	0.19945 v.
	10:05,	" "	0.19950 v.
	10:10,	" "	0.19958 v.
	10:15,	" "	0.19970 v.
	10:18,	" "	0.19993 v.
	10:20,	" "	0.20010 v.
	10:25,	" "	0.20018 v.
	10:30,	" "	0.20004 v.
	10:35,	" "	0.20008 v.
	10:38,	" "	0.20015 v.
	10:41, broke the circuit.		

The average value of the current was 0.00019964 which flowed for one hour 26 minutes or 5160 seconds and gave 1.0301 coulomb. As one coulomb deposits 0.00033385 gram of zinc there was deposited in the 35 grams of mercury 0.0003486 gram of zinc.

Immediately after the circuit was broken the cell was rocked and the measurements of this amalgam against the constant electrode were taken.

1 minute	0.094707
5 minutes	0.094705
11 minutes	0.094704
10 hours	0.094883
15 hours	0.094944

There was no drift here for several hours. The value 0.09470 is evidently the correct one for this $1/10^5$ amalgam (the current was broken somewhat too soon so that the concentration of this amalgam was really $0.996/10^5$).

Zinc was now deposited in the 34.9902 grams of mercury in compartment *c*. The current was 0.00011814 which remained absolutely constant for the 14 minutes and 35 seconds it was depositing zinc. This gave 0.10336 coulomb which deposited 0.000034987 gram of zinc. It was found necessary to rock the cell for about 5 minutes before the readings became at all constant.

5 minutes	0.12448
10 "	0.12453
15 "	0.12462
20 "	0.12471
25 "	0.12471
35 "	0.12480

There is evidence of considerable loss here. The original value of about 0.1245 is probably near the correct one.

Compartment *d* contained 34.9889 grams of mercury. A current of 0.0001175 was passed for 88 seconds which gave 0.010341 coulomb and deposited 0.000003500 gram of zinc. The cell was rocked for two minutes and then measured.

2 minutes	0.151+
3 "	0.153+
4 "	0.1550
5 "	0.1555
6 "	0.1558
7 "	0.1562
10 "	0.1575
25 "	0.1587
12 hours	0.1664

The potential of this $1/10^7$ amalgam was variable during the first few minutes but at the end of four minutes it became constant enough to be followed in the fourth place decimal. The value 0.1550 may be taken as an approximation to the correct value.

Compartment *e* contained 34.9849 grams of mercury.

A current of 0.00001386 amp. for 75 1/5 seconds gave 0.0010423 coulomb and deposited 0.0000003525 gram of zinc. The cell was then rocked for 1/2 minute and measured.

1 minute	0.23+	7 minutes	0.435
2 "	0.35+	25 "	0.479
3 "	0.40+	30 "	0.511
4 "	0.41	4 hours	0.7031

The behavior of this $1/10^8$ amalgam was decidedly different from any previous one. The amalgam never became constant and in four hours the value had risen to 0.703 which is about the value that pure mercury falls to when allowed to stand in an oxygen free zinc sulphate solution.

A great many measurements have been made on pure mercury against the two-phase standard in these cells, the same precautions being used to exclude oxygen as in the case of the dilute amalgams. The value at first was about 1.09 but in time this settled down to about 0.74, usually something less than 0.75. After four hours then there was no more zinc in the $1/10^8$ amalgam than there was before any zinc had been deposited by the current.

After three days zinc was again deposited in this mercury in compartment *e*. It was thought probable that the amalgam had lost some zinc while the current was still depositing it so a larger current was used. 0.000123 ampere for 8 4/5 seconds gave 0.001084 coulomb and deposited 0.0000003669 gram of zinc.

After 1 minute the e. m. f. was	0.18+
2 minutes	0.19
3 "	0.21
5 "	0.25
35 "	0.50
2 days	0.714

In this case where the time required to deposit the zinc was only about 1/10 of that previously used a much lower value was obtained for the initial reading. This is also in good agreement with the idea of an equilibrium between the mercury and zinc sulphate since the zinc from the first $1/10^8$ amalgam would have reduced the concentration of mercury ions in solution and so there would have been fewer present to remove the zinc from the second $1/10^8$ amalgam.

After 3 days this amalgam had apparently lost all of its zinc. Zinc was again deposited in this mercury by 0.00000235 amp. for 43 4/5 secs. which gave 0.00010315 coulomb and deposited 0.00000003502 gram of zinc. The cell was rocked during the whole time of deposition:

1 minute	0.24
2 minutes	0.27
5 "	0.408
30 "	0.514

In a few hours the value rose to the equilibrium value of about 0.7+.

In the following table the e. m. f. measurements are given between amalgams varying in concentration from that saturated at 25° to one containing one part of zinc in one billion parts of mercury. In the column marked observed the value of each amalgam measured against the 2 phase is given.

Amalgams	Observed V	Differences	Calculated
2.220/100	0.000000		
2/100	0.000890	0.000890	0.001340
1.8/100	0.001829	0.000939	0.001351
1.4/100	0.004260	0.002431	0.003226
1/100	0.007795	0.003535	0.004320
5/1000	0.015620	0.007825	0.008898
2/1000	0.026768	0.011148	0.011763
$1/10^3$	0.035470	0.008702	0.008898
$1/10^4$	0.065000	0.029530	0.029560
$1/10^5$	0.094700	0.029700	0.029560
$1/10^6$	0.12450	0.029800	0.029560
$1/10^7$	0.1550	0.030500	0.029560
$1/10^8$	0.185	0.0300	0.029560
$1/10^9$	0.24	0.0550	

The Nernst equation for concentration cells is $E = RTln C_1/C_2$ where C_1 and C_2 in our case represent the concentration of the zinc in the mercury. Changing to Briggs' logarithms for 25° we get $\pi = 0.029560 \log C_1/C_2$.

As has been observed by previous workers the e. m. f. between the concentrated amalgams is much too small to agree with the above equation. There is very good agreement in the range from 2/1000 to $1/10^7$ and even to $1/10^8$ if the first reading is taken.

In the case of amalgams more dilute than $1/10^8$ it was impossible to take any measurements before the amalgam had lost part of its zinc. In fact the potential measurements seem to leave no doubt that in a short time both the $1/10^8$ and the $1/10^9$ amalgams had lost all of the zinc that had been deposited in them. It is well known that oxygen dissolved in the solution about a zinc amalgam does remove the zinc. There is little doubt that the glowing platinum wire in the cell removed all oxygen from the vapor phase and it seems that the agitation of the electrolyte for days with the two-phase amalgam, which contained over 200 million times as much zinc as the $1/10^8$ amalgam, would have removed any residual oxygen from the solution. Considering all of these points it seems very unlikely that zinc was removed from these very dilute amalgams by oxygen.

The equilibrium between mercury and zinc in the amalgam and in solution undoubtedly follows the relation;

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}$$

where P_1 and P_2 represent the concentrations of zinc and mercury in the amalgam and p_1 and p_2 their respective concentrations in solution. In our case P_2, the concentration of mercury in the amalgam and p_1 the concentration of zinc in solution are constant. The mercury in solution is mercurous mercury, but as has been shown by Ogg[1] the ions are composed of two atoms each and carry a double charge so

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[1] Loc. cit.

that $n_2 = 2$ and for zinc $n_1 = 2$. The equation reduces to $P_1 \times p_2 = K$ and K is evidently a very small number. If mercury is brought into a zinc sulphate solution mercury should go into solution and zinc be deposited in an equivalent quantity in the mercury until the equilibrium constant has been satisfied. The measurements of the e. m. f. between pure mercury and the two-phase electrode have indicated this very thing. The initial high value of about 1.09 has always settled down to about 0.7+ indicating a deposition of zinc in the mercury. This reaction must be electrolytic so that when one double gram atom of mercury has passed into solution a gram atom of zinc has been deposited. It is thus seen that the actual concentration of zinc in the mercury is dependent on the relative volumes of mercury and solution, at the same time the reaction must proceed until $P_1 \times p_2 = K$. Before any zinc was deposited in the mercury in cell No. 6 the e. m. f's. between the two-phase amalgam and the mercury in the different compartments were measured. It may be observed that this same gradation of values has been found in many other cases so that this may not be considered a chance effect.

A two-phase	B mercury	C mercury	D mercury	E mercury	F $1/10^4$
—	0.97	1.00	1.04	1.01	X

From these values it appears that the mercury nearest the compartments containing amalgams had acquired the most zinc. In the case of the two-phase amalgam, P_1 of the above equation is constant and relatively very large so that p_2 must be relatively very small. This amalgam would then tend to remove the mercury ions thrown into solution by the pure mercury in the other compartments, so that the mercury in the compartments nearby would have to continue giving ions to the solution in order to preserve the equilibrium.

When zinc was deposited electrolytically in the mercury, mercury was also deposited in proportion to their concentrations, but since the solution was saturated with zinc sulphate, while the concentration of mercury was exceedingly small, it is safe to assume that the zinc deposited corresponded to the coulombs passed even in the most dilute amalgams. The deposition of zinc disturbed the equilibrium and the zinc began at once to leave the amalgam and replace the mercury ions in solution until the equilibrium condition was again reached. In the cell used where the volume of mercury was about 1/6 of that of the electrolyte the equilibrium e. m. f. between mercury and the constant electrode fell to about 0.7 + and could be reached from either side.

It seems that the concentrations of our $1/10^8$ and $1/10^9$ amalgams were of the order of magnitude of the concentration of the mercury ions in solution. As was to be expected this is a somewhat greater dilution than was found by Hulett and Delury[1] in the case of cadmium amalgams.

Summary

The chief results of this investigation are: A determination of the composition of the zinc amalgam saturated at 25°. A determination of the relation $D_{25°} = 13.5340 - 0.0859\,p$, where p = grams of zinc in 100 grams of mercury, between the density and composition of zinc amalgams.

Measurements on the electromotive forces of zinc amalgams at 25° extending from the saturated amalgam to a dilution of 1 part of zinc to one billion parts of mercury. The observations were all based on a constant reproducible electrode and so are directly comparable.

The discovery of a region between two grams of zinc to 1000 grams of mercury and 1 gram of zinc to 10 million of mercury where the potentials of any two amalgams conform to the requirements of the gas laws. Beyond this dilution the potential fell off so rapidly with the time that no accurate measurements could be taken, which indicates that the reac-

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[1] Loc. cit.

tion $\mathrm{Zn} + \overset{++}{\mathrm{Hg}_2} \leftrightarrows \overset{++}{\mathrm{Zn}} + 2\mathrm{Hg}$ is a reversible one and that a definite equilibrium is established in the system mercury, zinc sulphate and water.

My sincere thanks are due to Dr. G. A. Hulett at whose suggestion this work was undertaken, and owing to whose valuable assistance the work has been brought to its present state.

Princeton, December, 1909.

NEW BOOKS

Vergangenes und Künftiges aus der Chemie. *Biographische und chemische Essays von William Ramsay. Deutsche, um eine Autobiographische Skizze vermehrte Ausgabe übersetzt und bearbeitet von Wilhelm Ostwald. 17 × 24 cm: pp. vi + 296. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1909. Price: linen, 8.50 marks; bound, 9.50 marks.*—The volume opens with an autobiographical sketch of the author. Ramsay's early training in Glasgow was essentially along inorganic and analytical lines. Quite naturally he went to Bunsen's laboratory in Heidelberg. It does not appear whether he liked it there or not; but he soon went to Fittig's laboratory in Tübingen, ostensibly because many of his friends were there or had been there. That meant a temporary change to organic chemistry. From 1874 to 1880 Ramsay drilled the medical students of Glasgow in general chemistry, handling four groups of men each year. During this period he gave lectures upon organic chemistry and did a good deal of work with the pyridine bases because there happened to be a large supply of them in the laboratory. The determination of vapor densities of some of the dipyridine derivatives seems to have been the thing which turned his mind to what we now call physical chemistry and when he moved to Bristol in 1880 he continued the work on molecular volumes of liquids, gradually passing from that to the general study of boiling point curves.

In 1887 Ramsay was called to University College in London where he still is. He was probably the first man in England to perceive the importance of van't Hoff's paper on osmotic pressure; and the work on the osmotic pressure of metals in mercury was the immediate result. Under Ramsay's guidance Linder and Picton began their work on colloids while Shields in 1892 worked out the relation between surface energy and molecular weight, first suggested by Eötvös.

Ramsay's knowledge that heated magnesium absorbs nitrogen led him to make use of this reaction when he joined forces with Rayleigh in a search for an explanation of the fact that nitrogen from the air was denser than nitrogen prepared from chemical compounds. The discovery of argon followed.

While trying in vain to make compounds of argon, Ramsay's attention was called by the mineralogist Myers to a statement by Hillebrand that certain uranium minerals give off large quantities of gas when heated. Ramsay followed up this lead and discovered helium. In consequence of the work done years before on boiling point curves, Ramsay naturally thought of fractioning liquid air and liquid air residues with the result that krypton, neon and xenon were added to the list of elements. That helium was a decomposition product of the radium emanation was first suggested by Rutherford and Soddy but the experimental proof of this remarkable fact was furnished by Ramsay and Soddy. Ramsay's later work on the radium emanation is well known.

To my mind Ramsay's career brings out clearly the importance of discussing one's work with others and of working with a definite plan in mind. If Ramsay had belonged to the intensely secretive type it is probable that Rayleigh would not have welcomed him as a collaborator and it is certain that Myers would not have called his attention to Hillebrand's paper. While Ramsay would doubtless have discovered helium sooner or later, he might easily have been set back a couple of years had his temperament been different. So far as one can judge from the published accounts, Ramsay has not experimented in a blind way. He has always started in to solve a definite problem and while he has often bagged bigger game than he expected, the result has been due far more to skill than to luck. The work on liquids was clearly systematic. The work on argon was based on the legitimate conclusion that if there was something else in atmospheric nitrogen it was not likely to be taken up by magnesium in exactly the same proportions in which it occurred in the atmospheric nitrogen. The discovery of helium was an unexpected one; but Ramsay knew that gas was given off and he was working at the definite problem of determining what the gas or gases were in the minerals examined. From the periodic table it appeared probable that there were other inert gases besides argon and helium. The natural place to look for them was in the air and Ramsay found them. Dewar was the man who had had the experience with the liquefaction of gases but he set himself a different problem. The discovery of the formation of helium from the emanation was the result of a deliberately planned experiment to determine the spectrum of the emanation. If one wishes, one may say that Ramsay has been fortunate to the point of genius in the problems he set himself; but the important thing is that no single one of his discoveries has been the result of purposeless experimenting.

The historical essays consist of sketches of Black, Kelvin and Berthelot; of a paper on the early period of chemistry, and of a paper on the great London chemists, Boyle, Cavendish, Davy and Graham.

The last half of the book is taken up by an article on the functions of a university and by seven chemical essays entitled: How discoveries are made; Becquerel rays; what is an element? the periodic grouping of the elements; radium and its products; what is electricity? the *Aurora borealis*.

In the paper on discoveries Ramsay points out that the man who fishes for salmon is very likely not to catch anything; but if he is successful, his reward is great. On the other hand the fellow who fishes for perch is pretty safe to get a basketful; but he is not looked up to with awe and admiration except by the very young who are still in the bent pin stage. Having selected one's problem, the way to attack it is to ask oneself some intelligent question in regard to it which shall be of such a nature that the answer to the first question shall suggest a second question, that the answer to that shall suggest a third question, and so on. If one follows this plan, one can start anywhere and be sure of making discoveries. Whether they will be important ones or not is on the knees of the gods. While this is an absolutely safe rule for making discoveries, it is a rule which very few people can apply. There is first the difficulty of asking oneself the intelligent question and then the difficulty of finding the answer to it. With each succeeding question and answer these difficulties usually increase.

Among the other essays the most interesting one is perhaps that on the *Aurora borealis*. Ramsay believes that the northern lights are due to electrical discharges through krypton and he has devised a laboratory experiment which duplicates some of the conditions actually observed in the heavens. Since this essay was published, the hypothesis has received additional confirmation from Collie's discovery of the flashes which are given out when neon is shaken with mercury. It now seems probable that the electrical discharge acts first on the neon and then on the krypton.

This is distinctly a book on which one can spend a few hours with great profit. As was to be expected, the translation has been done admirably though Ostwald's rendering of the English phrase "sour grapes" was new to the reviewer. *Wilder D. Bancroft*

Jahrbuch der Elektrochemie und angewandten physikalischen Chemie. *Begründet und bis 1901 herausgegeben von W. Nernst und W. Borchers. Berichte über die Fortschritte des Jahres 1905. Unter Mitwirkung der Herren P. Askenasy, P. Berl, K. Elbs, F. Harms, J. Hess, H. Ley, J. Meyer, M. Roloff, O. Sackur, herausgegeben von Heinrich Danneel. XII. Jahrgang. 17 × 25 cm; pp. xiii + 1049. Halle: Wilhelm Knapp, 1909. Price: paper, 30 marks.*—The volume for 1905 appears in 1909 instead of in 1906. This is a serious drawback and it is much to be hoped that the editor will be able to catch up again before many years have passed. The extraordinary value of the volume is shown by the fact that the book is very useful even though three years late.

In the scientific part, the material is classified under the headings: natural constants; book notices; apparatus; periodic system and valence; phase rule; reaction velocity and mass law; catalysis; thermochemistry; theory of ions; theory of electrons; osmotic pressure; colloids; applications of physical chemistry to medicine and physiology; conductivity and the constitution of solutions; chemical and electrical energy; polarization and electrolysis; electrical phenomena in gases, and radioactivity.

Under applied electrochemistry the headings are: production of current; inorganic processes and products; organic compounds; electrolysis of the alkali chlorides; technical electrochemical apparatus; electroplating and allied subjects; book notices.

Among the many interesting things in this volume we may cite: the theory of the alkali storage battery; electrolytic chromium; the discussion as to the absolute zero in potential measurements; the use of chloride in copper refining; and the new construction of the carborundum furnace. *Wilder D. Bancroft*

Elektrochemie geschmolzener Salze. *By Rich. Lorenz and F. Kaufler. (Handbuch der angewandten physikalischen Chemie. Herausgegeben von Prof. Dr. G. Bredig). Band II.: Abteilung I. 16 × 25 cm; pp. vi + 84. Leipzig: Johann Ambrosius Barth, 1909. Price: paper, 3,60 marks.*—The volume on the electrolysis of fused salts is to appear in three parts of which this is the first. The subject is discussed under the headings: properties of fused salts; methods of work; Faraday's law; electromotive forces; theory of ions; special part. In the special part the authors discuss the obtaining of the metals by electrolysis of fused baths. The book is evidently not intended to be a technical one as may be seen from the very limited amount of space devoted to Castner's sodium process and to the aluminum process of Hall and Héroult. On the other hand the book is extremely good in the parts concerned with polarization, with Faraday's law, etc. The section on the conductivity of fused salts is also extremely full. *Wilder D. Bancroft*

Elementary Modern Chemistry. *By Wilhelm Ostwald and Harry W. Morse. 13 × 19 cm; pp. xi + 291. Boston: Ginn and Company. Price: bound, $1.00; mailing price, $1.10.*—In the preface the authors say:

"The beginner in the study of chemistry finds interest and pleasure, first of all, in the remarkable new facts which are placed before him, and this is both natural and desirable. No one can master the science without much study of properties and reactions, and minute acquaintance with as many phenomena as possible is a fundamental requisite. Modern chemistry has, however, a number of general laws which appear everywhere through it, connecting various facts in the most interesting way. Before study has gone very far it becomes necessary to begin the statement of these laws and to indicate how the facts already learned group themselves about them. Two purposes are served by this method of presentation. First a real *science* of chemistry begins to unfold itself to the student, and second, the acquisition of more new facts is made easier and more interesting.

"We have planned in this book to present a sufficient number of facts and experiments to fill the time usually devoted to a first course, and at the same time we have endeavored to fit these facts, as far as possible, to the simpler of the general laws now firmly established as the basis of the science of chemistry."

The headings of the chapters are: substances and properties; melting and solidification; pure substances and solutions; combustion; the metals; water; hydrogen; air; acids and bases; combining weights; electrolysis; gas volumes; the halogen group—chlorine; bromine and iodine (fluorine); sulphur; sulphuric acid; hydrogen sulphide; nitric acid; ammonia; phosphorus; silicon; sodium; potassium; ammonium; calcium (barium, strontium, magnesium); aluminum; copper; iron; lead; mercury; silver; tin; gold and platinum; the periodic system; alloys.

Any book by Ostwald is sure to have some good qualities and this one is no exception. Taken as a whole, the book is rather a disappointment. It is a little difficult to see why copper should come after calcium and aluminum. There may be some reason why the order: copper, iron, lead, mercury, silver, tin, and gold is better than any other order; but there is nothing in the text to show what it is.

The book is full of careless and inadequate statements. On p. 3 there are figures showing the way in which a section of granite looks if seen under a microscope, once when illuminated by ordinary light and again by polarized light. The two figures are very different but no explanation is given of the difference or even why there should be a difference.

On p. 6 we find the statement that "any solid whatever can be changed into a liquid if its temperature is raised to a high enough point." Two pages later it is stated that "a few substances pass from the form of a solid directly into that of a gas, without melting; they are said to *sublime*." In a sense both these statements are true; but they are not both true under the same experimental conditions and there is nothing to show how these two statements are to be reconciled.

On p. 12 we read that "the name 'solution' is given to homogeneous bodies with changing boiling and freezing points, because they can be made by 'dissolving' one body in another; that is, by bringing together two phases which act on each other to produce a single phase. There are three kinds of solution—solid, liquid and gaseous." It is not clear that a solid solution can have a boiling point at all and there certainly are a great many which do not have a freezing point which can be realized experimentally.

On p. 27 the authors say that "the difference in price between a pound of aluminium, which costs about forty cents, and the same weight of aluminium in the form of clay, which costs almost nothing, is a measure of the amount of energy contained in the element aluminium compared with the amount contained in the oxide." This is a picturesque way of putting it; but the student might ask whether the energy changes when the price drops below thirty cents. If not, which price is the measure of the energy? Exception might also be taken to a statement which implies that purified aluminium oxide costs almost nothing. While it may be true that "in tropical lands the clays are very often nearly pure aluminium oxide," the ordinary clay is not. In a popular article it is permissible to say that aluminium is made from clay; but such a statement is misleading in a book on chemistry.

On p. 116 the authors discuss the precipitation of metallic copper from solutions by means of zinc. They state that the anion has no influence on the reaction and they suggest testing this statement by placing a zinc rod in each of the solutions, cupric nitrate, cupric chloride and cupric bromide. It is perfectly true that zinc will precipitate copper from each of these solutions; but the student should not be taught at first to consider these three cases as identical. His attention should rather be directed to the fact that cuprous chloride and cuprous bromide are the stable products so long as any cupric salt is left in solution.

On p. 178 the authors say that "in America we have no very large salt beds, and we are therefore dependent on salt from the ocean and from salt springs and lakes for our supply." As a flight of the imagination, this is unsurpassed.

Under sodium, p. 180, the authors say that the reducing action of the cathode is a very strong one. In this particular case they must mean the reducing action at the cathode, not of it.

Throughout the book the words cathode and cation are mis-spelled. Ramsay's name is changed in two places in which it occurs. The translator speaks of hypochlorite but of hypoiodate. The quotation from the preface, with which this review opened, may be taken as a fair sample of the English and of the punctuation.

The illustrations are very good, with two exceptions. In the calcium carbide furnace, p. 209, the hottest part of the furnace is apparently at the bottom, far away from the arc. On p. 227 the cut illustrates a method by which copper might be refined but it does not represent anything actual. In this country nobody refines copper with a lot of small anodes hung on a bar. The artist was apparently thinking of silver refining. It would have represented actual facts rather better if the cathode had been made thinner than the anodes.

Wilder D. Bancroft

EQUILIBRIUM IN THE SYSTEM, MERCURIC CHLORIDE-PYRIDINE

BY RUSSEL SMITH McBRIDE

In the case of pyridine compounds only a few of the immense number listed have been studied in the light of the phase rule. These are the chloride, bromide, iodide and nitrate of silver investigated by the solubility method[1] and the copper salts studied by the vapor pressure method by Tombeck.[2] Preliminary experiments suggested by Professor Kahlenberg showed that the double salt formed with mercuric chloride might advantageously be studied by the solubility method.

In 1884 Monari[3] gave the first description of compounds of mercuric chloride and pyridine. Four years later Lang[4] described the compound $HgCl_2.C_5H_5N$ and this was again prepared by Groos in 1890.[5] Ladenburg,[6] working with aqueous solutions containing an excess of HCl, made the compound $C_5H_5N.HCl.2HgCl_2$. Pesci[7] has described the preparation and properties of all three of the known compounds which contain only mercuric chloride and pyridine. These are: $HgCl_2.2C_5H_5N$, $HgCl_2.C_5H_5N$, and $3HgCl_2.2C_5H_5N$. Reitzenstein[8] and Naumann[9] have since prepared one or more of these by new methods and recognized them as the same compounds.

In order to determine the limits of stability of these

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[1] $AgNO_3$—Kahlenberg and Brewer: Jour. Phys. Chem., **12**, 283 (1908); AgCl—Kahlenberg and Wittich: Ibid., **13**, 421 (1909); AgBr, and AgI—Kahlenberg and McKelvey (not yet published).

[2] Tombeck: Ann. Chim. Phys. (7), **21**, 433 (1900).

[3] Monari: Revista di chim. med. farm. 2, 190 (1884); see also Jahresber., 1884, 629.

[4] Lang: Ber. chem. Ges. Berlin, **21**, 1586 (1888).

[5] Groos: Liebig's Ann., **228**, 73 (1890).

[6] Ladenburg: Jahresber., **247**, 5 (1888).

[7] Pesci: Gaz. chim. Ital., **25**, II, 428 (1895).

[8] Reitzenstein: Liebig's Ann., **326**, 313 (1903).

[9] Naumann: Ber. chem. Ges. Berlin, **37**, 4610 (1904).

compounds and their solubility in pyridine the following work has been done.

Materials Used

The mercuric chloride used for all the work was a "C. P." sample for analytical purposes. It was carefully tested by analysis, three determinations giving the results 100.00, 100.09, and 100.10 percent, showing it to be of a high quality. It contained no mercurous salt or other impurity in detectable amount.

The pyridine used was a sample from Kahlbaum, which had been standing over solid caustic potash for more than two months before distillation for use. The fraction boiling between 114° and 116° was used.

The set of weights used for all of the analytical work was standardized by Richards' method, no error greater than 0.1 mg being possible from this source. The thermometers employed were compared with three standard instruments, two from the Reichsanstalt, and one from the Bureau of Standards, and the zero and one hundred degree points determined. The thermometers were graduated to 0.1° and estimation to 0.01° was always made, so that the error was certainly less than 0.05°.

Method of Analysis

Two methods of determination of the mercury in the samples were available, namely, gravimetric as HgS, and electrolytic as free metal. The latter was tried but soon abandoned as the former proved more rapid and accurate. All results which are given have been determined by the method described below, which is a modification of that described by Treadwell.[1]

Several variations of the method, such as washing the precipitate with hot or cold water, precipitation from hot or cold solution, extraction with carbon bisulphide to remove free sulphur or washing with alcohol to aid in the rapidity of drying, cause no apparent variation in the accuracy. The

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[1] First English edit., Vol. 2, p. 133.

presence of pyridine when neutralized by a slight excess of HCl was shown to have no detrimental effect. The physical character of the precipitate seemed better, however, when the precipitation was made in cold solution. Under these conditions there was much less tendency to form a slimy precipitate tending to creep up the sides of the beaker and crucible. The speed of washing the precipitate was greatly increased by the use of hot water, and the time of drying materially lessened by a final washing with alcohol.

One radical change was found necessary in the method of washing. Before use of hot water, two or three portions of hydrogen sulphide water were used. Unless this precaution was observed the results were invariably too high. The precipitate was dried on a Gooch filter at 115° for one and one half hours. Exclusive of this time of drying, the method as thus modified required less than twenty minutes for each determination after the sample had been weighed. The accuracy leaves nothing to be desired.

Method of Solubility Measurement

For the range 12° to 90° a water thermostat was employed. The temperature was controlled by an ordinary toluene gas regulator. Up to 30° it was necessary to pass a stream of cold water through a lead coil immersed in the bath in order to cool it to the desired temperature. Above 60° a thin layer of paraffine on the surface of the water aided greatly in the temperature control by prevention of evaporation. Radiation was greatly reduced by insulating the tank with a layer of cotton. No difficulty was experienced in maintaining the temperature within a range of 0.1° for five or six hours at a stretch, while in many cases the maximum variation was less than 0.05°.

Saturation of the solution was secured by continuously stirring, with a glass spiral, a mixture of the solid and liquid phases. Samples of the liquid were removed at intervals of one to two hours and saturation was assured by the agreement in composition of successive samples. Access of water was prevented by tightly stoppering the tube and introducing the stirrer through a mercury seal. That the arrangement was thoroughly tight, was evident from the fact that no odor of pyridine vapor was observed, even at the higher temperatures.

When a sample was desired, the stirrer was removed and the solid allowed to settle for about ten minutes. The density of the solid was so great that in most cases the liquid could be at once sampled by means of a pipette. As an added precaution, however, the tip of the latter was covered with a filter to prevent entrance of any solid particles. The liquid (about 2 cc) was run into a glass stoppered weighing bottle and quickly stoppered. At no time was the solubility tube removed from the thermostat. At higher temperatures the pipette was heated slightly above the temperature of the solution to prevent solidification of the sample.

The liquid after cooling was weighed, dissolved in dilute hydrochloric acid, diluted to 300 cc and analyzed as above described. A sample of about 2 grams, giving a precipitate usually greater than 0.3 gram, gave very satisfactory results.

For the determination at 0° the solubility tube was immersed in finely chopped ice, and the stirring was done by hand. Otherwise the method was very similar to that employed with the thermostat. The temperature variation was less than 0.1° in this case also.

At —22° and —33° salt with ice and calcium chloride with ice respectively were used. In the former case, the temperature range was —21.65° to —22.0°, a toluene thermometer being used. At the lower temperature a variation of 0.4° seemed unavoidable, even when using a Dewar tube as container. The results at —33° are thus an approximation, certain only within 0.5°.

Melting-point Method

Over the range 0°–80°, as has been noted, the errors were not greater than 0.1°. At 80° and above, the degree of accuracy was notably lessened because of three factors: the increased difficulty of temperature regulation, errors introduced by loss of pyridine while sampling, and finally the greatly increased time required to obtain equilibrium in the meta-stable region. This led to the use of the melting point method which was of equal accuracy and permitted much greater speed.

The principle involved in this process is merely the determination of the temperature at which the last of the solid phase in contact with the solution disappears. The tube shown (natural size) in Fig. 1 was employed. The bulb was filled with the desired mixture and then sealed at A as shown. The tube was fastened to the side of a thermometer graduated to 0.1°, the bulb and the cistern of the thermometer being very close together. The two were immersed in a bath of sulphuric acid and slowly heated, shaking them carefully to mix the liquid and solid in the bulb thoroughly.

Fig. 1

The heating was continued until all but the last traces of solid were liquefied. It was then cooled slightly (1° or 2°) until increase in the amount of solid was apparent. By several heatings and coolings the exact temperature could be determined within 0.3° except in a few cases where the limit was 0.5°.

This method prevented any possibility of supercooling of the liquid, as solid phase was always present. The chance of superheating was extremely small as the bath was stirred and heated very slowly. At the final testing, the bath varied less than one degree during a period of ten or fifteen minutes and the thin-walled bulb certainly attained the exact temperature of the acid within 30 seconds. Distinctly noticeable variation in the quantity of solid present could be detected by a change of 0.3°, within one minute.

In several cases it was possible to determine two points on different curves with the same sample. The meta-stable point was always difficult and often impossible to obtain. When heating a sample slowly, the approach to a meta-stable curve was always indicated by partial liquefaction; in the majority of cases, however, the new solid formed and the whole again solidified before the meta-stable point of equilibrium could be exactly determined. The method of analysis has been described and was of equally satisfactory character with these samples.

The Solid Phase

The testing of the solid phase presented the greatest difficulty in all cases. Near the ordinary temperatures, the mixture of solid and liquid was separated by a suction filter. The crystals thus obtained were freed from adhering mother liquor by filter paper and preserved *in* glass stoppered weighing bottles until analyzed. At higher and lower temperatures, the filtration was made *in* the thermostat by inserting an inverted filter directly into the solubility tube. The separation was thus accomplished at the exact temperature of the equilibrium.

The difficulty of removal of all adhering liquid without loss of the pyridine of the compound itself made the results somewhat irregular. It should be noted that the solid $HgCl_2.2C_5H_6N$ loses pyridine rapidly in the air, giving the lower forms.

As all the points on the curves at higher temperatures were located by the melting point method, a special determination as to the character of the solid phase was required for each. It was possible, however, to tell, in the melting point determinations themselves, from the *appearance* of the solid, on which of the three curves the point under investigation should lie.

The solid, for which the curve ABC (Fig. 3) represents the solubility, appeared in long needle-like crystals, tending to form in radial groups or cross-like aggregates. The crystals in equilibrium on the curve BE were likewise needle shaped, but tended to group themselves in parallel bundles. The high temperature compound CEF showed little crystalline form, but appeared granular.

The apparatus illustrated in Fig. 2 is the form finally used to separate out these compounds for analysis. The jacketing liquid in J for the compound BE was water; for CEF a mixture of toluene and xylene, boiling at 118° was used. The solid was removed from the liquid phase by use of an inverted suction filter, which was immersed in the mixture in the inner tube A and filtration thus accomplished at the desired temperature, as already mentioned.

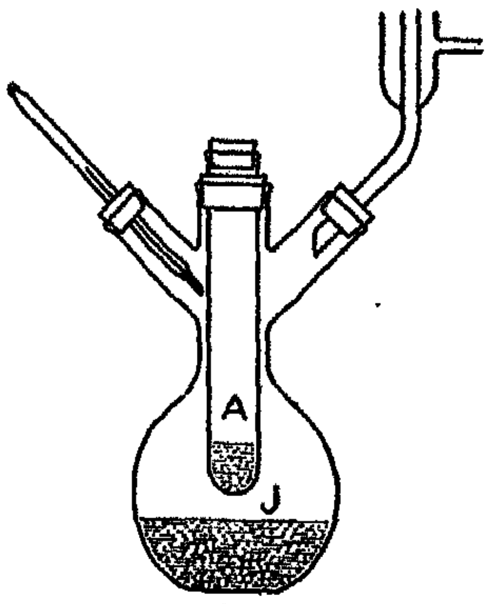

Fig. 2

The mercury content of each solid was determined. No ultimate analysis of the compounds was considered necessary as the percent of mercury shows them to be the three compounds already prepared and analyzed as described in the literature.[1] .

Results and Curves

The results of the solubility measurements and the melting point determinations are given in Tables 1 and 2 respectively, and in the curves following.

In attempting to continue the curve CEF higher than 145° it was found that reduction of the mercuric to mercurous chloride was so rapid at these temperatures, that no satisfac-

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[1] Loc. cit.

TABLE 1.—SOLUBILITY RESULTS

Composition of the liquid in equilibrium with solid $HgCl_2.2C_5H_5N$

No.	Temperature	Time hours	Sample	HgS obtained	Percent $HgCl_2$	Average
1	12.58°	6.0	2.4490	0.3646	17.36	
2		7.5	1.8979	0.2819	17.32	17.34
6	18.78	0.5	1.9738	0.3345	19.76	
7		1.0	2.0256	0.3433	19.77	
8		2.0	1.8210	0.3086	19.77	
9		2.5	1.9222	0.3165	19.81	19.78
12	23.58	1.3	2.0737	0.3834	21.56	
13		2.3	2.0432	0.3774	21.55	
14	23.62	3.3	2.0881	0.3880	21.67	21.59
15	27.23	1.0	1.6960	0.3291	22.63	
16		2.0	1.9890	0.3856	22.61	
17		3.0	1.9715	0.3837	22.70	22.65
19	31.05	1.0	2.2153	0.4640	24.43	
20		2.0	1.9749	0.4146	24.49	
21		3.0	2.1067	0.4421	24.48	24.46
22	40.90	1.5	2.2705	0.5709	29.29	
23		2.5	2.0090	0.5043	29.28	
24		3.3	2.1561	0.5416	29.31	29.29
25	50.10	1.3	1.9679	0.5888	34.90	
26		2.0	2.1102	0.6335	35.00	
27		3.0	2.0768	0.6219	34.93	34.94
28	60.03	1.3	2.2577	0.7812	40.37	
29		2.0	1.9590	0.6773	40.35	
30		3.0	2.0625	0.7136	40.36	40.36
31	70.15	0.5	1.5845	0.6279	46.23	
32		2.5	1.5808	0.6290	46.42	
33		3.5	1.8585	0.7406	46.46	46.44
34	80.15	2.5	1.3396	0.5897	51.36	
35	80.18	5.0	2.1077	0.3720	51.48	
36	80.22	5.5	1.0534	0.4671	51.72	51.52
37	90.38	2.0	0.3315	0.1555	54.72	
38		3.5	0.8609	0.4081	55.30	(omit)
42	0.02	1.0	1.3491	0.1520	13.14	
43		2.0	1.6330	0.1840	13.14	13.14
44	—21.95	1.0	2.2648	0.1517	7.81	
45		2.0	2.2376	0.1504	7.84	
47	—21.75	5.5	2.1358	0.1450	7.92	7.86
48	—33.0	0.5	2.6427	0.0586	2.59	
49	—32.6	1.0	2.1820	0.0550	2.94	2.76

TABLE 2.—MELTING POINT DETERMINATIONS.

A. Equilibrium with the solid $HgCl_2.2C_5H_5N$

No.	Temperature	Sample	HgS obtained	Percent $HgCl_2$
35	70.8 ± 2	0.6624	0.2599	45.77
29	74.6 ± 2	0.5469	0.2250	48.00
36	75.2 ± 2	0.3991	0.1655	48.38
30	76.4 ± 2	0.8856	0.3731	49.15
10	78.0 ± 2	0.6507	0.2773	49.72
34	78.7 ± 2	0.4475	0.1932	50.37
31	82.5 ± 2	0.4710	0.2115	52.40
33	89.0 ± 1	0.4016	0.1943	56.45
26	90.8 ± 2	1.0219	0.4994	57.01
20	94.1 ± 3	0.7326	0.3773	60.09

B. Equilibrium with the solid $HgCl_2.C_5H_5N$

36	74.7 ± 1	0.3991	0.1655	48.38
32	83.5 ± 3	0.3461	0.1499	50.53
28	86.5 ± 3	0.6609	0.2967	52.37
13	87.3 ± 2	0.8176	0.3645	52.02
27	90.4 ± 2	0.5486	0.2514	53.41
18	90.4 ± 3	0.8017	0.3682	53.58
33	97.0 ± 3	0.4016	0.1943	56.45
25	99.5 ± 3	0.3674	0.1767	56.07
26	99.5 ± 5	1.0219	0.4994	57.01
24	100.5 ± 2	0.5769	0.2852	57.84
20	104.1 ± 2	0.7326	0.3773	60.09
12	104.2 ± 2	0.5178	0.2707	60.72
19	104.7 ± 3	0.3490	0.1764	58.97
4	107.0 ± 5	0.4218	0.2280	63.06

C. Equilibrium with the solid $3HgCl_2.2C_5H_5N$

12	94.7 ± 5	0.5178	0.2707	60.72
8	95.2 ± 2	0.6982	0.3637	60.77
17	106.4 ± 3	0.6659	0.3535	61.93
11	109.8 ± 3	0.4562	0.2447	62.58
4	113.6 ± 2	0.4218	0.2280	63.06
21	114.0 ± 3	0.5953	0.3224	63.18
6	115.7 ± 2	0.3439	0.1874	63.57
14	118.2 ± 2	0.7676	0.4217	64.09
9	124.2 ± 3	0.7482	0.4170	65.00
22	129.4 ± 3	1.1768	0.6620	65.63
23	145.5 ± 2	0.4001	0.2389	69.66

tory results could be obtained. The low temperature work was not attempted below —33° as the expense for solid carbon dioxide or other refrigerant required seemed hardly warranted by the small practical or theoretical value which these results might have at this time.

The curve plotted in Fig. 3 and shown more in detail in

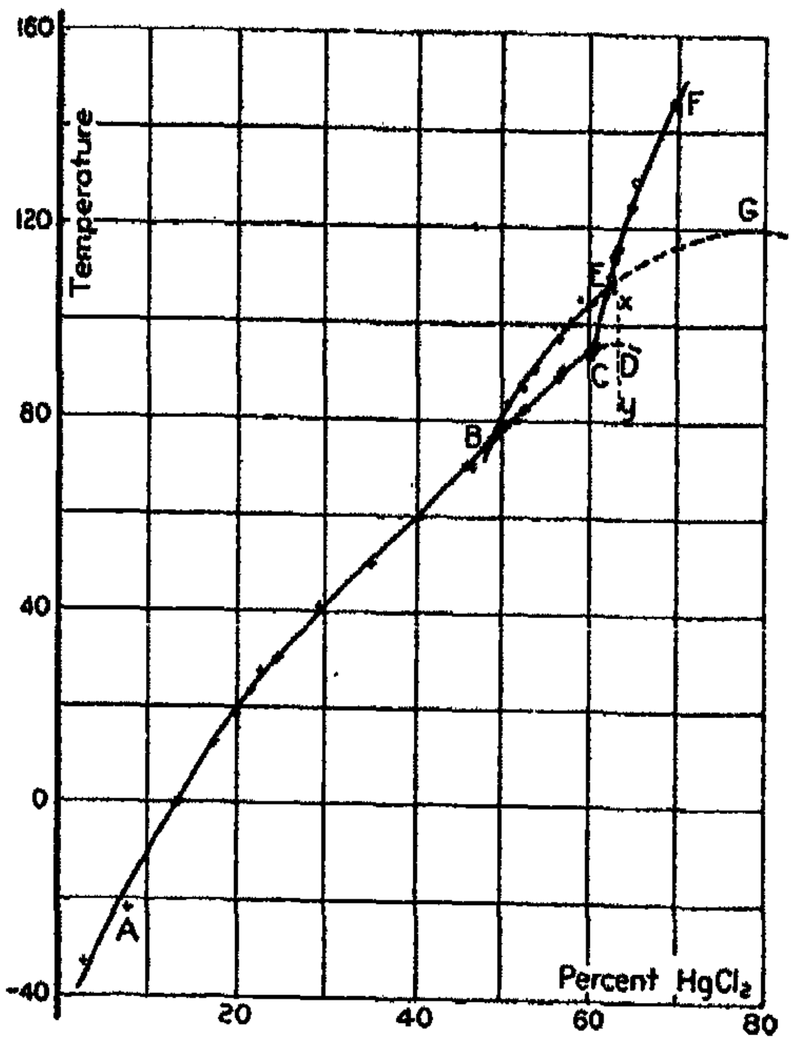

Fig. 3

Fig. 4 shows the transition points B and E at 76.0° and 106.2° respectively and the meta-stable transition point C at 94.7°. The curves BC and CE represent meta-stable equilibrium. The dotted portion CD has not been experimentally confirmed but the curve ABC must continue in very nearly this direction, through a melting point and therefore a maximum D on the line XY, which represents the composition of the solid phase, *i. e.*, 63.14 percent $HgCl_2$. The point D is certainly within one degree of the point plotted (96.0°) as shown by the direction of the portion BC which was located by experiment.

This point D and the whole curve show that the melting point 108°, as given by Pesci for $HgCl_2.2C_5H_5N$, was not a true melting point but a point of equilibrium on the projection of BE into the meta-stable region. The true melting point (96° ± 1) is so far over in the unstable region that it is not strange that it was thus undiscovered by him in a single determination.

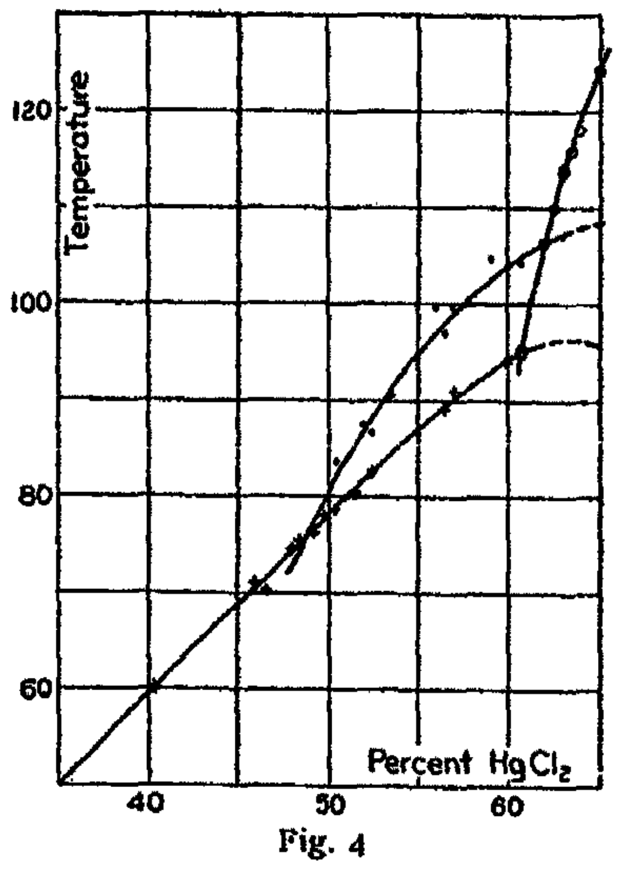

Fig. 4

The same author in describing $HgCl_2.C_5H_5N$ says it softens at 120° and is all liquid at 180°. From an examination of the curve the explanation is evident. The point 120° is the true melting point but it is far out in the meta-stable region at G, on the continuation of the curve BE. At the point G there must be a maximum in this curve at about 120° and it undoubtedly has the form, if not the exact location, shown in the dotted line EG. The point at which Pesci observed his compound to be all liquid is a point on the upper end of EF (not shown). It lies very close to the curve of Fig. 3 when that is extended to 180°, the temperature which he gives as the point of complete liquefaction.

The change of direction in the curve ABC below —22° would suggest that a new solid may exist at these lower temperatures. At —22°, however, the analysis showed it to be the same as above 0°. This matter has not been studied further.

Summary

1. An essential variation in the method of determination of mercury as sulphide has been noted.

2. Fourteen solubility measurements of mercuric chloride in pyridine are given, four of these in duplicate and ten in triplicate.

3. A new method of melting point determination for phase rule work is described, and thirty-five measurements made by it are given.

4. The complete curve of stable and meta-stable equilibrium for the three compounds of pyridine and mercuric chloride, namely: $HgCl_2.2C_5H_5N$, $HgCl_2.C_5H_5N$, and $3HgCl_2.2C_5H_5N$, has been plotted from —33° to +145°. The two stable and one meta-stable transition points are thus accurately located and the true meta-stable melting points of the first two named are located approximately.

5. The probability of a new compound of mercuric chloride and pyridine, existing below —22°, has been indicated.

6. The correct interpretation of Pesci's observations has been given, showing the necessity of study by phase rule methods in order to gain correct interpretations of phenomena of solutions.

The author takes pleasure in thanking Professor Kahlenberg at whose suggestion this research was undertaken and in expressing appreciation of the valuable assistance and encouragement of Dr. J. H. Mathews, under whose immediate direction it has been pursued.

Laboratory of Physical Chemistry,
University of Wisconsin.
June, 1909

THE PHOTOGRAPHIC PLATE. III

BY WILDER D. BANCROFT

THE EMULSION. PART III

The difference in sensitiveness between collodion and gelatine plates shows that there is an effect due to the nature of the medium in which the silver salt is suspended. It is not a simple matter to decide to what the effect is due, and it will be well first to see what is known in regard to the matter.

Lüppo-Cramer[1] believes that the sensitizing action of gelatine is negligible and he is therefore forced to find another explanation[2].

"If we exclude the possibility of the medium playing any part during the exposure, the only alternative is to attribute the effect of the colloid to an action on nascent silver bromide or to an action on silver bromide during the process of ripening. If we compare gelatine with collodion, we notice one fundamental difference, that gelatine is soluble in water and collodion in a mixture of alcohol and ether. I have previously shown that this difference is fundamental because the substances which ordinarily coarsen the grain of the emulsion lose part of their efficiency in alcoholic solution.[3]

"My experiments on the mercuric iodide emulsion[4] gave me a new clue. When mercuric iodide is emulsified in gelatine, the yellowish white modification is obtained, while the much more sensitive red form is obtained when gum arabic is used as binder. It seemed probable that a careful study of the conditions would enable me to show that different modifications of the silver halides are formed during emulsification. Since the two forms of mercuric

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[1] Jour. Phys. Chem., 14, 145 (1910).

[2] Lüppo-Cramer: Phot. Correspondenz, 40, 673 (1903).

[3] Ibid., 40, 89 (1903).

[4] Eder's Jahrbuch der Photographie, 17, 30 (1903).

iodide are very easily recognized on account of the marked difference in color, I studied this compound more carefully. It may be stated in advance that the halide emulsified in gum arabic is not to be compared with the one precipitated from aqueous solution. My mercuric iodide plates have a very fine grain. When examined under a magnification of one thousand diameters, the grain is seen to be distinctly finer than that of the ordinary dry plate; no crystalline structure can be detected. One might nevertheless assume that the formation of the yellow modification in gelatine was due to the greater viscosity of the emulsifying solution. Numerous experiments have shown that the red halide never forms even in extremely dilute gelatine solutions while the yellow form is not obtained from gum arabic solutions of any concentration.

"Caseine solution behaves exactly like a gelatine solution, the emulsion always containing the yellow modification of the iodide. For this reason I have also made comparative experiments with a mercuric iodide caseine emulsion obtained as follows: Twenty grams of purest caseine were shaken up with 400 g H_2O and were carried into solution by the addition of the least possible amount of ammonia. An ammonia solution (sp. gr. 0.91) was diluted to one-tenth and 15 cc of this taken. A few drops of ether were added to the solution to get rid of the troublesome foam. Twenty grams of potassium iodide were added to the clear caseine solution, and then 20 g $HgCl_2$ dissolved in 200 cc of hot water.

"I was not able to find another medium like gum arabic which would give the red form of the mercuric iodide emulsion. No emulsion was formed when the iodide was prepared in starch solutions of different concentrations. Instead, a coarse-grained, red product separates which is very like what one gets by precipitation from water solutions. The following experiment seemed to me of importance as showing that a relatively small amount of gelatine will cause the formation of the yellow mercuric iodide even in a solution containing gum arabic.

"A solution, containing 100 cc of a ten percent gum arabic solution, 15 cc of a ten percent solution and 5 g KI, was heated to 45°. To this was added a boiling solution of 5 g $HgCl_2$ in fifty of water. The yellowish white form of the iodide was obtained. We get the same result if we substitute 25 cc of an ammoniacal caseine solution of the gelatine solution. If 10 cc of the gelatine solution are added instead of fifteen, the pure yellow form is not obtained but rather an intermediate product having a pinkish orange color. From these experiments one is tempted to conclude that gelatine and caseine have a specific emulsifying effect, exceeding that of gum arabic; and that in the gum arabic emulsion we have a product which resembles more closely the product obtained by precipitation under ordinary conditions.

"Further experiments seem to indicate, however, that gum arabic has a positive effect. If mercuric iodide is formed in a one percent gum arabic solution, it is pinkish orange, while in a corresponding gelatine solution it is a pure yellow. These experiments prove conclusively that the medium has a tremendous effect on the form in which a precipitate occurs. At present we are quite unable to say anything definite in regard to the nature of this effect."

Later experiments by Lüppo-Cramer[1] with silver bromide emulsified in gelatine, caseine and gum arabic showed that the emulsions obtained with caseine and gum arabic are much less sensitive than the one obtained with gelatine. "After the emulsification the caseine emulsion and the gum arabic emulsion were made to solidify by addition of gelatine and the soluble binder was then washed out whereby the 'sensitizing' action of the gelatine was the same for the three emulsions. The difference in the sensitiveness could not be due either to the size of the grain of the emulsion or to the reducing action of the binder."

When silver iodide is emulsified[2] in gum arabic the sen-

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[1] Eder's Jahrbuch der Photographie, 18, 436 (1904).

[2] Lüppo-Cramer: Ibid., 20, 385 (1906).

sitiveness is ten to a hundred times as great as when the salt is emulsified in gelatine.

Schloemann[1] has made experiments on the sensitiveness of silver bromide when suspended in a silicic acid gel. I quote from this paper.

"Experiments with an emulsion of silver bromide in silicic acid are of importance for our knowledge of the photochemical reaction when silver bromide is exposed to light, because in this case the formation of the latent or of the visible image cannot depend in any way on the action of an organic binder, as may be the case with gelatine, collodion, agar-agar, starch, gum arabic, etc. It is well known that the presence of such binders during the exposure has been supposed by some to be an important factor in the photochemistry of silver bromide. As instances of this I may cite the tanning theory of solarization and the often disputed belief that the latent image consists entirely or in part of an organic silver salt. These are questions which cannot be decided off-hand by experiments with silver bromide containing no binder. It seemed desirable therefore to prepare a silver bromide emulsion in an indifferent, inorganic medium and to study the behavior of the latent image both as regards physical development after fixing and as regards the action of concentrated nitric acid. The sensitometry of such an emulsion is also a matter of interest.

"At the suggestion of and together with Professor Karl Schaum, the author undertook to work out the preparation of an emulsion of silver bromide in silicic acid and to make experiments of the kind indicated. The most important results of the investigation shall now be given.

Preparation of a Colloidal Silicic Acid Solution

"Lobry de Bruyn[2] describes the following method of preparing an emulsion of silver bromide in silicic acid. Into each of two flasks he places 10 cc sodium silicate (sp. gr.

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[1] Phot. Correspondenz, 43, 466 (1906).

[2] Recueil Trav. Pays-Bas, 19, 236 (1900).

1.09) + 5 cc nitric acid (sp. gr. 1.08) and then adds 5 cc of a tenth-normal silver nitrate solution to one flask and 5 cc of a tenth-normal potassium bromide solution to the other. When the solutions in the two flasks were mixed, a white milky emulsion was obtained which was said to gelatinize in two or three minutes. According to a further statement of Lobry de Bruyn the sensitiveness of such an emulsion exceeds that of a ripened silver bromide gelatine.

"When these experiments were repeated carefully, it was found that in consequence of the high concentration of the silicic acid solution gelatinization took place too soon, so that it was scarcely possible to mix the silver and the bromide solutions satisfactorily even when working rapidly. It was seldom possible to pour several plates, one after another, from the same emulsion. A still more disturbing factor for our experiments was the formation of large amounts of potassium nitrate during the precipitation of the silver bromide.

"In order to work under the most simple conditions, we prepared a supply of colloidal silicic acid by means of dialysis. We diluted 30 cc of a water glass solution (sp. gr. 1.30) and 30 cc pure concentrated hydrochloric acid[1] each with 120 cc distilled water and then poured the acid into the silicate solution, stirring all the while. The mixture was dialyzed in two portions. By using running water, this process could usually be finished in about three days. We made a satisfactory dialyzer out of a beaker, 15 cm in diameter, by removing the bottom and covering the opening with pig's bladder which had been purified by treatment with alcohol. Since the stock solution gelatinizes very readily when apparently pure, it is not safe to carry on the dialysis until all of the hydrochloric acid and sodium chloride has been removed. The dialysis should be stopped at the point where an addition of silver nitrate still causes a

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[1] Commercial water glass must always be tested as to its specific gravity and diluted if necessary. Pure concentrated hydrochloric acid can be used without test.

slight opalescence. Immediately before using, such a solution should be dialyzed again until no opalescence can be detected. It is then ready for use. The gelatinization of the sol takes place readily on heating or on addition of electrolytes, especially ammonium carbonate.

"E. Jordis[1] has discussed the question whether we should consider a solution of silicic acid as pure when it does not opalesce with silver nitrate. He found that it was scarcely possible to free a silicic acid sol or gel completely from the electrolytes used in preparing it. Owing to the amphoteric character of the silicic acid, small amounts of hydrochloric acid or caustic soda are held back because the silicic acid can react with the hydrogen ions of the one or the hydroxyl ions of the other. This explanation assumes a chemical reaction between the sol and gel and the substances which give rise to the sol. We may instead be dealing with a case of absorption or adsorption. It is still an open question which hypothesis is the more satisfactory.

"Graham[2] considered the colloids as entirely pure after dialysis and he was familiar with the fact that the sol is more stable in presence of a trace of acid or base. According to his view this is a case of protective action.

Preparation of Silver Bromide Silicic Acid Plates

"For the experiments to be described the silver bromide silicic acid emulsion was made up as follows:

I	II
35 cc silicic acid sol 5 cc KBr 1 : 10	35 cc silicic acid sol 2.5 cc $AgNO_3$ 1 : 10

"In the dark-room solution II was allowed to drop from a separatory funnel into solution I. When this was done carefully, an extremely fine-grained emulsion was obtained which was allowed to stand for half an hour in the dark.

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[1] Zeit. Elektrochemie, 11, 288, 835 (1905).

[2] Liebig's Ann., 121, 1 (1862).

This was filtered through flannel and poured upon glass plates which had been cleaned with pumice. About 10 cc of the emulsion was used for a plate 9 cm x 12 cm.

"The filtration of the emulsion was necessary to remove coarse-grained, precipitated silver bromide which is not embedded in the gel and which is very apt to fog because the developer comes in contact with it on all sides. The plates were placed in light-tight pasteboard boxes so that the slowly solidifying emulsion might gelatinize without being removed. When silicic acid solutions have stood for a while, they gelatinize rapidly. When freshly-prepared they sometimes need to be inoculated with ammonium carbonate, especially if the temperature of the room is low. As a rule the film is completely solidified at the end of four to six hours, so that the plates can then be washed in order to remove the excess of potassium bromide. The washing is continued until the wash water does not cloud on addition of silver nitrate.

"Among the more noticeable properties of the silicic acid plate is the one that its opacity is low, like that of a wet gelatine plate having a low sensitiveness. When examined in transmitted daylight the general color of the film is bluish white. After prolonged exposure to direct sunlight the film becomes gradually grayish black.

"If the silver bromide silicic acid emulsion is ripened in a way analogous to the ammoniacal silver oxide method, the plate then becomes blackish violet very quickly when exposed to daylight. Unfortunately, this rapid increase in the sensitiveness to light could not be taken advantage of in this investigation because the presence of ammonia was to be avoided and also because ammonia affected the rate of solidification of the sol in a way which could not be allowed for.

"When the emulsion dries it becomes somewhat brittle and tears loose from the glass. This was not prevented by superposing a film of gelatine containing chrome alum, and we therefore made our experiments with plates which were still moist.

Determination of Sensitiveness

"To determine the relative sensitiveness to light of our moist silver bromide silicic acid films we made use of a tube sensitometer, arranged in a form more suited to our purpose than the one which R. Luther[1] recommended for obtaining graded intensities of light. In order to obtain a greater exactness, we replaced the cardboard disk by one of zinc and bored round holes with a drill instead of making them rectangular. Each hole stood to the one following it in the ratio of 2 : 1. The surfaces of the sixteen holes were as follows, the values being in square millimeters:

Table I

181	128	90.5	64.0
45.3	32.0	22.6	16.0
11.3	8.0	5.7	4.0
2.8	2.0	1.4	1.0

"The centres of the holes were arranged at equal distances, four to a row, on a zinc disc, 9 cm x 12 cm. Over each opening there was placed a tube, ten centimeters in length, made out of a dead-black paper. The ends of all the tubes were held in a cap provided with sixteen, equally large, circular holes. A second sensitometer, just like the first one, was fastened to it so as to make a double-barrelled sensitometer. With this it was possible to compare our silicic acid films with gelatine plates, the two being exposed under identical conditions. The whole was placed in a tin box, the inside of which was painted a dead black, and the bottom of which was arranged to accommodate two plates lying side by side.

"Luther puts the error at 10–15 percent when square holes are cut in cardboard. A greater accuracy can be obtained with circular holes bored in sheet zinc. The linear diameters of the single holes could be determined to ±0.05 mm and those of the same size to within ±0.025 m. The

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[1] Zeit. phys. Chem., 30, 635 (1899).

larger holes were checked by means of expanding callipers and the smaller ones in an indirect way by means of callipered brass rods for each hole.

"In this double-barrelled sensitometer a silicic acid plate was placed alongside of a Hauff transparency plate which had been allowed to stand in water for half an hour. In order to get a diffused light we placed the apparatus at a distance of one meter from a window covered with several layers of silk paper. We developed with the standard ferrous oxalate developer, recommended by J. M. Eder,[1] and fixed our plates in a twenty percent thiosulphate solution.

"With an exposure of three seconds, with eight minutes development, and with the temperature of the developer 18° C, the liminal value (*Schwellenwerth*) was reached by the gelatine plate in the fourteenth field and by the silicic acid plate in the third field, the moist plates being examined, after development and fixing, with white paper pressed against the backs.

"From Table I it appears that the hole in the third field is forty-five times as large as that in the fourteenth field. With the same time of exposure this is also the ratio of the amounts of light. Since it takes forty-five times the amount of light to produce the same photochemical effect on the silicic acid plate as on the gelatine plate, we may say that a Hauff transparency plate is forty-five times as sensitive as our silicic acid plate—always assuming the general validity of Bunsen and Roscoe's intensity law.

"When left a long time in the developer, the silver bromide silicic acid plate shows a strong tendency to fog. The dried edge, where the silver bromide is not surrounded by a swelled jelly, blackens in a short time when in contact with the developer. This was perhaps what caused Lobry de Bruyn to say that silicic acid films are more sensitive than ripened gelatine films.

"A microscopic investigation showed that the silver

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[1] Eder's Handbuch der Photographie, 5th Ed., 3, I, 213 (1902).

bromide grain, and also that of the reduced silver in the silicic acid gel was extremely fine."

It seems rather a pity that Schloemann should not have made some experiments as to the degree of sensitiveness which could be obtained by ripening his silicic acid plates. Now we know only that such plates can be made considerably more sensitive and nothing more. The reason for the omission seems to be that Schloemann was interested chiefly in the problems of the latent image and of solarization instead of the theory of ripening. Only two years ago Cooper and Nuttall[1] published a paper on the use of agar-agar as a medium for carrying the silver salts. I quote rather extensively from this paper.

"Last year, I was approached by Mr. P. Gillard, and asked to take up a new paper which he claimed to be his own invention. Demanding that he should demonstrate his process to me, I gave him facilities to do so in my laboratory. The paper was to be a self-toning paper in agar, containing gold and platinum, and having certain properties. Some of these papers were undoubtedly good, but one could not be certain of the result of any particular coating. Mr. Gillard failed very materially, in that he could not turn out consistent results. These failures are of great interest, however, and I suppose that the difficulties, which prevented him from turning out consistent results, are the same as would be encountered by others trying to use agar. Therefore they will be of interest, and we think we can point out the reasons and how to overcome them. We may mention here that Messrs. Morgan and Kidd are turning out agar P.O.P., and therefore it is possible for others to do so; moreover there are agar papers on the market in Germany. It is quite obvious to us that agar can be used as a medium for plates and bromide paper.

"Mr. Gillard's failures were chiefly:

"(1) The agar solution was not clear, containing small granules.

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[1] Phot. Jour., 32, 11 (1908).

"(2) In making the emulsions one found that it would become thin and limpid, and would not set.

"(This was termed peptonizing; but the term is quite wrong, as peptones are nitrogen compounds, whereas agar contains no nitrogen, and therefore cannot be peptonized. We use the term de-gelatinize therefore.) This second fault would occur, sometimes in making the emulsion, sometimes when made and while coating; sometimes it went limpid as a whole, while at other times it occurred in parts, causing a peculiar granular appearance.

"(3) Agar does not dissolve in water, unless heated to 100° C, *i. e.*, the temperature of boiling water.

"(4) If cooled to 32°-35° C it sets very quickly and then will not dissolve again unless boiled once more; if this be done with an emulsion it is often quite spoilt.

"(5) When he added his gold chloride to the emulsion, it was necessary to get it on to the machine without a moment's delay, otherwise the gold was reduced to the metallic state before the emulsion was on the paper. The causes of these difficulties, and methods to overcome them, will be explained later.

"When I inquired of Mr. Gillard what knowledge he had of agar, I found that practically nothing was known; I could get no books on the subject, so that it was necessary to set to work to look up references to it, and to ascertain its properties. This is the work which Mr. Nuttall and myself have undertaken.

"The first question is: 'What is agar?' 'To what class of substance does it belong?' It has been shown by Payen and Porumbaru that it does not contain nitrogen, therefore it is not a proteid, peptone or albumen; nor yet is it a proteid or an albuminoid, *i. e.*, it is not a gelatine, nor a glue; it differs very materially from all these in its properties. It seems that it must be placed amongst the more complex carbohydrates, celluloses, starches and gums. On oxidation with nitric acid the two former yield oxalic acid, whereas the gums and agar-agar yield mucic acid.

For this reason Allen classifies it as a gum. Senier also classifies it as a gum. It has been shown by Payen[1] to be similar to, or to yield, pararabin, or beet-sugar gum. From its properties it appears that this is the correct group in which to put it, therefore, though in many of its properties it is anomalous.

"As bought, it is in the form of long translucent, stringy pieces, tough, dry and hard. Soaked in water, it swells up as do gelatine and the gums. The soaked substance dissolves in water when boiled, and then only slowly. Our method of dissolving it is to cut up the agar into small pieces; soak them in running water for some hours; then place in distilled water; heat the water until it boils, and continue the boiling for a quarter of an hour, stirring vigorously the whole time. If the boiling is not continued long enough two things will be noted; firstly, that the solution is lumpy, *i. e.*, that the agar has not dissolved completely; and, secondly, that it is more difficult to strain.

"For bacteriological purposes the treatment at the Cambridge laboratory is to soak the agar in a 1 percent solution of acetic acid for twenty-four hours, wash out the acid in running water, and dissolve up by boiling. We may mention in passing that the acid has no ill effect; we have treated several lots in a similar manner with good results, but the treatment seems to be unnecessary.

"Having dissolved the agar, we proceed to strain it, in order to retain solid impurities. This we do in practice through nainsook. The solution is then fairly clear, but contains a large quantity of peculiar, slightly opaque specks, and is not quite transparent as gelatine is. This renders it useless for use in emulsions for plates, but the solution can be made perfectly clear by filtering. At Cambridge it is filtered through a special paper in a large funnel, the whole being enclosed in a steam-jacketed chamber which keeps the agar hot. (The paper can be bought from any dealers

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[1] Jahresbericht, 1859, 562.

in chemical apparatus.) We dissolve each gram of air-dried agar in 50 cc of water, which makes a 2 percent solution. This is then filtered at as high a temperature as possible through a hot Buchner funnel, using a pump, the flask being placed in hot water. Such a solution is quite clear and transparent.

"This forms the solution of gelose. Such a solution has the following properties, though in giving these we must note that the age of the sea-weed seems to have some effect on the properties; our results do not quite agree with those of earlier workers.

"A solution of agar in water, sets when cooled, the temperature at which it sets being about 33°–35°. It sets very rapidly when cooled to the setting temperature, more rapidly than gelatine. The gelatinizing property is very great; it is said to be ten times as great as gelatine. Stanford puts it down as eight times as great; Allen states that gelose will form a jelly with 500 times its own weight of water.

"Peculiarly enough, and entirely different from gelatine, a solution of gelose can be boiled for a long time without becoming much less viscous. Indeed, we frequently evaporate a solution which is too weak by boiling until it is quite thick. We may boil some solutions for an hour or more. Any agar which remains over from an experiment is allowed to set, and is kept for some days; when making an emulsion, we boil it up with more water and evaporate off the excess. We found that after boiling for a quarter of an hour, the agar solution was slightly less viscous, but that continued boiling, within reason, does not make much difference for practical work. The boiling solution must be vigorously stirred in order to prevent it from being burnt; if burnt, it is quite useless for emulsions, as it produces a very dirty color. This peculiarity is of importance. Gelatine is a nitrogen compound, and when hydrolyzed by boiling or by heating with acids or alkalies, it forms various compounds, amongst which are leucine and glycocoll and ammonia. Leucine is ammonia in which one hydrogen atom is replaced by the caproic acid group; it is an amide. Glycocoll is ammonia in which one hydrogen atom is replaced by the acetic acid group; it also is an amide. These two compounds are such as one would expect to cause fog in an emulsion, just as ammonia does, and we think that the spoiling of emulsions in gelatine may be put down to this cause in part. Now agar cannot form such compounds though it may form aldose compounds which would reduce the silver; certainly if heated with water under pressure, gelose is hydrolyzed and yields a sugar. This may account for some of the difference between working in agar and gelatine.

"On soaking agar and squeezing to extract the surplus water, we noticed that some matter appeared to be washed out. We took some agar and soaked in distilled water, poured off the water through a filter paper, and added a further quantity of distilled water. We repeatedly poured off the water in which the agar was soaked, at intervals of about an hour. The washings were then evaporated to dryness, and it was found that 18 percent had been washed out of the agar by the water, for the filter paper would have retained any solid matter.

"Air-dried agar usually contains about 21 percent moisture driven off at 100° C.

"The percentage of ash in our sample was 0.487 percent.

"The density of a solution of agar at 50° C is less than that of water at 50° C. We attempted to determine if the density could be used to ascertain the amount of agar in solution, but this has not been done up to the present.

"The viscosity of a solution of agar is much greater than that of gelatine with the same percentage of solid. We have estimated that a solution of gelatine of definite strength is about as 'thick' as a solution of agar containing 1/8 of the amount percent, this agreeing with the figures given by Stanford.

"Barker's P.O.P. formula contains 8 percent of gelatine; Valenta's contains 9.6 percent; Beadle's contains 11 percent; so that a solution of agar 1–1 1/4 percent, or 2 ozs. to the gallon, should be sufficient. We recommend that those trying agar for the first time should start with a 1 1/2 percent solution.

"A solution of 3 percent is difficult to use, as it is too thick. We find a 1 percent solution is most convenient, though a 2 percent solution is quite easily worked. A 1 percent solution is about as thick as an 8 percent solution of gelatine. If two emulsions containing the same amounts of chemicals, except that the medium in the one is gelatine, and in the other is agar, and if the solutions are of the same 'thickness,' then the amount of agar will be one-eighth the amount of gelatine; in coating a plate or paper with these solutions and drying, one will get the same amount of silver per square foot, but only one-eighth of the amount of medium when using agar. In the case of paper this would not matter so much perhaps, but with plates it means that the pellicle will be extremely thin. It will be of great interest to ascertain what influence this has, on the sensitiveness of the emulsion and on the development. If the pellicle is so much thinner, the light will be able to act more rapidly on the sensitive salt and should give increased rapidity. One would expect that in development, the developer would penetrate more rapidly and therefore develop more energetically; on that account also less exposure should suffice. In that case, one should be able to obtain plates of extreme rapidity, great latitude, and with a fine grain. Would the gradation be as delicate, however? The plates which we made worked like wet plates; they were developed and washed as quickly. One of them will be shown to-night which was intensified with mercuric chloride and potassio-silver cyanide three times, and completely washed, all within 5 minutes; it will be seen that (though the plate is badly coated) there is a total absence of the stain which would have existed had the intermediate washings been incomplete. This emulsion was matured by being plunged in boiling water for 5 minutes. The speed was about 65 H and D.

"The following do not form a precipitate with the solution of gelose:

1. Copper sulphate
2. Lead acetate (normal)
3. Nickel sulphate
4. Mercuric chloride
5. Iron chloride
6. Iron sulphate
7. Potassium bichromate
8. Potassium chloroplatinite
9. Platinum chloride
10. Gold chloride
11. Chlorine
12. Bromine water
13. Iodine
14. Chromic acid
15. Picric acid
16. Formalin.

"The following give a precipitate with the solution of gelose:

Basic lead acetate
Mercuric nitrate
Tannin
Phospho-tungstic acid
Alcohol."

"Alcohol will precipitate a solution of gelose, if added in sufficient quantity. A solution containing 1 1/4 percent of the solid dried at 100° C (about 2 percent ordinary dry agar), is precipitated by adding about 40 percent of rectified alcohol; whereas it appears that, to a solution containing 2 1/2 percent of the solid dried at 100° C, even more than 40 percent may be added without definite precipitation. If a solution of agar be poured into excess of 90 percent alcohol, a white precipitate is formed at once, which collects into a coagulum, which can be separated by muslin or filter paper. Payen states that precipitation of agar by alcohol is not a good method, as it increases the percentage of ash, or solid matter. In our experiment, the ash before precipitating was 0.487 percent, but after precipitation by alcohol it was 4.06 percent; though we think this is somewhat excessive. Certainly part of the agar is left in solution in the alcohol, because, on evaporating, the alcoholic filtrate to dryness, a gummy mass is obtained. . Is this part of much importance to the photographer? At present, we cannot say.

"Like gelatine, when heated with acids or alkalies, the setting property is destroyed. This will be dealt with later.

"Though the presence of small quantities of mineral acids in the solution causes it to lose the gelatinizing property, yet the solid substance soaked in water can be treated in the cold with dilute acids and alkalies without doing much harm. Hydrochloric and sulphuric acids, however, dissolve the agar; Payen says that it is dissolved by the concentrated acids, to form a hard brown mass which is insoluble in almost any ordinary reagent. We have found that it forms a brown solution, but we have not obtained the hard, insoluble mass. The solid agar can be boiled with glacial acetic acid without much change; but if containing water it dissolves the agar on heating. The 1 percent solution used for soaking, will have no detrimental effect, but will keep in solution all iron salts contained in the water, and so tend to prevent discolorations. Agar soaked in 10 percent acetic acid, however, then washed, and dissolved, had lost considerably in viscosity.

"The effect of alkalies on agar is to make the solution lose its setting properties, but at the same time it makes it a little more sticky and gummy. With a fresh solution of agar, if one puts one's finger into it the adherent drop soon separates from the main part of the solution; but when heated with a small quantity of alkali, the solution becomes somewhat more sticky and the drop does not immediately separate from the main part of the solution.

"On adding borax to a solution this effect is greatly augmented and the solution becomes so sticky (tacky)that one can draw out strings of the substance some feet in length. On rubbing between the finger and thumb it will be noticed that the untreated solution has more 'body' but is much less 'tacky.' We are of the opinion that this property will be found of great use in the practical application. We have coated paper with such a solution quite readily. The solution treated with borax in this manner sets, though much more slowly than when not so treated. The resulting jelly is much less friable and seems to be more tenacious.

"The reaction with iodine is peculiar. On adding iodine either in potassium iodide or in alcohol, to a hot solution of gelose in water, the light yellow colour, due to the iodine, remains. On cooling, however, the yellow changes to a red purple, very much like that of iodine vapor. On heating, the purple changes to a yellow once more; the purple is developed again on cooling, and one can cool and warm repeatedly, with the same effects. There is not a perfectly sharp temperature at which this takes place, but it is between 27° C and 29° C. This darkening and lightening can be detected when so dilute as 1 part in 10,000. On adding hydrogen peroxide to the mixture of gelose and iodine and warming, the red purple given when the solution is cooled changes to a blue similar to that given by iodine and starch. This disappears on warming, and reappears on cooling; but it is quite transient, and the exact conditions determining this blue color, and its cause and meaning, have not yet been ascertained.

"Agar will absorb a small quantity of iodine, and also of bromine, the amount being 1.65 percent, whereas gelatine absorbs 6.21 percent, at 15° C. This difference will be of interest in considering any theory of the latent image in agar as compared with that in gelatine. We may say that, though one would suppose, on theoretical grounds, that on this account agar would be less suitable for emulsion work than gelatine, this is not so. We find that its physical properties are not inferior to that of gelatine, and with scarcely any maturing one can prepare a comparatively fast emulsion. We shall show some lantern slides, made on plates with a speed of about 65 H and D. It has been mentioned that a pellicle of agar will be about one-eighth as thick as a similar one of gelatine; so that the comparative ability to absorb iodine will be 6.2 percent for gelatine, and 1.65/8 = 0.2 percent for agar; that is to say that, per area, gelatine will absorb about thirty-one times as much iodine as will agar.

"Silver nitrate forms no precipitate with a solution of gelose, but on mixing a hot solution and keeping hot, darkening in color takes place; this also occurs slowly at 50° C, different samples varying considerably in the time necessary for the darkening to take place. But in any case, even boiling, it is not less than ten to twenty minutes, and may be quite a long time, so that one has sufficient time for making an emulsion. If a small quantity of hydrogen peroxide be added, no discoloration takes place at 50°; but whether this is due to the oxidation of any aldehyde formed, to the acid, we cannot say at present. Citric acid also acts as a preventive of discoloration, but not so much so as hydrogen peroxide.

"Silver-ammonia-nitrate gives no reduction at 50°, only on boiling. The solution of agar which has been boiled for some time gives but little more reduction than that which has been freshly made.

"We find that our sample of agar does not form a peculiar compound with silver nitrate, similar to that produced with gelatine.

"Fehling's solution is not reduced by a fresh solution of agar; but by boiling with acids (such as sulphuric acid) the gelose is hydrolyzed to form a sugar which reduces Fehling's, and which gives a precipitate with phenyl hydrazine. This is being further studied, and the sugar is being identified.

"The distillate of a solution of agar boiled with dilute sulphuric acid, gives only a very slight colour with aniline acetate, so that no furfuraldehyde is formed, and there is no pentose group existing as such in the agar. It forms a very slight precipitate with phenyl hydrazine. The further study of these sugars and the products of hydrolysis are not of sufficient interest to the photographer to include here, but will be dealt with later.[1] It may be that agar is a glucoside, somewhat similar in constitution to fucose, a product also obtained from some varieties of sea-weed.. Glucosides, on boiling with dilute acids, give one of the sugars as a product of hydrolysis.

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[1] See Bauer: Jour. prakt. Chem. (2), 30, 367 (1884); and Muntz: Bull. Soc. chim. Paris (3), 37, 409 (1907).

"Sodium metaphosphate forms a gelatinous precipitate with a solution of agar, on boiling; gelatine gives no such precipitate.

"Tannin gives a precipitate with a solution of gelose when it is strong, but it dissolves on heating; the precipitate formed by tannin and gelatine is given in very dilute solution and does not dissolve on boiling in the presence of excess of tannin.

"Chromic acid seems to have no effect on agar, such as it has on gelatine; it does not form a precipitate, nor does it render it insoluble in water as it does with gelatine. Similarly potassium bichromate does not make it insoluble; neither does alum nor formalin. A mixture of agar and gelatine can be separated by adding formalin, evaporating to dryness, and extracting with hot water; the gelatine is insoluble, whereas the agar is dissolved. After being rendered insoluble in water, the gelatine may be dissolved in dilute acids and precipitated with tannin.

"Gold chloride does not give a precipitate with agar or gelatine solution; but platinum chloride gives a precipitate with gelatine and not with agar.

"It will be seen, therefore, that the difference between agar and gelatine is very marked. Agar gives no reactions with the colour tests for nitrogenous products; especially it gives no precipitate with picric acid, mercuric chloride, platinum chloride, chromic acid. Its reaction with iodine is distinctive, also that with hardening reagents.

Curves

"We have mentioned that many substances have a peculiar influence on agar in solution; it was also obvious that some chemicals had a greater effect than others; and we sought some method of ascertaining exactly what effect each of those we use would have on the solution. We considered that we should achieve our object by ascertaining the viscosity of the mixtures at varying intervals, since it is a property of great importance to the practical emulsion maker; so we adopted the method and apparatus of Ostwald. This is the one most used for such purposes, both in physical work and in technical determinations of such substances as gelatine, glues, etc., and we had every reason to suppose that it was the best instrument to use for our purpose.

"We found, however, that there were several objections and difficulties. The solution of agar contains minute solid impurities, and we found that they were precipitated, and by blocking the capillary caused serious errors in the rates of flow. It is extremely difficult to be certain of the strength of the solution of gelose owing to the fact that, to get it into solution, the water must be boiled and kept boiling for some time, so that a considerable amount of water is evaporated off. At first we thought that it was necessary to use a 3 percent solution, which is very viscous, too much so for the experiments and the emulsion making; we adopted this strength because we did not know what viscosity the actual maker obtained with his gelatine emulsions; Mr. Gillard used a 3 percent solution of agar, and we concluded that this must be the best strength, so that we persevered with a 3 percent solution for a considerable time. Great care has to be taken not to get any part of the apparatus cooled when manipulating the agar, and adding the chemicals. These and other practical difficulties have shown us that the method is not well adapted to the object in view—at least, not without several modifications.

"We have our results, and though we must admit that owing to the practical difficulties they are inaccurate, yet they are sufficiently accurate to be of interest, inasmuch as they give a fair estimate of the relative effect of the chemicals; as these relative effects are of extreme importance practically, we consider that it is worth while showing them. The whole, however, is being undertaken afresh, with a modified and different apparatus, using perfectly clear agar of a 1 percent concentration.

"The viscometers used by us are made with a wider capillary than usual and standardized with phosphoric acid, sp. gr. 1.5. In the most convenient ones, the time taken to run from the upper to the lower mark was about 60 seconds at 15°, or 24 seconds at 50°, that used for such chemicals as nitric acid took 383 seconds at 15°, and 113 seconds at 50°. In all experiments 3 grams of air-dried agar were dissolved in water and made up to a final weight of 103 grams. We consider that this is much too concentrated, and that a 1 percent solution would be better.

"The agar was soaked in running water overnight, dissolved in distilled water by boiling, boiled for a quarter of an hour, made up to the correct weight, strained, cooled to 50° C, then mixed with solutions of the chemical heated to 50° C, immediately placed in the viscometer and a reading taken.

"The curves, Fig. 1,[1] show the degelatinization, at varying intervals of time; we must repeat that they are not accurate owing to the difficulties of the work; but they illustrate the effects produced in actual work and so are instructive.

"In the case of nitric acid, deci-normal, it is seen that in ten minutes the solution is only 72 percent as viscous; after twenty minutes it is 64 percent; in sixty minutes it is 11 percent as viscous; if left longer it becomes only 8 percent as 'thick' as at the commencement.

"Tartaric acid, deci-normal, causes the solution to become only about 69 percent as thick, in twenty minutes; in time (about two hours) it will be 23 percent as viscous.

"The curve for acetic acid, normal, is very erratic; probably the capillary became somewhat choked after sixty minutes. But it certainly has a considerable effect.

"Citric acid, decinormal, has a small degelatinizing effect, and even after one hour it reduces the viscosity to no more than 80 percent.

"The effect of silver nitrate, normal, is marked at first,

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[1] [The cuts referred to in the text are not reproduced in this article.]

but after ten minutes there is not much alteration. The manner in which the line rises after a lapse of time is curious. The same peculiarity occurs in the curve for sodium hydrate.

"Sodium hydrate, normal, has a very considerable degelatinizing power.

"Sodium chloride has no effect whatever. Ammonium chloride, however, makes it more viscous, and in thirty-two minutes the solution has become 8 percent 'thicker.' It gradually becomes less viscous, and in about eighty minutes it returns to its initial viscosity.

"The effect of borax has been mentioned already. The curve has not been determined, as the capillary of the viscometer became blocked up.

"The next set of curves, Fig. 2, taken more exactly, show the comparative effect of citric, tartaric, and nitric acids. The results are very similar to those shown in the previous diagram. Nitric acid has a great degelatinizing power; tartaric acid is almost as potent. The effect of citric acid is very much less than that of either of the other two, and is never very great.

"The practical application of these results can now be seen. It preparing emulsions, such chemicals as free tartaric or nitric acid should be avoided; similarly, combinations of chemicals which react to produce free nitric or tartaric acid cause degelatinizing. In such a reaction as that between silver nitrate and iodine in solution, wherever a grain of silver iodide is formed, there is a concentration of nitric acid round it; this causes local degelatinization; hence the granular appearance of some of Mr. Gillard's emulsions; also it would cause coagulation of the silver haloid by destroying the colloidal nature of the medium. We found, in making emulsions, that this coagulation was a common accident, and we ascribe it to this cause. It should be mentioned that Rochelle salt, which Mr. Gillard frequently used, has an effect similar to tartaric acid, in its power of degelatinization.

"Mr. Gillard, in mixing some of his chemicals with the solution of gelose, did not dissolve them, but added them solid. This would cause excessive local concentration, and must have been responsible for the peculiar 'boiled rice' effect in his emulsions. We have repeatedly made emulsions to his formulae, quite successfully, but we dissolved the chemicals in water and added them gradually.

"An acid is required in a P.O.P. emulsion to make the paper keep, and preserve the whites. It will be seen from the curves that, of those examined, citric acid has less degelatinizing effects than others, and should be best adapted to that purpose. We have made many emulsions with it and have found it quite suitable.

"We are now in a position to discuss the failures of Mr. Gillard, mentioned previously, and to see how to avoid them.

"(1) The opacity was due to incorrect manipulation and can be overcome by filtering the solution of gelose at a strength of about one and a half percent.

"(2) The degelatinizing is due to the presence of certain chemicals in the emulsion, either added or formed by the reactions in emulsifying. The value of the curves will now be apparent. It has been shown that nitric acid, even in small quantities, has a very great degelatinizing effect; that tartaric and acetic acids are also detrimental; that citric acid does effect the viscosity, but not to any material degree. Therefore it is advisable to use citric acid, in preference to others, in order to make the paper keep.

"It should be noted that if tartaric acid is required in an emulsion, then the emulsion should be made very much thicker at first; so that the tartaric acid may reduce the viscosity to the required degree.

"(3) The difficulty of solution causes no trouble except in washing emulsions. We are told that one cannot dissolve the emulsion after it has been set and washed; but we show a sample of bromide paper, of about the same speed as 'Nikko,' also some lantern slides, all made with emulsion which has been washed and set, then dissolved. There was scarcely any fog at all in these during development.

"(4) The setting of the emulsion is due to careless manipulation. In pouring from one vessel to another, the second vessel must be heated to about 40° C. In coating also, the same point must be noted.

"(5) The reduction of the gold chloride was due to using the salt which reduces the gold most easily. In P.O.P. emulsions there is an excess of silver nitrate over the amount necessary to form the silver haloid, and this makes the reduction take place more easily. The notes on the reducibility of gold chloride should be of use here.

Apparatus for Drying Agar Coated Papers

"Since agar when once set is insoluble in water unless heated to boiling, it seemed to us that the paper off the coating machine could be dried very quickly by means of hot air. An experimental apparatus was made on a small scale. A long tubular wooden tube of rectangular section was made. The total length was 55 feet; it was about 10 inches wide and about 3 1/2 inches deep. Paper 8 inches wide was drawn through it. This paper was supported in the tube by glass rollers (made from glass tube) placed about 1 foot apart. The end into which the paper entered was open; the other end was closed by two pieces of wood covered with plush, pressed together. About 8 feet from the exit end a box was placed under the tube, and communication was made between the box and the bottom of the tube by means of holes bored through. At the same time, communication was made with the box and the top of the tube, by means of glass tubes. A large iron pipe leading from a blacksmith's bellows through a furnace opened into the box below the tube.

"The iron pipe was heated to redness, the air was blown through it by means of the bellows. The wooden tube having been made air-tight, the only exit from the air was at the open end where the paper entered. After blowing for some time the tube became heated up to temperatures shown in Fig. 4, the highest being 84° C, or 183° F. The temperatures were ascertained by means of thermometers let into the tube by means of corks.

"The solution was then put into the pan and the paper coated and drawn through the wooden tube as shown in Fig. 3, A and B. After running for a short time, the paper on the receiving roll was quite dry, and by tearing open the box at a distance of 36 feet from the paper-inlet end, it was seen that the paper was perfectly dry there; it may have been dry before it reached that point, but we could not ascertain this, as the tube was nailed up. The speed at which the paper was being drawn through was ascertained by taking the time for a mark to run through the tube, and was found to be 4 feet per minute. A wooden shuttle 3 feet long was used to pull the commencement of the paper through the tube and to lead it over the rollers. Two strips of tape drawn through the apparatus under the paper, served to support it and prevent it from breaking. Baffle plates were inserted in the tube to mix the air, and to keep it on to the upper and lower surfaces of the paper.

"It will be noticed that the hottest air met the driest part of the paper, so as to complete the desiccation, and that the paper was dried from both sides.

Rate of paper	4 feet per min.
Time taken to dry	11.5 per min.
Highest temperature	84° C. = 183° F.
Lowest "	43° C. = 109° F.
Distance at which the paper was dried	36 feet.

"From these figures it will be seen that the agar-coated paper can be dried quite readily in a short time.

"In conclusion it is hoped that though our work is necessarily incomplete, yet enough has been done to form the basis of future study and also to assist the practical user in the chief of his difficulties. Agar-agar has certain advantages over gelatine and we firmly believe that its use will be much more common in the future. Its cheapness is no inconsiderable item, the cost being less than gelatine and only about one-eighth the amount being used. Its insolubility in water under a temperature of 80°–90° C enables very hot water to be used in washing; at the same time, prints can be dried with extreme rapidity over a naked flame. Certain chemicals can be used in agar which cannot be added to gelatine, such as platinum chloride. The pellicle of agar is very much thinner than that of gelatine—about one-eighth the thickness—so that toning, washing, and other manipulations can be carried out much more quickly."

The change in the colour of an emulsion during ripening indicates qualitatively a change in the relative sensitiveness to light of different wave-lengths. The quantitative side of the matter has been brought out clearly by Eder[1] and I quote from him.

"It must not be overlooked that light is changed in composition by passing through silver bromide films. Unripe emulsions make the transmitted light reddish and therefore absorb chiefly the shorter wave-lengths, the blue and the violet. A highly ripened silver bromide appears bluish gray and is much more transparent for the blue and violet lights. Addition of silver iodide makes the film more yellow and causes a correspondingly greater absorption for blue. Of course the amount of the absorption depends on the thickness of the film.

"Gaedicke[2] has made measurements on the transparency of ripened films of silver bromide gelatine. Six films were placed in a pile. When the upper one received an exposure to the amount of 120 meter-candle seconds, only 33 M.C.S. came through to the second film, 9 M.C.S. to the third, and 2.6 M.C.S. to the fourth, while the fifth and sixth films received no perceptible light. Each film therefore absorbed 13/18 of the light and let 5/18 through. The absorption coefficient of these films is therefore 13/18 = 0.722, while the transparency coefficient, or penetration coefficient, as Gaedicke calls it, is 5/18 = 0.278. The absorption depends on the thickness of the film, on the size of the silver bromide

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[1] Eder's Handbuch der Photographie, 5th Ed., **3**, I, 79, 140–148, 149–150 (1902); Akad. Wiss. Wien., **90**, II, 1097 (1884).

[2] Eder's Jahrbuch der Photographie, **14**, 5 (1900).

grain, and on the volume ratio of silver bromide to gelatine, which is usually 1 : 7.

"Abney[1] found somewhat different figures. He determined at the same time the spectral transparency of the silver bromide gelatine by placing six films in a pile, exposing them to the spectrum and developing. He discovered, and demonstrated by photographs of the spectrum, that a silver bromide gelatine film absorbed all the light from the edge of the violet and ultra-violet, about half the light in the blue, and very little in the yellow. It looks as though this gave us a means of determining the absorption factor of a silver bromide film and of explaining why and to what extent the maximum effect of the spectrum in a thick film is displaced from that in a thin film. The thicker the film, the easier it is for one to photograph the lower end of the spectrum. With a thin film it is very difficult to obtain photographs down through the yellow. It has often been noticed that the red end of the spectrum can be photographed better with a thick film than with a thin one."

"The action of the solar spectrum on the different silver emulsions is of real importance because it is only in such investigations that we get the effect due to a pure color.

I. Action of Solar Spectrum on Silver Bromide and Silver Chloride Gelatine without Development

"If a solar spectrum, produced by glass prisms, is allowed to act on silver bromide and silver chloride gelatine emulsions until these latter darken without a developer, the following phenomena may be noted. Both unripe and highly sensitive silver bromide show about the same decomposition as occurs when a developer is used, except that the exposure must be much longer in the former case. With highly sensitive silver bromide there is a slight action even in the red (Abney). When no developer is used, silver chloride gelatine is changed most along the stretch between blue and violet just as is the case when a developer is used. With

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[1] Eder's Jahrbuch der Photographie, 14, 302 (1900).

pure silver chloride the action of the spectrum sinks very rapidly to nothing near the blue. An addition of silver citrate makes the silver chloride much more sensitive for blue, green and yellow. A mixture of silver chloride and silver citrate is therefore affected by a large number of different rays, which is advantageous when making copies. As a matter of fact, such mixtures are used for copying processes on glass, etc.

II. Silver Bromide in Gelatine Emulsion with Development

"Silver bromide behaves differently towards the solar spectrum according to whether it is emulsified in collodion or gelatine. The curve for the action of the spectrum has already been given.[1] Silver chloride and silver iodide show similar differences when emulsified first in one and then in the other substance.

"H. W. Vogel[2] pointed out:

"(1) Silver bromide collodion always shows a maximum sensitiveness at G (wave-length 410–438).

"(2) Silver bromide gelatine shows a maximum sensitiveness in the clear blue (wave-length 450 with variations from 420 to 460[3]). It makes no difference whether the bromide is precipitated hot or cold, whether the emulsion is boiled or not boiled, digested or not digested. Boiling, digesting or treating silver bromide gelatine with ammonia, has the effect only of increasing considerably the sensitiveness for the other colours, violet, ultra-violet, green and red, the increased being less for the less refrangible rays.

"(3) The so-called green silver bromide, obtained by addition of ammonia to collodion emulsion, is not identical

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[1] Eder's Handbuch der Photographie, 2nd Ed., 1, 241 (1892).

[2] Phot. Mittheilungen, 19, 33, 94, 108 (1882).

[3] According to O. Lohse the maximum action of the solar spectrum, produced by a glass spectograph, is about $\lambda = 440–430$ for silver bromide gelatine plates. In the blue at F $\lambda = 470$, only about one-fourth the maximum effect can be observed while three-fourths of it can be obtained at $\lambda = 452$, Eder's Jahrbuch der Photographie, 8, 271 (1894).

with the green silver bromide of the ripened emulsion. It shows a maximum at G.

"(4) Silver chloride collodion shows a maximum of sensitiveness at the two Fraunhofer lines H and K (wave-length 309–403).

"Naming the silver bromide according to its color, white or green, does not give any definite information in regard to its nature, especially since an excess of potassium bromide or of silver nitrate affects the color. Consequently Vogel calls the silver bromide in the gelatine emulsion blue-sensitive silver bromide from the position of its greatest sensitiveness in the spectrum, and the silver bromide in the collodion emulsion indigo-sensitive silver bromide.

"We are most interested in the silver bromide gelatine emulsion. Eder[1] has published a long account of the action of the solar spectrum on silver bromide gelatine emulsions in different stages of ripening. In this work Eder used a 'large spectrograph' and a small direct-vision one, both from Steinheil. The latter gives almost no spectrum in the ultra-violet, the limit of visibility extending but little beyond H.

"The two instruments have a marked effect on the apparent chemical action of the solar spectrum. The combined flint and crown glass prisms in the direct-vision spectroscope weaken the visible violet very much. For this reason the spectrum obtained with this instrument has surprisingly little effect on silver bromide and silver chloride gelatine in the violet. This is most marked with silver chloride gelatine, developed with ferrous citrate. In the large spectrograph with flint glass prisms the maximum action is at H at the beginning of the ultra-violet. In the small direct-vision spectrograph the maximum lies between G and F. The difference between the two curves is so great that it is hard to believe that the two curves refer to the same silver salt.

"In my large spectrograph the maximum action is even

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[1] Akad. Wiss. Wien., 90, II, 1097 (1884).

displaced noticeably when the blue-green is made to replace the extreme violet in the middle of the field of vision. Thus it is pretty unsafe to base conclusions as to modifications of silver bromide and chloride on determinations of the maximum of sensitiveness.[1] It is the more surprising therefore that the maxima for the sensitizing action of dyes in red-yellow and green are so strongly marked that, according to my observations, they appear in the same place quite independent of the instrument used, though they vary more or less in intensity with the distribution of light."

"The following experiments were all made with the large Steinheil spectrograph and the results are therefore comparable."

"If one mixes silver nitrate solution with an excess of ammonium bromide in presence of gelatine, there is formed a finely divided, pulverulent silver bromide which appears red by transmitted light. Plates covered with this emulsion[2] are dried and exposed for a short time to the solar spectrum produced by a spectrograph with glass prisms. When the plates were developed with ferrous oxalate or with alkaline pyrogallol, an action was obtained from the violet to the blue green (H nearly to F) with a maximum one-third of the way from G to F, at about $\lambda = 440$. With a longer exposure the action extends both ways to M and E. Curve 3, in Fig. 1, gives a graphical representation of the relative intensities of action for the different parts of the spectrum, with intensity as ordinates and the Fraunhofer

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[1] For instance, Vogel's classification of silver bromide into blue-sensitive and indigo-sensitive modifications, a distinction which does not follow from Abney's observations.

[2] The following formula for making such an emulsion has proved practical: 30 g silver nitrate are dissolved in 250 cc water and just so much ammonia added as will dissolve the precipitate completely again. Then 20 g ammonium bromide and 30-45 g hard gelatine are dissolved in 250 cc of hot water and the two solutions mixed at 30°-35°, the silver solution being added in small portions to the bromide solution, and this latter being shaken vigorously. The emulsion is then poured into a flat dish standing in cold water. After the emulsion has solidified, it is cut into small pieces and washed with water.

lines as abscissas. The dotted line shows the blackening after a short exposure and the solid one the blackening after a long exposure.

"If the ammoniacal emulsion, mentioned in the last foot-note is digested at 30°-40° for half an hour, the silver bromide changes to the finely-divided, granular modification. The grain of the silver bromide coarsens, and a thin film allows blue light to pass, and the total sensitiveness to white light increases. At the same time the sensitiveness to violet and to green increases, and the maximum sensitiveness is now about half way between G and F. The action is not so intense between G and F; the curve is flatter. With longer exposure the curve stretches out on one side to N and on the other side to D and beyond (Curve 4, Fig. 1). This curve represents the spectrographic behavior of most of the commercial dry plates.

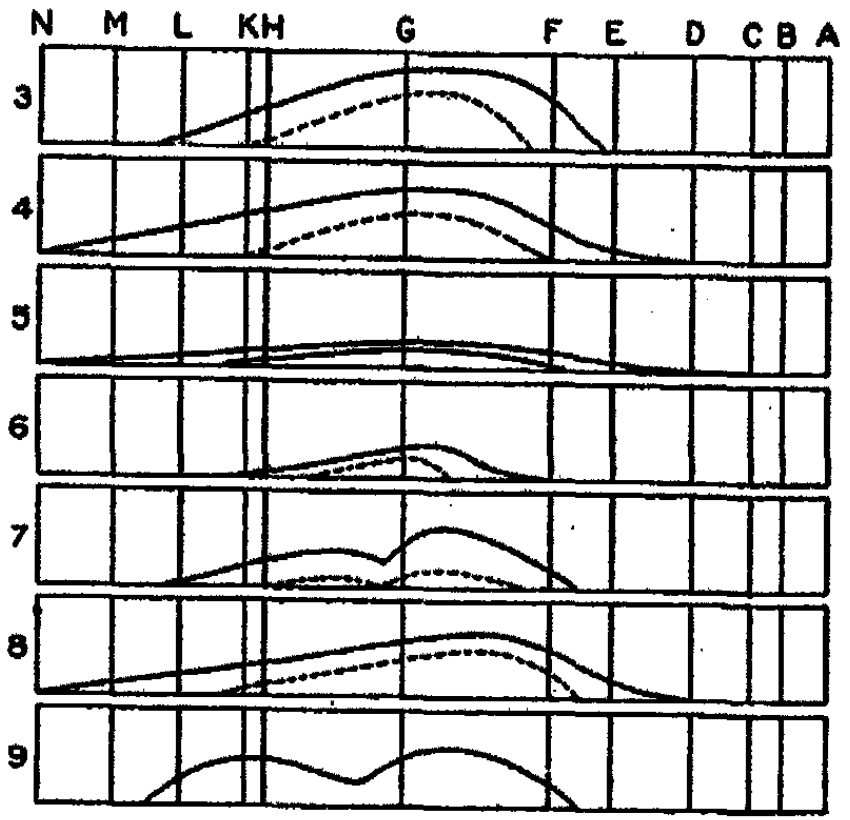

Fig. 1

3-5. Different modifications of silver bromide
6. Silver iodide
7. Mixed silver bromide and silver iodide
8. Ripened silver bromiodide
9. Mixed silver chloride and silver iodide
Dotted lines refer to short exposures, solid lines to longer ones

"When the digestion is carried on three to ten times as long as is necessary to obtain the results described in the preceding paragraph, the silver bromide is nearly ready to decompose. At the same time the curve of the spectrum action changes. It flattens more and more; there is no sharply marked maximum; and the photographic image lacks intensity. The sensitiveness to white light increases and also the sensitiveness to the less refrangible rays (Curve 5).

"We obtain Curve 5 if we digest for a long time the emulsion prepared according to the formula on page 231; but it can be obtained with greater certainty by keeping the gelatine content of the liquid very low, to one-half percent for instance, while the digestion is going on, adding the rest of the gelatine after the digestion is ended. Similar results are obtained by the method known as 'Henderson's cold emulsion.' The total sensitiveness of such an emulsion is very high and the details are well given in the shadows but the high lights are blurred[1] (Eder).

"These statements refer to glass spectrographs and sunlight. They therefore correspond to the results obtained by the usual methods of photography where glass lenses are used.

"Lenses and prisms of rock-crystal (quartz), fluorite, or Iceland spar are much more transparent than glass for ultra-violet.[2] With these the action of the spectrum is very uniform all the way from the blue-green to the extreme

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[1] Photometric experiments with a scale photometer show that such silver bromide gelatine films give a developable image even with a very short exposure, but the intensity of the image does not increase proportionally to the amount of light and soon reaches a maximum which is not increased by a longer exposure. Such pictures therefore lack modelling in the high lights. This can be expressed more accurately if we make use of the conception of the "characteristic curve." We can say definitely that the characteristic curve is affected not only by the development, etc., but also by the modification of the silver bromide present in the emulsion. The results with the spectrograph are in harmony with this.

[2] For the transparency of different kinds of glass as compared with quartz, see Eder and Valenta. Eder's Jahrbuch der Photographie, 9, 310 (1895).

ultra-violet (λ = 2200 or 2000). Concave gratings give the same result. For ultra-violet of very short wave-lengths (λ less than 2000), the ordinary silver bromide gelatine plates are not much good because the gelatine film absorbs these rays too much and prevents their reaching the silver bromide (Schumann). Pure silver bromide is extremely sensitive, however, for rays of the shortest wave-length.

"The atmosphere also absorbs rays of short wave-lengths so that with ordinary gelatine plates in the air it is not possible to photograph the ultra-violet beyond λ = 1850. For still shorter wave-lengths, it is necessary to use a silver bromide, which is sensitive to the ultra-violet and a vacuum spectrograph.

III. Silver Iodide in Gelatine Emulsion with Development

"When silver iodide is precipitated in presence of an excess of potassium iodide it is several hundred times less sensitive to light than silver bromide. If the exposure is very long and if the development is done with alkaline pyrogallol, a weak image is obtained at G. With still longer exposure the image extends towards H and towards F, with a maximum one-third to one-half the way from G to F (Curve 6). On the other hand, it is very sensitive to the extreme ultra-violet,[1] λ = 1900.

"If washed silver bromide gelatine is mixed with 10–50 percent of washed silver iodide gelatine, there is a slight decrease in the sensitiveness of the mixture towards white light. The intensity of the image decreases a good deal; but the plates are clearer and show less tendency to form halos. Two maxima are found in the spectrum, one between G and H followed by a minimum[2] and another maximum, usually a stronger one, between G and F. This latter is caused by the silver iodide. An emulsion made up of mixed

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[1] Schumann: Eder's Jahrbuch der Photographie, 11, 357 (1897).

[2] This minimum is also obtained when a little potassium iodide is added to a pure silver bromide gelatine and the plates are poured without any long digestion.

silver iodide and silver bromide gelatines is therefore quantitatively more sensitive in the blue than a pure, ripened silver bromide gelatine, such as is shown in Curves 4 and 5. Curve 7 represents the silver bromide and silver iodide mixed as an emulsion. The extension of the curve towards the ultraviolet and the green usually lies between Curves 3 and 4.

"This behavior of a mixed silver iodide and bromide was first noticed by Abney, whose results were confirmed by the observations of Eder. It was still a question whether these two maxima remained distinct when the emulsion was digested for a long time or whether they merged into one. Schumann claimed that they did, but it was denied by others.

"Eder's experiments showed that heating for half an hour to an hour actually caused the two maxima to change into one. The same result was obtained if silver nitrate was added to a mixture of potassium iodide and bromide so that silver iodide and silver bromide were precipitated simultaneously. The sensitiveness of such an emulsion to the less refrangible rays is greater than that of a pure silver bromide emulsion. The maximum action is displaced somewhat towards F and there is a distinct action even beyond F so that the correctness of Schumann's statements is established. Curve 8 shows the behavior of silver brom-iodide. The best results are obtained with a mixture containing one formula weight of silver iodide to eight to twenty formula weights of silver bromide. Emulsions containing more silver iodide are more sensitive to green but those with only small amounts of silver iodide[1] give stronger and handsomer pictures.

"The photographic action of silver brom-iodide emulsions seems to point to the existence of some sort of compound of silver iodide and bromide. This is the less improbable because a mixture containing equivalent weights of silver iodide and silver chloride shows a remarkable lowering of the melting-point.

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[1] Not exceeding five percent of silver iodide.

IV. Silver Chloride in Gelatine Emulsion, with Development

"When silver chloride gelatine is developed with ferrous citrate or with ferrous oxalate and potassium bromide, it proves to be less sensitive to white light than silver bromide. The maximum sensitiveness is further over in the violet or ultra-violet than is the case with silver iodide and silver bromide. The maximum is near KH, about at the dividing line between the visible violet and the ultra-violet. The action extends to N and to F, though only to L and to G when the exposure is short. When ten to thirty percent of a silver iodide emulsion is added to a silver chloride emulsion, two distinct maxima are obtained. The one due to the silver chloride is at H while the one due to the silver iodide lies about halfway between G and F (Curve 9). When the emulsions are digested or boiled, the two maxima become one, though not so readily as in the case of the silver bromiodide. With a chlor-iodide emulsion it is possible to use a stronger developer than with a silver chloride emulsion and yet not fog the plate. The sensitiveness of a chlor-iodide emulsion approximates that of silver bromide though without equalling it.

V. Effect of Colorless Substances on the Color-Sensitiveness of Silver Bromide Gelatine

"If silver bromide gelatine plates are bathed for a few minutes in dilute ammonia (say 2 cc ammonia in 100 cc water) and are then dried, the plates are about twice as sensitive to white light and give more intense pictures. Such plates are in general more sensitive to the solar spectrum without there being any increase in the sensitiveness towards special groups of rays. Since the ammonia evaporates during the drying, its action can only be due to a molecular change in the silver bromide."

"The solution of silver bromide in ammonia actually deposits microscopic crystals when evaporating, as Elsden[1] has showed. They also are formed when silver bromide

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[1] Photographic News, 1881, 17.

is precipitated in presence of much ammonia. Depending on the concentration of the solution, the crystals . . . vary in size from 0.02 to 0.2 mm. The thickness is about 0.001 mm. Crystals of this size are not formed by bathing silver bromide gelatine in dilute ammonia; but when ammonia evaporates from the moist plate, the silver bromide undoubtedly becomes crystalline and this may cause the increased sensitiveness to light."

"If a silver bromide gelatine plate is bathed in a dilute silver nitrate solution and is then tested in the spectrograph, we notice first an increase in the total sensitiveness. On closer examination we find that the relative sensitiveness for the less refrangible rays has also increased somewhat. Many dyes are more powerful colour sensitizers in presence of traces of silver nitrate (Eder, December, 1885). This is especially true of the eosine dyes and of others which form organic silver compounds or which are not decomposed by silver nitrate."

The general theory of optical sensitizers has already been discussed at length;[1] but there are some points in regard to the matter for which it is still necessary to quote from Eder.[2]

"If a photographic plate is to reproduce the colors with the same values as seen by the human eye, the orange at C and the clear blue at F of the solar spectrum should be about equal in intensity, while the yellow near D should be eight times as strong as the blue, the yellow-green near D about ten times as strong and the green at E approximately three times as strong; whereas the violet should be only about one-tenth as strong as the blue. As yet, no silver bromide gelatine process has been discovered which satisfies these requirements completely. By interposing yellow glasses or dyes, it is possible, however, to weaken the blue to such an extent that with stained silver bromide plates the yellow

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[1] Bancroft: Jour. Phys. Chem., 12, 318 (1908).

[2] Eder's Handbuch der Photographie, 5th Ed., 3, I, 149, 150, 153, 154, 168 (1902).

green is much more powerful than the blue and the violet. The action in the red and the orange is then lacking. Eder has proposed the name 'orthochromatic' for plates which, by optical or chemical means, give all the colors with the relative values as seen by the eye. This is now an accepted term along with 'isochromatic' and 'color-sensitive.' Everybody knows that, with the plates ordinarily used, orange and yellow come out almost black and much darker than dark blue and violet which act almost like white.

"The orthochromatic plates of commerce are usually sensitized for yellow green. In addition to the sensitiveness of the silver bromide in the violet and the blue, there is an increased sensitiveness for the green and the yellow, between the Fraunhofer lines E and D. With these plates it is possible to photograph the sodium (D) line with sufficient intensity. These plates are usually dyed with erythrosine, less often with eosine, quinoline red, or some other dye. Even though there is no real sensitiveness in the red, these plates are suitable for reproducing pictures and colored objects of all kinds, for taking landscapes in the mountains, and for cloud photographs. Pure reds, such as mercuric sulphide, only act slightly on erythrosine and therefore appear black when photographed. Since such colors only appear occasionally in paintings and elsewhere, one can help out by retouching. If one insists on the exact photographic reproduction of the red, one must use other sensitizers. . . . Lumière in Lyons makes plates which are sensitive in the red. When plates are simultaneously red-sensitive, yellow-sensitive, and green-sensitive, they are called panchromatic. They are usually less sensitive for any given color than plates which are sensitized especially for that color and which are of importance for three-color printing."

"The best concentration varies with the nature of the dye. It is well to start with an addition of 2–4 mg per 100 cc of emulsion or to dissolve this amount in water and to bathe the dry plate in this solution for two to five minutes. If the dye has a strong coloring power, a weaker solution should be used. With some dyes, having only a slight coloring power, the concentration must be ten times as great. With eosine one ten-thousandth of one percent is enough to sensitize the emulsion perceptibly with the characteristic band in the yellow green, although the eye cannot detect any reddish color. The dye can apparently be removed completely from such gelatine emulsions by washing for many hours and yet its sensitizing action can still be detected by means of the spectrograph.

IX. Effect of the Degree of Ripening of the Silver Bromide Gelatine on the Ease with Which it is Sensitized by Dyes

"As a rule color-sensitizing is possible both with colloidal, unripe, pulverulent, silver bromide and with ripened, highly sensitive silver bromide, either in a gelatine emulsion or more readily in a collodion emulsion. It must not be overlooked that ripened, highly sensitive silver bromide is in itself somewhat, though not much, more sensitive to the less refrangible (red and yellow) rays than unripened silver bromide. Such a silver bromide can be sensitized for the red more readily than unripe silver bromide. The observation has often been made that different dry plates are not all sensitized equally readily.[1] These are points which are not yet properly understood.

X. Effect of Silver Bromide, Iodide and Chloride on the Color Sensitizing

"The nature of the silver salt in the photographic plate has an effect on the sensitizing action of the dye. As a rule, one can say that pure silver bromide plates are the most suitable for experiments with sensitizers. Silver chloride can also be used and the relative increase in sensitiveness is often greater than with silver bromide (Eder). Owing to the lesser absolute sensitiveness, silver chloride is not used much in ordinary negative processes. Pure silver iodide

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[1] The author [Eder] always uses the silver bromide plates of Schleussner in Frankfort a.M. or of Schattera in Vienna.

gelatine cannot be sensitized to any extent by dyes even by such as eosine which have a powerful sensitizing action on silver bromide. Brom-iodide emulsions with more than two percent iodide are much less readily sensitized than pure silver bromide emulsions. It is practicable, however, to sensitize emulsions containing up to five percent of silver iodide. For spectrum analysis such plates are desirable on account of the sensitiveness near the line F.

"The presence of relatively large amounts of potassium bromide or of similar restrainers in the emulsion modifies the sensitizing action of dyes. The sensitizing band becomes surprisingly weaker and the orthochromatism of the plate suffers."

XIV. The Manner of Dyeing Silver Bromide Gelatine

"The sensitizers differ extraordinarily in the degree to which they make the silver bromide plates sensitive to the less refrangible rays, red and yellow. The result is also affected by the way in which the dyes are applied to the silver bromide plates. The dyeing of the silver bromide gelatine may be done in two ways: by adding the dye to the liquid emulsion or by bathing the finished, dry plate in an aqueous or an alcoholic solution of the dye. The alcoholic solution is usually not so satisfactory as the aqueous one because alcohol does not penetrate the gelatine readily.

"When making dry plates on a commercial scale it is usual to add the color-sensitizer to the washed and remelted emulsion and then to pour the dyed emulsion on glass plates by means of a pouring machine. Erythrosine and eosine plates can also be made by adding the dyes before the materials for the emulsion are mixed; in other words, to the bromide or to the ammoniacal silver oxide solution. If ammoniacal silver oxide is used, the dye must be stable in presence of ammonia. When the emulsion is dyed in this way, a good deal of the dye must be added because a good deal, though never all, of the dye is removed by the subsequent washing.

"When an emulsion is sensitized on a small scale, for laboratory experiments, it is more convenient to bathe commercial dry plates in a solution of the dye. The bathed plates often work better than the others, especially if ammonia is added. The advantages of the bathed plates show in greater color-sensitiveness.[1] It is helpful to give the plate a preliminary bath in aqueous ammonia. When preparing orthochromatic plates, V. Schumann[2] recommends a preliminary bath of 200 cc water and 0.25–2.0 cc caustic ammonia, which makes the film more porous. After two minutes the plate is taken out, allowed to drip, washed for two to four minutes in a cyanine solution (100 parts water, 1–2 parts ammonia, 5–10 parts alcohol, 2–5 parts alcoholic cyanine solution 1–500), and then dried.

"A preliminary treatment with ammonia gives a similarly good effect with many other dyes, such as eosine, erythrosine, nigrosine, glycine red, etc. It has also been recommended to add alcohol to the ammonia bath in order to cause a more rapid drying (80 cc water, 20 cc alcohol and 2 cc ammonia).[3] Under these circumstances it is well to add a corresponding amount of alcohol to the subsequent dyeing bath to prevent the formation of streaks.

"A mere surface contact of the dye with the silver bromide gelatine is enough to cause a distinct sensitizing. One can even sensitize silver bromide gelatine plates by superposing dyed collodion or alcoholic solutions, which do not go in very deep. This was first pointed out by Abney[4] and was afterwards recommended by Ives;[5] but this method of

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[1] Finished plates, when bathed in an eosine solution, are four times as sensitive to yellow green as is the case when the dye is added to the melted emulsion (Schumann, October, 1885). The same thing is true for erythrosine and for the colors of the eosine and cyanine groups.

[2] Phot. Wochenblatt, 1885, 395; 1886, 49.

[3] P. Ruh. Phot. Correspondenz, 35, 243 (1898).

[4] Phot. News, 1888.

[5] Ives proposed covering the gelatine plate with an alcoholic solution of the dye (1 : 1700), drying, washing with water, and drying again (Eder's Jahrbuch der Photographie, 4, 59 (1890)); but Bothamley found that there was no advantage in this.

sensitizing is usually quite insufficient.[1] The plates are not sensitive because the dye must be intimately mixed with the silver bromide if it is to produce the maximum effect.[2] Nevertheless, there are scattered cases where pure alcoholic solutions of dyes can be used successfully for sensitizing. Thus alcoholic cyanine solutions have but little sensitizing action if poured on silver bromide gelatine plates and then dried; but if the plate is then laid for a moment in water, the gelatine swells, some cyanine dissolves and penetrates a little way into the emulsion, with the result that the plate is quite sensitive to orange while wet.

"A distinct proof, that the sensitizing action of dyes on dry plates varies with the treatment, is furnished by Hinterberger's[3] careful experiments on cyanine. He repeated the work of Weissenberger, Debenham and Schumann.

"Weissenberger recommended bathing the silver bromide gelatine plate in a very dilute cyanine solution (1 : 5000000), which is made colorless with a trace of acetic acid. When the plate was dried, the acetic acid evaporated and left the cyanine behind with its blue color. With this small amount of dye, the sensitizing action is so slight that it can scarcely be detected even in the orange. When the amount of cyanine is increased, the sensitiveness to blue decreases while there is an increase in the sensitiveness to orange yellow, yellow green, and red. When the amount of cyanine becomes very large, the screening effect causes the sensitiveness to those last colors to decrease with the exception of a small strip near A. The best form of Weissenberger's method is to bathe the plate for a couple of minutes in a solution made up of one liter of water, 2 cc alcoholic cyanine solution (1 : 500) and one drop of acetic acid. The plate is dried after the bath.

"Debenham recommended bathing the plate in a pure alcoholic cyanine solution (1 : 2000), drying in the air in an

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[1] Wellington: Phot. News, 1885, 415.

[2] H. W. Vogel: Phot. Mittheilungen, 25, 117 (1888).

[3] Eder's Jahrbuch der Photographie, 11, 379 (1897).

absolutely dark room (which takes several minutes), bathing in pure water for two or three minutes, and exposing the plate *while wet.*

"The conclusions which Hinterberger drew from his comparisons were:

"(1) Schumann's method is uncertain and usually gives impure and fogged plates.

"(2) Weissenberger's method is reliable. The plates are very clear and quite sensitive; but the sensitiveness only covers the blue and a narrow strip in the orange between C and D.

"(3) Debenham's method is reliable. The plates are fairly pure and very sensitive. The color-sensitiveness extends over red, orange, yellow, yellow green, and blue to dark blue and is only broken by minima in the red at *a* and in the green between E and F. The disadvantage is that the plate must be exposed wet."

One of the very important things about the medium forming the emulsion is the way in which it retards the action of the developer on the unexposed silver bromide. I quote from Lüppo-Cramer:[1]

"When people have discussed the theory of the latent image, they have ignored entirely the fact that, when silver bromide is precipitated in aqueous solution, it is readily reduced by the developer even without exposure to light. This fact proves conclusively that it is not necessary to assume a reduction as the result of exposure to light. The following experiment shows that the mere enclosing of the silver bromide grain in a sheath of the medium is not the cause of a normal, emulsified silver bromide not being reduced unless it has been exposed to light. If silver bromide is precipitated from aqueous solution and is then suspended in a gelatine solution, it is reduced promptly and completely by a developer solution."

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[1] Phot. Correspondenz, 38, 222 (1901).

In a later paper on "The Reducibility of Precipitated Silver Bromide," Lüppo-Cramer[1] returns to this subject.

"In the course of my papers on the latent image, I have often had occasion to call attention to the fact, first observed by Abney,[2] that silver bromide precipitated in the dark from aqueous solution by an excess of bromide, is reduced instantaneously by a developer solution. In this respect it does not differ from silver bromide which has been exposed to light for a short or a long time. Years ago Andresen[3] established this fact by quantitative analysis and the author's work on bromhydroquinone (adurol) has confirmed the results obtained by Andresen under the conditions specified by him.

"At the Fifth International Congress for Applied Chemistry, the results of Andresen were called in question by Schaum. I therefore repeated the experiments and found that, with ordinary developer solutions such as Andresen used, the unexposed silver bromide was reduced instantaneously. No difference could be detected between the behavior of the unexposed silver bromide and that of silver bromide which had been exposed to light. Although the iron developer is usually slow during the first stages, yet it reduces at once silver bromide precipitated according to Andresen's directions. If one adds potassium bromide to the iron developer (1 cc KBr, 1 : 10, to 80 cc developer) a difference can be detected between the rate of reduction of an unexposed silver bromide and of one that has been exposed for a few seconds to daylight. The difference is more marked if one uses metol and sulphite without alkali. This solution causes an instantaneous reduction of silver bromide which has been exposed for a few seconds, while the unexposed silver bromide requires 30–40 seconds for reduction.

"The coarsely flocculent, precipitated silver bromide is therefore capable of photographic action though we must characterize it as fogging badly. The very much finer sil-

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[1] Phot. Correspondenz, 40, 671 (1903).

[2] Eder's Jahrbuch der Photographie, 12, 420 (1898).

[3] Ibid., 13, 143 (1899).

ver bromide, used by Schumann[1] in the plates sensitive to ultra-violet, fogged readily, which is probably the cause of Schumann's using a halide emulsified in a very little gelatine in his later work.

"At present we are not able to say how the colloidal media make exposed and unexposed silver bromide act so differently toward developer solutions that certain emulsions can be developed for hours without the unexposed silver bromide being reduced. The matter will be discussed in a later section."

According to Schaum[2] the matter is not so complex.

"We must say a few words in regard to the action of developers on silver bromide containing no binder. It has frequently been stated, even quite recently, that silver bromide containing no binder is reduced equally rapidly whether it has been exposed or not. The inaccuracy of this statement has been proved by Luther's experiments. We also have had no difficulty in showing by development the action of light on our silver bromide layers, which were obtained by precipitating from concentrated neutral solutions with an excess of bromide, while Luther used much more dilute solutions and an excess of hydrobromic acid. If one uses developers with the concentration usual for gelatine plates, many of them, such as ferrous oxalate or edinol, cause a complete blackening almost instantaneously. The complete reduction takes place somewhat less readily with adurol, hydroquinone, or Belitski's developer; metol acts the slowest. If one wants good gradation and freedom from fog, it can be obtained by taking one of these last developers and diluting to one-half with water. The gelatine is the cause of the slow reduction of silver bromide in the emulsion film as compared with the reduction of silver bromide containing no binder.

"The effect of the binder on the development, especially

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[1] Sitzungsber. Akad. Wiss. Wien., **102**, IIa, 994 (1893); Drude's Ann., **5**, 349 (1901).

[2] Eder's Jahrbuch der Photographie, **18**, 75 (1904).

in the case of gelatine, has been ascribed by Abney[1] to a mechanical retarding. This point of view is supported by our experiments. Precipitated silver bromide was suspended[2] in gelatine solution. Plates poured with this emulsion developed glass-clear with concentrated developers after exposure.

"Every trace of the organic matter was removed from a washed, ripened silver bromide taken from a ripened Schleussner emulsion; and the silver bromide was allowed to settle on a piece of ground glass. This silver bromide is reduced much more rapidly than the freshly-precipitated bromide. It is possible however to develop an image on this silver bromide by using a metol developer diluted to one-half and allowed to act only for a short time. After this silver bromide has been emulsified again in gelatine, a photographic image can be developed quite well even with concentrated developers. If a sedimentary silver bromide layer is merely coated with gelatine, the development is retarded considerably. If there are other differences—apart from differences in degree of ripening—between silver bromide precipitated in gelatine and silver bromide precipitated in water but afterwards suspended in gelatine, these seem to be that the suspended silver bromide is reduced more rapidly than the emulsified silver bromide. Quincke's[3] explanation applies here, namely, that solutions of silver bromide and gelatine are formed which have very complicated properties. Such solutions occur of course to a much greater extent when an emulsion is formed than when silver bromide is suspended in gelatine. In these solutions the unexposed silver bromide is less readily reduced than when it is merely protected by a coating of gelatine, because a solution of silver bromide and gelatine has a lower bromine pressure than pure silver bromide. The formation and properties of such solutions should be suffi-

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[1] Eder's Jahrbuch der Photographie, 12, 420 (1848).

[2] [It is not clear whether the author means suspended or emulsified. If he means the latter, the experiment proves nothing.—W. D. B.]

[3] Drude's Ann., 11, 1100 (1903).

cient to account for many other phenomena, such as the great differences between collodion and gelatine emulsions.

"The sensitiveness of silver bromide containing no binder depends on the nature of the precipitating bromide. This point is now being studied in detail.

"The phenomenon of ripening is usually referred to a coarsening of the grain and to the action of gelatine (slight reduction or, according to Quincke, the coagulating of turbid media). We found that our layers containing no binder show the phenomenon of ripening if they are heated to 65° either when moist or dry. At the end of 70 minutes we obtaind an increase of sensitiveness from 5° Scheiner to 9°. After heating for five hours to 65°, the plate fogged at once in the developer. When heated under water, the sensitiveness increased though not to anything like the same extent. While the gradation is pretty bad with the unripened layers, it it quite good with the ripened layers."

While we are on the subject of silver bromide precipitated from aqueous solution, it is interesting to note that, according to Weisz,[1] the precipitated silver bromide is more sensitive to light, the finer the grain, which is the exact opposite of what is usually believed in regard to the emulsified silver bromide.

"The concentration for preparing the milky silver bromide was originally the same as Luther's: one volume of N/20 $AgNO_3$ to one volume N/10 HBr. Higher concentrations than these make the grain coarser and produce a less sensitive plate. A less excess of hydrobromic acid makes the grain finer and the plate more sensitive. When there is an excess of silver nitrate during precipitation and sedimentation, the layer does not hold together and floats off during the experiments. The slightest trace of thiosulphate on the surface of the glass has the same effect and it is therefore desirable not to clean spoiled plates with thiosulphate[2]

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[1] Zeit. phys. Chem., 54, 322, 351 (1906).

[2] I avoided gelatinizing the exposed plates before development. Luther: Zeit. phys. Chem., 30, 628 (1899).

if fresh silver bromide is to be precipitated upon them.

"The temperature of the silver nitrate and hydrobromic acid solutions should be between 15° and 19°. During sedimentation, all jarring of the dish must be avoided as far as possible. In the summer I could not get any satisfactory plates, though I do not know why. Perhaps the temperature was too high during sedimentation.

"The time of sedimentation is of great importance. If the milk settles too rapidly, one can be certain of getting irregular, mostly insensitive, plates with a silver bromide layer which does not cling to the glass. If the sedimentation is allowed to go on too long, the plates fog in the developer. This is because the finest silver bromide particles settle too, as dust on the surface of the layer and cause the fogging. If such a plate is cleaned vigorously with a brush, it becomes much less sensitive to light and does not fog in the developer any more."

"I divided a precipitation of silver bromide . . . into three fractional precipitations. The liquid layer was seven centimeters deep and I allowed the bromide to settle for five days, then sucked off the supernatant milk and let that settle on fresh plates for six days. The third time, the mixture was allowed to stand for two months. I thus had three fractional sedimentations, T_1, T_2, T_3, of which T_1 had the coarsest grain and T_3 the finest. There were four plates of each type. This experiment confirmed the opinion previously expressed; because the plates T_2 were about four times as sensitive as the plates T_1. . . . Plates T_3 fogged completely in the developer, which was what was to be expected."

The special idiosyncrasies of a plate sensitive to ultraviolet are brought out clearly in a paper by Schumann[1] from which I quote:

"It is known that the sensitiveness to light and the intensity of the gelatine dry plate decreases considerably

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[1] Drude's Ann., 5, 349 (1901).

as we pass from the wave-length 220$\mu\mu$ to the shorter wave-lengths. I have previously shown[1] that the cause of this decrease is the insufficient transparency of the gelatine. Silver bromide itself shows no such decrease in sensitiveness. There is also no decrease in sensitiveness if the silver bromide is used in presence of very small amounts of gelatine. It is on this fact that I based my earlier process of preparing plates sensitive to ultra-violet, which enabled me to investigate the regions beyond 185 $\mu\mu$. As I have previously stated, this process had many faults. I have been busy until recently in attempts to overcome these faults. In this way I have gradually succeeded in making plates which surpass the earlier ones considerably in purity, in delicacy of gradation accompanied by sufficient intensity, and in reliability.

"The essential features of the improved process are as follows: A silver bromide emulsion is prepared which is very rich in silver. This is allowed to solidify and is washed thoroughly.[2] It is then melted in presence of a very large excess of water [in order to dilute the gelatine], is filtered, and is poured on plates laid horizontally. The silver bromide is allowed to settle for half an hour and the emulsion is then poured off. The fine layer of silver bromide remaining on the plate dries quickly because it is so thin. The plate may be used as soon as it is dry. Still better results are obtained if the heavier particles of silver bromide are removed before the emulsion is filtered. The formation of the layer on the plate takes place as before but requires several hours instead of half an hour."

"If, instead of silver bromide, the emulsion contains other silver halides or mixtures, the photographic properties are different. The following are the most important conclusions which I have reached in regard to this matter:

"(1) Silver chloride gelatine, prepared with an excess of potassium chloride, is moderately sensitive, lacks strength, has a tendency to fog, and yields a fine-grained picture.

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[1] Sitzungsber. Akad. Wiss. Wien, 102, IIa, 415, 994 (1893).

[2] [Apparently no attempt is made to ripen the emulsion.—W. D. B.]

"(2) Silver iodide gelatine, prepared with an excess of potassium iodide, develops glass-clear and very intense, yields a coarse, black grain; but is distinctly less sensitive than silver bromide gelatine.

"(3) Silver iodide gelatine, prepared with an excess of silver nitrate, differs from the preceding in that it is nearly twice as sensitive. On account of its uncertain behavior in the developer, it is much less to be recommended than the silver iodide gelatine prepared with an excess of potassium iodide.

"(4) Silver chlor-iodide gelatine, prepared with an excess of potassium chloride, fogs very little and yields a very fine grain; but lacks intensity.

"(5) Silver chlor-iodide gelatine, prepared with an excess of potassium iodide, fogs easily, becomes a dirty, brick-red color when developed with pyrogallol and soda, and yields fine-grained pictures which are lacking in intensity.

"(6) Silver brom-iodide gelatine, prepared with excess of potassium bromide, is highly sensitive, excessively intense; it fogs readily to the point of complete opacity. The grain increases sometimes so much as to form small lumps. It is useless for spectrographic purposes.

"(7) A mixture of silver chloride gelatine and silver iodide gelatine, gives powerful negatives, free from fog, with soft half-tones and a fine grain. It is the only plate made by the improved process which ranks at all with silver bromide gelatine for the preparation of plates sensitive to ultra-violet light.

"(8) A mixture of silver bromide gelatine and silver iodide gelatine gives coarse-grained negatives of great intensity, and free from fog. The plates are only slightly sensitive.

"All the preceding statements in regard to size of grain refer to the plate after it has been developed and fixed. The grain of the emulsion and of the undeveloped plate is distinctly smaller on the average. The size of the grain of the developed plate depends on the silver iodide content of the layer and also on the amount of potassium bromide added to the developer."

"The first few days after it is prepared, the plate is not very sensitive and it is also lacking in intensity. During this period it will stand extraordinarily strong developers, solutions of concentrations which could not be used on a dry plate without danger of fog. There is no danger of the layer coming loose from the plate. The layer shows an extraordinary power of withstanding certain chemicals. It is not attacked by fuming nitric acid, concentrated sulphuric acid, hydrochloric acid, or potash solution 1:3. Fuming nitric acid does not destroy either the latent or the developed image. Even though the greater part of the silver is dissolved in the latter case, the image remains in all its details. The acid merely decreases the intensity. This behavior of the light-sensitive coating is the more surprising because one of its constituents, gelatine, is readily soluble in nitric acid. From this we must conclude that in this case the degree of solubility of the gelatine depends on the thickness of the film.

"On standing, the sensitiveness and the intensity of the plate both increase. At the end of a couple of weeks the increase in both is quite marked. From then on, it is the intensity which increases the more rapidly. I have usually obtained the best results with plates which were one to two months old. In the third month fog begins to be noticeable. Glass-clear negatives can be obtained however by adding plenty of potassium bromide to the developer. Plates[1] kept in dry air have even given excellent results at the end of two years. The only change is a marked decrease in the sensitiveness. Since the clearness of the picture can

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[1] To test the effect of moisture on the keeping properties of the film, I have placed a series of differently prepared plates in tightly closed vessels of glass and of zinc, using sulphuric acid in some cases as drying agent and phosphorus pentoxide in others. The plates were shielded from light and at the end of twenty-two months they were exposed to the aluminum spectrum from blue to the wave-length 185 $\mu\mu$. The results stated in the text were based on these experiments.

only be obtained in this case by increasing the amount of potassium bromide, whereby the time of development is increased considerably, the use of such old plates is not to be recommended."

"On account of the extraordinary fineness of the lines the spectrum on a plate sensitive to ultra-violet can stand a very high magnification. The spectra obtained with a very narrow slit give distinct line images when magnified a hundred fold. All the same, the grain of such a negative is by no means as fine as one might expect from this and from the size of the distinctly smaller emulsion grain. Since the ordinary dry plate will not stand so high a magnification, this can only be due to the greater (five-fold) thickness and the relatively much greater gelatine content of the light-sensitive layer.

"If an ultra-violet and a very slightly sensitive silver bromide gelatine plate are exposed to a uniform white light, the latter receives a developable image much sooner than the former. The ultra-violet plate is less sensitive to the visible rays. The same thing is true for most of the ultra-violet spectrum. It is only at about 231$\mu\mu$ that the ultra-violet plate begins to accomplish more than the gelatine plate, the image then becoming more intense and also sharper. As we pass towards the still shorter wave-lengths, this difference becomes so marked that the energy distribution and the intensity undergo a complete change in the field between 220 and 200$\mu\mu$, a region in which, as every observer knows, negatives are characterized by lack of intensity and of gradation. All photographs of this region of the spectrum are more valuable as showing the absorption spectrum of gelatine than as showing the sensitiveness of the silver bromide. It is much the same also with the stretch between 231$\mu\mu$ and the green of the spectrum where intensity and sensitiveness also depend on the gelatine though in a different way for the gelatine here acts as a sensitizer and increases the sensitiveness of the silver bromide to a marked extent, as everybody knows. From this it follows at once that all measurements of light intensity, which depend on differences in the density of the spectrum image, have only a relative value. Since the absorption effect and the sensitizing effect of the gelatine undergo marked fluctuations, it follows that the measurements hold strictly for the particular plate actually used and not for the dry plate in general. Plates from different makers may therefore give widely differing results. In spectroscopy this is more important than is usually supposed because the degree of brightness of the different rays is taken as proportional to the blackness of the photographed lines. As a matter of fact, equal differences of brightness in the visible spectrum and in the more refrangible ultra-violet correspond to different degrees of blackness and not to the same. It is not even necessary to prove the case by taking such extreme instances, by comparing remote portions of the spectrum. It will suffice to take the blue of the spectrum where very different degrees of sensitiveness to light will be obtained with plates of different makes, depending on the way the emulsion has been prepared. In addition to the gelatine, it is the silver iodide,[1] to be found in most plates, which determines by its amount the degree of sensitivenesss to white light and also to green blue light. While silver bromide gelatine, for instance, is practically not sensitive to the hydrogen line H_β and to that portion of the spectrum, this region comes out strong in silver bromiodide gelatine because silver iodide displaces the maximum of sensitiveness towards the red so that H_β equals the brilliant H_γ in intensity.

"For these reasons a plate, having a uniform sensitiveness over the whole spectrum, would be a very important addition to our equipment for making spectrographic measurements. The ultra-violet plate comes the nearest to satisfying these requirements of any plate that we have on account of its sensitiveness to the rays which can be photographed

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[1] Most manufacturers of dry plates add varying amounts of silver iodide to the emulsions. There are plates on the market which contain no silver iodide and which are very popular, especially in scientific circles.

only in a vacuum and because of its uniform reproduction of the remainder of the spectrum. To illustrate to what extent this latter is true I give two spectra[1] of the spark between aluminum terminals, photographed under the same conditions with increasing time of exposure. The first was taken on an ultra-violet plate and the second on a gelatine dry plate. A comparison of the two shows: how entirely differently they represent the energy from the same source of light; how poorly the commercial plate is adapted for photographing the more refrangible portion of the ultra-violet as far as 185$\mu\mu$; and how slightly its sensitiveness to light corresponds with that of pure silver bromide, which my earlier experiments have shown to be not only sensitive to all the rays from the blue portion of the spectrum to the shortest wave-lengths but also to be nearly uniformly sensitive to all these rays. It is also worth noting that the extremely small amount of gelatine used increases the sensitiveness of the ultra-violet plate in general and gives it the power of reproducing gradations. It is this which makes it possible, in spectrum work, to obtain the soft half-tones which cannot be obtained with silver bromide alone. If one covers a glass plate with pure silver bromide, it gives all the lines, which can be developed at all, with approximately the same maximum intensity of which the layer is capable.

"A further advantage of the ultra-violet plate consists in its lack of sensitiveness to the diffused light in the photographic apparatus, which makes great trouble in certain cases, when using ordinary plates. For instance, if one tries to photograph the spectrum beyond 185$\mu\mu$, using a gelatine dry plate, the plate fogs before the image has obtained sufficient strength; it fogs so completely that only the most active lines remain visible. This fog is caused by rays which are scattered inside the lenses and the prisms, and which reaches the plate as diffused light. Since the diffused light consists chiefly of rays which have been refracted less and therefore of the rays which have the most effect on the dry

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[1] [Not reproduced in this article.]

plate, it is not surprising that they should have a very strong fogging effect. Owing to the lack of a suitable light filter it has not proved possible so far to keep this diffused light completely out of the spectrum apparatus. All that we can do is to weaken it. This can be done easily by cutting down the light coming through the slit by shortening the slit to about one-third of a millimeter. This is the only way to obtain photographs of electrical discharges from the wave-length, 185$\mu\mu$, to the limit of the ultra-violet action on the dry plate 182$\mu\mu$. Since the ultra-violet plates are only slightly sensitive to the visible rays and the adjacent ultra-violet rays, the diffused light does not trouble them. It is therefore possible to make the slit as long as may be desired without having to fear fogging, no matter how long the exposure."

"There is another peculiarity of the plate which I must mention briefly. With the intense illumination which we get with a wide slit, heavy electrical currents, and a prolonged exposure, I have repeatedly obtained solarized spectra. Under these conditions the lines appear as pale strips surrounded by an edge of increased blackness caused by irradiation in the layer. That we are not dealing with a plain case of spectrum reversal is shown by the form of the dark edges. They occur at the ends of the lines as well as at the sides. Since this phenomenon only occurs occasionally, it is of more importance photochemically than spectroscopically. These results conflict with the observations of Abney; and some rays will cause solarization of silver bromide without the intervention of oxygen. My exposures were all made in a vacuum or in a hydrogen atmosphere having an excess pressure of several centimeters. Since the reversal cannot take place during the development of the image, it follows that the fact discovered by Abney does not hold for ultra-violet plates and that it therefore depends on the photographic plates used by Abney.[1]

"In 1893 I published an account of a process for mak-

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[1] [If Schumann had tested this conclusion he would have been in a position to have worked out a satisfactory theory of solarization.—W. D. B.].

ing plates which were sensitive to ultra-violet light.[1] In this process I added a great deal of water to an emulsion containing relatively little gelatine and poured the solution into deep dishes, in which the silver bromide settled upon glass plates placed therein. Many hours were necessary to produce the light-sensitive deposit, after which the emulsion was decanted and the plates were dried in a horizontal position. It is clear that the old process and the new one are very similar. It would be quite wrong, however, to reason from this to the photographic nature of the two makes of plates. The two have nothing in common beyond the sensitiveness to ultra-violet, the rapid fixing and drying, and the behavior when potassium iodide is present in the developer. In other respects they differ, and very considerably in some points.

"The most remarkable difference is in the behavior towards silver iodide. The emulsion made by the old process could stand quite a good deal of silver iodide; but the improved plate fogs so as to be quite useless. Many efforts have been made to introduce silver iodide into the sensitive film, but they have all failed on account of the ease of reduction and the excessive intensity which results therefrom. After many futile experiments I have succeeded in getting soft negatives, fairly free from fog, by means of stand development lasting seven hours; but it is clear that so lengthy a process of development is of little value for spectroscopic work.

"The improved process is much more dependent on the quality of the gelatine than the older one was. A gelatine, which formerly could be used successfully, now gave rise to a series of unexpected irregularities. Besides spots of various kinds, the films had the unpleasant peculiarity of becoming covered with numberless cracks, shaped like the tails of comets and varying up to 2.5 cm in length. This occurred within a few minutes after the emulsion had been

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[1] Schumann: Akad. Wiss. Wien, 102 IIa, 994 (1893).

poured off and while the plate was still wet. Of course this made the plate useless.

"In another case, one of our best German gelatines gave films which were so slightly sensitive that we could not even reach the wave-length $185\mu\mu$, which can be obtained without any trouble with the ordinary dry plate. When these plates were bathed in warm water (38°) for ten minutes, their character changed completely and they became surprisingly sensitive to ultra-violet. In this case, the water therefore plays the part of a physical sensitizer. Its sensitizing action is due in part to the fact that the gelatine melts enough so that the upper portion of the sensitive layer is freed from the coating which absorbs the light. It is also due in part to the fact that the continued heating increases the tendency of the silver bromide to reduce. The sensitizing action of the water on such a plate exceeds anything which I have ever noticed in my years of work with emulsions sensitive to ultra-violet. Unfortunately this treatment causes spots and dry zones of varying sensitiveness so that plates of this type are not to be recommended. Another objection is that the keeping qualities of the plate are decreased by the sensitizing bath.[1]

"Out of all the different kinds of gelatine which I have tried, only one has always given good results. This is the previously mentioned, soft, English gelatine, which is known to the photographic trade as Nelson's No. 1. I therefore advise anybody who wishes to make these plates to begin with this gelatine and no other.

"Plates made by the older method required dilute developers, while exceptionally concentrated developers could be used with the improved plates, at any rate so long as the plates were new. The chief merits of the improved plates are reliability and a more equal sensitiveness. This was ob-

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[1] It is surprising that it is not possible, by this means, to increase the sensitiveness of the ordinary plate to the shortest waves of lights. Experiments along this line gave negative results. The half of the plate which had been bathed developed to the same wave-length as the unbathed portion.

tained by letting the coarser particles of silver bromide settle to the bottom of the dish and keeping them off the glass plate.

"The photographing of crowded groups of lines showing marked differences of energy is a very severe test of a plate. My earlier plates did not stand this test very well. In them the lines often spread out enough to give a band, in which only the most intense lines could be detected. This difficulty was due chiefly to a lack of half tones. Owing to the finer gradations of the negatives obtained by the improved process this trouble has disappeared.

"I have previously called attention[1] to the peculiar action of potassium iodide when added to the developer used for ultra-violet plates. I found that a few drops of a one percent solution brought the image out more quickly and increased its density but also tended to produce a heavy fog which, however, did not appear simultaneously over the whole film as is the case with other plates. This fog began at the edges and crept slowly in to the centre. I have tried to avail myself of the accelerating action of potassium iodide by bathing the improved plate before exposure in an aqueous potassium iodide solution and then drying. The result did not come up to my expectations. The troubles were the same as with the old plates.[2]

"When it is a question of representing accurately the total photographic energy of a source of light, the ultra-

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[1] Schumann: Sitzungsber. Akad. Wiss. Wien., 102, II*a*, 1014 (1893).

[2] The action of a potassium iodide bath on the film varies with the concentration. I have tried solutions running from 1 : 1000000 to 1 : 15 and have found that even the small quantity of potassium iodide in the first solution has a weak sensitizing action. This is not much more marked with the 1 : 100000 solution but increases distinctly as the concentration goes up to 1 : 25000. With a concentration of 1 : 12500 we get a heavy fog along the edge. With increasing concentration the fog spreads over the whole plate and finally a point is reached at which the silver bromide is dissolved. A solution of potassium iodide 1 : 1.5 fixes an ultra-violet plate three to four times as fast as a solution of sodium hyposulphite 1 : 3. Gelatine is also dissolved at ordinary temperature by a potassium iodide solution. This makes it seem possible to extend the fixing of an ultra-violet plate to include the gelatine itself, which would have certain advantages when it came to enlargements. I made some experiments of this sort but the results were not satisfactory.

violet plate is superior to all others from the blue to the shortest wave-lengths. When one does not care about the region beyond 220$\mu\mu$, the gelatine dry plate is the best. The sensitiveness of the improved plate to the ultra-violet becomes striking at 220$\mu\mu$ and increases rapidly as the rays become more refrangible. The gelatine dry plate gives out at 182$\mu\mu$. It is not absolutely lacking in sensitiveness for the shorter waves; but the spectrum which it gives is a false one. In consequence of the absorbing action of the gelatine, all spectra, even though discontinuous, develop as a continuous, faint band which does not correspond in any way to the energy differences of the different waves of the source of light under examination. Therefore the ultra-violet plate is the only one that can be used for photographing the spectrum beyond 182$\mu\mu$."

In these three papers I have tried to give a fairly complete account of our knowledge in regard to photographic emulsions so far as this can be obtained from a study of the literature. I have tried to give a fair statement of the arguments for and against each particular hypothesis. The subject has been considered under the following heads: methods of preparation; amount of silver in film; sensitiveness of film to light; methods of ripening; limits to ripening; inhomogeneity of emulsion; reducing action of some gelatines; question of reduction during ripening; theories of ripening; state of silver bromide in film; behavior of mixed emulsions; opacity; coarsening of silver bromide grains; effect of water content and of gelatine content; effect of chemical and optical sensitizers; effect of medium; increased sensitiveness to different lights; sensitiveness of precipitated silver bromide to development; the ultra-violet plate. While it will take a great many experiments and a great deal of time to establish a satisfactory theory of the emulsion, it should not be difficult to develop a working hypothesis which will bring order out of chaos and which can be extended, modified or corrected as may prove desirable. In the next paper I shall try to present such a working hypothesis.

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ON THE ENERGY RELATIONS OF SOLUTE AND SOLVENT

BY M. M. GARVER.

In a former paper[1] attention was called to the fact that an expression for the maximum work done during the dilution of a dilute solution was independent of any force action on the part of the dissolved substance. Further study of the experimental evidence afforded by osmotic phenomena serves but to strengthen my conviction of the general soundness of the views therein presented, except as to minor details; in some respects those are open to modifications. The main fact, however, that the phenomena of osmosis all arise from and are most simply explained in terms of the activity of the solvent instead of the solute, seems beyond doubt when the deductions from such a view are considered as a whole. The object of the present paper is to show how a few of the many experimental facts available may be interpreted in the light of the proof that the dissolved substance takes *no active part* in the production of the maximum work done during dilution. And if the part it plays in the production of work be purely a passive one, may not the same passivity be traced throughout the whole range of the phenomena connected with dilute solutions? The question seems one worthy of investigation in view of the important part taken by osmotic pressure in modern science. But at the very outset we are met by the fact that osmotic pressure has been used as a measure of the work done in separating the constituents of a solution *and has given perfectly consistent results from that point of view.* The statement, then (with proof which cannot be doubted), that the dissolved substance plays only a passive part in the production of work would make osmotic pressure dependent on the activity of the solvent. Practically all of the text-books speak of osmotic pressure as a pressure exerted by the dissolved substance

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[1] Jour. Phys. Chem., 13, 679 (1909).

and yet use it as a measure of work done on or by the solution. Here is an evident conflict that requires clearing up. Either the alleged "proof" is false or a reinterpretation of osmotic pressure is demanded. If no defect can be found in the proof then a re-examination of the experimental evidence is absolutely necessary.

Evidently the first thing in order is a re-examination of the proof that the maximum work done during the dilution of a dilute solution is independent of any activity of the solute. However, the proof may readily be verified in different ways. The simplest and most satisfactory method will probably be afforded by evaluating the integral regarded as proof and showing that it leads directly to accepted canonic forms.

In the former paper (op. cit.) an expression for the maximum work was obtained from $dW = gh\,dm$ which gives $W = \rho g\int_{h_1}^{h_2} h\,dv$ where g is the attraction of gravity, ρ is the density of the solvent, v its volume and h a variable height. Before this can be evaluated it will be necessary to find the functional relation between h and v subject to the condition that the work between the limits is a maximum. Using the same device described in detail in the former paper, we may at any point regard h as constant and gradually change the volume by adding solute—so slowly that the equilibrium will not be disturbed, the vapor condensing will keep the concentration constant. Now the integral will take the form

$$W = \rho gh\int_{v_1}^{v_2} dv.$$

This is still a maximum, but gives the entire work due to dissolving (instead of diluting) an unknown, but definite mass of solute. It will serve to give the functional relation between h and v when the work is a maximum for a definite mass of solute, h arbitrary and the volume varied between

v_1 and v_2. We have, then, $W = \rho gh\,(v_2 - v_1)$, which becomes ρghv when v_1 is negligibly small. (We may start with as small a volume as we please.) Since the work is a maximum for that amount of solute, we may write

$$W' = \rho ghv = \text{const.}$$

Hence we see that h varies inversely as v, therefore $hdv = -vdh$ and $v = W'/\rho gh$. Therefore making the substitutions and integrating we have

$$W = W' \int_{h_1}^{h_2} \frac{dh}{h} = \rho ghv \log_e \frac{h_2}{h_1}.$$

If for ρgh we write p, and for $\frac{h_2}{h_1}$ write its equal, v_1/v_2, we have $W = p\,v \log \frac{v_1}{v_2}$ the accepted canonic form, for the maximum work obtainable through *diluting* a solution between the limits above indicated, v_1 and v_2.

Except as a verification we are not just now interested in the canonic form. Let us examine and analyze our results. In the first place it may be noted from the selected order of the limits, since $h_1 > h_2$, that work done *on the* solution is positive; work done by the solution, negative.

It is well also to note that the text-books also give the osmotic pressure $P = \rho gh$ or an equivalent expression; but this result is obtained only by assuming the validity of the application of van't Hoff's form of the general gas equation.

From the fact that pv, or $P\,V$, represents the maximum work, the maximum work must be proportional to P; and since the maximum, or limiting, value of P was always understood and used it would not fail to give consistent results. But from the present method of deriving the expression for the maximum work there is as yet no evidence to show that ρgh represents a pressure beyond the fact that in mechanics ρgh represents the pressure per unit area of a fluid column.

In the van't Hoff equation there was always an ambiguity attached to the term "volume." The present method leaves no doubt as to the volume represented but leaves ρgh ambiguous. What does it mean? Since $\rho v = m$, the full expression ρghv may be written $W = mgh$, the work in dyne-centimeters, or foot poundals, or work expressed in terms of displacement against resistance. Since work, energy, can always be expressed in terms of Fs or P V and *must* be expressed in some such way in order to be intelligible, or comparable, we may reason that since W and v are definite physical quantities, ρgh must represent a definite physical pressure. It is numerically equal to what has been called osmotic pressure and *is* a physical pressure because it represents the ratio between work and volume. Let us endeavor to interpret it without introducing any hypotheses as to the constitution of matter or making any assumptions not warranted by experimental and dynamic considerations.

It was noted above that the maximum work obtainable by dissolving a solid in a liquid under certain specified conditions, *was just sufficient to lift the entire mass of the pure solvent to a height which would serve to equilibrate the vapor pressures of the solution and pure solvent at the point of contact.* This is important and must be borne in mind in connection with the development of the subject. In the ideal experiment detailed in the former paper, the *vapor* lifted itself just that height. This fact, in connection with the other fact, that no evidence of activity on the part of the solute was traceable, suggests an assumption, purely dynamic, which will be justified if it leads to results experimentally verifiable.

Since in the derivation of the maximum work we found that the energy came from the solvent, we might assume that all the energy taking part in the work is proportional to the amount of solvent in the solution. This is evidently the case from $pv = W$ and in such cases as we have been considering where the work is done by rising vapor, but is not so evident in the osmotic cell or during the passage of the solvent through a semi-permeable wall. Now Planck[1] shows that in the case of gases the pressure of the gas that does not pass through the semi-permeable wall has no influence, whatever its pressure, on the equilibrating pressures of the gas that *can* pass through. Therefore, whatever the pressure of the dissolved substance, we may neglect it and state the conditions of equilibrium as though it were absent. This of course is assuming the above law to hold for liquids. Let us consider the osmotic cell with an open manometer tube just for the sake of visualizing the operation. We may also imagine it under a cover with the air exhausted.

The assumption that all the energy engaged in doing work comes from the solvent is equivalent to assuming that the ratio of the energy per unit volumes of the liquid to vapor is the same for both solution and pure solvent. The condition of equilibrium then, since the liquid can pass through the semi-permeable wall, will be given by assuming that since energies are proportional to pressures,

$$\frac{p_1}{P_1} = \frac{p_2}{P_2} \text{ or } \frac{p_1}{p_2} = \frac{P_1}{P_2}$$

where p_1 is the vapor pressure of the pure solvent, P_1 the inwardly directed pressure of the pure liquid solvent, p_2 the vapor pressure of the solution and P_2 the outwardly directed pressure of the liquid solution,—the effect at any point of contact being assumed proportional to amount of material acting at that point or element of area. We may write these ratios

$$\frac{p_1 - p_2}{p_1} = \frac{P_1 - P_2}{P_1}$$

which will be constant for a given concentration but will vary with the concentration. Therefore $p_1 - p_2 = Cp_1$. $P_1 - P_2 = CP_1$. But $p_1 - p_2$ being a difference in vapor pressures, and $P_1 - P_2$ being a difference in liquid pressures due to solvent only, we may write

$$p_1 - p_2 = \rho' gh \text{ and } P_1 - P_2 = \rho gh \text{ (osmotic pressure)}$$

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[1] Treatise on Thermodynamics. Translated by Ogg, p. 210.

where ρ' is the average density of the vapor of the pure solvent and ρ is the density of the liquid solvent and h is the height necessary to equilibrate the pressures whether liquid or vapor. Eliminating gh we have

$$\frac{p_1 - p_2}{\rho'} = \frac{P_1 - P_2}{\rho}$$

or regarding the differences as very small and integrating, from o to p, or P, we get $\frac{dp}{\rho'} = \frac{dP}{\rho} \therefore \frac{p}{\rho'} = \frac{P}{\rho}$ or, $pv = PV = RT$ by the gas laws, on substituting volumes to replace densities.

It may be noticed that the key to the above deduction turns on the assumption that the two opposed pressures are proportional to the amount of material of the solvent, whether liquid or vapor, acting in opposite directions on opposite sides of the areas where they are to be equilibrated. This is assumed to apply to the non-homogeneous layer between the vapors as well as to the semi-permeable wall between the liquids. The assumption is seen to be the simplest possible required to explain the dynamic facts, and was suggested by the height of the liquid column representing the maximum work. Why should equilibrium be established at just that height? Evidently because the energy concerned was exactly proportional to the quantity of substance available to produce the observed action.

It should be observed that no molecular or atomic or corpuscular constitution of matter was assumed, but purely dynamic relations. The kinetic theory assures us that the activity of the molecules of a substance depends upon the absolute temperature alone and is independent of the liquid or vapor state. The result of the above deduction really depends on this being true; the result may be taken as a corroboration.

There is an entirely different method of deducing the value of ρgh considered as a pressure, and, in some respects, is preferable since the deduction does not depend upon osmosis but does depend upon the possibility of separating by filtration the constituents of a solution. In fact the equilibrium method above given just occurred to me while writing; the filtration method was originally in mind and accounts for the phraseology of the first part of the paper.

On the assumption that we are dealing only with what might be called a mechanical, or physical, solution of a solid in a liquid unaccompanied by chemical action by which heat is liberated, $pv = W$ represents the total *mechanical* work, or free energy, available by completely dissolving a given quantity of solid in the volume v of solvent. When no heat or other energy is received from outside sources, the heat, whether work be done or not, will be taken from the solvent. If the operation be conducted isothermally, heat will be taken from the surroundings whether mechanical work be done or not. But the fact that work *may be done and transformed* into heat while the volume changes from v_1 to v_2, compels us to conclude that in either case, whether work has been done or not, since initial and final states are the same if conducted isothermally, then if it be possible by any mechanical means whatever to restore the solution to its original state after dilution, the mechanical work necessary must be greater, or in the limit equal to, the maximum work possible to be obtained by dilution. To suppose that less than this minimum be sufficient, is equivalent to supposing that unlimited work can be done by means of the heat of the surroundings. This possibility is denied by the second law of thermodynamics. Therefore, if W is the maximum work possible to be obtained by diluting a solution from the volme v_1 to volume v_2 and the process of restoration be one of filtration through any septum, the minimum work required cannot be less than

$$W = \int_{v_2}^{v_1} P\,dv = -\int_{v_2}^{v_2} p\,dv,$$

where P is the minimum filtration pressure necessary and dv the increment of volume swept through. During a state of equilibrium in the absence of mechanical motion, $P = -p$ since the two pressures are oppositely directed. Here no hypothesis need to be offered to account for the resistance to filtration, although the mind may eagerly seek an explanation. This filtration pressure answers all the requirements necessary to satisfy the equation

$$W = pghv \log \frac{v_1}{v_2}.$$

It is entirely independent of any hypothesis as to the constitution of matter and of any phenomena of osmosis except those arising from interacting vapors and liquids, and might have been deduced had Pfeffer's experiment never been observed. Professor Ostwald refers to an experiment,[1] without, however, giving any details in which the filtration pressure above referred to is demonstrated experimentally. This, I take it, is the *fundamental fact* which may be deduced from general dynamic principles and demonstrated experimentally. Since it is entirely independent of any hypothesis it furnishes a rational dynamic basis for a theory of solutions. From the fundamental equation $W = \int P\,dv$ we obtain at once a rational dynamic definition of filtration pressure above referred to in the form $P = \frac{dW}{dv}$ or the work per unit volume of solvent which must be done in separating solute and solvent. Osmotic pressure is, then, dynamically considered, the hydrostatic pressure arising through osmosis which just balances the filtration pressure just defined. It is evident that pressure arising from the osmotic process cannot exceed this limiting filtration value which, if exceeded, will reverse the process that produced it. This limiting value has been used under the name of osmotic pressure and has consequently given consistent dynamic results; but physically, osmotic pressure has no significance or existence except as the hydrostatic pressure produced by osmosis through semi-permeable septa. The fanciful idea that there is an occult kind of osmotic pressure

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[1] Ostwald: Principles of Inorganic Chemistry. Translated by Findlay, p. 650.

"that would break the glass if it reached it," arises from an overstrained analogy.

There is, however, yet another aspect to this value of P, in the equation $pv = PV$. This equation was derived from considerations of static equilibrium based on the kinetic equilibrium between the active masses of solvent whether liquid or vapor. From it we should be able to obtain the "intrinsic pressure," as it is called, of the liquid solvent. Two cases by two different methods will suffice.

Let us take 1 gm of water at 0° C. From tables we find that its pressure in the vapor state is $\frac{.46}{76}$ atm. and its volume 204 liters, or 204000 cc. Since V in the liquid state is 1 cc we have $P = pv = \frac{.46}{76} \times 204000 = 1235$ atmospheres. This does not mean that there is, during equilibrium, such a pressure actually existing, but that under certain circumstances *such a force would have to be reckoned with.* In terms of molecules, it means merely that in the liquid state, at that temperature, we have 1235 times as many molecules acting through a given element of area as we find in the vapor state. In terms of mass-action there is 1235 times as much mass concerned in the liquid state as compared with the vapor state under standard conditions.

This value, 1200 atmospheres, for the intrinsic pressure of water at 0° C, may be corroborated by substituting experimental values in the equation expressing the conditions of equilibrium between vapor and liquid and liquid solution,

$$\frac{p_1 - p_2}{p_1} = \frac{P_1 - P_2}{P_1}.$$

In Sentner's Physical Chemistry,[1] p. 105, is quoted an experiment from Smits where the following numerical values are given for an aqueous sugar solution at 0° C:

$$\frac{0.00705}{4.62} = \frac{29.0358 \times 18}{1000 \times 342}.$$

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[1] Outlines of Physical Chemistry, G. Sentner, 1908.

Here $p_1 = 4.62$ and $p_1 - p_2 = 0.00705$. Calculating $P_1 - P_2$, the osmotic pressure, from the above data, we get $P_1 - P_2 = 1.9$ atmospheres. Therefore P_1, the intrinsic pressure, $= 1240$ atm.

An example ready at hand taken from Nernst[1] will illustrate the influence of molecular weight on intrinsic pressure of a liquid in the case of benzene at 80° C. Here $p_1 - p_2 = 9.26$, $p_1 = 751.86$. In like manner, as above, we find the osmotic pressure $P_1 - P_2$ of benzene at 80° C under the given conditions to be 3.75 atmospheres (Nernst gets 3.78 instead of 3.75 through using p_2 for p_1). By substitution we get

$$\frac{9.26}{751.86} = \frac{3.75}{P_1}.$$

where P_1 is the intrinsic pressure of benzene at 80° C. $\therefore P_1 = 304$ atmospheres.

Summary and Conclusion

Attention has been called to certain inconsistencies between the experimental facts and the nomenclature arising from the theory that osmotic pressure is a direct function, or property, of the solute. I have shown how a number of fundamental facts may be interpreted without reference to osmosis at all,—merely as activities of the solvent brought into play by the presence of a foreign substance. In addition, I have shown how a new and important set of facts is brought to light by the application of the principle of mass-action to deriving an equation of equilibrium between the vapor and liquid states having the simple form

$$\frac{p_1 - p_2}{p_1} = \frac{P_1 - P_2}{P_1}.$$

This equation affords a simple means of determining the intrinsic pressure of a liquid by comparatively simple and direct experimental measurements. It is more fundamental than the general gas (van't Hoff's) equation for that can

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[1] Nernst: Theoretical Chemistry, 4th ed. Translated by Lehfeldt, p. 138.

readily be derived from it as shown in the text. By a direct measurement of vapor pressure and osmotic (or filtration) pressure, without reference to the number of molecules concerned, the intrinsic pressure of a liquid solvent may be determined.

In the light of all the evidence adduced, can there be longer any reasonable doubt that the present theory of osmotic pressure is open to revision?

State College, Pa.,
Jan. 10, 1910

CONTRIBUTION TO THE THEORY OF PERIODIC REACTIONS

BY ALFRED J. LOTKA

It lies in the nature of the law of mass-action that every simple (isothermal) reaction approaches its equilibrium asymptotically. In systems, on the other hand, in which several reactions go on simultaneously, the possibility of other modes of approach to equilibrium (or to a steady state) arises. A case of this kind, which presents some features of special interest, is treated below.

Consider the following series of consecutive reactions, each of which we will suppose to be (practically) irreversible:

1. $a \longrightarrow A$
2. $A \longrightarrow B$
3. $B \longrightarrow C.$

It is to be understood that the capitals refer to substances in the state of "dilute" gas or solution, while the small letter *a* denotes a saturated vapor or solution in contact with its condensed phase. It is further to be assumed that the conversion of *a* into A is slow as compared with the establishment of equilibrium between the condensed phase and its vapor or solution, so that the concentration of the latter may be regarded as practically constant, and diffusion effects may be left out of consideration.

Then the equations expressing the rate of change of the concentrations of the substances A and B are:

$$\frac{dc_A}{dt} = H - k_1 c_A \qquad (1)$$

$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B \qquad (2)$$

where H, k_1 and k_2 are constants, and the symbols c_A c_B have the usual meaning.

Now let the substance B influence autocatalytically its own rate of formation, and let us further assume that this influence follows the simplest possible law, so that we can write for k_1 in (1):

$$k_1 = kc_B \qquad (3)$$

Equations (1) and (2) then become

$$\frac{dc_A}{dt} = H - kc_Ac_B \qquad (4)$$

$$\frac{dc_B}{dt} = kc_Ac_B - k_2c_B \qquad (5)$$

The complete solution of equations (4) and (5), giving the entire course of the reaction, presents difficulties. Of the final stages in the process, however, which are of special interest, we can very easily obtain a representation.

Let us first of all simplify equations (4) and (5) by changing the scale of time reckoning, and by fusing some of the constants. We will put

$$T = kt \qquad (6)$$

$$h = \frac{H}{k} \qquad (7)$$

$$K = \frac{k_2}{k} \qquad (8)$$

Making these substitutions in equations (4) and (5), we have

$$\frac{dc_A}{dT} = h - c_Ac_B \qquad (9)$$

$$\frac{dc_B}{dT} = (c_A - K)c_B \qquad (10)$$

A further transformation is suggested by the reflection that the system will ultimately settle down to a steady state when

$$\frac{dc_A}{dT} = h - c_Ac_B = 0 \qquad (11)$$

$$\frac{dc_B}{dT} = (c_A - K)c_B = 0 \qquad (12)$$

i. e., when

$$c_A = K \tag{13}$$

$$c_A c_B = K c_B = h \tag{14}$$

$$c_B = \frac{h}{K} = L \tag{15}$$

Instead of reckoning with absolute concentrations c_A c_B, let us then reckon with the excess

$$x = c_A - K \tag{16}$$

$$y = c_B - L \tag{17}$$

of the existing over the ultimate concentrations. Introducing these in equations (9) and (10) we thus finally obtain

$$-\frac{dx}{dT} = xy + Ky + Lx \tag{18}$$

$$\frac{dy}{dT} = xy + Lx \tag{19}$$

Now in the last stages of the process, when the steady state is nearly reached, x and y are both very small, and we can neglect the product xy. Equations (18) and (19) then finally by elimination of y and x respectively, lead to the differential equations of the second order

$$\frac{d^2x}{dT^2} + L\frac{dx}{dT} + KLx = 0 \tag{20}$$

$$\frac{d^2y}{dT^2} + L\frac{dy}{dT} + KLy = 0 \tag{21}$$

in which we recognize the well-known "damped vibration" type. The reaction is periodic provided that

$$L < 4K.$$

The solution of (20) and (21) in that case, written in the simplest form, is

$$y = y_0\, e^{-pT} \cos qT \tag{23}$$

$$x = \frac{1}{L}\frac{dy}{dT} = -z y_0 e^{-pT} \sin (\varphi + qT) \tag{24}$$

$$= \quad M e^{-pT} \sin (\varphi + qT) \tag{25}$$

where

$$p = \frac{L}{2} \tag{26}$$

$$q = \frac{\sqrt{4KL - L^2}}{2} \tag{27}$$

$$Lz = \sqrt{p^2 + q^2} \tag{28}$$

$$\sin \varphi = \frac{p}{\sqrt{p^2 + q^2}} \tag{29}$$

$$\cos \varphi = \frac{q}{\sqrt{p^2 + q^2}} \tag{30}$$

The constant y_0 is the value of y at time $T = 0$, as is evident from (23). The origin of time is arbitrarily so chosen that equation (23) contains no sine term.

No reaction is known which follows the above law, and as a matter of fact the case here considered was suggested by the consideration of matters lying outside the field of physical chemistry.[1] It seems interesting, however, also from a purely chemical point of view, to note that in a system in which consecutive reactions take place in the presence of an autocatalytic decomposition-product, we have the requisite conditions for the occurrence of a "periodic" process. And in the simple case here considered we have two consecutive reactions of equal period, each following the law of "damped vibrations," and the one lagging behind the other by an angle depending on certain coefficients characteristic of the reactions, but independent of the initial concentrations.

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[1] The growth of living matter is obviously autocatalytic at least in form. It has been shown by T. Brailsford Robertson (Arch. f. Entwickelungsmech. d. Organismen, 1908, p. 581) that the growth of man and other organisms can be represented with close approximation as the resultant of two components, each following the law of a reversible monomolecular autocatalytic reaction. The rather close agreement of the calculated with the observed values seems rather surprising. For the circumstances which ultimately bring the autocatalytic reaction to a standstill are the decreasing concentration of the substances entering into the reaction, and the increasing concentration of the reaction-products. It is not obvious what are the analogous conditions (if any) which set a limit upon the mass of the full-grown organism.

NEW BOOKS

General Inorganic Chemistry. *By Charles Baskerville. 13 × 19 cm; pp. vii + 357. Boston: D. C. Heath and Co., 1909. Price: bound, $1.50.*—In the preface the author says:

"The value of a text-book depends upon its teachableness. The teachableness of a book or method, however, depends also upon the teacher, his spirit and the conscientious interpretation of the serious but opportune responsibility that he enjoys. What is contained within these pages has been tried with a large number of students in general chemistry through several years. Satisfactory results have been obtained. That is why it is now offered to others.

"The author has unhesitatingly used every source of information and all devices suggested by other teachers which appealed to him, to make the work effective. The material has been so arranged as to accomplish the most in the least time. Much has been omitted, and the temptation to omit more has been resisted with difficulty.

"A knowledge of elementary physics has been assumed, but where the border territory of chemical physics has been entered, sufficient of the general principles involved has been recapitulated, but without detail, to present a logical sequence. No effort has been made to get away from the conception of atoms, yet enough of the modern theories of physical chemistry has been presented to show the student the entrancing fields of interest to the specialist and the scientific methods he makes use of therein. A distinct effort has been made to keep theory and fact in proper proportion, yet some very definite statements are made; but it is assumed that the teacher will explain that some of the laws are true only within limits.

"Many historical errors handed down through generations of texts have been corrected. Many methods of preparation used by the al-chemist and given in texts these days have been omitted. As a rule, only methods which illustrate principles have been given."

After an introductory chapter and one on the chemical elements, the author takes up hydrogen, oxygen and ozone. Then come three chapters on water, one on the halogens and one on the halogen acids. The alkali metals are discussed in chapter ten and then we have two chapters dealing with nitrogen, ammonia, the atmosphere, the noble gases, liquefaction of gases, etc. Three chapters on carbon and the carbon derivatives come next and then one on the periodic law. After that we have the negative series of groups VI and V, the positive series of group II, groups III and IV, the negative series of groups V, VI, and VII. Radium and radioactive phenomena naturally have a chapter to themselves and then we have one on the iron metals and one on the platinum metals. One chapter is given up to the hydrides and two to the halides. Next we have a chapter on the determination of molecular weights, and one on the theory of electrolytic dissociation. There are then seventeen chapters on the oxides, sulphides, carbonates and nitrates. The last three chapters are on the carbides and nitrides, the compounds of carbon and nitrogen, and alloys.

This is not the usual arrangement but it is perhaps none the worse on that account. Considering compounds with reference to acid radicals instead of basic radicals has the advantage that it brings the first year work more in line with the second year work in qualitative analysis. The book is written in a free and easy style and the author has taken pains to introduce miscellaneous information on: the amount of water evaporated by an acre of green plants; the question of water supply; the action of filter beds; the fixation of nitrogen by leguminous plants; the amount of sulphuric acid from the chimneys of New York; the caking of table salt; photography, etc.

The reviewer doubts the statement, p. 177, that nickel plating is usually done from a cyanide solution. The account of fractional crystallization, p. 164, applies only to cases in which solid solutions are formed. The author has generalized from his own special experiences. It is not clear what is meant by the statement, p. 252, that "silica melts transiently at + 1800°."

The reviewer objects strongly to the second sentence of the following quotation, p. 9: "Compounds are composed of simple substances and always in definite fixed proportions, which fact gives us the *law of constancy of composition or definite proportions*. We know of no exceptions to this law, and we know the composition of many tens of thousands of compounds." The reason that we find no exceptions is that we define a compound as a substance of constant composition, and we refuse to call any other substances compounds. So long as we do this, there can be no exceptions. Curiously enough, the author is quite clear as to this when it comes to the definition of an element. On p. 16, he says: "With the final establishment of the law of the conservation of matter by Lavoisier in the last quarter of the eighteenth century, the idea (of the transmutation of the elements) appeared to be doomed from an experimental point of view. Within the past decade a new element, radium, has been discovered. Under certain conditions it changes into another element, helium. The transmutation of the elements has been experimentally demonstrated. While these statements appear to be contradictory, in fact they are not, when the terms used are clearly understood. By our definition, radium cannot be an element, because its molecule breaks up into something else, yet it has a recognized place in the table of elements. This latter fact is due to an agreement among chemists to recognize a substance as an element which, under proper conditions, exhibits a spectrum showing characteristic lines possessed by no other element and possesses a definite combining weight. Radium satisfies these two requirements and constitutes an exception to the general proposition of the consistency of atoms in an elementary molecule. If we retain the term *element*, and there is no indication of its being discarded soon, its definition must be broadened."

The only reason why radium is an exception is because we have three distinct tests for an element according to Baskerville. If we had only one and stuck to it, we should have no exceptions. That is what we do in the case of compounds and what some people still do in the case of elements.

The author is a bit lax in his use of the phrase 'chemical affinity.' On p. 6 it means chemical energy while on p. 105 it does not seem to mean anything. Neither use of the phrase is to be commended. It is also inaccurate to say that we cannot measure any case of chemical affinity accurately because chemical actions are always accompanied by heat effects, often by electricity as well, and frequently by light, and even sound.

The reviewer was pleased to see that Kahlenberg's recent work was referred to under dialysis, p. 238.

This volume is well worth a careful consideration by teachers because it presents an entirely different point of view from that taken by Alexander Smith in his excellent book. In the latter, the amount of what is usually called physical chemistry is extraordinarily large. In Baskerville's book it is relatively small. There is a reference to osmosis and to the phase rule, and there is a chapter on electrolytic dissociation. That is really about all. The time-honored fetich of the solubility product is not mentioned so far as the reviewer has noticed. There is practically nothing on the mass law or on the reaction velocity. Is there a winning type and, if so, which of these books comes the nearer to it? It is an interesting question which the reviewer is quite unable to answer, owing to his lack of experience in the teaching of freshmen. It seems probable, however, that the difference between the two books depends in part on the amount of time spent in recitation work and on the ratio of instructors to students. The larger these two factors are, the more ground can be covered and consequently the more physical chemistry can be taught in the first year. Whether these relative conditions actually exist at the University of Chicago and at the College of the City of New York is a matter on which the reviewer has no information. *Wilder D. Bancroft*

Histoire du Développement de la Chemie. *Depuis Lavoisier jusqu'à nos Jours. By A. Ladenburg. Traduit sur la 4e édition allemande par A Corvisy. 16 × 25 cm; pp. ii + 388. Paris: A. Hermann and Fils, 1909. Price: paper, 15 francs.*—The German edition has been reviewed (12, 293) and it is a pleasure to welcome the French translation. The author's view of the advantages of a study of the historical development, p. 3, are worth quoting.

"In addition to the real advantage, that the study of the history of the science enables us to understand the present status, there is one which is of much more value to the student, that we are able to form a correct opinion of the theories. If we examine the past, we see how opinions have changed. We see that hypotheses which appear to be established firmly will some day be given up. We perceive that we live in a period of transition, that the ideas we hold are merely the precursors of future ideas, and that they will not long satisfy the needs of science. From our historical studies we learn that the laws which we formulate are not intangible truths or sacred revelations and that they can only be considered as a provisional statement of facts collected in a methodical way and said to be explained by the laws. We recognize that these laws have not come forth suddenly from the brain of a single man, as Minerva sprang from the head of Jupiter. The ideas on which they rest have developed slowly and the facts of which they are the synthesis have been obtained by the work of many before the law describing them was formulated by somebody or perhaps by several people at the same time. Further, the study of history tends to weaken our faith in the authority of the masters, which is harmful to science since it checks individual originality. It teaches us, on the other hand, that theories are essential to progress. Though the substance of science lies in the experimental data, its real intellectual importance is obtained only when the isolated observations are brought under one head by a hypothesis, so that really the present development of a science depends much more on the method of explaining the observations than on the observations themselves."

After discussing the conflict between Berthollet and Proust, the author goes on as follows:

"I have treated this subject at some length because I consider it very important. We are dealing with a general proposition which is one of the foundations of our theoretical concepts. It makes a distinction between mixtures and compounds. The laws of chemistry apply only to the latter and not to mixtures. It is therefore necessary in many cases to know with which class of substances we are dealing; but what is to be our criterion? You will read in the elementary books that compounds are homogeneous while mixtures can very often be decomposed into their constituents by mechanical means. It is also stated that in compounds the properties of the initial substances have disappeared while they are preserved in mixtures. Finally, the constancy of the proportions is given as a distinctive characteristic and I should like to say a word in regard to this. There are instances where mixtures cannot be distinguished from compounds by their general behavior; only an analysis will settle the question. We prepare the substance by different methods if possible and we see whether it always has the same composition. We have thus returned to the question discussed by Berthollet and by Proust. The first believed that compounds can have varying compositions while the second claimed that substances can combine only according to a limited number of definite proportions. We *define* a substance as a compound when the ratio of the constituents is constant.

"I do not know whether you have grasped the differences between these two conceptions. It is only when one has to decide whether one has a mixture or a compound, that one appreciates the full importance of the question. We still lack the general test, applicable to all cases, which Berthollet demanded of Proust. Of course we have some criteria, such as crystallization, the constancy of the melting point of a solid or of the boiling point of a liquid; but these are not enough. I have only to mention the phenomena of isomorphism to remind you that mixtures may also crystallize. Roscoe has shown that solutions of hydrochloric acid, hydriodic acid, etc., in water are really only mixtures and yet you know that they have a constant boiling point. To distinguish between mixtures and compounds is one of the most difficult and most important of problems and it is one to which sufficient attention has often not been paid. If you study chemical memoirs, you will soon see that many errors have resulted from this negligence. Often, people have written formulas for substances and have based theoretical conclusions on the existence of these substances before they had proved that these really were compounds."

On p. 327 the author says that the importance of the phase rule has sometimes been exaggerated. Perhaps he would have modified this statement if he had realized that the phase rule gives the criterion for which he has sought in vain.

On p. 299, a misprint makes the author say that the theory of valence has been of great value in inorganic chemistry when he really meant the opposite of this.

The most satisfactory portions of this excellent book are those dealing with the development of organic chemistry. The work of Liebig, Dumas, Laurent, Gerhardt and Williamson is presented with great clearness. One has only to read the two prefaces, written in 1869 and 1907 respectively, to see what it is that appeals most to the author. *Wilder D. Bancroft*

Traité de Physique. *By O. D. Chwolson. Ouvrage traduit sur les Éditions russe et allemande par E. Davaux. Édition revue et considérablement augmentée par l'auteur, suivie de Notes sur la Physique théorique par E. Cosserat et F. Cosserat. Tome deuxième, quatrième fascicule. 16 × 25 cm; pp. 641–1188. Paris: A. Hermann. 1909. Price: paper, 17 francs.*—In this volume the author treats the diffraction, double refraction and polarization of light. At first sight there might seem to be little in this which would appeal to the chemist; but a closer examination reveals such topics as the rotation of the plane of polarized light, the color of crystals under crossed nicols; the phenomena of flowing and of liquid crystals; the behavior of salts in flexible films of gelatine, etc.

The following quotation in regard to fluorescence, p. 837, is distinctly interesting. "When discussing the phenomena of fluorescence, we have seen that the light sent out in all directions by fluorescing substances is generated in the interior of these substances when they are illuminated and especially when the exciting light is rich in short wave lengths. If a fluorescent substance shows double refraction, it is clear that the rays which it emits must be polarized in the two planes. One might expect that the both polarized rays would be of the same intensity provided the substance was not dichroic. Nevertheless, Grailich discovered in 1858 that sometimes the rays were polarized more completely in one plane than in the plane perpendicular to it. At the spot *where the fluorescence is formed in the interior of the crystal*, a vibration takes place more readily in a given direction than in the one perpendicular to it."

There is another paragraph in connection with flowing crystals, p. 901, which must be quoted without translation because the meaning is obscure:

"Mais, avant tout, les forces observées dans les organismes (force musculaire, mouvement ciliaire, formes pseudopodes, courants protoplasmiques, etc.) paraissent toutes se ramener aussi a celles observées dans les cristaux liquides et solides, car elles sont, d'après la découverts de Th. W. Engelmann, toujours liées a l'existence de substances biréfringentes, qui, pendant l'action de la force, en suite de transformations chimiques, changent leur biréfringence, ou la perdent, et qui prennent naissance par le travail effectué directement aux dépens de l'energie chimique disparue (sans perte, comme dans la transformation de l'energie chimique en chaleur, dans une machine à vapeur par exemple). Il n'y a qu'une force qui puisse produire une telle circulation d'énergie, savoir la force morphologique des cristaux liquides et solides et des substances anisotropes amorphes analogues (tendons, nerfs, etc.). Le travail que cette force peut accomplir dans les transformations polymorphiques ou chimiques du cristal, c'est-a-dire dans tout changement des molécules, est déterminé directement par ce changement; cela ressort de ce que si l'action de la force est. empêchée, il en est de même de la transformation ou du phénomène chimique, ce qui peut se faire par une force suffisamment grande exactement opposée. Une recherche plus précise pourrait conduire a la construction de moteurs, qui non seulement utiliseraient l'énergie chimique aussi avantageusement qu'on le fait jusqu'ici, mais posséderaient en outre un poids tres petit. Elle pourrait aussi conduire a éclaircir le role de *l'ame* sur l'organisme."

The last half of the volume is given up to a discussion of the theory of deformation by E. Cosserat and F. Cosserat. It is doubtful whether many chemists will be able to do anything with the mathematics in this section.

Wilder D. Bancroft

Les Découvertes modernes en Physique. *By O. Manville. Première partie: Électricité et matière. Deuxième partie: Les ions et les électrons dans la théorie des phénomenès physiques—La matière et l'ether. Deuxième Édition revue et augmentée. 14 × 22 cm; pp. ii + 463. Paris: A. Hermann, 1909. Price: paper, 8 francs.*—The book is divided into two parts, which are practically our old friends theory and application. The first part deals with the fundamental experiments on electricity and matter and with the evolution of the ideas which have lead up to the conception of an electron. The subject is treated under the headings: electric discharge through liquids; electric discharge through gases; ionization of gases; the electron; introduction to the electronic theory of matter; induced radioactivity; electronic theory of matter.

The second half of the book deals with the part played by ions and electrons in the theory of physical phenomena. The subject is treated under the headings: ionized liquid media; ionized gaseous media; non-ionized gaseous media; ionized solid media; matter and ether.

The author calls attention to an extraordinary number of minor misprints and the reviewer has noted a good many mis-statements which are due to ignorance and not to defective reading of proof. Granting all that, the fact remains that the author has undertaken a very difficult task and that he has produced a readable and a suggestive book. Take the chapters on magnetism as a single instance. Anybody really working at the subject would have to go back to the original sources of course; but the author gives a pretty good comparative statement of the different points of view. It is so good that it brings out with great clearness, though quite unconsciously, that the present theories of magnetism are written by physicists for physicists. Until some chemist has worked out a better theory, it is not certain that a chemist could do better than the physicists; but certainly no chemist would treat inversion points with the airy disregard which characterizes the physicists. *W. D. B.*

OSMOTIC EXPERIMENTS WITH COLLODION MEMBRANES

BY J. HOWARD MATHEWS

Because of the results obtained by Kahlenberg[1] and others with membranes and solvents other than those which have been so extensively studied since the time of the classical experiments of Pfeffer—results which are quite opposed to the generally accepted views of the nature of the process of osmosis—it seemed desirable to extend the study to still other membranes, solvents and solutes. From the results obtained by Kahlenberg it would seem that osmotic pressures are merely equilibrium pressures, and that in the process of osmosis there is always a current in both directions, though in some cases the major current is so great in comparison that the minor current becomes almost insignificant. In other words, there is in reality no such thing as a truly semipermeable membrane. The experiments made seem to indicate that whether passage of the solvent through the membrane takes place or not is, in the first place, dependent upon the specific nature of the membrane and solvent employed and, secondly, upon the relative attraction between membrane and solvent and solute and solvent. The solvent must be of such nature that it is taken up by the membrane: it must be capable of wetting and permeating it. The solution bathing the other side of the membrane must have an attraction for the solvent greater than that between membrane and solvent, the result being that the solvent is extracted from the membrane by the solution and more solvent is thereupon taken up by the membrane, to be again extracted in turn. We then have a continual process of transfer of solvent through the membrane and into the solution. At the same time some of the solution permeates the membrane and passes out into the pure solvent, so that we have a current in both directions. In every case so far studied a small

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[1] Jour. Phys. Chem., 10, 141 (1906).

quantity, at least, of the solute has always been found to pass through the membrane. This passage of solute through the membrane is not in any way due to imperfections in the membrane, but is a part of the osmotic process itself.

Collodion is a substance quite different chemically from the membranes ordinarily used, and it lends itself nicely to such qualitative experiments as were here desired. It is essentially a nitro-cellulose (of uncertain structure) in solution in a mixture of ether (about 75 percent) and alcohol (about 25 percent) The membranes were prepared by pouring out a layer of collodion on the surface of mercury. When sufficiently dry to be handled, but still quite moist on the lower side, the membrane was picked off the surface of the mercury, stretched over the end of a thistle tube and securely tied with strong thread. The edges were then trimmed down smooth and painted with fresh collodion. When dry the membrane so formed was very tight and exceedingly thin: and, if carefully made, gave no evidence of mechanical leaks. The membranes so made varied from 0.002 inch to 0.004 inch in thickness. Their tensile strength is remarkably great. They are so strong that they can scarcely be broken with the hands. After preparation, the membranes were placed over a large steam coil and left to dry for several days at least, in order to dry out all the ether and alcohol.

If the membrane exerts a selective action in such a way that only those liquids can go through which themselves have an affinity for the material composing the membrane, we should expect that such liquids as carbon bisulphide, carbon tetrachloride, benzene, the paraffine hydrocarbons, etc., which have no solvent action on the collodion, would not pass through the membrane; while, on the other hand, such liquids as are somewhat similar in chemical character to the membrane would be able to pass through it. Since collodion is a hydroxyl bearing body we should naturally expect that liquids containing hydroxyl groups, such as alcohols, would be imbibed by it;[1] and, on the other hand,

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[1] Compare, Kahlenberg, Vice-presidential address, Science, Jan. 14, 1910.

that the hydrocarbons would not. How far this conclusion is verified will be seen from the following experiments.

Ethyl Alcohol and Camphor.—Ethyl alcohol (96 percent) does not dissolve the membrane at once but it does wet it and exerts a slow solvent action upon it. A block of pure camphor, cut in the shape of a cube with sharp edges, was placed upon a collodion membrane. The lower side of the latter was bathed with 96 percent alcohol. Within a few minutes it was observed that the surface of the camphor appeared wet and within a half hour the sharp edges of the block had become dull and rounded. At the end of two or three hours there was a strong alcoholic solution of camphor within the osmometer and this kept on increasing in quantity for a couple of days at the end of which time the solid block had entirely disappeared, only the solution remaining. A considerable amount of camphor was thus taken through the membrane into the outside compartment, as was to be expected.[1]

Mercuric Chloride in Alcohol.—Mercuric chloride is quite soluble in alcohol. A solution of mercuric chloride in 96 percent alcohol was placed within an osmometer and 96 percent alcohol placed outside. Within a few minutes the level of the solution in the osmometer began to rise and continued to do so for several hours, until a total rise of about 20 cm had been attained, whereupon the level sank again. The outer liquid was tested and found to contain a considerable quantity of mercuric chloride. After standing a week, the level within was 2.5 cm below the initial point, and the membrane was greatly distended.

In all experiments where diffusion through the membrane takes place rapidly, the minor current, *i. e.*, the passage of the solute through the membrane, is very much in evidence, and *vice versa.* In all cases where it takes place rapidly, the membrane becomes weakened and distended. It is also found, invariably as far as we know, that after the maximum

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[1] Compare a similar experiment by Kahlenberg (Jour. Phys. Chem., 10, 170 (1906)), who used a rubber membrane.

pressure has been attained the level begins to sink again. No adequate explanation of this phenomenon has yet been advanced. It is likely, however, that it is due to some change in the membrane caused by the passage of the solvent through it. Possibly it has a greater bearing on the process than we realize.

Ethyl Alcohol plus Iodine, and Carbon Bisulphide.—Iodine is considerably more soluble in carbon bisulphide than in ethyl alcohol. Carbon bisulphide has no action upon collodion membranes. A solution of iodine in 96 percent ethyl alcohol was placed outside of the osmometer and pure redistilled carbon bisulphide placed within, the level being marked immediately. Three minutes thereafter, the carbon bisulphide, about 50 cc in volume, had become pink throughout, due to iodine. The intensity of color increased rapidly and the level of the carbon bisulphide began to rise, slowly. At the end of two days it had risen to a height of about 5 cm., and had then commenced to fall again. At the end of a week, the level within and without was the same, and the membrane was badly disintegrated by the alcohol.

The explanation of this experiment is not difficult. The carbon bisulphide was not imbibed by the membrane, while the alcohol was imbibed and carried iodine along with it. The carbon bisulphide, inside, being a better solvent for iodine than is alcohol, extracted it from the latter, whereupon the alcohol took up more iodine from the solution outside and this in turn was given up to the carbon bisulphide. We have here merely a partition experiment. The membrane impedes the process, the carbon bisulphide being insoluble in it. The alcohol, being capable of permeating the membrane, serves as a carrier of iodine through the membrane to the carbon bisulphide. Since the two solvents are miscible, and since carbon bisulphide has no action on the membrane, it was to be expected that alcohol would also pass out from the membrane into the carbon bisulphide, thus causing the level to rise.

At the close of the experiment, the membrane was removed and examined. It was found to be opalescent, due to iodine. Its thickness was the same as before the experiment (0.004 inch), and its strength seemed unimpaired.

Carbon bisulphide was shown to have no action on the membrane in the following way. Three disks cut from a dried membrane were carefully weighed. Their combined weight was 0.1173 grams, their combined area approximately 6 sq. in., and their individual thickness 0.002 of an inch. The circles were placed in a strong solution of iodine in carbon bisulphide, where they remained twelve hours. They were then removed, rinsed with ligroin, and quickly dried and weighed. They had gained in weight but 2 mg. In appearance they were quite unchanged, except for the opalescence caused by the iodine. The thickness remained the same, the edges were sharp, no sogginess was evident and their strength seemed unimpaired.

Since this these membranes have been bathed with carbon bisulphide for months without any determinable change. Iodine does not cause any deep-seated change in the nature of the membrane, as it does in the case of rubber, which it greatly weakens.

Carbon tetrachloride, chloroform, and the hydrocarbons are similar to carbon bisulphide in their inactivity toward collodion. Pyridine, nitrobenzene and the esters dissolve the membranes very quickly, and cannot be used. Ethyl benzoate has a peculiar action on collodion films. Instead of swelling up and softening, the film remains firm, but presents a ground glass appearance after the solvent has acted for a short time.

Carbon Tetrachloride plus Iodine, and Carbon Bisulphide.—Iodine is very soluble in both of these solvents. A solution of iodine in carbon tetrachloride was placed outside of an osmometer and pure carbon bisulphide placed within. In a short time the carbon bisulphide had become colored, but by no means as quickly as in the preceding experiment where alcohol was used. The level of the liquid rose for a short time, after which it began to fall again, slowly. After standing a week, the membrane was examined and found to be unaffected, to all appearances at least. Its strength was unimpaired and its thickness was 0.004 of an inch.

The converse of this experiment, *i. e.*, with the iodine dissolved in the carbon bisulphide with pure carbon tetrachloride on the other side, gave similar results, the iodine passing through the membrane in small amounts, though the membrane seems unaffected by either solvent. An exceedingly minute trace of alcohol remaining in the membrane would undoubtedly account for the passage of iodine through it. The membranes employed in this experiment were used a few days after making, and may not have been as dry as they should have been. Greater care in drying was thereafter used.

That iodine in itself is not capable of passing into the collodion without a suitable carrier is shown by the following experiment.

Crystals of iodine were placed upon the upper surface of a membrane whose lower surface was bathed with carbon bisulphide for several months. No iodine appeared in the carbon bisulphide, though the upper surface of the membrane showed a slight opalescence due to iodine deposited upon it.

The alcohols are capable of wetting collodion. The solvent action of methyl alcohol is so great that a membrane 0.004 inch thick lasts but a few seconds. The solvent effect decreases as we go higher in the series, *i. e.*, as the proportion of hydroxyl becomes less and less, and we more nearly approach the hydrocarbons, the latter class of substances being incapable of wetting collodion.

In 96 percent alcohol collodion is fairly permanent. A dried film was subjected to the action of 96 percent alcohol for a week, at the end of which time the membrane was quite firm but had bagged somewhat; however, it was still very strong. This membrane was thereupon put into absolute alcohol and it dissolved in a few minutes. It went into solution like gelatin into water. Fresh membranes, after careful drying, were put into absolute alcohol, and they went into solution in a short time. Anhydrous propyl alcohol has a slower action than ethyl alcohol, and isoamyl alcohol has so slow an action that the membrane seems almost unaffected after being submerged in it for at least six months, though the membrane is wetted. The following experiments were made with alcohols as solvents.

Copper Oleate plus Ethyl Alcohol, and Ethyl Alcohol.—A solution of copper oleate, which had been carefully dried, in 96 percent alcohol was placed inside an osmometer and 96 percent alcohol was placed on the outside. The level remained practically unchanged, and copper oleate went through the membrane freely. The membrane was found to be greatly weakened, and badly disintegrated.

Propyl Alcohol plus Copper Oleate, and Propyl Alcohol.—A solution of dry copper oleate in propyl alcohol was placed inside of an osmometer and anhydrous propyl alcohol placed on the outside. Three days later the level of the solution had risen 1 cm and on the following day the membrane broke, due to the solvent action of the anhydrous alcohol.

Isoamyl Alcohol plus Copper Oleate, and Isoamyl Alcohol.—A 5 percent solution of dry copper oleate in isoamyl alcohol was placed inside of an osmometer and pure anhydrous isoamyl alcohol placed on the outside. No change was apparent for the first three months. At the end of three and a half months the level had risen slightly. This has continued steadily, though slowly, until now at the end of thirteen months the level has risen 57 mm. There seems to be no copper oleate in the outer liquid, but there is a fine grayish sediment deposited along the inner surface of the membrane. The membrane has commenced to sag very slightly and is evidently becoming somewhat weakened by the continued action of the alcohol.

Isoamyl Alcohol plus Copper Oleate, and Carbon Bisulphide.—Carbon bisulphide and isoamyl alcohol are miscible in all proportions and the former is a good solvent for copper oleate, much better than is the alcohol.

A 5 percent solution of copper oleate in isoamyl alcohol was placed within an osmometer and carbon bisulphide placed without. At the end of a week the level had risen twelve inches. This continued until finally a height of over eighty inches was attained, after which the experiment was discontinued.

The explanation of the action is evidently as follows: Isoamyl alcohol was imbibed by the membrane and the imbibed alcohol coming in contact with the carbon bisulphide on the other side takes it up and enables it to pass through into the alcoholic solution of copper oleate, for which it has a great affinity, whereas alone it would not be capable of going through, because it does not wet the membrane.

Some isoamyl alcohol naturally passed out into the carbon bisulphide. The membrane became somewhat weakened in consequence of the imbibition of the alcohol.

That the above explanation is the correct one is shown by the fact that when a solution of copper oleate in carbon bisulphide is separated from pure carbon bisulphide by a collodion membrane no action takes place. The solvent is incapable of penetrating the membrane without a carrier, such as alcohol.

Another experiment which also leads to the same conclusion regarding the necessity of a carrier is as follows: A solution of sulphur in carbon bisulphide, in which it is quite soluble, was separated from pure carbon bisulphide by a collodion film. Although the liquids bathed the membrane for several months, no carbon bisulphide passed through. No carrier of carbon bisulphide was present.

Iodine plus Potassium Iodide plus Water, and Water.— This experiment was quite similar to the one last described, the difference being that the solution of iodine was stronger and that water was used in place of carbon bisulphide. The solution was placed within the osmometer, and the solvent outside.

At the end of three weeks, a very slight rise in the level of the solution had taken place. At the end of five and a half months the level had risen twenty-five and one-half centimeters, whereupon it began to sink back again. Copious amounts of iodine passed out into the water outside.

This experiment makes it evident that water is responsible for the transfer of iodine through the membrane, in this and the preceding experiment; and that the reason that no rise was experienced in the former experiment, where carbon bisulphide and water were used, is that the two liquids are immiscible.

Glycerine plus Water, and Water.—A 50 percent solution (by volume) of glycerine in water was placed inside of an osmometer, and distilled water placed on the outside. The level rose about one centimeter the first twenty-four hours, and continued to rise regularly. The experiment was continued until a height of thirty centimeters was attained. Glycerine also passed out into the water outside. Here we have two hydroxyl compounds, both of which are capable of wetting the membrane. Evidently the mixture permeates the membrane more readily than pure water.

O-Kresol plus Isoamyl Alcohol, and Isoamyl Alcohol.—An osmometer was filled with a solution of *o*-kresol (approximately 25 percent) in isoamyl alcohol, and isoamyl alcohol was placed outside. The two liquids mix readily with each other. It should be remembered that isoamyl alcohol is but very slowly taken up by collodion, ordinarily. In this case the level of the solution rose 1 cm the first week and continued to rise for about five weeks, whereupon the level sank again, finally reaching its initial point at the end of an additional four weeks.

The relatively rapid rise was evidently due to the imbibition of kresol into the membrane, whereupon the alcohol is enabled to pass through the membrane more readily. Considerable quantities of kresol passed through into the solvent, until finally the concentration became about equal on both sides.

Sugar plus Water, and Water.—Water penetrates dry collodion but very slowly. The statement is often made that dried collodion is insoluble in water, which is practically true. Yet that water has some action is shown by the following experiment.

A rather strong solution of sugar in water was separated from pure water by a collodion membrane. No change was apparent for the first two weeks. At the end of three weeks the level had risen 1.5 cm, and this has continued until now at the end of six months the level has risen 14 cm. The membrane appears perfect, being taut and smooth and entirely unchanged in appearance.[1] Some sugar has passed through into the water outside.

This experiment is very similar to the ordinary experiment where parchment is used, save that collodion is much more impermeable to water and therefore the process goes on more slowly. As usual we have the major and minor current, in opposite directions.

Other experiments have been made with aqueous and alcoholic-aqueous solutions of boric and oxalic acids with the same general results, the main current being from solvent to solution but always accompanied by a minor current in the opposite direction. When the maximum height has been attained the level always sinks back again.

Effect of Dissolved Halides on Collodion.—Mercuric chloride when dissolved in water has no destructive effect upon collodion films, nor does it when dissolved in 96 percent alcohol. When dissolved in absolute alcohol, however, the membrane is disrupted almost immediately when the solution is poured upon it. The effect is the same as if the membrane had been seized by some powerful mechanical device and torn mechanically. Other halides, soluble in alcohol, produce the same effect, though their aqueous solutions do not. Antimony trichloride in alcohol acts just as does mercuric chloride.

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[1] Since the above was written the membrane has been allowed to remain in contact with the solvent and solution an additional eight months, with no apparent effect on the membrane.

Summary

1. Whether osmotic action through a membrane takes place or not seems to be dependent upon the solubility of at least one of the components in the membrane.

2. Whether an increase in volume of the solution takes place or not depends upon the miscibility of the solvents used.

3. The direction and extent of the osmotic action is evidently largely a question of relative solubility. The process is akin to a distribution process.

4. When osmotic action takes place it consists of a major and a minor current, in opposite directions, as has been previously pointed out.

5. It was noted repeatedly during these experiments that stirring of the liquids bathing the membranes served to hasten the osmotic process.

These conclusions afford an interesting confirmation of the results obtained by Kahlenberg from a study of other membranes and serve to emphasize the correctness of the views advanced by him concerning the nature of the osmotic process.

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February, 1910

THE ELECTROCHEMISTRY OF LIGHT. IX

BY WILDER D. BANCROFT

THE THEORY OF SOLARIZATION. PART III

In the preceding paper[1] I commented on Homolka's experiments with indoxyl as developer. When he gave the plate a preliminary treatment with bromine, he obtained an indigo image only and no silver image. When he treated the plate with stannous chloride and then developed, he obtained a silver image and no indigo image. At that time I had not seen Homolka's original paper and I could not tell what precautions he had or had not observed. Since then I have received a copy of this paper through the courtesy of the John Crerar Library in Chicago. I am happy to say that a number of precautions were taken. After the treatment with bromine water or with stannous chloride solution, the plates were washed for an hour in running water. In the case of the bromine a blank test was made upon a plate from which the silver bromide had been removed by means of sodium thiosulphate. This proves that possible bromine compounds of gelatine have nothing to do with the phenomenon and makes it reasonably certain that the error is one of observation. To check this point, Mr. Perley made some experiments with stannous chloride, using indoxyl as a developer, and found that an indigo image was formed under these circumstances. This matter may therefore be considered as settled.

One interesting conclusion may be drawn from this. Since stannous chloride produces an effect on the plate which is apparently equivalent to that of light and since the theory of Grotthuss requires that the action of light upon the silver bromide in a photographic plate shall be a reducing action, it follows that we ought to get the phenomena of solarization by treating the plate with a suitable reducing agent and

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[1] Jour. Phys. Chem., 13, 554 (1909.)

then developing the plate in an ordinary developer. This has been confirmed by Mr. Perley in my laboratory. One-fifth of a lantern slide plate was left unexposed and each successive fifth was exposed longer and longer to light. The plate was then developed for a definite time in a regular developer, the time of development being so adjusted that there was no visible reduction on the unexposed portion of the plate. If the exposures are properly timed, we get a clear strip where the plate has not been exposed, a moderate blackening for the first or shortest exposure, a strong black for the second exposure, a clear strip for the third exposure and a black strip for the fourth exposure. The first exposure is on the ascending portion of the curve representing degree of exposure and intensity of developed image. The second exposure should be at the top of this curve just where the solarizing exposure begins. The third exposure is at the end of the descending branch just where the solarizing exposure ends, and the fourth exposure is on the ascending curve corresponding to the second negative. A lantern slide of this sort is a much more satisfactory way of bringing out the relations than one which shows the graphical representation of the phenomena in the form of a curve. It was then necessary to duplicate this slide without the use of light. A plate was dipped one-fifth its length into a stannous chloride solution and kept there for a suitable length of time. It was then pushed down another fifth of the way into the solution and kept there for another period of time which was not necessarily the same as the first. This operation was repeated twice more and we then had a plate, one-fifth of which had not been immersed while the remaining fifths had been immersed for varying lengths of time. The plate was washed thoroughly and then developed for the same length of time in the same developer that had been used in the corresponding experiment with light. Qualitatively the results were just what they should be. Starting from the end which has not been immersed we had a light strip, a dark strip, a darker strip, a light strip, and a dark strip. Unfortunately the stannous chloride solution had acted on the gelatine to some extent and the developed plate was brown instead of black. The experiment was repeated, using sodium arsenite solution instead of stannous chloride. The result was quite satisfactory, the only criticism to be made being that the black of the second negative was not as intense with the arsenite solution as with the light. This is not surprising, because sodium arsenite is not a powerful reducing agent, and if the plate is left in the solution long enough to get a pretty thorough reduction to metallic silver, the gelatine is apt to suffer. A better black for the second negative can be obtained by substituting a dilute developer solution for the sodium arsenite solution; but then it becomes more difficult to time the first two exposures. It would probably be easier to duplicate the experiment with light absolutely by immersing in solutions of different concentrations, which would be equivalent to working with lights of varying intensity.

This series of experiments seems to me to offer a conclusive proof that the action of light is a reducing action and that solarization therefore is entirely a matter of the relative rates of reduction of the decomposition products of silver bromide by the developer used. Treatment with different chemicals before the development will affect the nature of the various decomposition products and will therefore affect the tendency to solarize in any given developer. Speaking broadly, any chemical which tends to dissolve silver from the latent image will check solarization while any chemical that tends to dissolve silver bromide from the latent image will increase the tendency to solarization. That solarization is merely the result of the relative rates of development is shown equally conclusively, but in another way, by the Waterhouse reversal. The exposure is so short that the latent image cannot be anything but the normal latent image so-called. By ripening the unexposed silver bromide we can get it to a state where it develops faster than the silver bromide which has been exposed. Of course this raises the whole question of the theory of ripening. I am treating this matter at considerable length in another series of papers. For our purpose it will suffice to say that the silver bromide complex in the unripened emulsion contains silver bromide, gelatine and water. The process of ripening consists in removing gelatine and water, one or the other or both, from the silver bromide complex. It does not involve a reduction and consequently the Waterhouse reversal is identical in principle with the ordinary reversal caused by long exposure. In both cases a silver bromide complex with a lower ratio of bromine to silver develops more slowly than a silver bromide complex with a high ratio of bromine to silver.

The experiments with the reducing agents show that the latent image obtained as a result of prolonged exposure to light is a reduction product and that the ratio of bromine to silver is therefore less than in normal silver bromide. These experiments show nothing in regard to the amounts of gelatine and water in the silver bromide complex. It is probable that these vary with the varying halogen content; but we have no method at present of proving this and consequently this point must be left undecided. If we could tell what changes take place in the gelatine and water content of the silver bromide complex as the ratio of bromine to silver decreases, it is possible that we might see more clearly why the maximum rate of development comes where it does for a given developer; but these facts are not essential to a general theory of solarization.

If we leave out of account the side reaction between the solution and the gelatine, and also the possible solvent action on the silver bromide,[1] we see that suitable solutions of

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[1] In a previous paper, Jour. Phys. Chem., 13, 571 (1909), it was stated that sodium hypophosphite dissolves silver bromide. Dr. Lüppo-Cramer very courteously called my attention to the fact that he was unable to confirm this statement. The sodium hypophosphite which we used was marked Sodium Hypophosphite C. P., and was bought from Baker and Adamson in 1906. Since the results that we obtained with it seemed to agree with those obtained by Carey Lea we did not make any tests for purity. We now find that it contains

suitable reducing agents in general and dilute developer solution in particular act like light and carry the silver bromide through the successive stages down to metallic or colloidal silver. Since dilute solutions are used in stand development, it seemed quite probable that these developers pushed the silver bromide along so that we were merely having a printing out process without light, in which case the visible image would really be the second negative and there would be a fundamental difference between stand development and ordinary development. If this entrancing hypothesis were correct, it should be possible to develop a positive by allowing an exposed plate to remain for a suitable length of time in a solution of the concentration suitable for stand development and by then developing it in an ordinary developer. This was tried by Mr. Perley; but the hypothesis proved to be wrong. A stand developer does not act like light and does not push the latent image along. A stand developer acts just like an ordinary developer except that it acts more slowly.

Since we have found that the ordinary stand developer carries the latent image down to metallic or colloidal silver without passing through the intermediate stages and since we have found that a diluted stand developer carries the latent image through the successive stages, we now have experimental proof for the two postulates[1] which were put forward last June as constituting the working hypothesis:

(1) The action of light on a silver halide corresponds to that of a direct current or of a fairly weak reducing agent. It causes the silver halide to pass through all the possible stages.

(2) A fairly strong reducing agent (a developer) does

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small amounts of sodium hyposulphite. Pure sodium hypophosphite has no perceptible solvent action on silver bromide and it give us pleasure to confirm Dr. Lüppo-Cramer's results. Whether Carey Lea's hypophosphite contained hyposulphite is a question which one can hardly answer definitely. If not, his reversals are due to the difference in the rates of development of a dried plate and a wetted plate.

[1] Bancroft: Jour. Phys. Chem., 13, 456 (1909).

not cause the silver halide to pass through all the possible stages and does reduce certain silver-halogen solid solutions or subhalides faster than others which contain less halogen.

The work on solarization is therefore finished with the exception of gathering up the loose ends. If a substance reacts slowly it will be a poor depolarizer and, in most cases not involving equilibrium conditions, it will be equivalent to a substance reacting more rapidly but having a lower potential.[1] If we apply this principle to Luggin's[2] work, we shall find that everything straightens out nicely and that the theory of solarization, as outlined, accounts for all the facts.

So far as one can judge from the meagre accounts, there is nothing in any of the reversals observed by Waterhouse[3] on stained plates which cannot be accounted for as the result of the dye acting as a color screen or a sensitizer or both. In Abney's experiments[4] with permanganate, bichromate, etc., the corrosive action on the latent image may be an additional factor; but it does not seem to me that this introduces any serious complications, though I admit that I should like to see these experiments of Abney repeated in a careful and systematic manner.

When we come to the alleged antagonistic effect of different lights, the so-called Herschel effect, we have a more serious difficulty to face. I have already pointed out[5] that "if we work with a sufficient quantity of pure silver halide in a closed space there will be an equilibrium pressure of the halogen corresponding to the chemical potential of each wave-length of light or to the chemical potential of any other form of energy, cathode rays for instance, which tends to set free the halogen. If we pass from light which causes one equilibrium pressure to light which causes another equilibrium pressure, we shall have a change in the dissociation

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[1] Cf. Luther: Zeit. phys. Chem., 46, 792 (1903).
[2] Jour. Phys. Chem., 13, 194 (1909).
[3] Ibid., 13, 11, 12, 27 (1909).
[4] Ibid., 13, 22 (1909).
[5] Ibid., 13, 465 (1909).

and consequently an antagonistic effect, which may or may not lead to a reversal, depending on the conditions of the experiment." This is entirely true but we are not dealing with equilibrium conditions in the case of an exposed dry plate and consequently the antagonistic effect of different lights can scarcely be important enough to be worth considering.

Since there is apparent ground for belief in the existence of such a phenomenon,[1] we shall have to consider the facts. Abney is one of the firmest believers in the phenomenon and I therefore quote a recent paper of his:[2]

"The photographer has to deal with the effect of white light on a photographic plate; and probably never has and never will deal with any other effect, but it is interesting from a scientific point of view to see whether the effect of white light gives the same effect as that kind of light to which the salt in the plate is sensitive. What I am describing is to be a repetition of experiments made a good many years ago by myself and which have been already published. It really comes under the heading of reversals of the photographic image. If we take ordinary bromo-iodized collodion and the silver bath as our photographic equipment and a spectrum as our light we shall find peculiarities in the image under certain conditions. Having prepared a plate with the bath and exposed it for a short time to the spectrum, we shall find on development that we have an image of the violet, blue and blue-green of the spectrum, and the green, the yellow, and red have not impressed the sensitive salt.

"Before placing in the spectrum let another similar plate be exposed to white light for a very brief period (enough, indeed, to cause a faintly marked fog if the plate were then and there developed), and then exposed to the spectrum. On developing the plate we shall find that the same colours as before impress the plate, but that where the red and orange fall the fog has become less intense than it is

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[1] Jour. Phys. Chem., 13, 2, 10, 13, 25, 295, 310, 313, 314, 316, 328 (1909).

[2] Abney: Phot. Jour., 32, 318 (1908).

in the surrounding parts. In other words, the red and yellow rays have undone part of the work that the white light has done. By placing a red or an orange glass in front of the slit of the spectroscope and giving a rather more prolonged exposure, the clearance of the fog may be made complete. Again, if the plate be exposed to a very feeble white light during exposure, the same results occur. The parts exposed to the red and yellow of the spectrum refuse to be veiled. Were this last experiment the only one, it might have been a moot point as to whether the mixture of red and yellow light on the white light did not cause the phenomenon—but the first experiment shows that it is an effect produced by the photographic material and not one by the light waves.

"We have then the facts before us that when the photographer is using such a kind of plate part of the effect due to some components of the white light is being undone by other components. If we call the work done by the blue and violet rays $+ m$ and that done by the red and yellow rays $- n$, then the total effect of white light is $m - n$. The exclusion of the red and yellow rays from the image should induce increased sensitiveness, but it is a matter for experiment to find whether the absorbing medium used would cut off more of the blue and violet rays than would be warranted by the loss of 'n'. It will be interesting further to find experimentally the proportionate values of m and n.

"The case of bromo-iodide of silver has been referred to in the above experiments, but other sensitive salts are equally liable to this reversing action by the rays of low refrangibility. The chloride of silver in its "red" state (red by transmitted light) acts in the same way, as does bromide of silver when its sensitiveness is not extended below the green. A salt of silver which is sensitive into the yellow, as is some bromide of silver, cannot be treated in the same manner, though it seems probable that, at the same time a reducing action is taking place, an oxidizing (or reversing) action is also at work, so that the total reduction is not a maximum. In so-called color plates rendered sensitive by means of coloring matter, we may have the same reversing action at work. It may be that the difference in gradation which plates exhibit in the different parts of the spectrum may be induced by some such cause as this.

"If we take the atomic weights of say silver bromide and of the silver sub-bromide (for the writer still holds firmly to the chemical theory of the photographic image), it will be found that the frequency of the different rays are in proportion to these atomic weights. Anyhow, from a scientific point of view there is much experimenting to be done in order to settle what causes the reversal. A telling experiment which I have described before, is to illuminate a sheet of white paper very feebly, and at the same time to throw a brilliant spot of red light on to the same paper. A plate exposed to the sheet of paper will show a certain density all over the paper except at that part on which the image of the red spot falls."

Lüppo-Cramer[1] does not believe in the phenomenon at all as the following quotation will show:

"Some very remarkable experiments were made by Waterhouse[2] in 1876. When collodion plates, either dyed or not dyed, were fogged by diffused light and then exposed to the action of the red end of the spectrum, a reversal was obtained so that the Fraunhofer lines from A to D came out as positives. Waterhouse remarked that the effect seemed due chiefly to over-exposure and possibly in part to the use of an alkaline developer.

"In a note to this article by Waterhouse, H. W. Vogel considers the peculiar action of the spectrogram merely as an ordinary solarization, the parts of the plate which have only had the exposure to diffused light blackening much more than the others, precisely as in Claudet's experiments. This simple explanation may account for Waterhouse's experiments, since Waterhouse obtained the same reversal in the

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[1] Phot. Corespondenz, 39, 134 (1902).

[2] Phot. Mittheilungen, 12, 247.

blue; but it will not account for the later experiments of Abney because Abney found a special reversing action in the red. On the other hand, in 1878 and before Abney's last paper on the subject, Vogel denied the accuracy of all observations tending to show special actions in the less refrangible end of the spectrum.

"Vogel[1] writes: 'I have photographed the whole visible spectrum on silver bromide from the ultra-violet to the infra-red. Sometimes there will be a different action in the red and ultra-red than in the blue and violet, and we get a positive instead of a negative. This is always due, however, to the presence of organic substances and to the influence of other rays .... If one works with pure silver chloride, silver bromide, or silver iodide, and pyroxyline, there is no sign of an alleged oxidizing action of the yellow and red rays and consequently no neutral point between D and E. On the contrary the light here has a fairly powerful reducing action decreasing gradually in amount as we pass towards the ultra-red.'

"Since I myself (Lüppo-Cramer) have made a number of experiments and have never detected any action of the red end of the spectrum which differed fundamentally from that at the blue end of the spectrum, I should have been ready to agree with Vogel if the phenomenon in question had not been observed by a man of Abney's standing. In my experiments I used a large Vogel spectrograph. The slit was 0.26 mm in width and, in front of it, there was placed a filter which only allowed yellow and red light to pass. As source of light I used an arc lamp running on fifteen amperes, and a condenser. Since the slit of the spectrograph was about in the focus, an alum cell was interposed in order to cut off any heat rays which might cause trouble.[2] In addition to highly sensitive dry plates I also made use of plates

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[1] Phot. Mittheilungen, 15, 47 (1878).

[2] I am indebted to Professor Miethe for kindly allowing me the use of the instrument in the photochemical laboratory of the technical school and for valuable suggestions.

coated with a collodion emulsion. These latter were treated as I treated them in my previous work on solarization. After the usual rinsing with water they were bathed for two minutes in a five percent aqueous glycerine solution so as to ensure good development in case the film dried during an exposure of several hours.

"The plates were previously fogged more or less thoroughly by means of diffused light. In every case the effect of the red light was the same as that of a much shorter exposure to blue light. I am quite unable to see how one is to explain the repeated observation of a specific reversing action of the red rays, because Vogel's assumption of the presence of other rays of light certainly cannot be justified in experiments by Abney and by Waterhouse. It is much to be hoped that experimenters will interest themselves in this matter because it would be very important if somebody could prove conclusively that red rays act in a fundamentally different way from blue rays."

In a later paper, Lüppo-Cramer[1] takes a more decided stand:

"At one time there was a lively discussion over the mysterious action of red and infra-red rays in causing solarization. I was not able to confirm this action[2] and the more recent experiments of Eder[3] have also given negative results. Eder was able to obtain abnormal solarization phenomena in different portions of the spectrum only when using stained plates. With undyed films the solarization was entirely normal. As was to be expected from the degree of sensitiveness of silver bromide the solarization began last in the red portion of the spectrum and the phenomena here were just what would have been obtained if blue light had acted for a correspondingly shorter time. The abnormal

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[1] Phot. Correspondenz, 43, 433 (1906).

[2] Lüppo-Cramer: Wissenschaftliche Arbeiten, 52 (1902).

[3] Eder and Valenta: Beiträge zur Photochemie und Spektralanalyse, 2, 172 (1904).

phenomena with color sensitizers are therefore probably due to secondary causes."

In a reprint which I have recently received, Lüppo-Cramer[1] repeats his disbelief in the so-called Herschel effect.

As a matter of fact the whole thing is quite simple and the apparent difficulties are due unquestionably to lack of care in stating the conditions under which the experiments were performed. Lüppo-Cramer, for instance, says that he could not get the so-called Herschel effect; but he does not say what he actually tried and his experiments are inconclusive for that reason. Now I know that the Herschel effect cannot exist and does not exist; but I know how to get what is called the Herschel effect. Abney is worse than Lüppo-Cramer in the matter of giving details. He tells us that if a piece of white paper is illuminated faintly but uniformly by white light and if a beam of intensely bright red light is allowed to fall on the center of the paper, the red spot will photograph lighter than the white paper. This is true if the exposure is long enough; but under these circumstances the experiment is worthless because it proves nothing. The amount of light falling on the red spot is equal to the amount of white light falling on any other equal surface of the paper plus the amount of red light. If the red light has any actinic value whatever, the spot will come out darker on the plate than the surroundings provided the exposure is not too long. If the exposure is too long the red spot will solarize first and will therefore appear light on a dark ground. This is a plain case of solarization and would occur equally well with a blue spot. If we did not know that we had an over-exposure we should call this a Herschel effect. The phenomenon will be more marked, the greater the actinic value of the red light relatively to the white light.

The experiments with the spectrum are just as simple. The blue will reverse before the red and we then have a special

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[1] Phot. Correspondenz, 46, 344 (1909).

reversing effect due to blue, provided we ignore the fact of an over-exposure. If we expose still longer, the red end will also reverse but we may easily reach the point at which the blue has reversed again giving the second negative. We then have a positive at the red end and a negative at the blue end. If we omit all reference to the time of exposure, we have a beautiful instance of "the antagonistic effect of red light." So far as our experiments go, this is the whole thing. Abney is right and so is Lüppo-Cramer; but a great deal of trouble would have been avoided if Abney had described his experiments carefully and if Lüppo-Cramer had then repeated those experiments.

Lüppo-Cramer[1] has recently published a paper on 'black lightning' or the Clayden effect.

"Various considerations caused me to believe that with the Clayden effect there might be an action on silver bromide similar to that produced by Röntgen rays. In a previous paper[2] I have shown that when Röntgen rays act on silver bromide, there is a setting free of bromine and also a physical change which I have called disintegration. Now the extraordinarily short electrical discharges, which produce the curious action on silver bromide which is known as the Clayden effect, bear a certain resemblance to the form of energy which manifests itself as Röntgen rays and which we consider to be sudden, almost explosive, shocks in the ether. My experiments confirm in a surprising way the hypothesis of a certain fundamental likeness in the action of X-rays and of the short, intense illumination of the Clayden effect. Electrical discharges gave me precisely the same effects which caused me to assume a disintegration of the grain when I obtained these effects during my investigation of the latent image produced by Röntgen rays.

"As a result of my experiments on the disintegrating action of Röntgen rays, I used Schleussner transparency

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[1] Phot. Correspondenz, 45, 525 (1908).

[2] Phot. Rundschau, 1908, 221.

plates exclusively in the following experiments and they gave brilliant results. In most of the experiments the plates were exposed to the electrical discharges in a very simple way. The plates were sometimes uncovered and sometimes packed in black paper; they were laid on a lead plate which was connected with the negative pole of the induction coil. The positive pole was a hanging metal point which was kept moving slowly about 10 cm above the film. The circuit was closed for one-half to one minute during which time a large number of electrical sparks passed over the plate. Of course it was not possible to identify each one of the sparks in the necessary check experiments. This arrangement made it possible to obtain a large number of discharges on each plate and since large plates (18 × 24 cm) were used, satisfactory checks were obtained on different parts of the same plate.

"The action of the electrical spark discharges on the silver bromide plates was precisely like that of the Röntgen rays:

(1) By daylight (without using any chemical reagents) the latent impressions 'develop' red on a greenish ground to a very considerable density so that prints can be made which can be reproduced.

(2) If a picture of the discharges which has been developed by light, is treated with chromic acid, the red silver bromide is bleached completely while the ground remains gray. This is like what happens with Röntgen rays. We account for it in terms of the disintegration theory by saying that the shocks of the discharges have produced a more finely divided silver bromide which yields a fine-grained photobromide and this latter is less resistant to oxidizing agents than the original photobromide.

(3) If plates which have been subjected to the discharges, are allowed to blacken in the light under a sensitizer (nitrite or silver citrate[1] until the whole plate 'fogs,'

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[1] See my article "On the Action of Röntgen Rays on the Photographic Plate," which will appear soon in "Fortschritte auf dem Gebiete der Röntgenstrahlen, 13, Heft 2.

a positive image is obtained by treating with chromic acid. The discharges appear light on a dark ground, which is just the reverse of what would happen if the latent image produced by light were treated in the same way.

"After I had established in this way the similarity between the action of electrical discharges and of the Röntgen rays, it was very important to determine whether here, as in the Clayden effect, it was a matter of the brief but intense light action of the spark or whether perhaps some special electrical property was the determining factor. The electric spark was therefore passed along the inside of a glass tube while the plate was placed outside and then exposed to the light of the sparks. When such a plate was afterwards exposed to daylight, an intense red color was obtained. An exposure in the camera was also developed, allowing the plate to darken in the light under nitrite or silver citrate. Though the action of electrical discharges upon silver bromide differs from that of ordinary light in that it causes a disintegration, yet this effect is not due to electrical peculiarities; but to the action of light for extraordinarily short periods just as is the case with the Clayden effect.[1]

"From these results it seemed probable that the Schleussner transparency plates would also show the Clayden effect especially readily. This was the more probable because B. Walter[2] had recently found the surprising fact that different makes of plates behaved very differently in regard to the Clayden effect. This guess of mine was confirmed and I obtained prints which, in addition to some bright flashes, showed 'black lightning' with an intensity such as I have never obtained with any other plates. This agrees with the other fact that this homogeneous, fine-grained emulsion is better than any for the Luther-Uschkoff experiment. A special after-exposure, such as is usually required for the Clayden effect, was not necessary in these experiments.

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[1] [Lüppo-Cramer apparently limits the Clayden effect to the photography of real lightning. This is not the usual practice.]

[2] Drude's Ann., 27, 93 (1908).

With the plates which were not covered, the diffused illumination which occurs simultaneously with the exposure to the electric spark was enough to fog the plate and the Clayden effect is due to the fact that the silver bromide is disintegrated to finer particles and therefore is less sensitive to ordinary light. There is thus a complete analogy with the action of the Röntgen rays which, according to Luther and Uschkoff[1] decrease the sensitiveness of the plate to light and subsequent development.

"It is not surprising that all the flashes on Plate I[2] do not come out black since the diffused 'after-exposure' will reach a higher value with the brighter flashes so that the decrease of sensitiveness caused by the disintegration is compensated thereby. Possibly this is the explanation for the bright center to some of the intense black flashes. Walter[3] writes in regard to this: 'If the spark was more powerful, it often happened that the less bright edges—the so-called aureole—were reversed while the inner portion developed in the proper way.' The explanation for the Clayden effect not appearing with many makes of plates is probably due to the fact that their grain is not readily disintegrated. The transparency plates are also admirably suited to this work because their relatively slight sensitiveness to light prevents the diffused exposure from being too powerful. It is also to be remembered that the ordinary solarization can only be obtained with difficulty and very incompletely with these plates.[4]

"In the paper[5] to which I have referred but which has not yet appeared, I have supported my assumption of the disintegration of silver bromide by Röntgen rays with citations from earlier investigators as to the visible change of structure caused by light and also by a quotation from Zehn-

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[1] Phys. Zeit., 4, 866 (1904).

[2] [Not reproduced in this article.]

[3] Phot. Centralblatt, 8, 396.

[4] Cf. Lüppo-Cramer: Photographische Probleme, 146 (1907).

[5] Fortschritte auf dem Gebiete der Röntgenstrahlen, 13, Heft 2.

der[1] as to the action of canal rays on silver bromide. Zehnder observed 'a marked change in the structure of the silver bromide film which looked almost like a corrosion.' Professor Zehnder wrote to me that this change in structure was visible before the development. In my experiments with Röntgen rays I tried in vain to detect such a visible change of structure; but the phenomenon could be seen quite clearly after the action of the electrical discharges. Not only the heavy branches of the discharges but also the finest ramifications were clearly to be recognized by orange-red light as shining streaks which became red very quickly when exposed to daylight. While this increased shininess is not conclusive proof of a disintegration, yet this direct observation of a change in structure, witnessed also by Mr. Guido Seeber,[2] increases the probability of the correctness of the disintegration theory for the case of the Röntgen rays as well.[3] In addition to the disintegration, there is also a removal of bromine when Röntgen rays or electrical discharges act on the plate, because the latent image can be developed physically.

"*Eder*[4] *was therefore right in assuming that the Clayden effect depends on a special principle of great importance for the theory of the latent image and that the recognition of this principle opens an entirely new chapter in the photographic action of light.* What has been hitherto considered as only hypothetically possible has now become extremely probable, namely that the action of light on the photographic film consists in a disintegration of the grain, though this cannot be proved in the case of the somewhat sluggish ac-

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[1] Drude's Ann., 12, 413 (1903).

[2] I thank Mr. Guido Seeber for repeated assistance in these experiments.

[3] [Lüppo-Cramer has himself recorded the appearance of a surface shine in the case of solarized plates. Jour. Phys. Chem., 13, 300 (1909). It is not clear why a shiny surface should indicate disintegration in one case and not in another. W. D. B.]

[4] Eder's Jahrbuch der Photographie, 14, 532 (1900).

tion of ordinary light,[1] though it is possible that it is a factor here also."

This theory of Lüppo-Cramer is interesting enough but to me it does not seem satisfactory. I am willing to concede the disintegrating action of light, especially of ultraviolet. I am not willing to concede that a mechanical disintegration of silver bromide causes a decrease in the sensitiveness when not accompanied by a change in the composition of the silver bromide complex. Even if this were to be proved, the theory would still fail to account for the bright centers to some of the dark flashes because the decrease in sensitiveness would be greatest where the disintegration is greatest. Lüppo-Cramer says that possibly the after-exposure is greater here and that this more than compensates for the decrease in sensitiveness; but he is merely juggling with words. If the decrease in sensitiveness, due to disintegration, is the important factor, the reversal should be more marked with the brightest flashes, which is not the case.

All difficulties disappear if we consider the Clayden effect as a case of solarization. With the bright flashes we get solarization and therefore a reversal. With the very bright flashes or with the bright centers of some of the other flashes, we get the second negative and therefore a re-reversal. Wood[2] duplicated the Clayden effect by exposing a plate to an arc light for a thousandth of a second or less. "It was found that as the duration of the light shock was increased the reversal became weaker, the images finally failing to appear at all on the plate, notwithstanding the

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[1] Trivelli's interesting exposition on the Clayden effect (Zeit. wiss. Photographie, 6, 239 (1908)) does not affect my opinion in the least. Trivelli considers that he has a case of the Clayden effect in which the keeping for several years of a celluloid film, which had been exposed in the ordinary way, is a sort of substitute for the diffused after-exposure. This interpretation is faulty because the first exposure has nothing to do with the Clayden effect. On the other hand, the discharges which sometimes occur with celluloid films and which often give 'reversed' or 'black lightning,' very probably depend on the Clayden effect.

[2] Jour. Phys. Chem., 13, 283 (1909).

longer duration of the flash. On still further increasing the duration, the images came out not reversed." This is exactly what should happen. The first exposures were on the descending or solarized portion of the curve while the last exposures were on the ascending portion corresponding to the second negative.

If Wood had used a less intense source of light than the arc or had put his plate farther from the source of light, his exposures could equally well have been made seconds, minutes, or hours, instead of thousandths of a second or less. While we must admire the ingenuity displayed in the experiments, it was a misapplied cleverness because it concentrated attention on the shortness of the exposure to the exclusion of the important factor of the intensity of the light and of the product of intensity into exposure.

Liesegang[1] has pointed out that some phenomena of reversal may be obtained with prints as a result of diffusion.

"The silver chloride papers, used for printing, usually contain a rather large amount of free silver nitrate in addition to the silver chloride. The silver nitrate is necessary because pure silver chloride would not darken sufficiently. The silver nitrate is called a chemical sensitizer and its function is to take up the chlorine which the light sets free from the silver chloride. If this reaction really takes place, there must be less silver nitrate in those portions of the film which have been exposed than in those that have not been. I have noticed a number of phenomena which indicate that this is actually the case. They seem to me to be worth recording because several matters are cleared up thereby.

"I have already called attention to one case some time ago:[2] I poured a mixture of gelatine solution and gallic acid over a glass plate. After the film has solidified I lay upon it an exposed silver chloride gelatine plate. The latter develops slowly to full intensity. When the picture is removed, one sees a negative image of the same picture on the

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[1] Phot. Correspondenz, 36, 78 (1899).

[2] Ibid., 35, 9 (1898).

gelatine film which contains the gallic acid. The silver nitrate has diffused from the unexposed and slightly exposed places to the other film and has there been reduced by the gallic acid. In the previous paper I left the explanation of the phenomenon to a future time. In view of the phenomena to be recorded in this paper, it is very probable that no diffusion of silver nitrate occurred from those portions which had received a great deal of light for the simple reason that there was little or no silver nitrate left there to diffuse.

"A similar phenomenon occurs if a printed silver chloride image is laid upon a jellied solution of sodium chloride. There is formed a negative image consisting of silver chloride.

"It is not necessary to work with a jelly in order to show the difference in rate of diffusion between the exposed and the unexposed portion. If an exposed silver chloride gelatine plate (Aristotype plate) is placed in a platinum toning bath, which contains some sodium chloride, the film becomes covered with white silver chloride on those portions which have received little or no light. This does not occur on the dark portions. This newly-formed silver chloride is on the outside of the gelatine film and can easily be rubbed off. (If the theory is right that the amount of free silver nitrate in the film decreases during the exposure, these differences in diffusion are easily explained in accordance with the fundamental principles laid down in my "*Chemische Reaktionen in Gallerten.*" Silver nitrate can diffuse from the film into the solution only if its solution has a higher molecular concentration than that of the chloride.) A similar covering of the unexposed portions of a silver chloride picture can be observed if it is wetted too little or not at all before being laid in a gold bath.

"We do not even need to study the behavior of plates and papers in baths in order to find such peculiar diffusion phenomena. I found a number of old prints on albumen paper which had lain for years in the dark, unfixed. It is well known that these papers become brown on the back if kept for a long while. This browning is due to a reaction between the free silver nitrate and the organic substance of the paper. In the prints referred to, the back was not colored at the places where the front was dark. The clear portions on the front corresponded to the dark portions on the back and consequently there was an intense negative on the back. This phenomenon is quite intelligible in view of the theory which I have outlined. The silver nitrate diffused into the lower layers of the paper and since there was less of it in those portions of the film which had been exposed to strong light, there could not be so much darkening in the corresponding places on the back.

"Such negative pictures on the back may sometimes occur in the physical development of under-exposed silver chloride images. I have noticed them if a print has been left for a long time in the dish without being moved provided the dish contained so little developer that the paper was only moistened. The phenomenon never occurs under normal conditions.

"If the amount of silver nitrate becomes small at the places where the light has been most intense, there is the possibility of solarization when physical development is employed. In this case it is not the gallic acid which does the developing but rather the nascent, metallic silver, and it is very hard to see how the intensification can go wrong. I have noticed however that the blackening does not increase in places which have received a great deal of light, such as the projecting edges of a paper which is being exposed under a very dense negative. We might call this a beginning of solarization because places, which have received much less light, blacken much more under the influence of the developer. Something similar is possible in the wet collodion process.

"I must mention an experiment in which an attempt was made to make use of this distribution of silver nitrate in a silver chloride print. If such a paper were coated with albumen, the albumen should be coagulated in the clear places by the silver nitrate there and should not be coagulated in the dark portions where the silver nitrate has been used up. In this way one might obtain a relief in albumen; but so far as I have obtained no results which are of practical value."

Scholl's experiments[1] on the clouding of silver iodide seem to be a case of disintegration by light. They have nothing directly to do with solarization and consequently we are not now interested in the question why the clouding is accelerated by oxygen or iodine. This explanation was offered by Bredig[2] the same year that Scholl's paper appeared.

"Lenard and Wolf[3] showed that certain substances appeared to disintegrate to a very fine powder when exposed to ultra-violet light (especially as negative pole of a dry cell). The presumption is a probable one that the silver bromide grain undergoes a similar disintegration in the light. As a matter of fact Schultz-Sellack[4] has noticed that silver halide crystals become cloudy in the light without any change of structure, and at last fall to pieces. If there is no allotropic change,[5] this agrees with the results of Lenard and Wolf. Schmidt[6] found that when silver halide salts were made cathodes in the air and were exposed to light, they dispersed electricity surprisingly readily. This is probably due to disintegration[7] with increase of electrical capacity."[8]

Much the same point of view is taken by Lüppo-Cramer[9] and this seems to me the rational point of view though I do not agree with all the conclusions drawn by Bredig and by Lüppo-Cramer.

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[1] Jour. Phys. Chem., 13, 209 (1909).

[2] Eder's Jahrbuch der Photographie, 13, 365 (1899).

[3] Wied. Ann., 37, 443 (1889).

[4] Pogg. Ann., 143, 441 (1871).

[5] Professor Ostwald tells me that he suspects that there is an allotropic change.

[6] Wied. Ann., 64, 718 (1898).

[7] The disintegrating action of light may perhaps be analogous to the shattering of a vibrating glass rod.

[8] Kaufman: Wied. Ann., 61, 552 (1897); Bredig and Pemsel: Archiv wiss. Photographie, 1899, Heft 2.

[9] Phot. Rundschau, 1909, Heft 10; Zeit. Kolloide, 6, 9 (1910).

Nipher[1] has given a diagram which purports to show the conditions under which one gets a negative, a positive, or nothing. As ordinates he plotted the illumination during exposure and as abscissas the illumination during development. His zero line first runs practically parallel to the axis of abscissas and then runs practically parallel to the axis of ordinates almost to the point where it reaches the axis of abscissas. The rectangular space inside these two lines is the field for negatives and the space outside the lines is the field for positives. This diagram cannot be right. In the first place, Nipher has overlooked completely the existence of the second negative. The field for positive images lies between the field for the first negative and the field for the second negative. This is not the only defect in the diagram. The form of the zero line, as Nipher has drawn it, seems to me quite impossible. We know that as we decrease the exposure, we must increase the illumination during development if we are to get a positive. Nipher's diagram does not show this and it was therefore certain that he had committed some error which vitiated his results. On going over his paper more carefully, I discovered the trouble. Nipher was studying the effects due to variation in the exposure and variation in the illumination during development. Consequently everything else should have been kept constant throughout the experiments. Instead of doing this he varied the composition of the developer[2] throughout and was therefore studying a system with at least three variables.

"The over-exposed negative and the under-exposed positive require the same kind of treatment. A restrainer must be used, whose function is to keep away the fog. The fog is incidental to an approach to a zero condition in which the plate will be blank. The restrainer does not change the character of the picture as regards positive and negative. It is not necessary to use it for what are called normal

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[1] Jour. Phys. Chem., 13, 245 (1909).

[2] Nipher: Jour. Phys. Chem., 13, 242 (1909).

exposures, when negatives are developed in the dark room, nor for normal exposures when positives are developed in the light. The amount of restrainer used must increase as the zero condition is approached. The amount needed may be as great as a twelfth of the entire bath in ten percent solution of potassium bromide, and this may be supplemented by the addition of from two to five drops of saturated solution of sodium hyposulphite.... The zero condition does not seem to be affected by varying the strength of the bath. If the plate be first placed for a minute in a normal bath, it may then be transferred to and developed in a bath as weak as one-tenth the normal strength. The positive and negative features are then the same as when developed in the normal bath. If the plate is first placed in the weak bath, the solution does not wet the film uniformly, and the plate appears as if it had been attacked by a painter's brush while the gelatin was soft."

Nipher's justification for varying his developer is that such a variation has no effect on the zero point. For the case of no illumination in the dark room, there were at that time experiments on record to show that a suitable exposure will develop either as a positive or as a negative, depending on the composition of the developer used. We must therefore conclude that Nipher's diagram does not represent any definite state of things and that the whole work will have to be done over again.

Lüppo-Cramer[1] states that the fine-grained Schleussner "D" plates show no normal solarization and that "silver bromide gelatine plates with an *extraordinarily* fine grain, such as the Lippmann plates, show no normal solarization phenomena at all even when they have been exposed so long that the direct photochemical change is distinctly visible after a preliminary fixing. Silver chloride gelatine plates act in the same way." In view of Lüppo-Cramer's experiments with nitrite, and with developers in the film, it is pretty

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[1] Jour. Phys. Chem., 13, 187 (1909).

safe to say that the trouble with the bromide plates is a failure to obtain the right conditions though, of course, one cannot be certain of this until the experiments have been repeated.

With the silver chloride plates, the case may be different. In the first paper on the theory of solarization, I tried to give an *a priori* proof[1] that solarization must occur. The more I think this over, the more convinced I become that I was wrong. At that time I said: "We know that the rate of development of an unexposed plate is practically zero when an ordinary developer is used. When the silver bromide has lost a little bromine through exposure to light, the plate can be developed and therefore has a definite rate of development. On the other hand, the rate of development of metallic silver is, of course, zero. The rate of development for a given plate and a given developer therefore passes through at least one maximum as the composition of the silver salt changes from silver bromide to silver." This is true and to the point provided that silver bromide forms a continuous series of solid solutions with silver. As this is not so, we need not consider this possibility any further. The statement is true under any circumstances provided we apply it, as I did, to the total amount of silver bromide and silver on the plate. It is not to the point, however, because there will be no solarization if the maximum rate of development, as given, comes at the composition at which silver just begins to appear. A more rational way to draw the diagram would have been to refer the rate of development to the single grain of silver bromide. In that case the axis of abscissas would have ended at the unknown composition beyond which silver begins to appear. So far as I can see now there is no way of predicting whether the curve would have passed through a maximum before reaching that point or not. It is purely a matter for experiment. For this reason it is impossible to predict whether silver chloride plates will or will not show solarization. In view of the analogies be-

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[1] Jour. Phys. Chem., 13, 457 (1909).

tween silver chloride, silver bromide and silver iodide, it is probable that silver chloride plates will solarize and that we have not happened to discover the fact. It is possible that they do not solarize under any circumstances and it is conceivable that the composition of the silver bromide complex in the Lippmann plates may be such that the maximum rate of development comes at the composition beyond which silver appears. Such a displacement of the maximum is not impossible and if it really occurs there will be no solarization. What actually happens must be determined experimentally. The theory takes account of the possible existence of two cases; but of course it cannot predict which one will occur in any given plate. Experiment has shown the occurrence of solarization in every case that has as yet been studied carefully but that does not prove that the Lippmann plate may not be in a class by itself.

If a man wishes to make practical use of the phenomenon of solarization by developing positives direct, he usually does not wish to make a long exposure. It may therefore be well to run over the different methods we have of obtaining positives with a relatively short exposure.

We have the method first suggested by Namias[1] in 1899 and now in regular use with autochrome plates, of developing a negative, destroying the developed image with acidified permanganate, fogging the plate, and developing again. This method is easy to perform and certain in its results. It involves a number of operations, however, and of course has nothing to do with solarization.

We can give a short exposure and can convert this into a solarizing exposure by exposing the plates to a diffused light afterwards. If this method is to be employed, it should be done in an intelligent way. Usually the plate is held up to the window for a moment. Since the actinic value of the sky varies from hour to hour, from day to day, and from month to month, a man who works in this way has nobody but himself to thank for the uncertain results which he gets.

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[1] Chimie photographique, 419.

The plate should be exposed for a definite time at a definite distance from a definite source of light. From Perley's experiments on developing in light[1] it seems probable that a green-blue light would be better than a white light.

A third method is the one worked out by Nipher of exposing the plate to light during development. To make this really satisfactory a green-blue light should be used.

A fourth method is to convert a short exposure into a solarizing one by means of chemical action. If a plate be placed in a very dilute developer solution for a suitable length of time and be then developed in the ordinary way, a positive will be obtained. The chief objection to this method is the possibility that the film may suffer during the long soaking.

A fifth method is to have a depolarizer in the film and thus to cut down the length of time necessary for an exposure. This method is interesting theoretically but of very little value otherwise. In the first place it does not cut down the time enough and, in the second place, it is sloppy and inconvenient.

The sixth, and probably the best, method is the Waterhouse reversal when performed in two stages.[2] In this method the unchanged silver bromide is ripened so that it reduces more rapidly than the bromide which has been changed by light. Since the changed silver bromide is in enormous excess after a short exposure, there is a danger of getting too dense a plate. While we have not, as yet, succeeded in decreasing the liminal value of the plate appreciably by this method, we can obtain an excellent positive with an exposure which yields a negative so thin as to be absolutely worthless.

The general results of these six papers on solarization may be summed up as follows:

(1) Experimental proof has been given for the two postulates of the working hypothesis:

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[1] Perley: Jour. Phys. Chem., 13, 645 (1909).

[2] Ibid., 13, 655 (1909).

(*a*) The action of light on a silver halide corresponds to that of direct current or of a fairly weak reducing agent. It causes the silver halide to pass through all the possible stages.

(*b*) A fairly strong reducing agent (a developer) does not cause the silver halide to pass through all the possible stages, and does reduce certain silver-halogen solid solutions or subhalides faster than others which contain less halogen.

(2) The theory has been applied to a large number of specific cases and has enabled us to account for all the known facts and to predict new ones.

(3) When the Waterhouse reversal is performed in two stages, it is possible to obtain a good positive with an exposure shorter than the one necessary to yield a good negative with the same developer.

Cornell University

AN INTRODUCTION TO THE STUDY OF THE SOIL SOLUTION[1]

BY FRANK K. CAMERON

The Soil

The soil, or that part of the land surface of the earth adapted to the growth and support of crops, is a heterogeneous mixture composed of solids, gases and a liquid, and containing living organisms. There are present: mineral debris from rock degradation and decomposition; organic matter from the degradation and decomposition of former plant and animal tissues; the soil atmosphere, always richer in carbon dioxide and water vapor and possibly other gases than the atmosphere above the soil; living organisms, such as various kinds of bacteria and fungi, with the products of their activities, notably the "nitrogen carriers" and the enzymes; and finally the soil moisture, a solution of products yielded by the above components and in equilibrium or approaching equilibrium with the solids and gases with which it is in contact.

In its relation to crop plants,[2] that part of the soil of immediate importance is the soil moisture. From this solution the plants, through their roots, draw all the material involved in their growth, except the carbon dioxide absorbed through their leaves. The soil solution is the natural nutrient medium from which the plants absorb the mineral constituents which have been shown to be absolutely essential to their continued existence and development. And from this solution plants sometimes absorb dissolved organic substances, but such absorptions are probably adventitious and incidental to the growth of the plant in a particular environment.

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[1] Published by permission of the Secretary of Agriculture.

[2] By crop plants are meant the ordinary green plants employed in agriculture. As is well known, the fungi as well as certain parasitic and saprophytic non-green seed plants obtain their nutriment in a very different way from ordinary green crop plants.

Therefore, the study of the soil solution is of the first importance in the investigation of the relation of the soil to plant growth, and in the following pages there is given an outline of our present knowledge of the chemical principles involved, with such discussion of the physical and biological factors as is essential to an orderly presentation of the subject.

Soil Management or Control

From the practical point of view the problem of the soil in its relation to crop production is like the problem of the factory or of any other industrial endeavor, in that it is a problem of management or control. The soil possesses this distinction, however, that it is both the raw material and the factory.[1] The processes involved are physical, chemical and biological, are always numerous and interdependent, and are never (speaking generally) exactly the same, so that each soil possesses marked individuality. No matter how soils may be classified, as for instance into provinces, series and types,[2] the fact remains that the soil of the individual field has properties which give it a crop-producing power, an adaptation to a specific crop or crop rotation, or a responsiveness to cultural treatment, which can not be anticipated in

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[1] According to S. W. Johnson—Some points of agricultural science, Am. Jour. Sci. (2), 28, 71–85 (1859)—"The soil (speaking in the widest sense) is then not only the ultimate exhaustless source of mineral (fixed) food, to vegetation, but it is the storehouse and conservatory of this food, protecting its own resources from waste and from too rapid use, and converting the highly soluble matters of animal exuviæ as well as of artificial refuse (manures) into permanent supplies."

[2] For definitions, see Soil Survey Field Book, 1906, Bureau of Soils, U. S. Dept. of Agriculture, pp. 15–24. On the ground that experience has shown that genetic classifications are the ones which have generally persisted and proved the most useful, objection might be made to the classification just cited. But a careful inspection of the results of the Soil Survey by the U. S. Department of Agriculture will show that while not categorically stating the fact, to all intents and purposes it has employed a genetic classification. This is exemplified by the fact that its delineation of soil provinces corresponds quite closely with the recognized physiographic provinces of the United States. See map accompanying Soils of the United States, by Milton Whitney, Bull. No. 55, Bureau of Soils, U. S. Dept. Agriculture, 1909.

any other field. Consequently, there is no possibility of reducing soil management or agriculture to the state of an exact science. That is to say, scientific investigation of the problems involved cannot be expected to yield absolute results, although furnishing the best possible basis on which to form judgments. Therefore, soil management, like other agricultural practices, is an art, more or less well founded on scientific principles, perhaps, but susceptible to much higher development as the scientific principles involved become better understood.

Aside from such devices as greenhouses, wind-breaks, etc., which have a local application only, there are three general methods of soil control: tillage methods, such as plowing and harrowing; rotation of crops; and the use of soil amendments or "fertilizers."

Our knowledge regarding tillage methods is generally considered to be fairly satisfactory. The purposes are well understood, namely, to break up and "fine" the soil, to keep down weeds, and by forming mulches to decrease the loss of water by evaporation. Not much increase is being made in our theoretical knowledge of this subject, although mechanical improvements in the implements of tillage are being and will undoubtedly continue to be made.

Our knowledge concerning crop rotations is fairly extensive, but it is almost entirely empirical. Some at least of the purposes served by a rotation of crops are fairly well known, such as the elimination of weeds or lower types of parasitic growth associated with particular crops; the introduction of humus by a grass crop or a green manure crop, especially by the *Leguminosae* with their symbiotic *Azobacteria*; the improvement in the structure or arrangement of the soil particles by alternating deep-rooted and shallow-rooted crops; the avoidance of continually growing a crop in the presence of its own excreta, and products of decay, etc.; and lastly, economic and market considerations.

Our knowledge of fertilizers, in spite of a vast amount of work and an enormous literature, is still very meagre and it also is almost entirely empirical; and this because studies on the subject have been dominated for three-quarters of a century by one theory almost to the exclusion of any other. The exponents of this theory have generally assumed that the action of fertilizers is on the plant rather than on the soil, and is independent of other factors. That is, while it is admitted that other factors influence plant growth, it has been held that the effect of the fertilizer is not to modify the influence of the other factors but to directly influence the plant by increasing its food supply. As a consequence, it has also been generally assumed that the influence of fertilizers is additive, that is, the increase in yield of crop is proportional to the increase in fertilizer added, and the increase in yield produced by adding two fertilizers is the sum of the increases which would have been produced by each alone. In this form the theory is essentially a quantitative one, and fertilizer practice should be easily susceptible of control by chemical analyses. But the large mass of data obtained from plot experiments shows that fertilizer effects are not additive. Indeed, the addition of some one or more fertilizer constituent is sometimes followed by a decreased yield. For example, about 20 percent of the trials of fertilizers on soils growing corn and reported by the American State Experiment Stations showed a decreased yield. And furthermore, in spite of the quantitative character of the theory, and the numerous analyses of soils and of plants which have been made, there is yet lacking any authoritative method for determining in quantitative terms the fertilizer needs of a soil. That analytical methods have a very restricted value in indicating even qualitatively the fertilizer needs of the soil is evidenced by the fact that within the past few years a number of the State Experiment Stations have publicly announced their unwillingness to undertake them.[1]

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[1] In this connection see: The texture of the soil, by L. H. Bailey, Cornell University Agr. Expt. Sta., Bull. No. 119 (1896); Suggestions regarding the examination of lands, by E. W. Hilgard, University of California, College of Agriculture, Circ. No. 25 (1906); Chemical analysis of soils, by William

The common procedure has been to define some arbitrary percentage limit in the soil, below which the soil is supposed to require fertilizers. But the amount of fertilizer to be applied is suggested on the indefinite basis of "experience." Thus, Hilgard, in an interesting discussion of this subject,[1] quotes Dyer as showing that "on Rothamsted soils of known productiveness or manurial condition, it appears that when the citric acid extraction yields as much as 0.005 percent of potash and 0.010 percent of phosphoric acid, the supply is adequate for normal crop production, so that the use of the above substances as fertilizers would be, if not ineffective, at least not a profitable investment." Hilgard himself sets limits as determined by strong hydrochloric acid digestion; thus a soil containing upwards of 0.45 percent potash (K_2O) does not need this substance as a fertilizer, while one containing below 0.25 percent does need it at once, and intermediate percentages indicate that potash fertilizers would probably be profitable; the corresponding upper and lower limits for phosphoric acid are set at 0.10 percent and 0.05 percent. But Hilgard points out that various things, such as the content of lime, or the texture of the soil, may materially alter these limits. In a very interesting set of experiments in which white mustard was grown in various soils, and these same soils diluted with various amounts of dune sand which had previously been extracted with strong hydrochloric acid, he found that the plants did best when the soils had been diluted with four times their weight of the extracted sand. This was the case even with a pulverulent

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P. Brooks, Massachusetts Agr. Expt. Sta., Circ. No. 11 (1907); Testing soils for fertilizer needs, by F. W. Taylor, New Hampshire Agr. Expt. Sta., Circ. No. 2 (1908); The uses and limitations of soil analysis, by J. T. Willard, The Industrialist, Kansas State Agricultural College, 34, 291 (1908); Soil analysis, by Wm. Frear, Pennsylvania Agr. Expt. Sta., Chem. Circ. No. 1; How to determine the fertilizer requirements of Ohio soils, by Chas. E. Thorne, Ohio Agr. Expt. Sta., Circ. No. 79 (1908); Concerning work which the station can and cannot undertake for residents of the state, by Joseph L. Hills, Vermont Agr. Expt. Sta., Circ. No. 3 (1909).

[1] Soils, by E. W. Hilgard, 1906, p. 339, *et seq.*

sandy loam; and with a black adobe, the best results were obtained when the diluted soil contained but 0.15 percent potash (K_2O) and 0.04 percent phosphoric acid (P_2O_5). It also appears that Hilgard regards soil analyses of value only in the case of virgin soils or soils which have long been out of cultivation, and in common with other authorities, he fails to point out how to determine the amount of fertilizer needed by lands.

It is clear, therefore, that the principles underlying the practice or art of soil management and crop rotation are in a state of development far from satisfactory, and scientific methods of soil control are yet wanting.[1] Recent activities in soil investigations, however, justify the hope that much improvement is to be anticipated, and the application of the modern methods of physical, chemical, and biological research to the soil problem promises a sure and probably rapid advance in this branch of applied science.

Soil Analysis and the Historical Methods of Soil Investigation

Owing to the labors of Davy, Boussingault, de Saussure, Liebig, Sachs, Knop, Salm-Horstmar, and other scarcely less distinguished savants, it has been clearly shown that *growing plants need certain mineral elements in order to maintain their metabolic functions*, and that *these mineral elements can be obtained, under normal conditions, from the soil.* All subsequent investigation has confirmed these statements and they can now be accepted as facts with as much assurance as any known law of nature.

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[1] It should, of course, be borne in mind that soil factors are not the only ones in crop production. Control by seed selection, breeding of standard types of plants, etc., may be, and probably is, more highly developed than control by soil factors. The same might possibly be claimed for moisture supply in irrigated areas; but on the other hand, such factors as the bacterial and lower life processes in the soil are generally under little or no control, and as a rule the amount and distribution of sunlight under none at all. A notable effort has been made in the last case with shade-grown tobacco (see Bulletins Nos. 20 and 39, Bureau of Soils, U. S. Dept. Agriculture) and a few cases are known where shade-crops are employed, but not in general agriculture.

The determination and formulation of these two fundamental facts came at a time when analytical chemistry was being rapidly developed and was finding wide and useful applications in numerous fields of activity. It was natural, therefore, that analytical chemistry should be enlisted in this new field of work, obviously of the first importance to the welfare of mankind. It was early found, however, that the chemical analysis of a soil fails to explain its relative productivity. In other words the content of a soil with respect to potash, phosphoric acid, or other mineral plant-food constituent, bears no necessary relation to its crop-producing power. Many cases were found where one soil "analyzed well" but did not produce as large a crop as another soil which "analyzed poor." To meet this difficulty a subsidiary hypothesis was brought forward, which rapidly gained general acceptance, although lacking experimental support.

This hypothesis supposes that the mineral constituents of the soil are present in two different chemical conditions or distinct kinds of combinations, one of which readily gives up its constituents to growing plants, while the other does not; and the constituents have, therefore, been called respectively "available" and "non-available." It would appear from his writings that Liebig regarded this distinction as applying to the "absorbed" or "adsorbed" mineral matter; that is, on the one hand the material held in or upon the soil grains by surface forces, and on the other the chemically combined constituents in the minerals themselves. We know that Liebig was much impressed by the absorption experiments of Way, and himself did much work in this field.[1] But the great body of soil investigators has evidently held to the opinion that there are two general classes of minerals in the soil. Some have held that the "available" potassium is held in zeolites or "zeolitic minerals an interesting example

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[1] Way was misled, as we now know, in considering the results of his absorption experiments with soils as merely metathetical reactions; see Absorption by soils, by Harrison E. Patten and William H. Waggaman, Bull. No. 52, Bureau of Soils, U. S. Dept. Agriculture, 1908.

often cited being glauconite or "green sand marl" which sometimes contains phosphorus as well as potassium;"[1] in minerals which are easily broken down by alkaline solutions, as by sodium carbonate solutions or ammonia; or in minerals which are easily broken down by organic acids supposedly excreted from the roots of growing plants, or formed by the decay of plant tissue.[2]

With the advent of this idea of a distinction between the available and non-available mineral plant-food elements in the soil, came attempts to distinguish them by analytical methods. Of these we now have a bewildering array, most of them frankly empirical. For instance, Hilgard, in his classical investigation of the cotton soils for the Tenth Census, treated his soil samples with an excess of hydrochloric acid, evaporated to dryness, extracted with water, and regarded the extracted mineral constituents as available. In Germany, a method similar to Hilgard's is now commonly used, while in France nitric acid is preferred generally because it is supposed to have peculiar solvent powers on soil phosphates. In the United States the "official method" of the Association of Official Agricultural Chemists is to keep 10 grams of the soil in contact with 100 cc of a solution of hydrochloric acid (specific gravity 1.115) at the boiling point of water for exactly 10 hours. In England the popular method is that proposed by Dyer, namely, to treat the soil with a 1 percent citric acid solution, this strength of solution being supposed at one time to represent the average acidity of root sap. Maxwell, in

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[1] The formation of zeolites in the soil has often been assumed, but has not yet been proven: see, Rocks, rock-weathering and soils, by George P. Merrill, 1906, p. 363.

[2] The classic experiments of Sachs, in producing etchings on marble slabs, and the etchings observed occasionally on rock surfaces are the proofs universally cited. The experiments of Czapek, who substituted slabs of aluminum phosphate and other substances for the marble, and those of Kossowitch, show that the action can be accounted for more satisfactorily and reasonably as due to dissolved carbon dioxide. In fact such etchings can be produced on marble slabs by laying platinum wires upon them and covering with moist soil, or cotton, or mats of filter paper; see Bull. No. 22, p. 14, and Bull. No. 30, p. 41, Bureau of Soils, U. S. Dept. Agriculture.

Hawaii, and afterwards in Australia, claimed good results for the extraction of the soil with a 1 percent solution of aspartic acid, this acid being employed on the erroneous ground that the organic acids of the soil are amido acids, and that these are the effective agents in dissolving the soil minerals and rendering their constituents "available."

The Kentucky Agricultural Experiment Station favors an N/5 nitric acid solution,[1] but does not recommend its use for soils of other localities, while in a contiguous state, the Tennessee Station favors the "official" method.[2] Many other methods have been proposed, but the foregoing are typical and sufficient to illustrate the present status of soil analysis.

It is clear that these several methods must give differing results. And it is not clear that any one of them is to be preferred to the others for any other reasons than analytical convenience. There is no reason to expect that the proportion of solvent to soil required in these methods bears any relation whatever to the mechanism of absorption by plant roots. And the attempts to simulate the properties of plant sap in some of these solvents are obviously illogical, for the plant sap does not come in contact with the soil grains, except through an accidental destruction of the plant.

Naturally, comparisons were attempted between the amounts of the mineral constituents extracted from a soil by these various solvents and the amounts taken up by crops growing on the soil. It was found, however, that the amount of any given mineral constituent extracted from the soil by a solvent is not, generally, the same as that taken up by the plant. Moreover, the ratio of one constituent to another in the extract bears no definite relation to the ratio of these constituents in the plant. Nevertheless many efforts were made to establish "factors." For instance, the percentage of potash extracted from the soil of a field by hydrochloric acid is some multiple of the percentage removed by a wheat crop;

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[1] Soils, by A. M. Peter and S. D. Averitt, Bull. No. 126, p. 66 (1906).

[2] The soils of Tennessee, by Charles A. Mooers, Bull. No. 78, p. 49 (1906).

it was sought to determine this multiple, assuming it to be a definite ratio and a natural constant, and it was designated as the potash factor. But there is a different factor for phosphorus, another for calcium, and still others for each and every constituent. The factors found for a soil from one area generally do not hold for a soil from another area. Again, different factors obviously must be used for different crops. And, finally, the whole scheme becomes hopelessly absurd when it is realized that the same crop will yield widely varying ash analyses, depending upon the cultural methods employed, the judicious selection of seed, the amount and distribution of rainfall and sunlight, and possibly other agencies, all of which affect the growth and absorptive functions of the plant to as great an extent as does the particular soil upon which it may be growing.

Moreover, from the purely analytical point of view the situation is no better. For instance, the addition of potassium in the amounts usually employed in ordinary fertilizer practice generally does produce a noticeable effect on the yield of crop. The average application of potash (K_2O) is certainly less than 50 lbs. to the acre. It is customary to consider the surface foot of soil as the region affected by the fertilizer, and an acre foot in good moisture condition weighs about 4,000,000 lbs. To be conservative, let it be assumed that 60 lbs. of potash have been added to 3,000,000 lbs. of soil. The official method of the Association of Official Agricultural Chemists calls for the determination of the potash in 2 grams of soil, which on the basis of the present assumption calls for the estimation of an added amount of 0.00004 gram of potash or 0.002 percent. Taking as an example the report of the Association of Official Agricultural Chemists for 1895[1] there are given the following results obtained independently by a number of analysts, on soils which had presumably been sampled by the referee with all possible care:

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[1] Proceedings of the Twelfth Annual Convention of the Association of Official Agricultural Chemists, Bull. No. 47, Division of Chemistry, U. S. Dept. Agriculture, p. 36 (1896).

Potash Calculated as Percent of the Fine Dried Earth

Analyst	1		2		3		4	
	Percent	Var.	Percent	Var.	Percent	Var.	Percent	Var.
A....	0.359	0.044	0.154	—0.002	—	—	—	—
B	0.345	0.030	0.112	—0.044	0.380	0.051	0.104	—0.050
C..	0.354	0.039	0.235	0.079	0.396	0.067	0.225	0.071
D....	0.260	—0.055	—	—	—	—	—	—
E....	0.373	0.058	0.179	0.023	0.365	0.036	0.175	0.021
F.....	0.210	—0.105	0.130	—0.026	0.220	—0.109	0.109	—0.045
G....	0.304	—0.011	0.125	—0.031	0.286	—0.043	0.158	0.004
Mean.	0.315	—	0.156	—	0.329	—	0.154	—

Not only do the individual determinations show differences far in excess of 0.002 percent, but the differences between each individual reading and the mean is greater than 0.002 percent, so that it is evident from these results that the analytical procedure fails to recognize appreciable amounts of the so-called available plant foods. Consequently the "acid digestion" of a soil fails of the purpose for which it was designed, and it is one of the mysteries of chemical history that so much time and energy have been devoted to such a hopeless quest.

This state of affairs is the more surprising when the limitations of the analytical procedure are considered. The data tabulated above indicate that the analyses were made with an exactness that justifies a statement to three decimal places, that is, to three significant figures; and in fact, as was shown, such is necessary if the figures are to have any significance regarding fertilizer applications. It is obvious that the analysis of a finely pulverized definite mineral or rock is less subject to error than a sample of soil sifted through a 2 mm mesh. Yet the U. S. Geological Survey commonly reports its analytical data to only two decimal places. What variation may be expected in duplicate determinations by the same analysts it is difficult to say, for such duplicates are not commonly published.[1] In spite of the widespread view that the chemical analysis of a soil is a statement of great accuracy, it is improbable that as usually determined the potash content is correct to three or even two significant figures; it is also doubtful if the phosphoric acid content is correct to even one significant figure, if the total amount is below 0.1 percent of the soil. That these determinations have a higher accuracy than here stated is not shown by an inspection of the literature including the fairly numerous results reported in the annual Proceedings of the Association of Official Agricultural Chemists.

It was early felt by some investigators that soil analyses were unsatisfactory for studying the relation of the soil to the food requirements of a crop, and a second method was devised, namely, the growing of a crop, and determining the amount of mineral constituents removed from the soil by analyzing the ash of the crop. From the point of view of practical soil management this procedure involves the serious difficulty of being first obliged to get the crop before determining what must be done to best get it. It apparently has the scientific advantage of directness in determining the mineral needs of the plant from the plant itself. If these needs were constant, the advantage would be real, but as already mentioned, one and the same plant may have a very different ash content as the result of different cultural methods, different climatic and seasonal factors, as well as different soils. Generally, a poor crop has a higher percentage of ash content than a good crop, and sometimes the poor crop may remove from the soil more in absolute amounts of some one or other of the ash constituents than does the good crop. The ratio of the ash constituents is by no means constant for any one crop, and of course varies

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[1] See: On the interpretation of mineral analyses, by S. L. Penfield, Amer. Jour. Sci., (4), 10, 33 (1900); The analysis of silicate and carbonate rocks, by W. F. Hillebrand, Bull. No. 305, U. S. Geol. Surv., 1907; Manual of the chemical analysis of rocks, by H. S. Washington, 1904, p. 24; Ueber Genauigkeit von Gesteinanalysen, von M. Dittrich, Neues Jahrbuch für Mineralogie Geologie und Palaeontologie, 2, 69 (1903).

with different crops.[1] Finally, it is now known that the amount of the several mineral nutrients which a soil must furnish to a crop in the earlier stages of growth is greater than the crop contents at maturity,[2] consequently an analysis of the ripe crop would not indicate the plant's drain upon the soil at all growing periods. So that, while ash analyses have taught some important things concerning plant growth, they have of necessity failed as guides or criteria of the crop-producing power of a soil, its fertilizer requirements, or its content of "available" plant-food.

A third method of soil investigation, also essentially analytical in character, is the plot or pot test. The difference between a plot or pot experiment is mainly one of size, although it is claimed, and with a certain amount of justice, that the plot experiment more nearly approximates actual practice, and should be given a somewhat different consideration than the more readily controlled pot experiment. Here again it has to be considered that seasonal factors and factors other than the soil play a relatively large part in the production of the crop, so that conclusions regarding the productivity of a soil can not be drawn from one season's crop. Also, nowadays it is recognized generally that continuous growing of one crop is an incorrect practice, and a rotation should be followed and repeated several times before conclusions regarding the productivity of the soil are justified. If, however, the rotation has been well managed, the cultivation, fertilizing and soil management generally been well done for sixteen, twenty or more years, the soil has materially changed, and there can be no assurance that the treatment then best for it, is that which was best at the beginning of

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[1] For a brief but comprehensive discussion of ash analyses see, The ash constituents of plants, etc., by B. Tollens, Expt. Sta. Rec., 13, 207–220, 305–317 (1901–02).

[2] Über die Nährstoffaufnahme der Pflanzen in verschiedenen Zeiten ihres Wachstums, von Wilfarth, Römer und Wimmer, Landw. Vers. Sta., 63, 1–70 (1905); Plant food removed from growing plants by rain or dew, by J. A. Le Clerc and J. F. Breazeale, Year Book, U. S. Dept. Agriculture, 1908, p. 389–402.

the experiment. Therefore the method throws no certain light on the productive power of the soil, or the availability of its mineral plant-food constituents. Although much has been learned from plot experiments, and especially from the better controlled pot experiments, they are inadequate to meet the fundamental problem of the relation of the chemical characteristics of the soil to its crop-producing powers.

The Plant-Food Theory of Fertilizers

The guiding principle in soil investigations for about three-quarters of a century and until the past few years has been the assumption that the principal function of the soil is to furnish mineral nutrients to the plant, and that, to supply a lack in the soil, fertilizers are added because of the mineral plant nutrients they contain.

This theory has apparently much to support it. It is attractively simple. It will be shown later, however, that this very simplicity is an argument against its validity.

Those substances which experience has shown to be useful soil amendments usually contain one or more of the constituents necessary to plant metabolism, commonly phosphorus, potassium, nitrogen or calcium. Fertilizers do not always produce increased yields of crops, but it has been usual to consider bad results as due to other more or less extraneous causes. Moreover, as will appear later, crop yield is as strongly affected by some substances containing no mineral plant nutrient as by ordinary fertilizers. Again, the plant-food theory has been apparently confirmed by the popular misconception that crop yields are decreasing. Government statistics, however, indicate very positively that crop yields are increasing in Europe as well as in America, more in areas where the acreage is stationary than in areas where the acreage is increasing, and in areas where fertilizers are not used as well as in areas where they are used. Analyses of European soils which have been cropped for centuries show no characteristic differences from the newer soils of the

United States.[1] It is true that, from bad management or other causes, individual fields where crop production has fallen off are not uncommon. But that such a condition is general or that it can be associated generally with a decreased content in the soil of any particular mineral substance or substances, is a conclusion not sustained by the available data.

The plant-food theory of fertilizers must now be regarded as entirely insufficient. Granting that it has been useful in the past and has occasioned much valuable work, it seems to have reached the point which another simple and temporarily useful theory, the phlogiston theory of combustion, reached shortly before the plant-food theory of fertilizers was evolved. Just as the phlogiston theory passed away when the elementary nature of oxygen was established and Lavoisier taught the scientific world how to use the balance, so the plant-food theory of fertilizers must pass with increasing knowledge of the relation of soil to plant and the application of modern methods of research to the problem.

The Dynamic Nature of Soil Phenomena

In soil investigations, until recently, the assumption has been made, more or less explicitly, that any given soil mass, as for instance a field, remains fixed or in place indefinitely. It has been admitted, of course, that some physical, chemical and biological processes might be taking place in the soil, but these have been regarded as relatively unimportant in their effects upon the soil mass *in toto*. It has been assumed that the only important change taking place in the soil is a loss of mineral plant nutrients, partly by leaching, partly by removal in the garnered crops. In other words, the soil has been regarded as a static system. This is a fundamental error. In studying the soil as a medium for crop production, we must consider the plant itself, or at

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[1] A study of crop yields and soil composition in relation to soil productivity, by Milton Whitney, Bull. No. 57, Bureau of Soils, U. S. Dept. Agriculture, 1909.

least that part of the plant which enters the soil, namely, the root; the solid particles of the soil; the soil water, or the aqueous solution from which the plant draws all the materials for its sustenance, excepting the carbon dioxide absorbed by its aerial portions; the soil atmosphere; the biological processes taking place. The one common characteristic of all these things is that they are continually in a state of change; therefore the soil problem is essentially dynamic.

The root of a growing plant is always moving.[1] The amount of motion may be small or large, depending upon the surrounding conditions or attendant circumstances, but cessation of motion means the death of the root. This becomes evident from a consideration of the mechanism of root growth. The living root absorbs and excretes water and dissolved substances through a restricted area just back of the root tip or the tips of the root hairs. While absorption is taking place, however, there is a deposition of denser material over the absorbing area, or "root corking." But coincident with the corking process, the tip is pushed forward between the soil grains into the nutrient medium, new cells are formed and a new absorbing surface continually brought into functional activity. A failure of the plant root to move forward in this way would mean a reabsorption of root effluvia with harmful consequences to the plant, or a corking over of the root without further formation of absorbing surface with consequent cessation of its functioning. This would mean the inevitable death of the root, and, if general, of the whole plant. It is clear, therefore, that root

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[1] In order to penetrate the soil, a living root must be capable of exerting large pressures, and indeed, the magnitude of these pressures has been determined for some cases. See, for citations of the literature, Pfeffer, Plant Physiology, translated by Ewart, 1903, Vol. 2, p. 124 *et seq.* But it can not be doubted that, in general, root movement is much facilitated and perhaps directed by movements among the soil particles. As the absorbing tip of the root removes film water from the adjacent soil grains, there is a necessary rearrangement of these grains with a shrinking away from the tip, which then moves forward by taking advantage of the movements among the soil grains.

penetration and absorption of plant nutrients is essentially dynamic.

The solid components of the soil are always in motion. Every soil, no matter how flat the area or how well protected by vegetal covering, suffers some translocation of soil material through rains, as is evidenced by suspended material in the run-off waters. On hillsides this is shown by the soil accumulating on the "up" sides of fences, especially stone fences. In the aggregate this movement is probably quite large everywhere. It is manifestly so in the watersheds of many of the world's important rivers as shown by their muddy waters and the formation of deltas, sometimes of great area and agricultural importance.

With the saturation or approach to saturation of the surface soil the particles are more easily moved among themselves by an extraneous force. It is very rarely that the surface of a field is a dead level. Consequently when the soil is wetted, the gravitational force on the individual soil grains produces a more or less pronounced "creeping" effect down hill. On decided slopes this soil creep is believed to be of great importance in connection with soil erosion.[1]

As important as is the translocation of material by water, quite as important probably is that produced by the winds. These are blowing all the time, uphill as well as

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[1] Soil erosion is undoubtedly one of the greatest economic problems of the time, and yet there is scarcely any subject about which there are current so many popular misconceptions. In the rivers and to those who use the rivers the water-borne soil material is an unmitigated nuisance, save probably to the few cultivators of low-lying lands who flood their fields for the sake of the silt deposited. To the upland farmer, however, erosion is not only a necessity of natural conditions which can not be avoided entirely, but under proper control it may be even a blessing. The scalded and gullied hillsides, a trial and unnecessary disgrace to the owner, are probably not the main sources of the material which finds its way to the river. On the contrary, what are regarded usually as well-tilled fields supply the greater part of the suspended material in the rivers. The problem of erosion on the farm is not merely to check gullying and scalding, and deepening of stream heads, but to so adjust both cropping system and cultural methods as to secure a reasonable translocation of surface soil material with a minimum contamination of the neighborhood streams. See Man and the earth, by Nathaniel Southgate Shaler, 1905.

down, and their range of action is thus far wider than is that of rain and flood. The effectiveness of the wind as a translocating agency is seldom realized or even suspected by the layman, although it is commonly known that the air always contains some dust, and dust storms are familiar phenomena. That soil material can be carried long distances is certain, however, as for instance the sirocco dust, often carried from the Sahara over Europe.[1] Dust carried high into the air by volcanic eruptions sometimes travels enormous distances, as in the case of the eruption of Krakatoa, when such material is reported to have traveled thousands of miles, and volcanic dèbris from the eruptions at Soufrière fell upon ships several hundred miles distant. Arctic explorers have reported the finding of wind-borne soil materials over the polar ice, and mountaineers have observed similar deposits on snow-capped peaks. Soil material on roofs and similar inaccessible places has been observed many times, and testifies to the continual activity of the wind. The burial of objects even of considerable size by wind-borne soil gives like testimony.

Measurements of the amount of action of wind in translocating soil material are rare and probably have a qualitative value only. But Udden[2] in what appears to be a conservative calculation, finds "the capacity of the atmosphere [over the Mississippi Valley] to transport dust is 1000 times as great as that of the [Mississippi] River." The wind seldom is carrying anything like so great a load as it is capable of carrying. That is, the wind in its attack upon the land surface does not ordinarily obtain so large an amount of material capable of being wind-borne as it is possible for the wind to carry when suitable material is artificially provided. It should be remembered that, speaking generally, the velocity

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[1] For a comprehensive discussion of wind as a translocating agent, see: The movement of soil material by the wind, by E. E. Free, Bureau of Soils, Bull. No. 68, U. S. Dept. Agriculture.

[2] Erosion, transportation and sedimentation performed by the atmosphere, by J. A. Udden, Jour. Geol., 2, 318–331 (1894).

of the wind is lower just at the surface of the ground than at heights above, and it is necessary to get the soil material above the surface before the wind can exercise its full efficiency as a carrying agent. Moreover, wind-borne material is constantly being deposited as well as being removed from the land surface. It is evident, however, that this movement of soil material by winds is very great, and there is no reason to believe that it is of any less importance in other areas than in the Mississippi Valley. It is also evident that the individual grains in any surface soil of any particular field or area are continually and more or less rapidly changing; and the farmer is not dealing to-day with just the same soil complex he faced a few years back, or will face a few years hence.

But besides the movements of the solid components of the soil by translocating agencies, other movements are constantly taking place. Whenever a moderately dry soil becomes wetted, it "swells up" until a certain critical amount of moisture is present above which there is a shrinking. But as a wet soil dries out again below the critical amount, there is again a shrinking. As it is always either raining or not raining, soils are always either getting wetted or are drying. Consequently the individual grains are continually moving about among themselves. A heavy object, such as stone, when left on the ground gradually sinks into it.[1] Earthworms, burrowing animals and insects are continually at work in most arable soils. The action of frost in "heaving" a soil is familiar to everyone. Not so well known, however, is the fact that the apparently superficial cracks which occur to a greater or less extent in every soil, under drought conditions, are in reality quite deep, extending well into the subsoil. By the edges breaking off, and by wind- and water-borne material being carried in, considerable surface soil is thus brought into the subsoil. Through these various agencies, therefore, the

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[1] On the small vertical movements of a stone laid on the surface of the ground, by Horace Darwin, Proceedings of the Royal Society of London, 68, 253-261 (1901).

solid components of the soil are continually subject to much mixing; subsoil is becoming surface soil, and to some extent *vice versa.* An important result of these various processes is the bringing into the surface soil of degradation and decomposition products from underlying rocks. The processes involved are essentially dynamic.[1]

The soil solution is also a dynamic problem. When the rain falls on the soil, a part, the "run-off," flows over the surface and finds its way into the regional drainage; a part immediately evaporates into the air, and is designated as the "fly-off;" a third part, the "cut-off," enters the soil.[2] The cut-off water penetrates the soil by way of the larger openings and interstices, and mainly under the influence of gravity. For convenience this downward-moving water is designated as "gravitational" water. It moves through the soil with comparative rapidity and a portion reappears elsewhere as seepage water, springs, etc. But with the return of fair-weather conditions at the surface, there is increased evaporation and augmentation of the fly-off, and there is developed a drag or "capillary pull" on the water below. A large portion of the cut-off thus returns to the surface, mainly through films over the surface of the soil grains and in the finest interstices.[3]

The soil atmosphere is continually in motion, following with more or less decided lag the barometric changes in the atmosphere above the soil. Moreover, the chemical and physical processes continually taking place in the soil involve the absorption or the formation of free carbonic acid, and it seems probable that all rain water penetrating the soil gives up some oxygen to the soil atmosphere. The bacteria and lower life forms are necessarily undergoing changes con-

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[1] It is clear that as the soil is continually changing through physical agencies, the chemical analysis of it can not be expected to furnish evidence as to the mineral constituents removed by crops or by leaching.

[2] This terminology has been suggested by Dr. W J McGee.

[3] Leather, however, thinks that the water returns from only a limited depth, some 5–7 feet: see, The loss of water from soil during dry weather, by J. Walter Leather, Memoirs of the Department of Agriculture, Agricultural Research Institute, Pusa, India, Chemical series, 1, 79–116 (1908).

tinually. In fact all components of the soil are continually undergoing, or are involved in, changes of one kind or another.

It is certain that investigation of the various motions and changes taking place in the soil is quite as important as investigation of the soil components, and that no clear idea of the chemistry of the soil can be obtained without it. The development of a rational practice of soil control is possible only when the soil is regarded from a dynamic viewpoint.

The Film Water

When a relatively small quantity of water is added to an absolutely dry soil or other powdered solid, there is some shrinkage in the apparent volume of the soil or powder. The water spreads over the surfaces of the solid particles in a film, and a rise in temperature shows that a noticeable energy change accompanies the formation of the film.[1] With further increments of water the apparent volume of the soil increases until a maximum is reached. The water content at which this maximum volume of soil can be attained is a definite physical characteristic for any given soil. What is popularly known as the "optimum water content" corresponds to this critical content.[2] It is the point at which further additions of water will not increase the thickness of the moisture film on the soil grains, but will give free water in the

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[1] See, in this connection, Energy changes accompanying absorption, by Harrison E. Patten, Trans. Am. Electrochem. Soc., 11, 387–407 (1907); see also the recent valuable research, Les dégagements de chaleur qui se produisent au contact de la terre sèche et de l'eau, par A. Muntz et H. Gaudechon, Ann. sci. agron. (3), 4, II, 393–443, 1909, where it is shown that probably a part of the heat is due to chemical combination between the water and the other soil components. To quote, "Ces diverses observations nous conduisent à penser, sans nous en donner toutefois la preuve absolue, que la fixation de l'eau sur les éléments terreux très fins et sur les matériaux organisés, est tout au moins, en partie, attribuable à une combinaison chimique qui se manifeste non seulement par un fort dégagement de chaleur, mais aussi par la soustraction de l'eau à des substances aux-quelles elle semble chimiquement liée."

[2] The moisture content and physical condition of soils, by Frank K. Cameron and Francis E. Gallagher, Bull. No. 50, Bureau of Soils, U. S. Dept. Agriculture, 1908.

soil interstices. Just as the apparent volume of a given mass of soil varies with the water content, and reaches a maximum at a critical moisture content, so do all the physical properties vary and have either a maximum or minimum value at this same critical moisture content. Thus the apparent specific gravity of a soil reaches a minimum, the force required to insert a penetrating tool becomes a minimum, while the rate at which a soil warms up reaches a maximum,[1] and the ease with which aeration takes place reaches a maximum. In fine, this critical water content is that at which the soil can be brought into the best possible physical condition for the growth of crops. The practical significance of the optimum water content is far greater than would be supposed from the attention given it hitherto by students of the soil. It is the content of soil water which the greenhouse man should strive to maintain, and which the irrigation farmer should seek to provide, instead of the overwetting so common to the practice of both. In general farming it is that moisture content at which the farmer will attain the best results in plowing and cultivating, and attain these results most readily.

With additions of water beyond the critical point, there is a presence of free water in the soil interstices accompanied by important changes in the soil structure. With continued additions, there is a more or less rapid decrease in the apparent volume; there is a tendency for the soil aggregates to break down and the "crumb structure" so greatly desired by agriculturists is less and less readily obtained, and working of the soil tends in some cases to produce that phenomenon known as "puddling." However desirable the property of puddling may be to the potter or the brick maker, to the farmer it is a bane to be avoided above all things. To overcome it requires his best skill, and it usually takes several years of patient effort to restore a puddled soil to good tilth.

The force with which the film water is held against the

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[1] Heat transference in soils, by Harrison E. Patten, Bull. No. 59, Bureau of Soils, U. S. Dept. Agriculture, 1909.

soil-grains has not been determined as yet with any degree of precision, but it is certainly very great. If a soil be saturated, that is, if so much water be added that further additions will cause a flow of free water, and the soil be then submitted to some mechanical device for abstracting the water, the moisture content of the soil can be readily diminished to the critical water content; but to diminish it further by mechanical means is not easy. The tenacity with which film water is held by the soil grains has been shown in several ways. In one of these, for instance, a semi-permeable membrane was precipitated in the walls of a porous clay cell, which was then filled with sugar solution having an osmotic pressure of about 35 atmospheres. When this cell was buried in a soil having a moisture content above the optimum, water flowed into the cell. On the contrary, when the cell was buried in another sample of the same soil having a moisture content well below the optimum, there was a marked flow of water from the cell. It would appear, therefore, that the attraction between the soil grains and the film-forming water was certainly greater than the solution pressure of the sugar.[1] Again, by whirling wetted soils in a rapidly revolving centrifuge,[2] fitted with a filtering device in the periphery, and developing a force equivalent on the average to 3,000 times the attraction of gravitation, the soils could not be reduced below the critical water content. From the results of Lagergren,[3] Young,[4] and Lord Rayleigh,[5] it appears that the force holding a very thin moisture film on the soil grains would be of an order of magnitude from 6,000 to 25,-

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[1] The chemistry of the soil as related to crop production, by Milton Whitney and Frank K. Cameron, Bull. No. 22, Bureau of Soils, U. S. Dept. Agriculture, 1903, p. 54.

[2] The moisture equivalent of soils, by Lyman J. Briggs and John W. McLane, Bull. No. 45, Bureau of Soils, U. S. Dept. Agriculture, 1907.

[3] Uber die beim Benetzen fein verteilter Körper auftretende Wärmetönung, von Lagergren, Bihang till K. sv. Vet.-Akad., Handl., 24, Afd. II, No. 5 (1898).

[4] Minchin: Hydrostatics and elementary hydrokinetics, 311, 1892.

[5] On the theory of surface forces, by Lord Rayleigh, Phil. Mag. (5), 30, 285-298, 456-475 (1890).

ooo atmospheres. This force, however, must greatly decrease with thickening of the film, as is shown by the fact that at the critical moisture content a small further addition of water produces no marked heat manifestation, though making a noticeable difference in the physical properties of the soil. Therefore, while recognizing that our knowledge of this force still lacks a desirable precision, it is nevertheless clear that the force is very great.

The function of the film water in maintaining the soil structure is undoubtedly important. A soil in good tilth, or good condition for crop growth, shows a peculiar structural arrangement of the individual soil grains or soil particles, which it is very difficult to describe in precise terms, but which is readily recognized in practice. This condition is usually described as a "crumb structure," either because of its appearance or because of the peculiar crumbly feeling which a soil in this condition gives when rubbed between the fingers. The individual grains of soil are gathered into groups or floccules. While other causes may be more or less operative in particular cases, it seems very probable that the film water is primarily the agency holding together the grains in these floccules. The obvious explanation is that the film is exerting a holding power because of its surface tension. It follows, therefore, that anything which affects the surface tension of water should affect the structure of the soil; that is, the flocculation or granulation of the particles. But certain agents which produce respectively flocculation or deflocculation, nevertheless modify the surface tension of the solution in the same direction, and in not widely varying degree. Similar difficulties arise in attempting to correlate "crumbing" phenomena with the viscosity of the film water,[1] and it must be admitted frankly that present views on this subject are very unsatis-

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[1] Equally unsuccessful is the attempt to correlate flocculating agents with changes in the density of water; see, The condensation of water by electrolytes, by F. K. Cameron and W. O. Robinson, Jour. Phys. Chem., 14, 1-11 (1900).

factory, and that more careful investigation is urgently needed on this fundamental and important problem. Not only is the absence of a satisfactory theory embarrassing in considering the problems of soil structure and a rational control, but the difficulties are no less in the equally important problems of the movement of film moisture, and the distribution of moisture in a soil.

The movement of moisture into a soil from an illimitable supply is a comparatively simple phenomenon, controlled by a rate law which may be expressed by the equation $y^n = kt$ when y is the distance through which the movement has taken place; t is the time, and k and n are characteristic constants for the particular soil and solution.[1] This formula also describes the rate of advance of a dissolved substance into the soil.

It has also been shown repeatedly by experiment that the movement of moisture is relatively rapid when the moisture content of the soil is above the optimum, but that the movement is exceedingly slow when the soil has a lower water content than the optimum; that is, the point at which the water is entirely in the form of film water. For instance, if a moderately wet sample of soil be brought into intimate contact with an air-dry sample of the same soil, there will, at first, be a relatively rapid movement of the moisture, but as soon as the wetted portion has been brought to the "optimum" condition, no further movement can be detected, although the experiment has been tried of leaving such samples together for months and with a difference of water content amounting, in the case of clay soils, to 15 or 20 per cent. Since the drought limit, or the soil moisture content at which plants wilt, is, for most soils, considerably below the optimum water content, the movement of film water is obviously a problem of the first importance from a practical point of view as well as of the highest theoretical interest.

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[1] See Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, p. 50 *et seq*; also, The flow of liquids through capillary spaces, by J. M. Bell and F. K. Cameron, Jour. Phys. Chem., 10, 659 (1906).

The movement of water vapor, or its distillation from place to place in the soil, is another problem often confused with the above. Its importance is not yet clear, although according to some investigators[1] it would appear that the addition of soluble fertilizer salts by causing a lowering of the vapor pressure of the water induces a distillation to that region from other regions of the soil as well as from the atmosphere above. This brings up the problem of the diffusion of water and other vapors through the soil. It has been shown that the soil "plug" retards the rate at which diffusion takes place but induces no other effect in the ordinary phenomenon of free diffusion. This fact is obviously of the first importance in the theory of mulches, but requires no further consideration here.[2]

The Mineral Constituents of the Soil Solution[3]

The mineral constituents of the soil are products of the disintegration, degradation and decomposition of rocks. The decomposition products are mainly silica in the form of quartz, ferruginous material consisting of more or less hydrated ferric oxide and alumina, and hydrated aluminum silicate. The ferruginous material, being deposited or formed in the soil in a very finely divided condition, frequently coats the soil fragments to such an extent as completely to mask their true character. But if a soil be thoroughly shaken with water, and especially in the presence of some deflocculating agent such as a slight excess of ammonia, as in the ordinary preparation of a soil sample for mechanical analysis,[4] the coating

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[1] Sur la diffusion des engrais salins dans le terre, par Muntz et Gaudechon, Comptes rendus, 148, 253–258 (1909).

[2] See, Contribution to our knowledge of the aeration of soils, and Studies on the movement of soil moisture, by Edgar Buckingham, Bulls. Nos. 25 and 38, Bureau of Soils, U. S. Dept. of Agriculture.

[3] For a more detailed discussion and citations of the literature, see The mineral constituents of the soil solution, by Frank K. Cameron and James M. Bell, Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, 1905.

[4] Centrifugal methods of mechanical soil analysis, by L. J. Briggs, F. O. Martin and J. R. Pearce, Bull. No. 24, Bureau of Soils, U. S. Dept. Agriculture, 1904.

material is generally removed quite readily, and the mineral particles appear as fragments and splinters of the ordinary rock-forming minerals. Sometimes these fragments are more or less worn and rounded at the edges, showing mechanical abrasion or solvent action; sometimes they show evidences of partial alteration and decomposition; but surfaces of the unaltered mineral individuals always are found. These unaltered minerals occur as fragments of all sizes, and are to be found in the sands, silts, and presumably in the clays. As might be anticipated, the minerals other than quartz generally show a tendency to segregate in the finer mechanical separations of the soil. The presence of these unaltered mineral fragments in the clays has so far defied direct experimental proof because of the limitations of the microscope, but from chemical reasoning and *a priori* considerations there can be but little doubt that they exist in the clays as in the coarser separations.[1]

An important result of researches on the minerals of the soil is the generalization that soils are far more heterogeneous than are rocks, and that *practically every soil contains all the common rock-forming minerals.*[2] This generalization is subject to some qualifications. It would hardly be fair to regard a beach sand, for instance, as a normal soil. Yet it is surprising how many minerals other than quartz can usually be found even in a beach sand. Opinions may differ as to just what are the common rock-forming minerals, and perhaps no two mineralogists or petrographers would give identical lists, but there are a number of minerals which would appear undoubtedly in every list, and these would be found generally in any soil. Again, it might happen that in any given sample of soil, no pyroxene, for instance, could be found; but ex-

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[1] See, The mineral composition of soil particles, by G. H. Failyer, J. G. Smith and H. R. Wade, Bull. No. 54, Bureau of Soils, U. S. Dept. Agriculture, 1909. Recent improvements in microscope methods make it possible to identify without serious trouble the mineral content of silts with a diameter as low as 0.005 mm, and many even of the clay particles have recently been determined with satisfactory accuracy.

[2] See Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, p. 9.

perience shows that it would never happen in such a case that no amphibole, chlorite, serpentine, or other ferro-magnesian silicates would be present. However distinct these minerals cited may be from each other morphologically or optically, they are much the same in their chemical characteristics, their solubilities and their reactions with water and such dilute solutions as exist in the soil. Hence from the point of view of the soil chemist they may be considered for all practical purposes varieties of one and the same mineral species.

It is not difficult to account for the heterogeneity of the mineral content of the soil. Many of our rocks are reconsolidated soils, and the alternating formation of rock and soil from the same materials is probably an agency, in some part at least, in the mixing of soil material. The action of water in carrying off and transporting surface material and in gullying and eroding sloping surfaces is probably a large factor. But this agency, like the first, is rather restricted and localized. Just as important as a mixing agency is the wind. This, unlike water, works uphill as well as down, and is more or less in action at all times, continually transporting soil material from place to place. Wind-borne dust on roofs of dwellings, on rocky mountain tops and similar places, where it could have been brought by no other agency than the wind, is sometimes found supporting vegetation. Many chemical and mineralogical analyses of wind-borne dust obtained from various locations show it to have generally the same essential characteristics as ordinary soils.

Aside from the quartz and ferruginous materials mentioned above, the major part of the soil minerals are silicates, ferro-silicates, alumino-silicates or ferro-alumino-silicates, of the common bases, sodium, potassium, calcium, magnesium, and ferrous iron. Other bases, such as lithium, barium, or the heavy metals may occasionally be present in appreciable amounts as may other types of silicates, or other mineral salts, but these may be regarded as more or less incidental and rarely affecting in any essential way the general character of the soil mass. These silicates or silico minerals are all somewhat soluble in water, and being salts of weak acids with strong bases, are greatly hydrolyzed. A convenient illustration is afforded by the well-known rock and soil mineral, orthoclase. Assuming its type formula, the reaction with water may be represented,

$$K.AlSi_3O_8 + HOH \rightleftarrows H.AlSi_3O_8 + KOH.$$

Under ordinary soil conditions, with a relatively large proportion of carbon dioxide in the soil atmosphere, the potash formed would be more or less completely transformed to the bicarbonate,

$$KOH + CO_2 + H_2O \rightleftarrows KHCO_3 + H_2O.$$

Confirmation of this view is afforded by the natural associations and known alteration products of orthoclase.

The acid of the formula $H.AlSi_3O_8$ is not known and is probably entirely instable under ordinary conditions, and breaks down with the separation of silica, to form the minerals pyrophyllite, kaolinite or kaolin, and diaspore according to the following equations:

$$H.AlSi_3O_8 - SiO_2 = H.AlSi_2O_6 \text{ (Pyrophyllite)}$$

$$H.AlSi_3O_8 - 2SiO_2 = H.AlSiO_4 \text{ (Kaolinite)}$$

$$H.AlSi_3O_8 - 3SiO_2 = H.AlO_2 \text{ (Diaspore).}$$

All three of these minerals and their corresponding salts have been found in nature as alteration products of orthoclase. It is probable that, under soil conditions, the principal metamorphic product of feldspar is kaolin (or kaolinite when it is crystalline), hydrated aluminum oxide being of much less importance[1] and pyrophyllite of doubtful occurrence. A still more interesting case, perhaps, because of the well recognized tendency of magnesium salts to form basic compounds, is the alteration of pyroxene, amphibole and olivine

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[1] See Ueber die Bildung von Bauxit und verwandte Mineralien, von A. Liebrich, Zeit. prakt. Geol., 1897, 212-214.

with the formation of a chlorite or serpentine, common associations in nature, which may be represented

$$MgSiO_3 + HOH \rightleftarrows MgSiO_3.nMg(OH)_2 + SiO_2.$$

It is tacitly assumed in the foregoing statements that the reaction between a silicate mineral and water is a reversible reaction. This is not definitely known to be the case, for the formation of the ordinary silicate rock-forming minerals in the wet way at ordinary temperatures has as yet been realized in only a few cases. The assumption has, however, some experimental support. Minerals have been often made in the wet way at somewhat elevated temperatures, especially interesting cases in this connection being the formation of orthoclase by Friedel and Sarasin[1] at slightly elevated temperatures, and the formation of zeolites by Gonnard.[2] Feldspars and zeolites are common natural associations, it being generally conceded that zeolites are alteration products of the feldspars through the action of water; but Van Hise[3] has pointed out that under conditions of weathering such as would obtain in the soil, the tendency is for the zeolites to alter to feldspars. Wöhler's classical experiment of recrystallizing apophyllite from hot water[4] is significant, for only the products of hydrolysis should be obtained if there is an irreversible reaction between the mineral and water. Lemberg found that leucite ($KAlSi_2O_6$) when treated with an aqueous solution containing 10 percent or more of sodium chloride, was partially transformed to analcite ($NaAlSi_2O_6.nH_2O$), potassium chloride being formed at the same time. The reverse reaction was also realized, that is, the partial conversion of analcite to leucite by treatment with a solution of potassium

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[1] Sur la reproduction par voie aqueuse du feldspath orthose, par Friedel et Sarasin, Comptes rendus, 92, 1374 (1881).

[2] Note sur une observation de Fournet, concernant la production des zéolites a froid, par F. Gonnard, Bull. Soc. min. France, 5, 267–269 (1882); Jahrb. Min., 1884, I, Ref. 28.

[3] U. S. Geol. Surv. Monograph, 47, A treatise on metamorphism, by Charles R. Van Hise, 1904, p. 333.

[4] Jahresb. Fortschr. Chemie Liebig and Kopp, 1847–48, 1262; note.

chloride, and similar transformations were carried out with the feldspars.[1] Lemberg's experiments are of especial value as they were carried out at ordinary as well as at high temperatures. It appears probable, therefore, that the hydrolysis of a silicate of the alkalis or alkaline earths is a reversible reaction. It should be noted, however, that Kahlenberg and Lincoln[2] have shown that probably, in very dilute solutions of alkali silicates, the hydrolysis is practically complete and the silica is nearly all present as colloidal silica and not as silicic acid. Nevertheless, at higher concentrations silicates are formed, and there is abundant evidence in nature that the alumino- or ferro-silicates are reacting with bases to form salts, for example such as the micas.[3] If the hydrolysis were quite complete, it would appear to follow that the reaction between water and the silicate is irreversible. In that case it is difficult to see how any silicate mineral could persist in the soil for any length of time, and all soils should soon become sterile wastes composed essentially of quartz, kaolin and ferruginous oxides. It has been suggested that the original mineral particles are protected from decomposition by the formation of a coating "gel."[4] If diffusion can take place through the gel, solution and hydrolysis of the mineral would proceed, although the presence of the gel would probably retard the rate of the reaction. If it be postulated, however, that diffusion through the gel does not take place, the minerals of the soil can have no influence on the composition of the soil solution, which is an unthinkable alternative. The presence of such gels in the soil has frequently been assumed, but satisfactory proof is generally wanting.

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[1] Ueber Silicatumwandlungen, von J. Lemberg, Zeit. deutsch. geol. Ges., 28, 519–621 (1876); Inaug. diss. Dorpat, 1877; Bied. Centbl., 8, 567–577 (1879).

[2] Solutions of silicates of the alkalis, by L. Kahlenberg and A. T. Lincoln, Jour. Phys. Chem., 2, 77–90 (1898).

[3] Van Hise, loc. cit., p. 693.

[4] For an experimental demonstration of the formation of such a gel, see, The effect of water on rock powders, by Allerton S. Cushman, Bull. No. 92, Bureau of Chemistry, U. S. Dept. Agriculture, 1905.

In general, the same kind of considerations developed for orthoclase hold for the other soil minerals. If minerals of this character be pulverized or ground reasonably fine and then be shaken with distilled water which has been previously boiled to eliminate the dissolved carbon dioxide, the resulting solution will give an alkaline reaction with such indicators as phenolphthalein or litmus.[1] If a soil be shaken up thoroughly with water, the resulting solution filtered free of suspended matter, as by passing through a Pasteur-Chamberland bougie, and then boiled to eliminate the carbon dioxide, in the vast majority of cases the solution will also give an alkaline reaction with phenolphthalein or litmus. The waters of most of our springs, ponds, creeks or rivers being natural soil solutions, give an alkaline reaction after boiling.

But the mineral content of these natural waters varies greatly. These waters are composed in part of the "run-off," in part of a portion of the "cut-off" waters, described above. This portion of the cut-off, normally, in passing through the soil goes mainly through the larger interstices. It is not long in contact with the individual soil particles and floccules, and because diffusion of dissolved mineral substances is quite slow, especially in dilute solutions, it takes up but little mineral matter from such aqueous films as it may intercept.

A different state of things exists with that portion of the cut-off water which returns towards the surface by reason of capillary forces, to form the great natural nutrient medium for plants. This water is moving over the soil particles in films, and with slowness. It *is* long in contact with successive fragments of any particular mineral and all the different minerals making up the soil. Consequently, it tends towards a saturated solution with respect to the mineral mass; and it follows that if every soil contains all the common rock-form-

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[1] In making such experiments in the laboratory or in lecture demonstrations, it is well to have the mass of water large in comparison with the mass of powdered mineral or rock; otherwise secondary absorption effects may occur and obscure the results of the hydrolysis.

ing minerals, every soil should give the same saturated solution, barring the presence of disturbing factors.[1] Disturbing factors, however, enter into all cases under field conditions, such for instance as the presence of some uncommon or unusual mineral in appreciable amounts, differences in temperature, surface effects, or extraneous substances. These will be considered later, but another disturbing factor requires immediate consideration.

In every soil, varying proportions of the soluble mineral constituents are present otherwise than as definite mineral species; that is, they are present as solid solutions, or adsorbed on the soil grains or perhaps absorbed in some other manner. The concentration of the liquid solution in contact with a solid solution or complex of absorbent and absorbed material is dependent upon the concentration in the solid phase, and consequently upon the relative masses of solution and solid. Thus, the concentration of a solution with respect to phosphoric acid, when brought into contact with so-called basic phosphates of lime or iron, is dependent in a marked way upon the proportion of solution to solid.[2] Consequently it is to be expected that an aqueous extract of a soil will vary in concentration with the proportion of water used; and that with the same proportion of water, different soils or different samples of the same soil will yield different concentrations.

How far absorbed mineral constituents affect the solubility of the definite minerals in the soil or influence the concentration of the soil solution, it is not possible to predict with any approach to certainty. Those soils which hold the

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[1] Feldspars certainly, and phosphorites possibly, are mineral components of the soil; and these substances when ground sufficiently fine have been added to soils with sometimes an increased production of crop. Other minerals, such as leucite, have given similar results. But also apparently pure quartz sand sometimes accomplishes the same results, as for example, in the experiments of Hilgard cited above. It has not been shown, however, that the addition of any of these substances produces an appreciable change in the concentration of the soil solution.

[2] The action of water and aqueous solutions upon soil phosphates, by Frank K. Cameron and James M. Bell, Bull. No. 41, Bureau of Soils, U. S. Dept. of Agriculture, 1907.

most moisture are generally the best absorbers. Moreover, the soluble mineral constituents of the soil, for instance potassium or phosphoric acid, are absorbed to a very high degree from dilute solutions. Consequently it is to be expected that variations in the concentration of the natural soil solution would be less than in aqueous extracts, when there is employed a constant and large proportion of water to soil.

Many attempts have been made to extract the solution naturally existing in the soil and to analyze it. The results obtained have not been very satisfactory, owing mainly to the mechanical difficulties involved. As pointed out above, the solution in a soil under suitable conditions for crop growth is held by a force of great magnitude. Nevertheless, by using powerful centrifuges, with saturated soil, it has been possible to throw out the excess of solution over the critical water content of the soil. In this way small quantities, generally a very few cubic centimeters at a time, have been obtained. The analysis of a few cubic centimeters of a very dilute solution is in itself difficult, involving necessarily more or less uncertainty as to the absolute value of the results. Nevertheless, the concentration of the soil solutions thus obtained, with respect to phosphoric acid and potash, varied but little for soils of various textures from sands to clays, and the variations observed could not be correlated with the known crop-producing power of the soils. The average concentrations of the soil solutions thus obtained lies in the neighborhood of 6-8 parts per million (p.p.m) of solution for phosphoric acid (P_2O_5) and 25-30 parts per million for potash (K_2O).[1] In the following table are given the results obtained by analyzing solutions extracted from different samples of loams and sands by means of a centrifuge. The crop growing on these soils and the crop condition at the time the samples were collected

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[1] In this connection it is interesting to note that recent investigations on the proportions of phosphoric acid, potassium and nitrates in cultural solutions best adapted to the growth of wheat, give the same ratio of phosphoric acid to potassium as the figures just cited show to exist normally in the soil solution.

are given in the table, and the percentages of water in the samples when placed in the centrifuge are also given.

ANALYSIS OF SOIL SOLUTION REMOVED FROM FRESH SOILS BY THE CENTRIFUGE

Soil	Crop	Condition of crop	Percent moisture	Parts per million of solution		
				PO_4	Ca	K
Leonardtown loam	Wheat	Good	22.0	6	17	22
Leonardtown loam	Wheat	Poor	25.2	10	9	19
Leonardtown loam	Wheat	Good	17.6	8	22	38
Sassafras loam	Clover	Good	19.7	5	18	19
Sassafras loam	Corn	Medium	17.5	8	13	36
Sassafras loam	Corn	Medium	18.3	8	83	25
Sassafras loam	Wheat	Good	18.8	7	44	34
Sassafras loam	Wheat	Poor	20.0	7	27	24
Sassafras loam	Corn	Good	17.3	8	24	25
Norfolk sand	Forest	Poor	10.0	5	18	31
Norfolk sand	Corn	Good	11.9	11	36	31
Norfolk sand	Wheat	Good	10.7	18	45	31
Norfolk sand	Wheat	Poor	11.2	8	38	24
Norfolk sand	Corn	Medium	10.6	9	65	35

The concentrations of the solutions obtained from the samples do not justify any correlation with the crop-producing power of the soils, nor with the texture of the soils. The wide variation in the concentrations with respect to calcium is probably due to the fact that all of the samples came from fields which had been limed, some quite recently, and that the content of carbon dioxide in the different samples varied. It is of special interest to note that the content of calcium in the solutions does not show any obvious relation to the content of phosphoric acid.[1]

An effort has been made to ascertain the mineral concentration of soil solutions as they occur naturally in the field.

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[1] For the literature of the earlier work on the composition of aqueous extracts of soils, see: How crops feed, by Samuel W. Johnson, 1890, p. 309 *et seq*; see also, On the analytical determination of probably available "mineral" plant food in soils, by Bernard Dyer, Jour. Chem. Soc., 65, 115–167 (1894); and Soils, by E. W. Hilgard, 1906, p. 327 *et seq.*

Because of the practical impossibility of extracting the actual soil solution, an empirical method was employed. Areas were selected where good and poor crops were growing near each other on the same soil types, and preferably in the same field. Samples of soil from under these crops were taken at several intervals during the growing season, quickly removed to a nearby laboratory, shaken thoroughly with distilled water in the proportion of one part of soil to five parts of water, allowed to stand twenty minutes and the supernatant solution passed through a Pasteur-Chamberland filter.[1]

As has been pointed out above, the aqueous extract of a soil thus arbitrarily prepared has no definite or causal relation to the soil solution in the field. It is certain that the solutions would not generally be the same. It should also be emphasized that such a procedure can not, as some investigators have assumed, afford a criterion between soluble and insoluble salts in the soil, else the proportion of water to soil used above some minimum would be immaterial as far as the amounts which go into solution are concerned. The proportion of water to soil is not immaterial, however, considering the chemical nature of the soil components and the results of experiment. Consequently, it is clear that the concentration of the soil solution is not simply the ratio of the amounts found in the aqueous extract, to the percentage of moisture in the soil, but something quite different.

Artificial solutions prepared in the manner described above should, however, furnish evidence as to whether or not there are recognizable differences in the soluble mineral constituents of good and poor soils respectively; and if such differences exist, whether they are consistent. That is to say, if the more productive soils also uniformly yield aqueous extracts of a higher concentration, then it would be a fair

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[1] Capillary studies and filtration of clays from soil solutions, by Lyman J. Briggs and Macy H. Lapham, Bull. No. 19, Bureau of Soils, U. S. Dept. Agriculture, 1902; Colorimetric, turbidity and titration methods used in soil investigations, by Oswald Schreiner and George H. Failyer, Bull. No. 31, Bureau of Soils, U. S. Dept. Agriculture, 1906.

inference that their natural soil solutions are maintained at a higher concentration than in the less productive soils.

Results obtained for several localities and several crops, taken from the original records, are given in the following tables.[1]

WATER SOLUBLE CONSTITUENTS OF SOIL

Locality, Salem, N. J. Soil type, Norfolk sand. Crop, wheat. Yield, good

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
March 10	0–12	13.2	12	5	12
	12–24	11.5	7	5	16
June 8	1–24	4.3	4	14	13
June 13	1–24	4.6	5	13	17
June 19	1–24	9.6	2	14	24

Locality, Salem, N. J. Soil type, Norfolk sand. Crop, wheat. Yield, poor

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
April 3	0–12	12.0	11	5	32
	12–24	12.0	10	3	22
June 16	1–24	9.3	4	29	20

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[1] The chemistry of the soil as related to crop production, by Milton Whitney and F. K. Cameron, Bull. No. 22, Bureau of Soils, U. S. Dept. Agriculture, 1903.

Locality, Salem, N. J. Soil type, Sassafras loam. Crop, wheat. Yield, medium

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
March 10	0–12	23.2	19	10	8
	12–24	21.6	11	10	14
March 14	0–12	22.3	18	8	18
	12–24	20.2	15	12	21
	24–36	20.3	18	17	16
March 20	0–12	19.3	7	10	21
	12–24	18.6	4	11	21
	24–36	12.6	5	12	21
June 16	1–24	22.5	4	24	23

Locality, Salem, N. J. Soil type, Sassafras loam. Crop, grass. Yield, fair

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
March 10	0–12	25.0	13	28	18
	12–24	23.8	7	26	13
	24–36	19.9	16	8	15
March 14	0–12	25.8	21	12	21
	12–24	23.1	8	12	15
	24–36	21.8	9	15	21
March 31	0–12	23.0	11	23	43
	12–24	21.6	8	20	34
April 2	0–12	24.8	8	16	41
	12–24	24.0	6	21	38
	24–36	21.4	3	11	25

Locality, Salem, N. J. Soil type, Sassafras loam. Crop, wheat. Yield, good

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
March 17	0–12	22.0	8	6	10
	12–24	18.1	8	15	14
March 17	0–12	18.3	10	15	Lost
	12–24	18.1	9	24	25
March 24	0–12	24.7	14	12	30
	12–24	22.3	8	11	38
March 26	0–12	23.4	4	16	16
	12–24	23.9	12	16	20
	24–36	22.4	8	3	21
April 2	0–12	25.6	8	16	30
	12–24	24.4	8	17	47
	24–36	21.6	8	11	38
June 5	0–12	5.2	14	51	23
	12–24	8.0	15	55	32
June 8	1–24	10.6	2	20	13
June 11	1–24	15.5	6	26	14
June 13	1–24	8.2	6	19	22
June 16	1–24	15.0	5	21	19
June 17	1–24	10.6	7	63	17

Locality, Salem, N. J. Solid type, Sassafras loam. Crop, clover. Yield, fair

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
March 20	0–12	20.8	5	15	32
	12–24	20.2	5	15	27
	24–36	18.6	5	12	36
March 26	0–12	26.8	9	31	20
	12–24	22.9	8	20	18
	24–36	22.5	4	14	20
June 6	0–12	8.1	8	16	17
	12–24	12.7	9	18	20

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, wheat. Yield, good

Date	Depth Inches	Moisture content Percent	Parts per million of over-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
April 27	0–12	21.8	5	10	12
	12–24	21.3	4	7	10
April 29	0–12	22.2	8	15	52
	12–24	21.8	4	11	38
May 1	0–12	22.4	7	14	23
	12–24	21.8	7	8	30
May 1	0–12	17.0	5	16	25
	12–24	21.0	5	7	19
May 9	0–12	15.0	13	34	28
	12–24	15.9	9	17	26
May 15	0–12	14.2	3	14	24
	12–24	19.9	4	13	25
August 14	0–24	15.0	6	11	13
August 15	0–24	15.7	5	3	17
August 15	0–24	16.4	8	15	15

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, wheat. Yield, poor

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
May 14	0–12	14.7	5	8	35
	12–24	19.9	4	4	30
May 23	0–12	7.8	4	7	22
	12–24	14.9	4	11	23
August 14	0–24	16.0	4	4	16
August 15	0–24	19.5	6	4	13

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, corn. Yield, good

Date	Depth Inches	Moisture content Percent	Parts per million of oven-dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
May 8	0–12	18.2	9	12	29
	12–24	18.9	10	7	26
May 18	0–12	18.2	3	24	38
	12–24	18.8	6	19	28
August 8	0–24	17.5	7	30	18

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, corn. Yield, poor

Date	Depth Inches	Moisture content Percent	Parts per million of oven dried soil		
			Phosphoric acid (PO_4)	Calcium (Ca)	Potassium (K)
May 23	0–12	16.6	5	12	22
	12–24	17.4	6	8	22
August 8	0–24	19.9	9	25	20
August 15	0–24	21.6	7	15	13

It will be observed that the results given in the above tables are expressed in parts per million of oven-dried soils, in order to have some definite basis of comparison, and because it was anticipated at the time the investigation was made that larger quantities of dissolved minerals would be found under the better crops, and *vice versa*. An inspection of the results, however, shows that no such correlation can be made, nor in fact can any consistent correlation be made between the dissolved material and crop, soil type, water content, depth of soil or part of the growing season.[1] It appears, therefore,

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[1] King, however, claims that the concentration of the soil solution with respect to mineral plant nutrients, is higher in the soils of the northern states than in the soils of the South Atlantic states. See Some results of investigations in soil management, by F. H. King, Yearbook, U. S. Dept. Agriculture, 1903,

that in so far as the field method of analyzing an arbitrarily prepared aqueous extract is competent, there is no evidence that there are important characteristic differences in the concentration of the mineral constituents in different soil solutions in the field.

The order of concentration of the soil solution can be approximated from the given data, if the assumption be made that in the preparation of the aqueous extract, soluble mineral constituents are of minor importance, other than the constituents already dissolved in the soil solution. The calculation is very laborious, is not exact, and on account of the assumptions made the actual figures obtained are of no especial value in any particular case. Remembering the method of making up the solutions from which these results were obtained, it would be sufficiently near the truth to assume an average moisture content of 20 percent, when the figures given here for the soil approximate those which would be obtained for the soil solution. More exact calculations have been made for a large number of such cases, and it has been found from this method of estimation that the average composition with respect to phosphoric acid would be about 6-8 parts per million, and for potash about 25 parts per million, figures which agree with the results obtained for the examination of solutions extracted from saturated soils by means of the centrifuge.

The results given in the foregoing tables were obtained under great difficulties, and in some part the variations they show are undoubtedly due to inevitable inaccuracies of analytical work done under such circumstances. Some of the variations may also be due to the disturbing influences in the soil referred to above. Experience has shown, however, that the preparation of an aqueous extract of the soil of any particular field is by no means a simple matter. Extracts made from

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p. 159-174. Bailey E. Brown has obtained some preliminary results which suggest that there may be seasonal variations with respect to some of the dissolved mineral constituents. See, Annual Report of the Pennsylvania State Experiment Station, 1908-9.

samples taken within a few feet of one another frequently show variations of the same order as with samples from entirely different fields, or even soil types. Differences in the preliminary drying out of the sample before the addition of the water, seems to result in the same order of differences as obtained between different soils. In consequence of these facts, and of the further fact that an arbitrary aqueous extract of a soil cannot be assumed to represent in any definite way the natural soil solution, the results of the field examination are inconclusive as to the concentration of the soil solution *in situ*. It is more necessary, therefore, that other lines of evidence should be sought as to the mineral characteristics and concentration of the soil solution. Such a line of evidence is found in certain percolation experiments.[1]

If a solution of a soluble phosphate be percolated through a soil, a part of the phosphate will be removed from the solution and absorbed by the soil; that is, there will be a redistribution of the phosphate between the soil and the water. As the process continues, however, relatively less and less phosphate is absorbed by the soil and the concentration of the percolate becomes more and more nearly that of the added solution. This absorption takes place more or less closely in accordance with the simple law that the absorption of phosphates by the soil, per unit of solution which is percolating, is proportional to the total amount of phosphate which the soil may yet take from that solution if percolated indefinitely. This law is expressed by the equation $dy/dx = K(A - y)$ where y is the amount absorbed, x amount of solution that has passed, and A is the total amount which can ultimately be absorbed by that particular soil from that particular solution. K is also a characteristic constant. If the percolation be maintained at constant rate, then t, time, can be substituted for x and the equation becomes $dy/dt = K(A - y)$, the

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[1] The absorption of phosphates and potassium by soils, by Oswald Schreiner and George H. Failyer, Bull. No. 32, Bureau of Soils, U. S. Dept. Agriculture, 1906.

ordinary rate equation for a monomolecular reaction of the first order, whether chemical or physical.

With such absorptions as are involved in soils, a clay exposes a greater amount of absorbing surface than does a loam or sand, and it will show the greatest absorption towards any particular solution, other things being equal. The curve showing the concentration of percolate, would lie lower for a clay than for a loam, or for a sand. This is illustrated in the accompanying sketch diagram, where *y* represents concentration of percolate and *t* represents time.

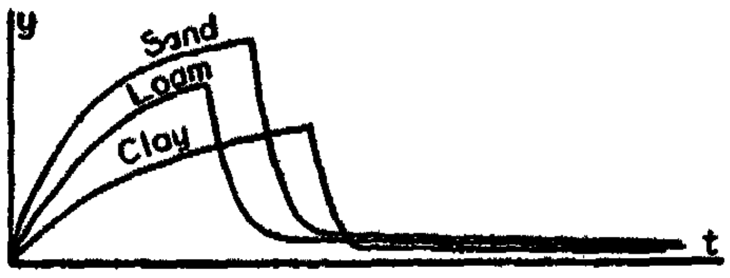

Fig. 1.—Absorption and leaching curves.

If after percolation has proceeded for some time (in some experiments for several weeks and until the soil contained 1 or 2 percent of phosphoric acid) pure water be passed through the soil, then, as soon as the previously used phosphate solution has been displaced, the concentration of the percolate drops, and continues practically constant for an indefinite period. Moreover, no matter what the soil may be as to texture or composition, the same concentration of percolate is obtained, namely, 6–8 parts per million, the concentration which the soils yielded prior to treatment with the phosphate solution. Similar experiments when the soils were treated with salts of potassium have given like results, although the curves obtained from passing pure water through the soils do not lie quite so close together; but the concentration of the percolate with respect to potassium generally lies somewhere between 25 and 30 parts per million.

The removal of a soluble constituent from the soil by percolating water appears to be described by a rate equation similar to that given above for absorption. If the rate of percolation be maintained constant this formula is

$$dx/dt = K(B - x)$$

where x is the amount removed by the percolation, with time t, K is a constant characteristic for the particular system under consideration, and B is the total amount of the constituent which may ultimately be leached out. In other words, the rate in any particular soil will depend upon the amount of the constituent still absorbed in that soil but has no necessary connection with the rate which would hold for the same amount of the constituent in any other soil.

Theoretically, two consequences follow from this law which require consideration here. The rate at which a constituent is removed gradually becomes less as percolation proceeds. If the soil contains an amount of the constituent approaching the total amount which it can absorb, as for instance is probably the case sometimes when large applications of lime have been made to the soil, the concentration of the percolating solution might be expected to change noticeably. Generally, however, a soil contains nowhere near as much phosphoric acid or potassium as it is capable of absorbing, so that the concentration of the percolating water changes but very little with respect to these constituents. It follows from the equation that if percolation continues uninterrupted, the concentration of the percolate, so far as it is determined by an absorbed constituent, must get less and less until it becomes a vanishing quantity. This state of affairs does not exist in the soil, however, for percolation by pure water does not continue uninterrupted for any length of time. The rise of the capillary water in the soil will, under normal conditions, enable the soil to reabsorb more of the ordinary mineral constituents than is removed by percolating waters. Further attention will be given the matter in another chapter.

Another but quite different line of evidence as to the probable concentration of the soil solution is furnished by the investigation of the solubility of certain phosphates.[1] It is popularly supposed that when superphosphate containing mono-calcium phosphate $CaH_4(PO_4)_2.H_2O$ is added to a soil there is a more or less permanent increase of readily soluble phosphoric acid in the soil, although a part "inverts" to the somewhat less soluble dicalcium phosphate $CaH(PO_4).2H_2O$. Such probably is far from a correct view of what actually takes place. The results obtained by studying the solubility of the different lime phosphates in water at ordinary temperature (25° C) can be expressed in a diagram similar to the accompanying sketch, which is much distorted for convenience in lettering. As the diagram indicates, when the concentration of the solution increases with respect to phosphoric acid, the lime is at first less and less soluble until the point represented by *B* is reached, then becomes more and more soluble until the point *D* is reached, from then on becoming less and less soluble, until the solution reaches a syrupy consistency. In contact with all solutions represented by points on the line *DE* the stable solid substance which can exist is mono-calcium phosphate, $CaH_4(PO_4)_2.H_2O$. Along the line *CD* the only solid which is stable and can continue to

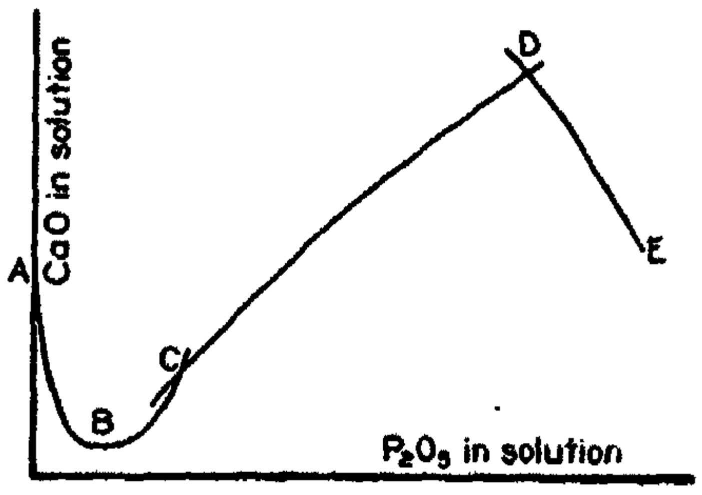

Fig. 2.—Solubility isotherm at 25° C for lime in aqueous solutions of phosphoric acid. Time point A is realized in a few minutes, but it requires days or even months to reach complete saturation at B.

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[1] For reference to the literature and detailed discussion see: The action of water and aqueous solutions upon soil phosphates, by F. K. Cameron and J. M. Bell, Bull. No. 41, Bureau of Soils, U. S. Dept. Agriculture, 1907.

persist is the dicalcium phosphate. From the point *C* the composition of the stable solid varies continuously with the concentration of the liquid solution. Therefore, these solids form a series varying in composition from pure dicalcium phosphate to pure calcium hydroxide. One of these basic phosphates, as they would ordinarily be called, has a less solubility than any other, as indicated by the point *B*. All solutions to the right of the point *B* have an acid reaction, while all solutions to the left possess an alkaline reaction. It follows from these facts that if we start with any lime phosphate corresponding to some point to the right of *B* and dilute it, or what amounts to the same thing in case it has been added to the soil, if we leach it, phosphoric acid will go into solution more rapidly than will lime until the composition of the residue is that of the basic phosphate stable at *B*. Similarly, if we start with a phosphate more basic, lime will be removed more rapidly than phosphoric acid, until the residue has the composition of the phosphate of lowest solubility. From this point, with continued leaching, the lime and phosphoric acid will dissolve in a definite ratio, which ratio is obviously that of the phosphate of least solubility. That is to say, if the leaching process is slow, as would be the case under soil conditions, the solution would have a perfectly definite concentration with respect to lime and phosphoric acid. What the ratio of lime to phosphoric acid may be, is of no particular interest in this connection, but the order of concentration of phosphoric acid is of interest. Owing to serious analytical difficulties, this has not yet been determined with any great precision, but by interpolating on the experimentally determined curve *AC*, this concentration is found to be somewhere in the neighborhood of 5-10 parts per million, figures close to those obtained for the concentration of the soil solution with respect to phosphoric acid by the previously described investigations.

Under ordinary circumstances, however, it is not probable that lime is the dominant base controlling the concentration of phosphoric acid in the soil solution, since the great majority of agricultural soils contain vastly more ferric oxide (more or less hydrated) than is equivalent to any amount of phosphoric acid that will ever be brought into the soil; and ferric phosphates are less soluble relatively than lime phosphates. Investigation of the relation of ferric oxide to solutions of phosphoric acid shows that the system is quite similar in many respects to the basic lime phosphates and water just described. When the ratio of iron to phosphoric acid in the solid is greater than that required by the formula of the norma phosphate, $FePO_4$, the aqueous solution will have an acid reaction and contain a mere trace of iron and an amount of phosphoric acid determined by the composition of the solid and by the proportion of solid to water. The basic ferric phosphates seem to be solid solutions which yield a very dilute aqueous solution when brought into contact with water. What the concentration will be under soil conditions is shown by the percolation experiments cited above.

The addition of other substances will in many cases affect more or less the solubility of the soil minerals. If these substances be electrolytes, they will generally, but not always, affect the solubility of the minerals as would be anticipated from the hypothesis of electrolytic dissociation. Thus, the addition of potassium sulphate lessens the solubility and hydrolysis of a potash feldspar or a potash mica. Contrary, however, to the indications of the hypothesis, sodium nitrate decreases the solubility of a ferric phosphate. While appreciable solubility effects take place with sufficiently high concentrations, laboratory experiments indicate that the addition of such substances, even in a liberal application of fertilizers, is not sufficient to produce any great effect on the concentration of the soil solution. Similarly, it has often been supposed that the ammonia, and nitrous and nitric oxides of the atmosphere carried into the soil by rain, or formed in the soil by bacterial action, affect the solubility of the soil minerals, but it is highly improbable that the concentration with respect to these agents ever becomes sufficiently high, as laboratory investigations show to be necessary to affect appreciably the solubility of the ordinary rock- or soil-forming minerals.

Rain brings from the atmosphere into the soil two agents, however, which do markedly affect the solubility of the soil minerals, namely, oxygen and carbon dioxide. The atmosphere within the soil contains normally a somewhat smaller proportion of oxygen than does the air above the soil. Rain in falling through the air absorbs or dissolves relatively more oxygen than nitrogen. Therefore when the rain water has penetrated the soil to any considerable depth there should be, and probably is, a liberation of dissolved oxygen into the atmosphere of the soil interstices. This dissolved oxygen in becoming liberated or when dissolved in the film water appears to be especially active towards the ferrous or ferro-magnesian silicates. These minerals are, moreover, as a class probably the most soluble of the rock-forming silicates. Consequently oxygen brought into the soil in this manner is one of the most important agencies in breaking down and decomposing such minerals as the amphiboles, pyroxenes, chlorites, certain serpentines, phlogopites and biotites; at the same time there is formed ferric oxide (more or less hydrated) and silica (probably as quartz) and magnesium. potassium, calcium or sodium pass into solution, probably as bicarbonates. That the concentration of the soil moisture may thus be made temporarily abnormal is not impossible, though scarcely probable.

The soil atmosphere has normally a decidedly higher content of carbon dioxide than the atmosphere above the soil. Consequently the soil water is always more or less "charged" with carbon dioxide, and the presence of the carbon dioxide decidedly augments the solvent powers of the water towards a great many and different kinds of rock-forming or soil minerals. What the mechanism of the reaction may be is far from clear. The obvious explanation, at least in the case of the ordinary silicates of the alkalis or alkaline earths, is that by forming bicarbonates of the hydrolyzed bases, the active mass of the reaction product with water is decreased and hydrolysis thereby increased. But this explanation is apparently insufficient to account for the effects sometimes observed. It has been shown that the passage of carbon dioxide through solutions of the silicates, will produce more or less slowly a precipitation of silica, and there seems little reason to doubt that it does induce to some degree a decomposition and consequent greater solubility of the silicates of the alkalis and alkaline earths. It also increases to an appreciable extent the solubility of the phosphates of iron, alumina, and lime. Therefore, the variation in the content of carbon dioxide in different soils, and its continual variation from time to time in any one soil, must be expected to produce corresponding changes in the soil solution with respect to such bases as potassium and lime, and also with respect to phosphoric acid. This has been verified experimentally by aqueous extracts of soils, the solutions being charged with carbon dioxide while in contact with the soils.[1] It is not conceivable, however, that any great difference can exist in the partial pressures of carbon dioxide in different soils which are in a condition to support crops, and therefore great absolute differences in the mineral content of the soil solution are not to be anticipated, nor are they actually observed.

It has long been held that the organic substances in the soil have an important solvent effect on the minerals. This assumption seems quite unwarranted in the light of our present knowledge, although it is not to be denied that occasionally there may be present in the soil some soluble organic substance which influences the mineral content. Generally it has been assumed that the effective organic substances influencing the solubility of the minerals are organic acids, of which a number have found their way into past and even current literature, and which have been designated as humic, ulmic, crenic, apocrenic, azohumic acids, etc. Their

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[1] See, for instance, the results obtained by Peter, Proceedings of the 19th Annual Convention of the Association of American Agricultural Colleges and Experiment Stations, Bull. No. 164, Office of Experiment Stations, U. S. Dept. Agriculture, 1906, p. 151 *et seq.*

existence is purely hypothetical and without experimental or other scientific verification, and calls for no further consideration here.

It is a widespread and popular notion that substances with a slight solubility also dissolve slowly, and that consequently the solubility of the minerals in the soil water must necessarily be a very slow process. This is, however, a misapprehension. It has been shown with a number of the common rock-forming minerals, that if they be powdered and then stirred into a relatively small volume of water, they dissolve very rapidly at first, and in a very short time, generally a few minutes, the solution is nearly saturated with respect to the mineral. Complete saturation, however, may require many days. The general shape of curve expressing the rate of solubility is shown in the accompanying figure.[1] For soils, this fact has been verified repeatedly, in the following way: a cell fitted with parallel electrodes is placed in circuit with a slide-wire[2] or Wheatstone bridge in such a manner that the resistance of the cell contents can be quickly determined. Distilled water is then placed in the cell and its resistance found. Generally this will be upwards of 100,000 ohms. The soil or rock powder under examination is then added to the cell, being rapidly stirred into the water contained therein.

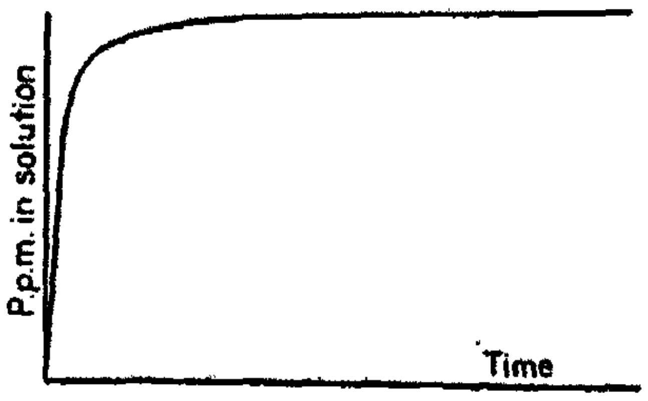

Fig. 3—Rate of solution of powdered minerals.

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[1] See, for example, Umwandlung des Feldspats in Sericit (Kaliglimmer) von Carl Benedick, Bull. Geol. Inst. Upsala, 7, 278–286 (1904).

[2] See Electrical instruments for determining the moisture, temperature and soluble salt content of soils, by L. J. Briggs, Bull. No. 15, Bureau of Soils, U. S. Dept. Agriculture, 1899.

The resistance drops to about 5,000 ohms within a short space of time usually three or four minutes. A further slight drop in the resistance generally takes place, but it requires days, and sometimes even months to become more than barely appreciable. In this manner it has been shown that the soil and many of the common soil minerals dissolve quite rapidly if they are sufficiently fine to offer a large surface to the action of the water. It would seem to follow, therefore, that in the case of the soil solution the concentration with respect to these constituents derived from the soil minerals, will be rapidly restored whenever disturbed through absorption by plants, leaching, or otherwise.

That the minerals of the soil, or a powdered mineral or rock-powder, will dissolve continually as the concentration of the solution in contact with it is disturbed by abstraction of a dissolved mineral substance, has been shown by numerous experimenters. An apparently obvious way to test this point would be to treat the soil sample with successive portions of water, and to analyze the successive portions for the dissolved mineral substances. This method, however, involves serious experimental difficulties, owing to the smaller sized mineral particles being suspended in the mother liquor, thus precluding satisfactory decantation and clogging filters. Moreover, such a process in no case simulates field conditions. To meet these difficulties, the soil or mineral powder has been placed between two porous media, as in the space between two concentric cylinders of unglazed porcelain, the space being closed by a rubber stopper. To the interior cylinder is fitted a stopper carrying a tube of insoluble metal, such as platinum or tin. This tube is bent into a goose-neck form, and just below the stopper the tube is perforated with a small opening. The whole apparatus is filled with water and set in a beaker, also filled with water. The metal tube is made the cathode in an electric circuit, a platinum or other suitable anode being introduced into the beaker. In a few minutes the dissolved and hydrolyzed bases pass into the cathode chamber, and as the water also accumulates in the chamber by electrolytic endosmosis, a solution of the bases dissolved from the soil minerals drops from the end of the metal goose-neck. By adding water to the outer beaker from time to time, a steady stream of alkaline solution has been obtained for months, and in no case yet has a soil thus treated failed to continue to yield up the bases it contains in its mineral particles. The acids, such as phosphoric acid for example, are of course found in the water outside the porous cells, and in the case of the phosphoric acid it also appears to continue indefinitely to be withdrawn from the soil.[1] It thus appears that as the products of solution and hydrolysis are removed, by such an endosmotic device as that just described or by the roots of growing plants, by leaching or otherwise, the soil minerals will continue to dissolve.

The foregoing arguments as to the concentration of the soil solution with respect to those constituents derived from the soil minerals, are based on the generally recognized principle that a material system left to itself tends towards a condition of stable equilibrium or final rest, that is, a condition where such changes as are taking place are so balanced that no change occurs in the system as a whole. But the soil is a system continually subject to outside forces and influences, and as pointed out above, is of necessity a dynamic system. It is doubtful in the extreme if any soil in place is ever in a state of final stable equilibrium. It would be natural, therefore, to expect and to find that even if the solution in the soil were directly dependent on the solubility of the soil minerals alone and were continually tending towards a definite normal concentration, actually this concentration would seldom if ever be realized. Most important in this connection is the fact that the concentration of the soil solution is always dependent in some degree upon the concentration of the soluble constituents in the solid phases in other than definite chemical combinations. Nevertheless, the evidence at hand indicates that the various processes taking place in the soil as a whole continually tend to form and maintain a normal concentration of mineral constituents in the soil solution.

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[1] For detailed description of the apparatus and experimental data, see Bull. No. 30, p. 27, *et seq.*, Bureau of Soils, U. S. Dept. Agriculture, 1905.

NEW BOOKS

Outlines of Chemistry. *A Text-Book for College Students. By Louis Kahlenberg. 14 × 23 cm; pp. xix + 548. New York: The Macmillan Company, 1909. Price: $2.60 net.*—This book carries the reviewer back to his undergraduate days. This is elementary chemistry as it used to be taught at all the American universities and as it still is at many of them. There is one chapter devoted to solutions, electrolysis and electrochemical theories; but except for that there is very little of what is ordinarily called physical chemistry. The arrangement of the material is as follows: hydrogen, oxygen, water, hydrochloric acid and chlorine; the laws of combining weights and combining volumes, and the atomic and molecular theories; ozone, allotropy and hydrogen peroxide; the halogens, acids, bases, salts, hydrolysis, mass action and chemical equilibrium; nitrogen, the atmosphere and the elements of the helium group; compounds of nitrogen with hydrogen and with the halogens; oxy-acids and oxides of nitrogen; sulphur, selenium and tellurium; carbon and some of its typical compounds; hydrocarbons and additional compounds of carbon; illuminating gas and flames; thermochemistry; silicon and boron and their important compounds; phosphorus, arsenic, antimony and bismuth; classification of the elements; the periodic system; the alkali metals; the alkaline earth metals; the metals of the magnesium group; solutions, electrolysis, and electrochemical theories; copper, silver and gold; the metals of the earths; lead and tin; chromium, molybdenum, tungsten and uranium; manganese; iron, nickel and cobalt; the metals of the platinum group.

To the reviewer it does not seem rational to take up boron and titanium before copper; but this book gives us another instance of how far we yet are from any agreement as to how to teach introductory chemistry. It seems to the reviewer as though the time were ripe for a discussion of the order in which the elements should be taken up, each man to give full reasons for his preference. There is good and sufficient reason for a great difference of opinion between those who believe in subordinating everything to the periodic law and those who do not. We cannot expect an agreement as to details between those who believe in putting in a lot of physical chemistry and those who do not; but it does not seem reasonable that the order should be silver, lead and iron in one book and iron, lead and silver in another. The reviewer is not pleading for uniformity of practice. That would probably be extremely undesirable. He does feel that those of us who do not teach elementary chemistry are entitled to know the reasons which give rise to this endless variety.

Apart from the question of classification, where each man's opinion is evidently much better than that of anybody's else, there are some errors of fact. On p. 23 is the statement that "the rate with which a chemical reaction proceeds is proportional to the chemical affinity that comes into play." While this is one factor determining the rate, it is not necessarily the decisive factor and there is serious trouble in store for the student who tries to make use of this statement.

On p. 57 we read: "If three elements, A, B and C, are able to form chemical compounds with one another, the proportions by weight with which A and B unite to form the compound AB, and the proportions in which A and C unite, also determine the proportions in which B and C unite with each other." Perhaps they do; but how about this case? One atomic weight of tin combines with either two or four atomic weights of chlorine. One atomic weight of copper combines with either one or two atomic weights of chlorine. Given these experimental facts as premises, the reviewer does not see how to apply the quotation so as to deduce the experimental fact that one atomic weight of tin combines with three atomic weights of copper.

On p. 87 the action of nascent hydrogen is said to be due to atomic hydrogen; but, if so, why is not the atomic hydrogen obtained with zinc like the atomic hydrogen obtained with copper?

In the present state of our knowledge it seems a pity not to have pointed out, p. 88, that the conversion of ozone into oxygen is a photochemical reaction. If one is to write the formula of hydrogen peroxide, p. 91, as H_2O_2, the formula of sodium peroxide should not be written NaO.

When making sodium or potassium persulphate, the yield is higher if one starts with the neutral salt and not with the acid salt as recommended in the text, p. 202. Further, the formula of persulphuric acid is not HSO_4.

With the author's extreme views on the electrolytic dissociation theory, it might have been supposed that he would take advantage of this opportunity to write a book which would be startlingly radical. He has done nothing of the sort. He has given a fair presentation of all debatable questions. Of course he does not reach quite the same conclusions that some other people have reached; but he has as much right to his opinions as the other people have to theirs. After stating the electrolytic dissociation theory, he points out that it is possible to duplicate all the typical ion reactions in non-conducting solutions. No one can deny that Kahlenberg has duplicated a surprising number of them. He also states that the bulk of the evidence is against the electrolytic dissociation theory. That is largely a matter of opinion. The reviewer would be willing to admit that many of the upholders of the electrolytic dissociation theory have made and are still making many absurd claims. He will also admit that Kahlenberg has shown the experimental weakness of many of these claims. The reviewer believes, however, that Kahlenberg's mission in life is to be a gardener with pruning shears and not a George Washington with a little hatchet. The reviewer looks forward confidently and with telescopic vision to the day when Kahlenberg will be recognized as one of the leaders in the movement to put the theory of electrolytic dissociation on a sound experimental basis.

For some unknown reason the publishers have lined the cover with brown wrapping paper and have put a blank page of brown wrapping paper at the beginning and the end of the book. *Wilder D. Bancroft*

Theorien der Chemie. *Nach Vorlesungen gehalten an der Universität von Kalifornien zu Berkeley. By Svante Arrhenius. Mit Unterstützung des Verfassers aus dem englischen Manuskript übersetzt von Alexis Finkelstein. Zweite neubearbeitete und bedeutend vermehrte Auflage. 16 × 24 cm; pp. ix + 233. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1909. Price: linen, 7.50 marks; bound, 8.50 marks.*—The first edition has been reviewed (11, 91) and we now have a second edition. Among the newer papers discussed or referred to, we find: Landolt's final conclusions on the conservation of mass; Ramsay's alleged synthesis of lithium and of neon, together with the criticisms by Mme. Curie and by Rutherford; the last papers of Jones and of Armstrong in regard to hydrates in solution; the work of Buckley and Jones on asymmetric nitrogen; Emil Fischer's work on alanine and the work of Bredig and Fajan on the catalytic action of nicotine; Nef's conclusions as to α-brompropionic acid; the work of Rosanoff and Prager on esterification; the work of Lenard and Crowther, of Wien, and of Gehrcke and Reichenheim on cathode rays and anode rays; the work of Rutherford on the α-particles and on the emanation; the views of Campbell and of McLennan on radioactivity; the work of Svedberg and of Ehrenhaft on the Brownian movements; Perrin's experiments with rubber emulsions; Hudson's studies on milk sugar; Morse's most recent work on osmosis; the views of Goldschmidt and of Acree in regard to esterification; Cohen's reply to Kahlenberg; and Lundén's work on amphoteric electrolytes.

These citations will give some idea of the thoroughness with which the book has been revised. *Wilder D. Bancroft*

Anleitung für das organisch präparative Praktikum. *By Franz Wilh. Henle. Mit einer Vorrede von J. Thiele. Mit zahlreichen Skizzen. 16 × 24 cm; pp. iv + 176. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1909. Price: linen, 4.60 marks; bound, 5.20 marks.*—The general arrangement of the experiments is as follows: substitution in the benzol ring; introduction of halogen; derivatives of the alcohols, acids, and aldehydes; oxidation; reduction; reactions of amines and diazo-compounds; carbon syntheses; the closing of rings; irreversible dissociation. The reactions seem to be well selected and the references to the original papers are exceptionally full. No equations are given and a number of questions are incorporated in the text. While there may be some difference of opinion as to the advisability of omitting the equations, everybody will agree that the questions serve a useful purpose. The reviewer's criticism is that they do not go far enough. Some day we may perhaps see a manual in which things are explained. Supposing we start with 100 grams KBr when making ethyl bromide, p. 41, why do we take 110 cc alcohol and 100 cc concentrated sulphuric acid? Why is the yield only 70–75 grams instead of about 90 grams? Why do Henle's directions differ from those of Gattermann? In spite of many admonitions from others, the reviewer sometimes wonders whether the methods of teaching organic chemistry are not exceptionally bad. The student learns manual dexterity; but it does not seem necessary to let his mind lie fallow throughout a whole laboratory course.

Wilder D. Bancroft

Les Bases physico-chimiques de la Chimie analytique. *By W. Herz. Traduit de l'allemand, par E. Philippi. 14 × 23 cm; pp. vi + 167. Paris: Gauthier-Villars, 1909. Price: bound, 5 francs.*—The German edition appeared in 1907 and we now have the French translation. In the preface the author says:

"In this volume my aim has not been to bring new facts but rather to make a choice among those already known and to present them in the most suitable form. I have attempted to set forth, from the point of view of chemical analysis, those portions of physical chemistry which I have found in my already long career as professor at the University of Breslau, to be the most serviceable in enabling people to understand analytical methods."

This is rather an interesting little book but not very well digested in spite of the preface. On p. 96 the author states that the analyst is often hard put to it to distinguish between a compound and a mixture. This is quite true and it is also true that the methods of physical chemistry will enable him to decide the matter. Unfortunately the author limits himself to the one case of alloys and it is still more unfortunate that he states that if we have a compound the freezing point curve will show a maximum. The budding analysts in Breslau must lead a very happy life if their difficulties can be removed in this easy way.

Wilder D. Bancroft

The Elements of Metallography. *By Rudolf Ruer. Authorized translation by C. H. Mathewson. First edition. 15 × 23 cm; pp. xvi + 342. New York: John Wiley and Sons, 1909. Price: $3.00 net.*—From one point of view, the author's, this is a very good book. The author has really written a book on the application of thermal analysis to the study of alloys. This of course involves a general study of one-component, two-component, and three-component systems. All of this is presented in so clear and satisfactory a manner that the book will be great value to many people. The only fault of the book is in its limitations. If the author had also discussed the microscopical methods of investigation with the same degree of thoroughness, he would have written a classic. As it is, the chapter on "investigation of structure" gives some information as to how to take photomicrographs; but practically nothing as to how to use the microscope so as to get results.

The Göttingen laboratory apparently takes the method of thermal analysis quite seriously. Really it is a rapid method for getting results which are sometimes right. It is a method which is of no value except when the changes in question take place rapidly and with a considerable evolution or absorption of heat. While useful in its place, it should never be relied on as the sole method. The Göttingen laboratory is forced to dodge the difficult problems and relies on others for the determination of the iron-carbon diagram for instance. While many binary alloys have been studied at Göttingen, it seems to the reviewer that all this work will have to be repeated. The zinc-antimony diagram will serve as an illustration and it is not an isolated case.

Since the reviewer believes that the method of thermal analysis is only of limited application, he regrets that an otherwise good book should be marred by a slavish adherence to a single method. *Wilder D. Bancroft*

ON THE RATE OF SOLUTION OF CASEIN IN SOLUTIONS OF THE HYDROXIDES OF THE ALKALIES AND OF THE ALKALINE EARTHS

BY T. BRAILSFORD ROBERTSON

(From the Rudolph Spreckels Physiological Laboratory of the University of California)

In previous communications[1] I have shown that when casein is shaken or stirred up in a solution of a hydroxide of an alkali or of an alkaline earth, it dissolves rapidly at first, but later, and especially after the solution has become acid to litmus, with extreme slowness. It appeared of interest to ascertain more precisely the time-relations of this phenomenon and their dependence upon the mass of casein or of hydroxide present in the mixture—upon the kind of hydroxide, etc. Accordingly the following experiments were undertaken.

The casein which was employed was Eimer & Amend's "C. P. Casein nach Hammarsten," specially purified by washing in water, alcohol and ether according to the method described in a previous communication.[2] It was dried at about 30° for about 12 hours, but not over H_2SO_4. Hence it contained traces of ether and a trace of water, too small to affect the accuracy of the determinations, but of considerable importance to the success of the investigation. Perfectly anhydrous casein only sinks in and is wetted by water or watery solutions with extreme difficulty and hence was not suitable for the present purpose. The same preparation of casein was employed in all of the experiments enumerated in Tables I–XVII inclusive. A fresh preparation of casein was employed in the experiments enumerated in Table XVIII.

A measured amount (usually 100 cc) of the fluid employed

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[1] T. Brailsford Robertson: Jour. Biol. Chem., 2, 317 (1907); 5, 147 (1908); Jour. Phys. Chem., 13, 469 (1907).

[2] T. Brailsford Robertson: Jour. Biol. Chem., 2, 317 (1907).

as solvent was placed in a beaker of squat form and 400 cc capacity and was agitated by a flattened glass rod which was bent at right angles, the plane of the horizontal arm being somewhat inclined to the vertical, so as to communicate an upward thrust to the rotating liquid. The horizontal arm of the stirrer was about $2^1/_2$ cm long and as near as possible to the bottom of the beaker; this was rotated at an approximately constant rate of about 1600 revolutions per minute by a small motor. While stirring, a weighed amount of the casein was dropped into the fluid. At stated intervals samples of the mixture were almost instantaneously abstracted by means of a 10 cc pipette which was provided with a rubber bulb. The samples were then very rapidly filtered through lightly-packed glass wool. The time occupied in filtration was never more than 30 seconds for the 5 and 10 minute samples, or more than 1 minute for the later samples. The refractive index of the filtrate from each sample was then determined.[1] Denoting the refractive index of the filtrate from any given sample by n and that of the pure solvent by n_1, the quotient $\frac{n - n_1}{0.00152}$ is the number of grams of casein dissolved in 100 cc of the solvent at the moment when the sample was extracted.[2]

The type of relation which was found to subsist between the time which elapsed after the introduction of the casein and the number of grams of casein dissolved in 100 cc of solvent is shown diagrammatically in Fig. 1, in which the abscissae represent minutes and the ordinates the number of grams of casein dissolved in 100 cc of solvent. It will be observed that the rate of solution is at first very great, but that it very rapidly falls off. It does not fall to zero, however, that is, the curve does not appear to approach an asymptote but is rather of a parabolic form. Nor does this appear strange when we observe that although, after two hours'

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[1] Using a Pulfrich refractometer which read the angle of total reflection accurately to within 1′, and a sodium flame as the source of light.

[2] T. Brailsford Robertson: Jour. Phys. Chem., 13, 469 (1909).

stirring, the rate of solution of the casein is very small, yet the solvent is still very far from being "saturated" with casein. The alkali-equivalent of 1 gram of casein, measured by neutralization of the excess of alkali by means of a strong acid,[1] is about 11×10^{-5} equivalent gram molecules but the proportion of the casein actually dissolved to the amount of base present in the solvent was always, in these experiments, ever after two hours of stirring, very much less than this.[2]

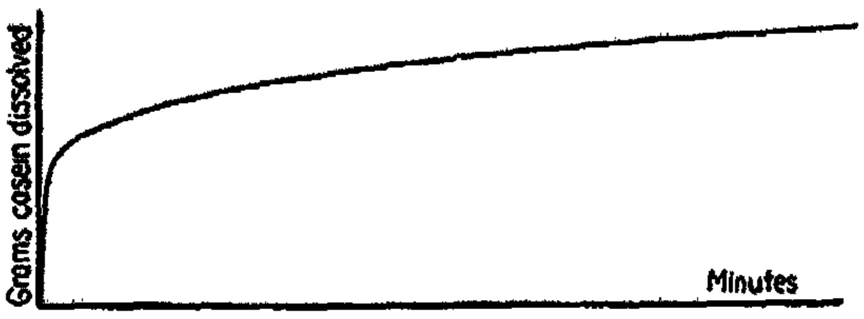

Fig. 1

The relation between the time of stirring and the quantity of casein dissolved does not appear to obey any of the ordinary chemical reaction—or solution-velocity formulae. Noyes and Whitney[3] have shown that the rate of solution of a crystalloid is at each moment proportional to the difference between the concentration at the moment and that required for saturation. This leads, for a constant rate of stirring and assuming that the surface of the crystalloid exposed to the action of the solvent is approximately constant during the progress of the experiment, to the equation $\log \frac{a}{a-x} = kt$, where a is the concentration at saturation, x is the concentration of the dissolved crystalloid at time t and k is a constant. We can

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[1] T. Brailsford Robertson: Loc. cit.

[2] It might be imagined that the solutions of the caseinates which are prepared by neutralizing the excess of base by a strong acid are "supersaturated" with respect to casein. I have, however, prepared a solution in this way containing 3 percent of casein in 0.0043 N KOH (1 g. of casein to 14×10^{-5} equivalent gram molecules of KOH) which has now been standing at room temperature with toluol in a sealed glass vessel for over four months. It is still perfectly stable and contains only a trace of precipitate, probably of paranuclein, derived from the casein by autohydrolysis.

[3] Noyes and Whitney: Zeit. phys. Chem., 23, 689 (1897).

compute a in the above equation, for casein, from the known alkali-equivalent of casein (1 g. = 11 × 10^{-5} equivalent gram molecules of base) and from the known amount of alkali present in the solution employed as solvent. But a few trials suffice to demonstrate that the relation between time and amount dissolved, for casein, does not even approximately obey this formula. The rate at which the velocity of solution falls off; the negative acceleration of the process; is far too great to permit of representation by this formula. Nor is any better agreement obtained if we insert, for the value of a, the actual number of grams of casein present in the mixture, or if, allowing for the diminution in the surface of the casein exposed to the action of the solvent, as solution proceeds, we endeavor to apply the relation $\frac{dx}{dt} = K(A - x)(B - x)$[1] where A is the number of grams of casein which the amount of alkali present in the solvent is capable of holding in solution, B is the number of grams of casein actually present in the mixture, x is the amount of casein dissolved at any given moment, and K is a constant. The relation between the time of stirring and the amount of casein dissolved, however, does obey, very accurately, the relation $x = Kt^m$, where x is the amount dissolved after time t and K and m are constants which vary with the nature and concentration of the alkali-solution employed as solvent and with the total mass of casein present in the mixture.

In the following tables are given the results of these experiments. The quantity of solvent employed was always 100 cc and the number of grams of casein initially added to it was always 5. For a reason which will shortly appear, no especial effort was made to maintain a constant temperature during the progress of an experiment, but at the head of each table are given the temperatures of the mixture at the beginning and at the end of the experiment. The temperature at the beginning of the experiment is always placed first. In

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[1] In its integrated form, $\log \frac{B(A - x)}{A(B - x)} = Kt$.

the column headed "calculated" are given the values of x calculated from the above formula, the constants K and m being determined from all of the observations by the method of least squares, employing for this purpose the form $\log_{10} x = m \log_{10} t + \log_{10} K$. The possible experimental error in the determination of the concentration of a casein solution by means of its refractive index is always ±0.07 gram per 100 cc. It will be seen that the differences ($= \Delta$) between the observed and calculated values of x are hardly ever greater, usually considerably less, than the possible error in the determination of the concentration of the casein in the filtrates.

TABLE I

Solvent: 0.00218 N KOH. Temperature 24°–21°

$K = 0.361$ $m = 0.154$

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	0.45	0.46	+0.01
10	0.51	0.51	0.00
30	0.64	0.61	—0.03
60	0.71	0.68	—0.03
120	0.71	0.75	+0.04
			$\Sigma\Delta = -0.01$

TABLE II

Solvent: 0.00435 N KOH. Temperature 25°

$K = 0.578$ $m = 0.187$

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	0.76	0.78	+0.02
10	0.89	0.89	0.00
30	1.15	1.10	—0.05
60	1.28	1.25	—0.03
120	1.35	1.42	+0.07
			$\Sigma\Delta = +0.01$

TABLE III

Solvent: 0.00653 N KOH. Temperature 24°

$K = 0.764 \qquad m = 0.208$

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	1.07	1.07	0.00
10	1.20	1.23	+0.03
30	1.60	1.55	—0.05
60	1.86	1.79	—0.07
120	1.99	2.07	+0.08
		$\Sigma\Delta =$	—0.01

TABLE IV

Solvent: 0.00870 N KOH. Temperature 26.5°

$K = 1.47 \qquad m = 0.169$

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	1.71	1.72	+0.01
10	1.91	1.93	+0.02
30	2.37	2.32	—0.05
60	2.63	2.61	—0.02
120	2.89	2.94	+0.05
		$\Sigma\Delta =$	+0.01

TABLE V

Solvent: 0.00870 N KOH. Temperature 18°–20°

$K = 1.48 \qquad m = 0.146$

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	1.84	1.87	+0.03
10	2.11	2.07	—0.04
30	2.43	2.43	0.00
60	2.70	2.69	—0.01
120	2.96	2.98	+0.02
		$\Sigma\Delta =$	0.00

TABLE VI

Solvent: 0.01088 N KOH. Temperature 21°–24°
K = 1.64 m = 0.168

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	2.09	2.15	+0.06
10	2.49	2.42	−0.07
30	2.95	2.91	−0.04
60	3.28	3.27	−0.01
120	3.61	3.67	+0.06
		ΣΔ =	0.00

TABLE VII

Solvent: 0.01305 N KOH. Temperature 25°–26°
K = 0.23 m = 0.142

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	2.74	2.80	+0.06
10	3.13	3.09	−0.04
30	3.66	3.62	−0.04
60	4.05	3.99	−0.06
120	4.32	4.40	+0.08
		ΣΔ =	0.00

TABLE VIII

Solvent: 0.01523 N KOH. Temperature 20°–22°
K = 2.42 m = 0.137

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	2.98	3.02	+0.04
10	3.31	3.32	+0.01
30	3.97	3.86	−0.11
60	4.30	4.24	−0.06
120	4.53	4.66	+0.13
		ΣΔ =	+0.01

TABLE IX

Solvent: 0.01740N KOH. Temperature 22°

K = 2.60 m = 0.153

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	3.30	3.33	+0.03
10	3.69	3.70	+0.01
30	4.48	4.38	—0.10
60	4.81	4.87	+0.06
120	(5.01)[1]	—	—
		ΣΔ =	0.00

TABLE X

Solvent: 0.00870 N NH_4OH. Temperature 20°–22°

K = 1.50 m = 0.141

Time in minutes	Gram casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	1.84	1.88	+0.04
10	2.11	2.07	—0.04
30	2.43	2.42	—0.01
60	2.70	2.67	—0.03
120	2.89	2.94	+0.05
		ΣΔ =	+0.01

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[1] That is to say, at some undetermined time previous to this all of the casein present had been dissolved. Only the first four observations were used in computing the constants.

TABLE XI

Solvent: 0.00870 N NaOH. Temperature 22°–23°
K = 1.33 *m* = 0.163

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	1.71	1.73	+0.02
10	1.97	1.94	—0.03
30	2.30	2.32	+0.02
60	2.63	2.60	—0.03
120	2.89	2.91	+0.02
		ΣΔ =	0.00

TABLE XII

Solvent: 0.00870 N LiOH. Temperature 20°–22°
K = 1.07 *m* = 0.213

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	1.51	1.51	0.00
10	1.71	1.74	+0.03
30	2.24	2.21	—0.03
60	2.63	2.56	—0.07
120	2.89	2.96	+0.07
		ΣΔ =	0.00

TABLE XIII

Solvent: 0.00870 N $Ca(OH)_2$. Temperature 20°
K = 0.778 *m* = 0.099

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	0.92	0.91	—0.01
10	0.99	0.98	—0.01
30	1.12	1.09	—0.03
60	1.18	1.17	—0.01
120	1.18	1.25	+0.07
		ΣΔ =	+0.01

TABLE XIV

Solvent: 0.01740 N $Ca(OH)_2$. Temperature 22°
$K = 1.63$ $m = 0.176$

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	2.11	2.17	+0.06
10	2.51	2.45	−0.06
30	3.03	2.98	−0.05
60	3.36	3.36	0.00
120	3.76	3.80	+0.04
		ΣΔ =	−0.01

TABLE XV

Solvent: 0.01740 N $Sr(OH)_2$. Temperature 21°
$K = 2.22$ $m = 0.141$

Time in minutes	Gram casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	2.77	2.79	+0.02
10	3.10	3.08	−0.02
30	3.63	3.60	−0.03
60	3.95	3.96	+0.01
120	4.35	4.37	+0.02
		ΣΔ =	0.00

TABLE XVI

Solvent: 0.01740 N $Ba(OH)_2$. Temperature 20°
$K = 1.34$ $m = 0.194$

Time in minutes	Grams casein dissolved in 100 cc solvent		Δ
	Found	Calculated	
5	1.85	1.84	−0.01
10	2.05	2.10	+0.05
30	2.64	2.60	−0.04
60	3.03	2.98	−0.05
120	3.36	3.40	+0.04
		ΣΔ =	−0.01

It is evident that equally concentrated solutions of KOH, NaOH, LiOH and NH_4OH dissolve casein with about equal rapidity, while solutions of the hydroxides of the alkaline earths dissolve casein much more slowly, $Sr(OH)_2$ dissolving the casein most rapidly, $Ca(OH)_2$ more slowly and $Ba(OH)_2$ more slowly still. This fact is perhaps of significance when viewed in the light of the facts that solutions of the caseinates of the alkaline earths become opalescent on heating, while those of the caseinates of the alkalies and ammonium do not,[1] that the caseinates of the alkaline earths will not pass through the pores of a clay filter, while those of the alkalies and ammonium readily do so,[2] and that in these and in other ways the caseinates of the alkaline earths give evidence of being present, in their solutions, in the form of more bulky molecules than those of the caseinates of the alkalies and of ammonium under equivalent conditions.

The amount of casein which is dissolved, in a given period of time, by a solution of KOH is, within the limits of accuracy of the determinations, *directly proportional to the concentration of the KOH-solution.* This is very clearly shown in Table XVII, in which *r* denotes the ratio of the number of grams of casein dissolved to the number of equivalent gram molecules (multiplied by 100) of KOH present in the 100 cc of solvent employed. It will be observed that this ratio, for any of the given times, is very nearly constant.[3]

A comparison of Tables IV and V at once shows that the temperature-coefficient of the velocity of solution is very small. The differences between the amounts of casein dissolved, after a given time, at 18°–20° and at 26° are only double the possible error of the determination for the 5- and 10-minute periods and only equal to the possible error for the remaining periods. So far as the accuracy of the method employed enables us to decide, therefore, the temperature-

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[1] W. A. Osborne: Jour. Physiol., 27, 398 (1901).

[2] W. A. Osborne: Loc. cit.

[3] At "saturation" of the alkali with casein the numerical value of this ratio would be 91.

TABLE XVII

Concentration of the KOH solution employed as solvent	0.00218 N	0.00435 N	0.00653 N	0.00870 N	0.01088 N	0.01305 N	0.01523 N	0.01740 N
Time in minutes	r	r	r	r[1]	r	r	r	r
5	21	18	16	20	19	21	20	19
10	23	21	18	23	23	24	22	21
30	29	26	26	28	27	28	26	26
60	33	29	29	31	30	31	28	28
120	33	31	31	34	33	33	30	—

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[1] Average of the two determinations at 26.5° and at 18°–20° respectively.

coefficient of the rate of solution, between the temperatures mentioned, is practically zero.[1] This agrees with the results of my previous investigations,[2] namely, that for temperatures lying between 20° and 36° the rate of solution of casein in solutions of the hydroxides of the alkalies is unaffected by temperature, while at higher temperatures the rate of solution in solutions of the hydroxides of the alkalies is increased and the rate of solution in solutions of the hydroxides of the alkaline earths is diminished.

This fact would, in itself, lead us to suspect that the process which determines the *rate* of solution of casein in solutions of hydroxides of the alkalies and alkaline earths is not chemical in nature.

That the rate of solution of the casein is not determined by the velocity of a chemical reaction occurring exclusively in the *liquid* phase is also shown by the fact that the rate of solution of the casein is dependent upon the mass of casein initially introduced into the mixture. Were the rate of solution of the casein dependent solely upon the velocity of a reaction between casein and the alkali, taking place in the liquid phase, then since, in the presence of undissolved casein, the liquid would always be saturated with casein, the rate of solution should be independent of the mass of undissolved casein. We are led to conclude, therefore, that the processes which determine the velocity of solution occur, in part at all events, either *within* or at the *surfaces* of the suspended particles of undissolved casein.

The relation between the amount of casein dissolved in a given time and the mass of casein initially added to the solvent is shown in Table XVIII and graphically in Fig. 2. The temperature of the mixtures was, in all of these experiments, 20°. It will be seen that the rate of solution increases, at first somewhat rapidly with the mass of casein added to the solvent, later more slowly.

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[1] It was for this reason, of course, that no special effort was made to maintain a constant temperature during the progress of the experiments.

[2] T. Brailsford Robertson: Jour. Biol. Chem., 5, 147 (1908).

TABLE XVIII

Grams casein added to 200 cc of solvent (0.010 N KOH)	2.5	5.0	7.5	10.0	12.5	15.0
Time in minutes	Grams dissolved	Grams dissolved	Grams dissolved	Grams dissolved	Grams dissolved	Grams dissolved
5	2.24	2.76	3.28	3.68	3.68	3.82
10	2.36	3.28	3.82	4.22	4.22	4.60
30	(2.50)[1]	3.96	4.86	5.40	5.40	5.66
60	—	4.60	5.40	5.92	5.92	6.18

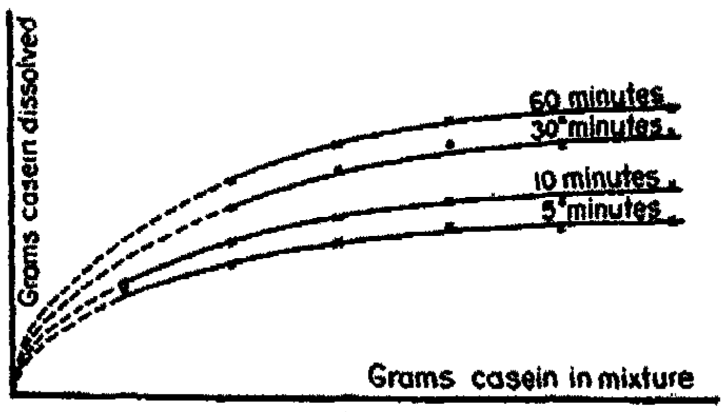

Fig. 2

The relation $x = Kt^m$ is, it is of interest to observe, the same as that found by Cameron and Bell[2] and later confirmed by Ostwald from the investigations of Goppelsroeder,[3] to subsist between the amount of fluid absorbed by a column of sand or of a strip of filter-paper and the time during which the fluid has remained in contact with a portion of its surface.[4] The values of the constants are also of the same order of magnitude as those found in these investigations. It is possible, therefore, that the *rate* of solution of the casein is primarily

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[1] That is to say, at some undetermined time previous to this all of the casein introduced into the solvent had been dissolved.

[2] Cameron and Bell: Bulletin No. 30, p. 50, Bureau of Soils, U. S. Dept. of Agriculture, 1905; Jour. Phys. Chem., 10, 658 (1906).

[3] Wo. Ostwald: 2 Supplementheft zur Zeit. Kolloidchemie, 1908, 20, der F. Goppelsroeder. "Neue Kapillar- und kapillaranalytische Untersuchungen" Verhandl. Naturforsch. Gesellsch. zu Basel, Bd. XIX, Heft 2, 1907.

[4] According to Cameron and Bell, Jour. Phys. Chem., 10, 658 (1906), this formula can be derived from the formula of Poiseuille for the flow of liquids through capillary spaces.

determined by the rate at which the particles are penetrated and wetted by the solvent, the processes of chemical reaction between the alkali and the casein and of diffusion of this compound into the liquid phase taking place at relatively great velocities.

It is, perhaps, not surprising that the factor which determines the rate of solution of casein should be the velocity with which it is wetted by the solvent, while that which determines the rate of solution of a crystalloid is the velocity with which the dissolved substance diffuses through a thin layer of saturated solution in immediate contact with the surfaces of the crystals. A crystal is only wetted upon its external surface, and the wetting, naturally, takes place instantly. A particle of casein (or, in general, of the solid or semi-solid phase of any colloid) is, however, comparable in structure with a sponge; the surface which may be wetted by the solvent is, per unit volume very much larger than that of a crystal and the solvent must, in wetting this surface, transverse a relatively immense network of minute capillary pores. Under such conditions the time occupied in wetting the surfaces of the particles may well be great compared with the time required for the dissolved substance to diffuse from these surfaces into the solvent, or with the time required for the accomplishment of the union between the protein and the alkali in the solvent.

Conclusions

1. If casein be stirred at an approximately constant rate in solutions of the hydroxides of the alkalies or of the alkaline earths, the amount dissolved is connected with the time which has elapsed since the casein was introduced into the solvent by the equation $x = Kt^m$, where x is the number of grams of casein dissolved, t is the time, and K and m are constants which depend upon the concentration and kind of hydroxide-solution employed as solvent, and upon the total mass of casein in the mixture.

2. The rapidity of solution is, within the limits of the accuracy of the determinations, unaffected by temperature,

for temperatures ranging between room-temperature and 30°.

3. Equally concentrated solutions of the hydroxides of potassium, sodium, lithium and ammonium dissolve casein at approximately the same rate. Solutions of the hydroxides of the alkaline earths dissolve casein much more slowly, $Sr(OH)_2$ dissolving it most rapidly, $Ca(OH)_2$ more slowly, and $Ba(OH)_2$ more slowly still.

4. The amount of casein dissolved by a solution of KOH in a given period of time is directly proportional to the concentration of the KOH.

5. The rapidity with which casein is dissolved by a given solution of a hydroxide of an alkali increases with the mass of casein present in the mixture. At first the increase in the velocity of solution with increasing mass of casein is rather large, but as the mass of casein is still further increased, the increase in the rapidity of solution is less.

6. Having regard to the smallness of the temperature-coefficient of this phenomenon, to the dependence of the rate of solution upon the total mass of casein present, and to the identity of the form of the equation $x = Kt^m$ with that which expresses the relation between the amount of a liquid absorbed by a column of sand or a strip of filter paper and the time, it is suggested that the factor which determines the rate of solution of casein in solutions of the hydroxides of the alkalies and of the alkaline earths may possibly be the velocity with which the casein particles are penetrated and wetted by the solvent.

INTRODUCTION TO THE STUDY OF THE SOIL SOLUTION[1]

BY FRANK K. CAMERON

Absorption by Soils[2]

A property of soils, affecting profoundly the composition and concentration of the soil solution, is absorption. It is generally recognized that soils are good absorbers for vapors, and this fact finds practical expression in the common practice of burying things with a disagreeable odor, such as animal carcasses, night-soil, etc. It is also well-known that dissolved as well as suspended material can be more or less completely removed from water by passing it through sand or soil, and this fact finds important application in water supplies for cities and towns, sewage disposal, etc. It was known as long ago as Aristotle's time that ordinary salt is partly removed from water by passing through sand or soil. In recent times the practical as well as theoretical importance of this phenomenon has led to considerable study and experimental research, so that our knowledge of absorption effects is now fairly extensive, though it can hardly be claimed that it is satisfactory. The absorption of a dissolved substance from solution by a soil may be one or more of at least three kinds of phenomena. It may be a mechanical inclusion or trapping, distinguished by the term *imbibition*, the most familiar and striking case being the absorption of water itself by a soil or sponge or similar medium. It may be a partial taking up of the dissolved substance to form a new compound or a *solid*

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[1] Continued from Jour. Phys. Chem., 14, 372 (1910).

[2] For a detailed discussion and citations of the literature, see: Absorption of vapors and gases by soils, by H. E. Patten and F. E. Gallagher, Bull. No. 51; and Absorption by soils, by H. E. Patten and W. H. Waggaman, Bull. No. 52, Bureau of Soils, U. S. Dept. Agriculture, 1908.

solution,[1] as probably is the absorption of phosphoric acid by lime or ferric oxide. Or it may be a condensation or concentration of the dissolved substance on or about the surface of the absorbing medium, a phenomenon known as *adsorption*. To prove the existence of adsorption definitely and conclusively in any given case is always difficult, if ever possible, but the existence of this phenomenon is the most logical explanation of many observations, and is generally admitted by chemists and physicists at the present time.[2] It is by adsorption, probably, that potash and ammonia are held by the soil when added in fertilizers.

That absorption is dependent in some manner upon the solubility of the dissolved substance in the particular solvent employed would seem to be obvious. But what the relation may be, if it exists at all, is not known. For instance, silk absorbs picric acid from solutions in water and alcohol but not from solutions in benzene, although the solubility of picric acid in benzene lies between its solubility in water and in alcohol.[3]

The absorption of any given dissolved substance from different solvents is markedly different. Most soils absorb methylene blue from aqueous solutions with great avidity, but washing out the absorbed dye with water is an extremely

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[1] That is, a homogeneous solid, which may be either crystalline or amorphous. Probably the readiest criterion for distinguishing between a definite compound and a solid solution, is that the former is stable in contact with a liquid solution of its constituents over a measurable range of concentrations, while the composition of the solid solution changes with every change in the concentration of the liquid solution in contact with it.

[2] A clear and apparently indisputable case of adsorption has been noted by Dr. H. E. Patten (Some surface factors affecting distribution, Trans. Am. Electrochem. Soc., 10, 67-74 (1906)). On adding powdered quartz to an aqueous solution of gentian violet, there is a distribution of the dye between the water and the quartz. A microscopic examination of the latter showed that the dye was concentrated in thin layers upon the surface of the quartz grains, from which it could be washed with water, no change in the quartz grains being noticeable.

[3] Absorption of dilute acids by silk, by James Walker and James R. Appleyard, Jour. Chem. Soc., 69, 1334-1349 (1896).

tedious and unsatisfactory process, although it can be readily and more or less completely removed from the soil by alcohol. As might be anticipated from this, it is known that the presence of one dissolved substance affects the absorption of another, but in what way can not, generally, be anticipated, although it would seem that the importance of this subject for manurial practice would invite further research.

From the same solution, different absorbents remove a dissolved substance in different degrees. Speaking generally, paper absorbs dyes more readily than do soils, while soils absorb bases more readily than does paper. Hence the reddening of litmus paper when in contact with a moist soil. Heavy soils or soils containing much hydrated ferric oxide absorb bases more readily than do light soils, but this is probably owing to relative amounts of surface exposed, for the same relation holds true with respect to phosphoric acid. Soils rich in humus are better absorbers than soils not so rich. But here again there is yet doubt as to whether the explanation lies in the amount or in the kind of surface acting.

From the same solvent different dissolved substances are absorbed quite differently by any given absorbent. This can be readily illustrated again by dyes. If an aqueous solution of a mixture of methylene blue and sodium eosine, for instance, be shaken up with a soil, or percolated through a column of soil, the methylene blue is absorbed the more quickly and completely and a partial separation of the two dyes can be readily effected, the separation being more or less complete according to the conditions of the experiment. In the same manner two salts in solution can be separated, partially at least. Soils absorb potassium more readily than sodium, magnesium more readily than lime, and ammonia more readily than any of these bases.[1]

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[1] The prompt absorption of a base by soils is shown by the following experiment: To some freshly boiled distilled water add several drops of alcoholic phenolphthalein, and then just enough base to produce a decided red color. If the solution be now passed through a short column of soil, cotton, shredded filter paper or similar absorbent, the percolate will be perfectly colorless. The red color will be restored, however, by adding a little of the base to the percolate.

The absorption from aqueous solutions of inorganic salts involves a most interesting complication. Just as a mixture of two or more dyes or salts in solution can be separated by the selective action of an absorbent, so can an electrolyte itself be decomposed or resolved. Thus, if a solution of potassium chloride be passed through a column of soil, or cotton, or paper, or any similar absorbent, the filtrate will not only be less concentrated than the original solution, but the potassium will be found to have been absorbed to a greater extent than the chlorine, that is, the percolate contains free hydrochloric acid. The importance of this phenomenon for the conservation of the desirable constituents of manurial salts, and the elimination or leaching out of the less desirable constituents is obviously great. Equally great perhaps, is the effect upon the reaction of the soil, whether it be rendered temporarily alkaline or acid, an effect of the very greatest importance for the growth of some of our common crop plants[1] and for the lower soil organisms, such as the bacteria, molds, together with ferments, enzymes, etc., many of which are very sensitive to the reaction of the media in which they may be, and which in turn are of undoubted importance in determining the fertility of the soil for higher plants.

The absorption of a dissolved substance from solution by an absorbent is in effect a distribution phenomenon and the simplest formula to give quantitative expression to such a distribution is $C/C^1 = K$ when C is the concentration in the liquid phase and C^1 the concentration in the solid phase, K being a characteristic constant for the particular case under consideration. When a chemical reaction or a change of state,

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[1] See, The toxic action of acids and salts on seedlings, by F. K. Cameron and J. F. Breazeale, Jour. Phys. Chem., 8, 1-13 (1904). It is quite conceivable, for instance, that if the drainage conditions were not exceptionally good under a heavy type of soil, it might be rendered temporarily unfit for clover or alfalfa by a heavy application of potassium salts or of sodium nitrate. The idea put forward by some authorities that too long-continued or overfertilizing renders soils acid, may have better foundation than their theoretical reasoning would seem to warrant.

chemical or physical, is involved in the absorption in either dissolved substance or absorbent the formula becomes $C^{n}/C^{1} = K$ when n is a function which may be very simple or very complex. Attempts to develop a precise formula of this general type for the absorption by some given soil, although such a formula would be desirable for theoretical and practical reasons alike, have uniformly failed. A sufficient reason for this failure seems to lie in the fact that most dissolved substances produce an appreciable effect on the granulation or flocculation of the soil particles, which is progressive with the absorption, so that a continual change of absorbing or effective surface is taking place as the absorption proceeds. Moreover, in the case of an adsorption, with the formation of a continuous film of the dissolved substance, a new kind of absorbing surface is developed. Hence n is a function of so difficult a character as to defy thus far any attempt at formulation.[1]

We cannot therefore predict in any quantitative way what will be the distribution of a soluble substance such as salts in commercial fertilizers, for instance, between the solid soil particles and the soil solution. Empirical experiments show, however, that with the amount of a soluble salt present under normal conditions in a humid climate, or as used in fertilizer practice, the absorption of ammonia, lime, potassium or phosphoric acid is relatively very great, and in a general way in about the order named.

Absorption is not an instantaneous process. However, the rate at which a dissolved substance is absorbed is generally quite rapid. That is, if a soil be stirred or mixed with an aqueous solution, the absorption takes place very quickly, in the absence of any outside disturbing influences. The law governing the rate of absorption by soils has not therefore possessed any great practical interest and has not been studied from a quantitative point of view, although it is known

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[1] The distribution of solute between water and soil, by F. K. Cameron and H. E. Patten, Jour. Phys. Chem., 11, 581-593 (1907).

qualitatively that the rate is increased by increasing the concentration of the solution, or by increasing the amount of the absorbent or at least its effective surface. Two rate equations are of interest in this connection, and have been carefully studied. The rate at which a salt or other dissolved substance will advance into an absorbing soil from a solution is given by the same equation as that describing the rate of advance of the water itself, $y^n = Kt$, where y is the distance and t the time. The constants n and K for the slower moving dissolved substance are different from those for the water. This equation has probably little importance for ordinary agriculture, for absorption by the soil from a large (and relatively illimitable) mass of solution is unusual. That it may have considerable importance in seepage, irrigation, and some soil engineering problems, seems quite likely.

The rate at which a soil will absorb a dissolved substance from a percolating solution is given by the equation $dx/dt = K(A - x)$, as has been pointed out above. More interesting and important, however, is the fact that this same equation describes the rate at which an absorbed substance is removed from the soil by leaching. In the case of soils in humid areas dx/dt rapidly becomes exceedingly small as x approaches A, that is, when the amount of soluble material in the soil becomes small, and is practically constant under such conditions, as has been pointed out above when describing the removal of potassium and phosphoric acid from soils by percolating waters. This formula has a special interest in considering the reclamation of alkali lands by underdrainage, a problem to which reference will be made later.

Both percolation experiments, as those cited above, and direct absorption experiments made by shaking up soils with solutions of the salts in question, show conclusively that the absorption phenomena taking place in the soil are in harmony with the direct solubility effects in tending to produce and maintain a solution of a normal concentration as regards those constituents which it happens are also derived from the soil minerals.[1] It is an interesting coincidence that nitric acid (in combination with various bases of course) is very little absorbed by most soils, and does vary in concentration, not only in different soils but in the same soil, between wide limits, and within short intervals of time.[2] The nitrates of the soil are not derived from minerals, and should more properly be considered with the organic constituents of the soil solution.

An important application of these views concerning absorption arises in connection with certain wide-spread notions concerning soil acidity. There is a popular belief that most soils are acid, that the soil solution contains some free acid, mineral or organic, other than dissolved carbon dioxide, and that a neutral or alkaline solution is necessary to the successful production of most of our crops. This belief is, however, unwarranted, for the vast majority of soils yield an aqueous extract which is alkaline when boiled to expel carbon dioxide, and some of our crops, for instance wheat, seem to thrive better in a slightly acid medium. This popular fallacy seems to have its origin in the fact that most soils when moistened and pressed against blue litmus paper, redden it. This reddening may sometimes be due to the actual presence of some acid, or to dissolved carbon dioxide, but is undoubtedly due in the majority of cases to selective absorption. Litmus

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[1] An extreme case is worth citing in this connection. Mr. W. H. Heileman in studying the influence of various kinds of alkali upon plant growth, added from 3-4 percent of sodium carbonate to soils known to be otherwise free from alkali. Wheat seedlings grown in the soils so treated showed no ill effects from the added salt. When distilled water was percolated slowly through the soils, or shaken up with them, the resulting solution contained the merest traces of the alkali.

The ordinary method of determining the lime requirement of a soil by adding lime water until the solution shows an alkaline reaction is another obvious absorption phenomenon, and is not dependent, as popularly supposed, upon the presence of acids in the soil. Soils, which by no possibility could contain any free acid, frequently absorb very large amounts of lime in this manner.

[2] Usually, in the growing season, the soil solution has a much higher concentration with respect to nitrates in the morning than it has in the evening.

is a red dye of an acid-like character, which forms a soluble blue salt with the ordinary bases. But it has been shown that most soils are better absorbents of bases than is paper, whereas paper is a better absorbent of dye, speaking generally, than is a soil. Consequently when moist soil is brought into contact with wetted blue litmus paper the base is absorbed more readily by the soil, and the dye by the paper, the latter therefore becoming reddened.[1] The only criterion for determining surely that a soil is acid, is to make an aqueous extract, expel the dissolved carbon dioxide by boiling, or by passing through the solution an inactive gas, such as nitrogen, and then to test the reaction of the solution. Acid soils undoubtedly do exist, but they are by no means common or wide-spread, and are to be regarded as exceptional and abnormal.

The phenomena of selective absorption suggest the important part which surfaces play in modifying and changing chemical reactions.[2] For instance, Becquerel[3] observed that a solution of copper nitrate or cobalt chloride diffusing from a cracked test tube placed in a solution of sodium sulphide, led to the formation of the corresponding sulphide, but in the

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[1] The reddening of blue or "neutral" litmus paper can be accomplished with various absorbents. By pressing the litmus paper between moistened wads of absorbent cotton the reddening can be readily accomplished, usually in the course of ten minutes to a half hour. That the phenomenon is not due to any adhering acid on the cotton can be shown in the following way: A litmus solution is carefully prepared so that there is a very small excess of base present over that required to give the blue color. A wad of absorbent cotton is carefully washed by repeatedly sousing it in distilled water from which carbon dioxide has been expelled by boiling. When the cotton has been thoroughly washed, it is stirred thoroughly in a portion of distilled water, free from carbon dioxide, then withdrawn by some appropriate instrument and allowed to drain for a few minutes. The litmus is added in fairly large quantity to the drainings, which should then have a blue color. Again stir the cotton in the water, and more or less quickly, depending on the amount and purity of the litmus preparation as well as the quantity of cotton used, the solution will become red.

[2] For references to the literature see, Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, p. 61 *et seq.*

[3] Note sur les reductions metalliques produites dans les espaces capillaires, par M. Becquerel, Comptes rendus, 82, 354–356 (1876).

crack the metal itself was precipitated. Experiments of Graham[1] show that when a solution of silver nitrate is percolated through charcoal, not only is there a selective absorption as is shown by the percolate containing free acid, but there is a chemical reaction involved, since the silver is deposited in metallic spangles in the interstices of the absorbent. Graham has shown, and since his time others, that often metals can be separated from solutions of their salts by such absorbents as charcoal.

It has been shown that the amount and kind of surface has a marked influence on the decomposition of hypochlorous acid, carbon dioxide, phosphine, arsine, and other compounds. Meyer and his associates, as well as a number of other investigators, have shown that the character of the surface of the containing vessel greatly affects the combination of hydrogen and oxygen. Many reactions have been investigated by van't Hoff, who concludes that both the nature and amount of surface exposed have an influence. The inversion of sugar is affected by the nature of the walls of the containing vessel, and its reduction by Fehling's solution is affected both by the walls of the vessel and the amount of cuprous oxide formed in the reaction. Alteration in the character as well as degree of a number of reactions by having them take place in capillary spaces has been observed by Liebreich, Becquerel, Lieving and other investigators. So-called "contact reactions," as in the production of sulphuric acid, are now familiar processes finding commercial applications. And the solubility of some substances at least, notably gypsum, has been shown to vary considerably with the size and consequent shape of the particles in the solid substance in contact with its solution.[2]

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[1] Effects of animal charcoal on solutions, by T. Graham, Quart. Jour. Sci., 1, 120–125 (1830).

[2] See especially, Beziehungen zwischen Oberflächenspannung und Löslichkeit, von G. A. Hulett, Zeit. phys. Chem., 37, 385–406 (1901). Löslichkeit und Löslichkeits Beeinflussung, von V. Rothmund, p. 109 (1907); Principles théoretiques des methodes d'analyse minerale, par G. Chesneau, p. 16–25 (1906).

It has been shown that soils will sometimes produce the blue coloration in alcoholic solutions of guaiac, which is characteristic of oxidases, and yellow aloin solutions are sometimes colored red. Hydrogen peroxide is decomposed by some soils even after they have been thoroughly ignited to get rid of all organic matter. But in how far these effects may be due to surface influences can not be positively stated; yet uncompleted investigations by Dr. M. X. Sullivan indicate that some of these phenomena at least must be attributed to specific influences (although probably of catalytic character) of particular soil components, such possibly as manganous oxide or ferric oxide; but the mechanism of the reactions is as yet largely speculative.

The soil is composed in large part of very fine particles of rounded shape, exposing relatively an enormous surface to the soil solution, and normally this solution is mainly under capillary conditions, so that we should expect that many reactions would take place quite differently in the soil from the way they would in a beaker or flask. This fact has been generally overlooked or ignored, and is probably the explanation of many of the apparently anomalous results hitherto reported in chemical investigations of soils. Abnormal solubilities, precipitations, oxidations or reductions are frequently found in the literature, and when their abnormality is noted at all, they are too often and with slight show of reason ascribed to indefinite bacterial action or more mysterious vital agencies. Many of them are undoubtedly the results of surface actions. Unfortunately, aside from some few studies of absorption phenomena, surface effects have received little or no attention from soil investigators, although obviously one of the most important and apparently fruitful fields, requiring immediate attention. Enough is known to justify the statement that the chemistry of the soil need not be, and probably is not, the chemistry of the beaker.

The Relation of Plant Growth to Concentration

That the concentration of the mineral constituents in the soil solution under normal conditions is competent for plant support, is shown by numerous experiments. Birner and Lucanus,[1] in an experiment that has long since become classic, found that they could raise wheat to maturity in a well-water, the concentration of which was approximately 18 parts per million with respect to potassium, and 2 parts per million with respect to phosphoric acid, while the corresponding concentrations of the soil solution are normally about 20–25 parts per million of potassium and 6–8 parts per million of phosphoric acid. Nevertheless Birner and Lucanus report that the wheat grown in the well-water throve even better than that grown at the same time in a rich garden mold. Since then many investigators in numerous trials have obtained similar results. Recently wheat, corn, and some of the common grasses have been grown to a satisfactory maturity in tap water with a concentration of about 7 parts per million of potassium and 0.5 part per million of phosphoric acid. And repeatedly wheat plants, grasses, cowpeas, vetches, potatoes and other plants have been grown in a satisfactory way in solutions made by shaking up a soil in distilled water and separating from the solid particles by means of filters of unglazed porcelain.

There can be no doubt, therefore, that the soil solution is normally of a concentration amply sufficient to support ordinary crop plants, and is maintained at a sufficient concentration, so far as mineral plant nutrients are concerned. Undoubtedly, however, variations in the concentration of the soil solution can, and often do, take place, and the results of laboratory experiment indicate that they probably produce effects on plants.

It has been shown in water-culture experiments with wheat, that if a given ratio of mineral nutrients be maintained, relatively small effect is produced on the growing plants by varying the concentration over a wide range, in one case from

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[1] Wasserculturversuche mit Hafer, von Dr. Birner und Dr. Lucanus, Landw. Vers.-Sta., 8, 128–177 (1866).

75 parts per million to 750 parts per million,[1] and this effect seems to be largely independent of the nature of the particular mixture of solutes. But varying the relative proportions of the mineral constituents has been shown by numerous experiments to produce very marked changes in the growth of plants. Not only does a control of the concentration and proportion of the mineral constituents of a solution produce a more rapid, or a slower growth, a greater or lesser total growth, but it produces differences in the character of growth; as for instance, causing the tops to grow relatively faster than the roots, or *vice versa*. However, many effects of this type can be produced, and sometimes more readily, by soluble organic substances, or mechanical agencies. The mechanism of these effects is by no means clear, in many cases. That other causes obtain than a sufficient supply of mineral nutrients will be shown in the following chapters. Experiments with wheat seedlings in water cultures, where the weight of the green tops was taken as the measure of growth, showed that the most favorable ratio was one of phosphoric acid (PO_4) to three or four of potassium (K), about the ratio which has been found to exist normally in the soil solution of humid areas of the United States, namely, 6–8 parts per million of phosphoric acid to 25–30 parts per million of potassium.

The Balance between Supply and Removal of Mineral Plant Nutrients

The mechanism of the solution and transport of mineral nutrients developed in the preceding pages makes it of interest to determine the relation between the possible or probable supply of mineral plant nutrients and crop demands over large areas. The inquiry can be formulated more specifically: Is the movement of mineral plant nutrients towards the surface soil equal to or in excess of the removal by drainage waters and garnered crops? Satisfactory data are yet wanting for anything like exact computations, but approximate

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[1] Effect of the concentration of the nutrient solution upon wheat cultures, by J. F. Breazeale, Science, 22, N. S., 146–149 (1905).

figures are available which appear sufficient for the present purpose.

The rainfall (R) can be considered as disposed in three portions, the fly-off (f), the run-off (r), and the cut-off (c). Stating this as an equation,

$$R = f + r + c.$$

The cut-off can be resolved into the portion (a) seeping through the soil to ultimately join the run-off, and the portion (b) returning to the surface to ultimately join the fly-off. Stated as equations,

$$\begin{aligned} R &= f + r + a + b \\ &= f + b + (r + a). \end{aligned}$$

In other words, the rainfall can also be considered as made up of the fly-off, the capillary water of the soil and the drainage from the area. According to Murray,[1] Geikie,[2] Newell,[3] and others, the drainage water for humid areas, or such an area as the United States as a whole, would be between 20 and 30 percent of the rainfall, the major portion coming from seepage water rather than surface drainage. Assuming the higher figure, and making the further very probable assumption that the capillary water in the soil (b) is never less than the fly-off or the water that evaporates during rain (f), it follows from the equations given that the capillary water is at least 35 percent of the rainfall. If we assume the lower value for the drainage, then the capillary water is at least 40 per cent of the rainfall, and if we assume the extreme case—that the fly-off is practically negligible—the capillary water becomes 80 percent of the rainfall. It appears, therefore, that in all probability the proportion of the cut-off water which returns to the surface as film water or capillary water is always greater, and generally much

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[1] On the total annual rainfall on the land of the globe, and the relation of rainfall to the annual discharge of rivers, by Sir John Murray, Scot. Geog. Mag., 3, 65–77 (1887).

[2] Textbook of Geology, by Sir Archibald Geikie, p. 484 (1903).

[3] *In* Principles and conditions of the movements of ground water, by F. H. King, Ann. rept. U. S. Geol. Surv., 19, II, 59–294 (1897–98).

greater, than the portion which seeps through the soil to join the run-off.

From the available data, it appears that the average concentration of the run-off waters of the United States is about 1.8 parts per million of potassium (K) and about 0.6 part per million of phosphoric acid (PO_4),[1] while the concentration of the capillary groundwater is some ten or twelve times greater. But even if these concentrations were the same, it is altogether probable that very much the greater part of the mineral plant nutrients dissolved by meteoric waters is continually, if slowly, moving towards the surface of the soil.

The average rainfall of the United States may be taken as approximately 30 inches. If it be assumed that the discharge into the sea is 25 percent, then the capillary cut-off water is at least 37.5, and probably nearer 70 percent of the rainfall. King's experimental work[2] indicates that the higher figure is much nearer the truth. Computing from the concentrations just cited, with the equations given above, it is found that approximately 3,500,000 tons of potassium (K) and 1,200,000 tons of phosphoric acid (PO_4) are carried into the sea annually from the United States, while from 48,000,000 to 100,000,000, tons of potassium and 18,000,000, to 40,000,000 tons of phosphoric acid are being carried towards the surface of the soil. If it be assumed that an average of one ton per acre of dry crop containing one percent potash and 0.6 percent phosphoric acid[3] be removed from the entire area of the United States, then the annual loss from this source would be 24,000,000 tons of potassium and 14,000,000 tons of phosphoric acid. Consequently, there is an ample margin between the losses by cropping and seepage waters, and the supply of capillary waters. It is true that cases exist where

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[1] Estimated from data in Bull. No. 330, U. S. Geological Survey, The data of geochemistry, by Frank Wigglesworth Clarke, 1908, pp. 53–90.

[2] King: loc. cit., p. 85.

[3] Estimated from Wolff's tables, How crops grow, by Samuel W. Johnson, 1890, appendix.

the production of vegetable matter is much greater than a ton to the acre, productions of five tons or even more being on record. But such cases occur only where the water supply is also greater, either through natural rainfall or artificial irrigation; and it should also be borne in mind that the production of so large a mass of green crop involves a considerable drawing power on the water in the soil in addition to the evaporation which would take place at the surface under ordinary conditions. In other words, the plant would then be playing no small part in drawing to itself its needed supplies of water and dissolved mineral nutrients.

The question may be asked, if the processes outlined above are generally operative, why accumulations of soluble mineral substances are not usually found at the surface of the soil. As a matter of fact such accumulations do occur normally when the evaporation at the surface is relatively large, that is, under arid conditions. And under humid conditions it appears to be a general rule that the surface soil contains more readily soluble or absorbed mineral matter than do subsoils.[1] No great accumulation occurs at the surface normally under humid conditions because the rainfall is sufficiently distributed throughout the year to enable the cut-off water to carry back promptly into the lower soil levels any excessive amount of soluble material, there to start anew its slower ascent towards the surface.

Calculations such as those here presented are at the best open to many objections, and it is wise to avoid giving them too much emphasis. So far as the available data justify any conclusion, however, it appears that the rise of capillary

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[1] See, for instance: Investigations in soil management, by F. H. King, Madison, Wis., 1904, p. 62 *et seq.* This tendency towards a higher content of absorbed soluble mineral matter in the surface soil has been amply confirmed by other experiments. It has been advanced as an argument against the assumption that the hydrolysis of the soil minerals is a reversible process. But as pointed out elsewhere in the text, many of the soil minerals can be made in the wet way at more or less elevated temperatures, and the more rational explanation is simply that at ordinary temperatures the rate of formation is exceedingly slow.

water is entirely capable of maintaining a sufficient supply of mineral nutrients for crop requirements; and furthermore, it is obvious that the problem of the supply of mineral plant nutrients is dynamic and cannot be successfully attacked by considerations which are essentially static.

The Organic Constituents of the Soil Solution

The organic substances in the soil are tissue remains, to a large extent of plants, and to a less extent of animals; and it is to be expected that there may be found also in the soil the substances excreted or thrown off by living organisms, substances which were in the organisms at the time of their death, and degradation and decomposition products derived from these. Moreover, there are to be anticipated numerous products of bacterial origin, secretions of algae, fungi, etc., so that the organic complex in the soil may contain numerous substances of widely different chemical characteristics. Degradation products of proteins, fats, and carbohydrates, as well as decomposition products, may be expected in almost any soil. But it does not follow that any particular organic substance (excluding, of course, carbon dioxide or nitrates) is to be found in every soil. No generalization regarding the organic substances in the soil can be made such as that formulated for the inorganic compounds. It is probable that further investigation will show certain organic substances or classes of substances to be common to most soils, but it is reasonably certain that many other organic substances will be found in only a few soils, or occasionally, and these latter will be often a prominent factor characterizing the particular soil in which they may occur.

Although no broad generalization is justified regarding the composition of the soil solution with respect to organic substances dissolved, nevertheless the extension of the methods developed in the study of the inorganic substances dissolved has led to a considerable knowledge of the organic ones.

In view of the facts shown in the preceding chapters, and at the same time recognizing that good and poor soils respectively must show differences in the soil solution if the fundamental thesis is valid as to the relation of soils to crop production, experiments have been made to investigate in a comparative way solutions obtained from good and poor soils of the same type, locality, and physical characteristics. For this purpose two samples of soil were taken from adjacent fields which had been under observation for two years. The soils were of the same type, Cecil clay, and were so similar in their physical characteristics as to be distinguished with difficulty in the laboratory. On one field a good crop of wheat was grown, followed by a good crop of clover and tame grasses. On the other field, the corresponding crops had been quite poor. The field yielding the good crops had been plowed somewhat deeper, and had previously received a moderate application of stable manure. Otherwise, so far as could be learned, the cultural history of the fields had been the same. For convenience, the sample from the first field will be designated "good," and from the other "poor."

Aqueous extracts from these soils were prepared, the same proportion of distilled water to soil being taken in each case, and the time of contact being the same. The solutions were freed from suspended matter by being passed through Pasteur-Chamberland bougies under pressure. Young wheat seedlings germinated at the same time, and selected carefully for uniformity of size and apparent vigor, were grown in these solutions for three days. At the expiration of this period the seedlings in the extract from the good soil were about five inches in height, and the roots were clear, clean and turgid. The plants in the poor extract were scarcely three inches in height, and the roots were assuming a slimy, unhealthy appearance and becoming flaccid at the tips. The plants were then all removed, the roots washed carefully in tap water; the plants which had been in the poor solution were placed in the good solution, and those which had been in the good solution were placed in the poor solution. At the end of four days further, the poor plants had surpassed in height the ones which had previously been in the good solution, and the roots had acquired the general characteristics of healthy plants. Those which had been originally in the good solution and then transferred to the poor, had made little additional growth, and the roots had become somewhat flaccid.[1]

This experiment was repeated several times, not only with the soils cited but with samples from adjacent good and poor spots in fields on several soil types from widely separated areas; for instance, Cecil clay from near Statesville, North Carolina; Sassafras loam from Maryland; Windsor sand from Delaware; and similar results were obtained. In other words, these water cultures produced plants which showed much the same differences, in kind and degree, as had been observed in the field. This was recognized as an important step forward, for it indicated that *whatever was making a difference in the crop-producing power of these soils in the field was transmitted to their aqueous extracts*, and methods for studying the chemical properties of solutions are far in advance of methods for studying mixtures of solids.

The soil extracts described above were subjected to a careful analysis for their mineral constituents. They were found to be practically identical in this respect. Further, the poor extract contained decidedly more nitrates than the good—from three to four times as much. It follows, therefore, that the difference in the soils which produced a good and a poor crop respectively, was not due to a difference in mineral plant nutrients, or other mineral differences probably, nor to their respective content of nitrates. Consequently, the poor solution was such, not because of the lack of anything, but because of the presence of something inimical or "toxic" to plant growth; and further, this something must be an organic substance or substances more or less soluble in water. This conclusion was confirmed in the following way:

Samples of the poor solution from the soil obtained

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[1] The success of this and of many of the following experiments was due in large measure to the skill and patience of Mr. James F. Breazeale.

near Statesville, N. C., were diluted twice, five times, and ten times, and wheat seedlings were grown in these solutions, using a sample of the good solution as a check. It was found after several days growth that the plants in the solution diluted tenfold were about as good, or perhaps slightly better, than those grown in the check solution. In every case diluting the poor solution had improved it for plant growth, and the higher the dilution the greater the improvement, in spite of the consequent dilution of the mineral plant nutrients. The only explanation of these results which has yet suggested itself is that the toxic organic substances present were less effective on dilution until the concentration reached a point where they actually became stimulative, as is common with toxins of every character.

Another set of experiments confirmed the conclusion that the poor solution contained some organic substance inhibitory to plant growth. A number of water cultures was prepared from the aqueous extract of the poor soil, and lime in various forms was added to the cultures. To two of the cultures lime carbonate and lime sulphate respectively were added in excess, so that there was in each case a powdered solid at the bottom of the containing vessel. At the end of two days the wheat seedlings which were growing in the vessels containing the powdered solids had decidedly outstripped those growing in all the others, the tops having the appearance of unusually good and healthy plants. The roots were of a very remarkable character, being exceptionally long, very turgid, clear, clean and translucent.

At once, new experiments were carried out in which there were added to the poor solution, precipitated ferric hydroxide freed from all adhering salts, precipitated alumina, shredded filter paper, absorbent cotton, or carbon black. In every case the same result was obtained as before, a much improved growth of top and a vastly better root development. Since, by no possibility could these various added substances have increased the concentration with respect to mineral nutrients, another explanation must be sought. Aside from their insolubility, the one property common to these various substances was the large amount of surface they brought into contact with the solution. The one obvious explanation of their effects on the growth of the wheat seedlings, therefore, is that they withdrew or absorbed from the solution some substance or substances deleterious to plant growth. As diluting with respect to mineral nutrients could not possibly be expected to improve the cultural value of the solution, the conclusion seems evident that the effect produced by these various absorbents was due to more or less complete removal from the solution, of organic substances inhibitory to plant growth. These experiments were then repeated in a modified form, by shaking the poor solution with such absorbents as precipitated ferric oxide or carbon black and filtering before adding the seedling plants. The solutions thus prepared proved very satisfactory nutrient media, although the decided elongation of the roots, always observed when the absorbents were in contact with the solutions, was not so noticeable with these filtered solutions.

The experiments just described were repeated with extracts from a number of soils which were supporting or had recently supported poor crops. The accumulated mass of evidence admits of no doubt that in many cases the apparent lack of fertility of a soil is due to the presence of some organic substance or substances soluble in soil water. This point established, there was studied the effect of fertilizers when added to aqueous extracts from poor soils.

A large amount of experimenting has been done on this subject. It has been found that the common commercial fertilizers, as well as many other substances, when added to the soil extract containing growing plants, sometimes improve the plants, sometimes the contrary. But, in general, those particular substances which improve any given soil for a crop also improve the aqueous extract of the soil for the growth of the same crop plant; *i. e.*, should a soil be known to respond well to the application of superphosphates when planted to wheat, then the probability is great that the aqueous extract of the soil will be improved as a culture medium for the wheat plant by addition of calcium phosphate. Particularly important in this connection are certain experiments with organic fertilizers.

A certain soil had been found to be quite unproductive with regard to wheat and ordinary tame grasses. It had been shown, however, that a much better growth of plants could be obtained if pyrogallol or better pyrogallol and lime were added to this soil some days before planting. An aqueous extract of this soil tested with young wheat seedlings produced but a poor growth, as did the soil itself. But with the addition of pyrogallol or pyrogallol and lime to the soil extract, and especially if the extract so treated were allowed to stand for a few days with free access of air, there was obtained a culture medium which yielded remarkably good results with wheat seedlings. Not only was there an excellent and increased development of tops, but the roots of the seedlings grown in the solution treated with pyrogallol were unusually long, turgid, clear and translucent. Here, then, there was obtained an increased amount and improved character of growth by the addition of a substance which contained only carbon, hydrogen and oxygen, and no recognized plant food. Other organic substances, such for instance as tannin, gave similar results.

With the recognition that the presence of organic dissolved substances in the nutrient medium produced effects on a growing plant of as great or even greater magnitude than those produced by inorganic dissolved substances, there was carried out a number of experiments to test more specifically such substances as might reasonably be expected to be present naturally in soils. The results thus obtained suggested experiments with other related substances. The first substance to suggest itself is stable manure. Taking it all in all, this substance is probably the most efficient as well as the most generally used soil amendment in the experience of mankind. The good effects produced by this substance have in the past been generally considered as due to the readily "available" potash, phosphoric acid and nitrogen it contains, but thoughtful experimenters and agriculturists have long doubted that this explanation is sufficient, since, after all, the mineral constituents of stable manure are usually small in amount, and out of all proportion to the effects resulting from its use. That some of the results are due to an improvement in the physical condition of the soil when manure is used has quite rightly been generally assumed; but to its content of nitrogenous components its value has in the main been ascribed.

A well-fermented aqueous extract of stable manure was prepared, and filtered free of suspended solids. Four equal volumes of this solution were taken. Three of these portions were evaporated to dryness in platinum dishes, and the residues incinerated. To the dishes containing the ash were added respectively nitric acid, sulphuric acid, and hydrochloric acid in slight excess, and the dishes again brought to dryness. Water cultures for wheat seedlings were then prepared.[1] Into one was introduced the given volume of manure extract; into another the ash from an equal volume of the extract which had subsequently been treated with nitric acid; and cultures with the ash which had been treated respectively with sulphuric and hydrochloric acid were similarly prepared. After ten days growth, the plants from the several cultures were compared. The plants from the cultures which contained the sulphates and the chlorides were not materially different from the plants grown in the check culture. The plants from the nitrate culture had larger shoots, but shorter roots than the check plants. But the plants grown in the culture to which the manure extract had been added directly had by far larger and better shoots, and the roots were incomparably superior to those grown in any other culture, being larger, thicker, better branched, clear, bright and translucent, and very turgid, very like the

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[1] Further studies on the properties of unproductive soils, B. E. Livingston, *et al.*, Bull. 36, 1907, and 48, 1908, Bureau of Soils, U. S. Dept. Agriculture.

roots obtained in cultures to which carbon black or precipitated ferric oxide has been added.

The results of this experiment, which has been repeated a number of times, using manure extracts of various origins, leave no doubt that it is the organic components of the manure which produce the characteristic effects, for the ash culture contained all and even more of the mineral constituents "available" in the original extract, and the nitrate culture excluded any explanation based on the nitrogenous content of the manure. This conclusion was supported by the results of another experiment.

To a manure extract was added alcohol, which precipitated most of the organic dissolved substances but very little of the inorganic ones. The precipitated organic matter was filtered off, dried carefully in a water oven to eliminate the alcohol, and then taken up in sufficient water to equal the original volume of manure extract. The filtrate containing the major part of the salts was boiled vigorously to eliminate the alcohol, and water was then added to restore the original concentration. A third solution was prepared by bringing together the organic and inorganic substances which had previously been separated as above described. The three solutions were used as water cultures for wheat seedlings, a solution of the original manure extract being taken for a check culture. The original manure extract and the reconstructed manure extract gave plants of about equal development. The culture containing the organic dissolved substances only gave plants of nearly, but not quite, equal development to those grown in the check culture. But the plants grown in the solution containing the dissolved minerals only, while fine plants and making what would ordinarily be considered a good development, were decidedly smaller as regards their aerial parts, and the roots were in no wise comparable to the roots of the plants grown in the cultures containing the dissolved organic substances.

This last experiment has been repeated, with dissolved substances prepared from another manure extract, but in this case the organic and inorganic substances were separated by dialysis. This suggested yet another experiment, in which it was sought to hasten the process of dialysis, by introducing electrodes into the manure extract, each electrode being surrounded by some porous membrane, either of parchment paper, or unglazed porcelain. Not only were the mineral constituents of the manure extract readily separated in this way, passing into the electrode chambers, as did also to some slight extent organic compounds, but also about the outer walls of the electrode chambers there was a marked segregation and deposition of organic materials. The organic substances deposited at the cathode were found to stimulate greatly the growth of wheat seedlings, while those deposited at the anode were found to retard the growth of seedlings. It seems probable, therefore, that stable manure contains organic components which produce as great or greater effects upon growing plants as do the inorganic substances it contains; that on the whole these organic components induce increased plant growth, but some of them, by themselves alone, would retard plant growth.

In a similar way green manures have been examined. If fresh clover, alfalfa, or cowpeas, be macerated and an aqueous extract thus prepared, it will in general be quite toxic to plants such as wheat; and if this extract be allowed to stand and ferment or sour the resulting solution will be totally unfit for the growth of seedling plants. But if the clover, alfalfa, or cowpea vines be allowed to wilt thoroughly before being macerated and extracted, or if they be macerated and incorporated with soil and allowed to remain thus for ten days or a fortnight before being extracted; then, the resulting solution will be quite stimulating to such plants as wheat, corn or the grasses, when added either to water or soil cultures. It would seem, therefore, that the mineral constituents of the legumes commonly employed as green manures are less important than the organic, in affecting the growth of crops subsequently planted, and the inhibitory or toxic action of fresh green manure seems to be recognized in the common practice of waiting some days after turning under a green manure crop before seeding to a new crop.

The wilting of a green manure involves a darkening and some blackening of the mass, with apparently some absorption of oxygen. This fact has suggested a trial of other organic substances which show a decided ability to absorb oxygen. Among such substances, pyrogallol stands preeminent. It has been shown that when pyrogallol, or better pyrogallol and lime, is added to certain soils, naturally low in productive power, and allowed to stand for a few days, these soils are readily brought into good condition and support good crops of wheat, rye, or grasses. Pyrogallol in water cultures is rather toxic to wheat plants, even in quite dilute solutions. But if the aqueous solution of pyrogallol be allowed to stand exposed to the air, and better if the solution be made slightly alkaline as by the addition of lime, oxygen is absorbed, and a dark brown or blackened solution is soon formed, which is stimulating to wheat seedlings. Many experiments have indicated it to be a general rule that soluble organic substances which are toxic to plant growth yield oxidation products which are harmless or positively beneficial.

The suggestion has been made that the well-known infertility of subsoils, when freshly turned up, is caused by the presence of alkaloids of the purine or codeine type, due to the activities of anaerobic bacteria. Water cultures and pot cultures show that while these substances do have a marked effect on plant growth, it is, frequently, quite beneficial; strychnine for example, in certain concentrations, produces a very decided stimulation in the growth of wheat seedlings. It is clear that some other explanation will have to be sought for the lack of fertility of subsoils.

A number of the substances which may be expected for one reason or another to be present in soils, have been investigated as to their effect on plants. In this connection may be cited the work of Livingston[1] and of Dachnowski,[2] who have studied the effect on vegetation of the organic substances dissolved in bog waters. In the following table are given the results obtained by growing wheat seedlings in solutions containing some one of a number of substances which might be expected to occur in a soil or to be derivatives of such substances. It will be observed that in the case of these dissolved organic substances, as has been repeatedly established with the inorganic ones, in concentrations sufficiently dilute not to be toxic, they generally show the opposite effect and appear to be stimulating.

Finally, a number of organic substances has been isolated from soils. Their composition, and in several cases their constitutions have been determined. The effects of these on plants, when they are present in the cultural media, have been studied. Thus, Shorey[3] was able to isolate picoline dicarboxylic acid ($C_6H_7NO_2$) from certain soils in Hawaii, and this same substance has since been found in several soils of the United States. In aqueous solutions it is quite toxic to wheat seedlings. Since then a number of other definite organic compounds[4] have been isolated from soils, including oxystearic acid ($CH_3(CH_2)_6.CHOH(CH_2)_9.COOH$), dihydroxystearic acid ($(CH_3(CH_2)_7.CHOH.CHOH(CH_2)_7COOH)$), agroceric acid ($C_{21}H_{42}O_3$), agrosterol ($C_{26}H_{44}O$), a pentosan-tetrose ($C_4H_8O_4$), arabinose ($C_5H_{10}O_5$), xylan ($C_5H_8O_4$), xanthine ($C_5H_5N_5O$), thymine ($C_{10}H_{16}$), paraffinic acid ($C_{13}H_{20}NO_5$), and a glyceride, monoacetin ($C_5H_{10}O_4$). Some of these, picoline dicarboxylic acid, dihydroxystearic acid and the pentosan just cited, are

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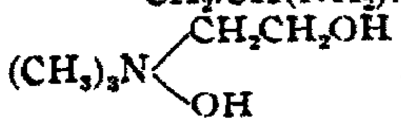
[1] Physiological properties of bog water, by B. E. Livingston: Bot. gaz., 39, 348–355 (1905).

[2] The toxic property of bog water and bog soil, by Alfred Dachnowski: Bot. gaz., 46, 130–143 (1908).

[3] Organic nitrogen in Hawaiian soils, by E. C. Shorey, report of Hawaii Experiment Station, 1906, 37–59.

[4] The isolation of harmful organic substances from soils, Oswald Schreiner and E. C. Shorey, Bull. 53, Bureau of Soils, U. S. Dept. Agriculture (1909).

Table I. Effect of Various Organic Compounds upon the Growth of Wheat Plants, with Especial Reference to Their Toxic Properties[1]

Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	Days	P. p. m.	P. p. m.	P. p. m.	
a Aspartic acid $HOOC.CH_2.CH(NH_2).COOH$.	10	500	100	—	Normal growth in concentration below 100 p. p. m.
b Asparagine $NH_2.OC.CH_2.CH(NH_2).COOH$.	9	—	—	—	No injury below 1,000 p. p. m.
c Glycocoll, $CH_2(NH_2).COOH$	9	—	—	—	Tops of all plants good. Roots slightly injured at higher concentrations
d Alanine, $CH_3.CH(NH_2).COOH$	10	—	500	25	Only roots were injured at 500 p.p.m.
e Leucine, $CH_3.(CH_2)_3.CH(NH_2).COOH$	9	—	—	—	No injurious action
f Tyrosine,  $C_6H_4\begin{cases}OH \\ CH_2.CH(NH_2).COOH\end{cases}$	11	—	10	—	
g Choline,  $(CH_3)_3N\begin{cases}CH_2CH_2OH \\ OH\end{cases}$	10	—	500	1	Roots affected more than tops

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[1] Certain organic constituents of soils in relation to soil fertility, by Oswald Schreiner, and Howard S. Reed, assisted by J. J. Skinner, Bull. No. 47, Bureau of Soils, U. S. Dept. Agriculture, 1907.

TABLE I—(*Continued*)

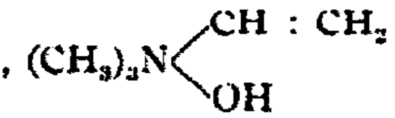
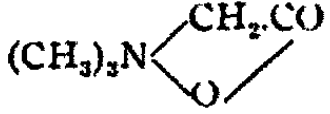
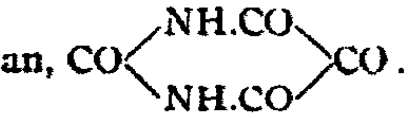
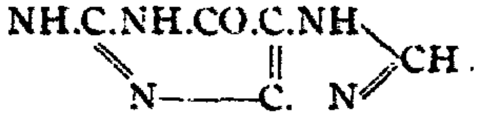
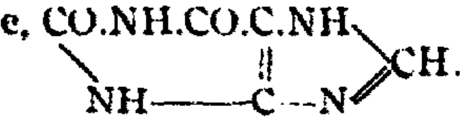
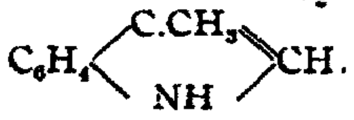
Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	Days	P. p. m.	P. p. m.	P. p. m.	
h Neurine, 	9	250	25	—	
Neurine (neutralized)	8	250	25	—	
i Betaine, 	9	—	—	—	No injury
j Alloxan, 	10	1,000	100	—	
k Guanine, 	12	—	—	—	Insoluble above 40 p. p. m. No harmful effects
l Xanthine, 	10	—	—	—	No injurious action.
m Guanidine, 	9	100	1	—	
n Skatol, 	9	200	50	—	Roots injured more than tops

TABLE I (Continued)

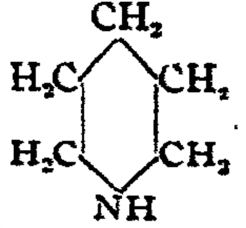
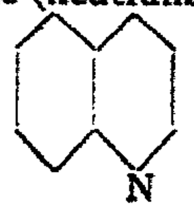
Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	Days	P. p. m.	P. p. m.	P. p. m.	
o Pyridine, C_5H_5N	9	—	50	—	In solutions of 50 p. p. m. and less the root growth was normal.
Picoline, $C_5H_4N.CH_3$	7	1,000	500	100	
Piperidine, 	7	250	25	—	
Piperidine (neutralized)	7	100	25	—	
Quinolin, 	6	500	5	—	
p Ricin	10	—	40	—	Insoluble above 50 p. p. m.
q Mucin	10	—	100	—	Not tested in concentrations higher than 100 p. p. m.

TABLE I—(*Continued*)

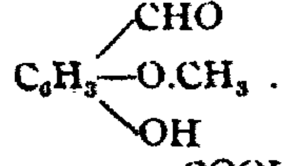
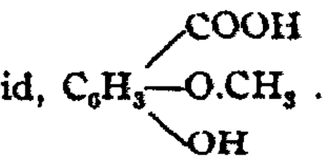
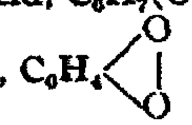
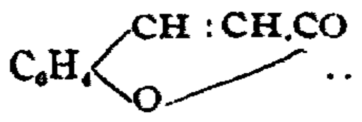
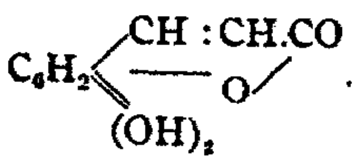
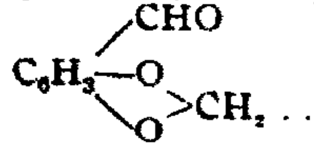
Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	Days	P. p. m.	P. p. m.	P. p. m.	
r Pyrocatechin, $C_6H_4(OH)_2(1,2)$	12	500	25	1	
s Arbutin, $C_{12}H_{16}O_7$	12	500	25	1	
t Phloroglucin, $C_6H_3(OH)_3(1,3,5)$	13	500	25	1	
u Vanillin,  $C_6H_3\begin{matrix}\diagup CHO\\ —O.CH_3\\ \diagdown OH\end{matrix}$	9	500	1	—	
Vanillic acid,  $C_6H_3\begin{matrix}\diagup COOH\\ —O.CH_3\\ \diagdown OH\end{matrix}$	7	100	25	5	
v Quinic acid, $C_6H_7(OH)_4.COOH$	10	500	100	—	
w Quinone,  $C_6H_4\begin{matrix}\diagup O\\ \vert\\ \diagdown O\end{matrix}$	9	100	1	—	
x Cinnamic acid, $C_6H_5CH:CH.COOH$	8	100	25	—	
Sodium cinnamate	12	—	100	—	Roots were stimulated in lower concentrations
y Cumarin,  $C_6H_4\begin{matrix}\diagup CH:CH.CO\\ \diagdown O\diagup\end{matrix}$	8	100	1	—	

TABLE I.—(Continued)

Remarks	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	Days	P. p. m.		P. p. m.	
z Daphnetin,  $C_6H_2\begin{matrix}CH:CH.CO\\ O\\ (OH)_2\end{matrix}$	12	—	50	—	Insoluble above 50 p. p. m. Roots somewhat injured
aa Esculin, $C_{15}H_{16}O_9$	13	500	1	—	
bb Piperonal (heliotropine)—  $C_6H_3\begin{matrix}CHO\\ O\\ O\end{matrix}>CH_2$	7	100	1	1	
cc Borneol, $C_{10}H_{17}(OH)$	10	100	1	—	
dd Camphor, $C_{10}H_{16}O$	8	300	5	—	
ee Turpentine, $C_{10}H_{16}$	8	500	10	—	

a. Aspartic acid has been found in young sugar cane and in seedlings of the bean and pumpkin.

b. Asparagine was first found in asparagus, but has since been shown to be relatively abundant in many species.

c. Glycocoll is one of the simpler and more common degradation products of proteins.

d. Alanine is a common degradation product of proteins and is related chemically to phenylalanine, and to tyrosine, which has been found in many plants.

e. Leucine, an amino-acid of a paraffine series and a decomposition product of proteids, has been found in certain mushrooms, vetches, lupine, gourds, potatoes, corn, etc.

f. Tyrosine is an important decomposition product of proteids, is widely distributed and found in many plants and fungi.

g. Choline is a derivative of certain lecithins and is found in many seeds and growing plants.

h. Neurine is a substance closely related to choline, and probably formed from it.

i. Betaine is closely related to both choline and neurine, and is found in many seeds and plants.

j. Alloxan is closely related chemically to convicine, which latter is found in beets and certain beans.

k. Guanine is a widely distributed nitrogenous body, and has been found in the seeds of vetch, alfalfa, clover, gourds, barley, sugar beets and sugar cane.

l. Xanthine, a substance closely related to guanine, has been found in a number of plants.

m. Guanidine, a substance chemically related to guanine, has been found in a number of plants of different species.

n. Skatol is a derivative of proteids and is a common product of the activities of some varieties of bacteria.

o. Pyridine has been shown to exist in soils, as such probably, by Shorey, who obtained it from certain soils in Hawaii.

p. Ricin is found in the castor-oil plant.

q. Mucin has been found in yams.

r. Pyrocatechin has been found in the bark of various trees, the berries of the Virginia creeper, the sap of sugar beets and in several varieties of willows.

s. Arbutin has been found in many plants, especially in some of the grasses.

t. Phloroglucin is easily derived from a number of plant constituents.

u. Vanillin forms readily from a glucoside, which is very widely distributed in many plants, and by some authorities is supposed to be a product of the decomposition of wood tissues.

v. Quinic acid, which is found with quinine in the cinchona bark, also occurs in beet leaves, certain hays, cranberry leaves, and occasionally in other plants.

w. Quinone has been shown to result from the action of a certain fungus, *Streptothrix chromogena*, common in soils.

x. Cinnamic acid is found in certain barks, and forms esters which have been found in the leaves of various plants.

y. Cumarin has been found in a large number of plants, including the grasses, beets, sweet clover, etc.

z. Daphnetin occurs in some species of *Daphne* and is closely related to cumarin.

aa. Esculin, as well as the corresponding esculetin, has been found occasionally in a number of plants.

bb. Heliotropine, or piperonal, has the odor of heliotrope and is found in flowers.

cc. Borneol occurs in needles of different varieties of pine, fir, spruce and hemlock, golden rod and thyme.

dd. Camphor is closely related chemically to borneol and is secreted by a number of plants; it is found in the wood of *Cinnamomum*, cinnamon root, in the leaves of sassafras, spikenard, rosemary, rosewood, etc.

ee. Turpentine is a constituent of many plants and coniferous trees.

toxic to growing plants; others are not. The origin and mode of production of these substances in the soil is, generally speaking, uncertain and obscure, and is yet one of the important fundamental problems confronting the soil chemist.

It is important to note that the organic substances thus far isolated from soils are of widely varying types, and with very different chemical characteristics. As pointed out above, almost any type of organic substance is likely to be found in soils, and the effects of any of them on growing plants can hardly be predicted from *a priori* considerations.

It has been found that as a general rule the continued growth of one crop in any soil results in a low crop production. Pot cultures have given even more pronounced results in the same direction. The explanation long accepted is that the soil has, as a result of continued cropping, become deficient in some one or more of the "available" mineral nutrients. Pot experiments, where the garnered crop was returned to the soil and still a diminished yield was obtained, throw doubt on this explanation. Still further doubt results from water-cultures which, by growing a crop in them, become "poor" for subsequent crops, although there is maintained in them an ample supply of mineral plant nutrients, and they are easily renovated by good absorbers. These facts find a more satisfactory explanation as being due to the production in the nutrient medium of deleterious organic substances originating in the growing plant itself. This idea seems to have been advanced first by De Candolle, in 1832,[1] to account for the beneficial results obtained by employing a rotation of crops. It appears to have been held by Liebig at one time, although he subsequently abandoned it in favor of the view that the benefits of a crop rotation are due to the several crops requiring different proportions of mineral nutrients, and that the disturbance of the balance in the soil produced by one crop is not unfavorable to the growth of some other crop. Although lacking direct experimental confirmation, this latter view of Liebig's has long prevailed among agricultural investigators, partly by reason of his authority, partly by reason of the dominance of the plant-food theory of fertilizers, and partly by reason of the fact that the ideas of De Candolle as originally advanced included certain errors soon detected. The trend of recent investigations has been distinctly in favor of a modified form of the view of De Candolle. It has been recognized that other factors enter into crop rotations, such as the elimination of associated weeds, various kinds of animal, insect and plant parasites, preparation of the soil by a deep-rooted crop for a shallow-rooted following crop, etc. It has come to be recognized that there are natural associations of plants, and natural rotations of vegetation certainly determined by other than plant-food factors. Thus, in the eastern United States, wheat is followed by ragweed naturally, while across the fence cocklebur and wild sunflower come in after the corn, the difference in vegetation being as sharply marked after the removal of the crops as when they still occupied the land. Analyses of the ragweed, for instance, although it is a shallower rooted crop than wheat, show that it takes from the soil as much of the mineral nutrients as does the preceding[2] wheat crop. The investigation of Lawes and

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[1] See in this connection, Further studies on the properties of unproductive soils, by B. E. Livingston, Bull. 36, Bureau of soils, Dept. of Agric., 1907, pp. 7–9.

[2] Mr. J. G. Smith has made a comparison between the potash and phosphoric acid content of the wheat and following crop of ragweed grown on a farm in Fairfax Co., Va. His unpublished results, with some others found in the literature, are given in the following table:

Gilbert[1] on fairy rings showed that the continual widening of the rings can not be satisfactorily explained by the comparison of the mineral constituents in the soil within and without the rings. Work at Woburn[2] on the effect of grass on apple trees finds no other plausible explanation than that the growing grass produces in the soil organic substances detrimental to young apple trees. A number of similar cases have been recorded.

Finally, although less work has been done in this direction with higher plants than with other organisms, it is now recognized as a general law of all living organisms that they function less and less readily as the products of their activities accumulate.[3] These products may, however, be inimical

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Material.	Potash K_2O Percent	Phosphoric acid, P_2O_5. Percent	Analyst
Wheat....................	0.76	0.52	Smith
Young ragweed...........	1.78	0.73	"
Ragweed in seed..........	1.28	0.35	"
Ragweed in seed and accompanying plants.........	1.18	0.39	"
Winter wheat in flower...	1.796	0.51	Wolff's tables in Johnson's "How crops grow," p. 376
Ragweed..................	1.79	0.41	DeRoode, in Bull. 19, W. Va. Agr. Expt. Stat., 1891
Ragweed..................	1.809	0.54	Burney, 2d. Ann. rept. S. C. Stat., 1889, p. 146

On the whole, ragweed seems to require and take from the soil about as much mineral matter as does wheat. It is stated by some of the dairy farmers near Washington, who cut the mixture of ragweed, other weeds and grass following wheat, for a hay crop, that the weight of the ragweed crop is generally heavier than that of the wheat crop. Therefore the ragweed actually removes more mineral matter from the field than does the wheat. These facts lend no support to the popular notion that wheat "exhausts" the soil of its "available" mineral plant nutrients. For analyses of a number of common American weeds, see Analyses of the ashes of certain weeds, by Francis P. Dunnington, Am. Chem. Jour., 2, 24-27 (1880).

[1] Note on the occurrence of "fairy rings," by J. H. Gilbert, Jour. Linn. Soc., 15, 17-24 (1875).

[2] Second, third and fifth reports of the Woburn Experimental Fruit Farm, 1900, 1903, 1905.

[3] It may not be amiss to point out here that this general law holds for all dynamic phenomena. In chemistry, for instance, the general law is well recognized that the rate of reaction diminishes with increase in the active mass of the reaction products.

neutral or even stimulating to other organisms.

This problem has been investigated critically by direct experimentation, growing wheat, and other seedlings in water and agar cultures.[1] It has been shown that wheat renders the culture media unsuitable for subsequent wheat crops, though it can be reclaimed or renovated by treatment with such absorbents as carbon black, or by other methods.[2] Wheat did about as well when grown in a medium which had previously supported a growth of cowpeas as when planted in a fresh medium; poorer results were obtained after oats; no crop produced such poor results in the succeeding wheat crop as did wheat itself.

It is yet a matter of dispute as to whether the substances thus added to nutrient media are truly excretory products of the plant, sloughed off or otherwise eliminated from the surface of the roots, or further elaborated by bacterial or other agencies before becoming effective. These are important problems for the plant physiologist and the soil chemist alike. It is beyond dispute, however, by reason of a large and increasing weight of evidence, much of it direct experiment, that, as a result of the growing of plants, soils and the soil water do contain organic substances; harmful to the plant or organism eliminating them; harmful, innocuous, or even stimulating to other plants or organisms.

For the elimination from the soil of toxic or inhibitory organic substances, whether excreted by roots or otherwise produced, several methods are more or less effective. When, as is sometimes the case, the substance is volatile, it may be removed by heating, distilling with steam, or passing a current of air through the soil or cultural medium. These methods, while effective in the laboratory and possibly applicable to greenhouse conditions, are naturally inapplicable to field conditions. In this last case the obvious procedure is to in-

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[1] Some factors in soil fertility, by Oswald Schreiner and Howard S. Reed, Bull. No. 40, Bureau of Soils, U. S. Dept. Agriculture, 1907.

[2] Soil fatigue caused by organic compounds, by Oswald Schreiner and M. X. Sullivan: Jour. Biol. Chem., 6, 39–50 (1909).

crease as much as possible the absorptive powers of the soil; to secure the best possible drainage; and with these, the best possible aeration of the soil.

It has been found that, in general, a cultural medium which has been rendered unfit for the continued growth of a crop, is readily renovated by treatment with oxidizing agents, and is sometimes rendered even better than ever by such treatment, which would suggest that the oxidation products from plant effluvia may be even beneficial to the plant. To this end the growing plant seems itself to be an active agent, apparently attempting automatically to protect itself against the products of its own activities. It has been pointed out by Molisch[1] that root secretions have an oxidizing power, apparently of an enzymotic character. Some doubt of the validity of Molisch's work has been raised by Czapek, Pfeffer, and others, nevertheless it is now accepted that while intercellular autoxidation or reduction processes may take place in living roots, the higher plants, such as our common crop plants, also show a more or less well-developed extracellular oxidizing power in the neighborhood of the root tips and root hairs.[2] That this oxidizing power displayed by growing roots is enzymotic is indicated by the fact that artificial culture media frequently display it also after plants have been grown in them for a short while.[3]

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[1] Uber Wurzelausscheidungen und deren Einwirkung auf organische Substanzen, von Hans Molisch, Sitzungsber. Akad. wiss. Wien., Math. nat. Kl., 96, 84–109 (1888).

[2] The rôle of oxidation in soil fertility, by Oswald Schreiner and Howard S. Reed: Bull. No. 56, Bureau of Soils, U. S. Dept. Agriculture, 1909.

[3] From considerations as yet highly speculative, a different type of oxidation by roots might be anticipated. It is recognized that in the absorption of mineral nutrients by plants a certain amount of selection enters. For example, a plant with its roots in a solution of potassium chloride absorbs more potassium than chlorine, relatively, and free hydrochloric acid is left in the solution. Obviously in the absorption, work is done, and a possible explanation is that water is decomposed at the absorbing surface of the root, with the liberation of oxygen. Theoretically, it ought not to be difficult to investigate this by a study of the energy changes during absorption, but growing plants do not lend themselves readily to such experimentation.

It has been shown that the oxidizing action of growing roots is generally promoted by having the cultural medium slightly alkaline or neutral rather than acid. It is also promoted by the addition of various mineral salts, notably by nitrates, phosphates, or lime salts. Potassium salts promote the oxidation but slightly, and in some experiments have even produced a slight decrease. The corresponding sodium and ammonium salts are more favorable than those of potassium. It appears altogether probable, therefore, that the mineral salts in commercial fertilizers may have some importance in this connection.

The fact that the oxidizing power of roots is more marked when grown in aqueous extracts of soils in good tilth than in extracts made from soils in poor tilth, shows that cultural methods are no less important in field practice than are fertilizers in promoting this important activity of plants. There is little reason to doubt that oxidizing agencies other than plant roots (bacterial for instance) are more or less active in every arable soil, and numerous investigations, among which Russell's researches[1] are conspicuous, leave little doubt that oxidation processes are promoted by good tilth. It is apparent, therefore, that by the activities of the plant itself as well as other agencies, the general tendency in soils is the destruction of or rendering innocuous harmful plant effluvia or other organic substances, and to this end are effective each of the three methods of soil control generally practiced, namely, tillage, crop rotation and fertilizers.

Among the organic components of the soil none have greater importance and interest than those containing nitrogen or as they are frequently called the nitrogen carriers. Conspicuous among these are the nitrates. While it is now generally conceded that ammonia and other nitrogen compounds can be taken up by higher plants and elaborated by them under special conditions, it nevertheless remains true that plants

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[1] Oxidation in soils, and its connection with fertility, by Edward J. Russell, Jour. Agric. Sci., 1, 261–279 (1905); Pt. II. The influence of partial sterilization, by Francis V. Darbishire and Edward J. Russell, 2, 305–326 (1907).

draw their needed supplies of nitrogen from the soil solution, mainly in the form of nitrates. The problems presented by these nitrogen carriers are mainly bacterial[1] and physiological, but certain features are of direct importance to the soil chemist and to a study of the soil solution. It is now known generally that there are many kinds of nitrifying and denitrifying bacteria in soils, and that probably every arable soil contains several species, or varieties at least of both kinds. With good tilth and consequent aerobic conditions, nitrifying processes prevail, and with poor tilth or in subsoils, anaerobic conditions and denitrifying processes prevail. Warmth, moisture, the reaction of the soil, and perhaps other factors markedly affect the activity of the organisms of the soil solution. Another important factor is that the absorptive powers of the higher plants are markedly affected by sunlight, so that, especially on bright and clear days, there is generally a higher concentration of nitrates in the soil solution in the morning than in the evening. This fact would seem to affect seriously the value of some recent and extensive investigations where it has been sought to classify soils by their content of water-dissolved nitrates. Nitric acid is more readily leached from soils than are most other acid radicals. Consequently nitrates, like other organic components of the soil solution, and unlike the inorganic components, tend to vary greatly in concentration.

Fertilizers

It is generally recognized that the great practical problem confronting the soil chemist is the proper use of soil amendments or fertilizers. The farmers of the United States now spend annually for fertilizers upwards of $100,000,000. It is estimated by various authorities that a large fraction, perhaps as much as three-fourths, of the material represented

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[1] The fixation of atmospheric nitrogen by bacteria, by J. G. Lipmann, Bull. 81, Bureau of Chemistry, U. S. Dept. of Agriculture, 1904, pp. 146–160; A review of investigations in soil bacteriology, by Edward B. Voorhees and Jacob G. Lipmann, Bull. 194, Office of Experiment Stations, U. S. Dept. of Agriculture, 1907.

by this expenditure is misapplied for lack of intelligent direction. Yet all of this enormous mass of fertilizers can be used to advantage. Great as it is, it is relatively small beside the total which will, and must, be used in a no distant future, with the growth and development of intensive methods of cultivation consequent upon the rapid settling of the country, the practical disappearance of new lands and the increase in money value of the old lands. The commercial importance of the problem, therefore, makes it desirable that special emphasis should be given to fertilizers from the point of view developed in the preceding chapters. It should be recalled that the use of fertilizers constitutes one of the three great general methods of soil control, and further that while tillage methods, crop rotations, and fertilizer applications can be used to supplement one another, no one of these methods can be expected to take satisfactorily the place of another.

Crop production is dependent upon a large number of factors. Upon the rainfall, both as to the amount and distribution; upon the sunlight, as to amount and distribution; upon the chemical and physical properties of the soil; soil bacteria and other biologic agents; enzymes in the soil; biological factors in the plant, and probably many other things. Opinions do and will continue to differ as to what these factors are, but at least every one agrees that they are many.

Attempting to formulate these factors develops fundamental difficulties, since it is not positively known how far the variables are dependent or independent, and we have no idea as to the nature of the function or functions. The weight of existing evidence favors the view that all the factors are dependent variables, although numerous attempts have been made from time to time to show that some one factor, such as the rainfall for instance, or the mean annual temperature, or available plant food, is *practically* an independent factor. Although it should be rather easy to determine experimentally the nature of the function, if any of these various factors were independent, this has never been done, and this fact is itself a strong argument that all the factors in crop production are dependent on one another.

When there is introduced into the equation a factor for any one of the methods of soil control, *i. e.*, tillage, crop rotation, or fertilizers, it becomes even more apparent that the function is determined by dependent variables, for the new factor always more or less affects several if not all of those already cited. For instance, fertilizers certainly affect the chemical properties of the soil, its physical properties, the soil bacteria, perhaps the plant-food supply, the oxidation of plant effluvia and other factors. It is obvious, therefore, that a satisfactory theory of fertilizer action can not be a simple one but must of necessity be complex; and the same statement is no less true as regards tillage and crop rotation.

The recognition of the fact that the action of fertilizers is a complex function depending upon many factors and groups of factors which vary among themselves and with each individual soil, carries with it the conviction that an exact or quantitative fertilizer practice, while theoretically possible, is probably unattainable, since methods for the solution of such complex functions are generally wanting. It is not surprising, therefore, that the empirical experience of the past has failed to develop a quantitative practice. However disappointing this may seem at first sight, the prospect is not altogether hopeless, for this point of view indicates a systematic scheme for experimentally determining a qualitative, but nevertheless rational, fertilizer practice. The dominance of the plant food theory of fertilizers in the past, shutting off, as it has, a rational attack of the problem, is causing the annual waste of millions of dollars in misapplied fertilizers, and it is of scarcely less economic than scientific importance to investigate and extend our knowledge of the effect of soil amendments upon the many factors in crop production. With a knowledge of the effect of fertilizers upon the physical, chemical and biological factors in crop production, and of the nature of the interdependence of these factors, will come the ability to manage intelligently the individual field for the particular crop. This knowledge can only come by attacking the problem from the dynamic view-point, and so far as the soil factors are concerned, they can apparently be studied best as they affect the properties of the soil solution.

While it seems certain that some fertilizer effects are directly upon the soil and secondarily upon the plants, it cannot be doubted that in others, the phenomena are more directly concerned with the absorption by and the metabolism within the plant. And until these plant processes are better understood, nothing approaching a satisfactory practice can be anticipated. Why and how plants exercise the selective powers they appear to possess are fundamental questions yet to be answered. The important effects sometimes produced by adding to the nutrient medium such substances as manganese salts which are not necessary to the growth of the plant, can no more be neglected than the study of the phosphorus needs. The presence in the soil universally of substances other than the recognized mineral nutrients,[1] may very well have a significance for plant production hitherto unsuspected, for the fact that an organism can continue to function in the absence of a substance is no argument, much less proof, that it would not function better with that substance present. Recent investigations showing that animal organisms are sometimes more resistant to certain toxins and diseases under starvation conditions or when ingesting substances unnecessary to normal development, suggest the possibility at least of similar phenomena with plants. It is at any rate clear that the practical problem of the best production of plants from soils is not merely one of providing a relatively large supply of potassium, phosphorus and nitrogen.

In this connection it is well to consider what constitutes a commercial fertilizer. It must be a substance, the addition of which either directly or indirectly affects the properties of the soil or the growing plant; it must be obtainable in large quantities and from a source or sources of supply not readily

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[1] See, for instance, "Barium in soils," by G. H. Failyer, Bull. No. 71, Bureau of Soils, U. S. Dept. of Agriculture, 1910.

exhausted; and it must be cheap. Of the many substances filling the first condition, all those which fulfil also the other conditions are used as fertilizers, with the exception of common salt and human excrement. In spite of the fact that it does not contain a conventional plant food, sodium chloride appears to produce results quite similar to those produced by the usual fertilizer salts. Its use has been followed generally by an increased yield of crop, but occasionally by a decreased one, and it appears not improbable that further investigation would show sodium chloride to have a considerable value as a fertilizer. Human excrement or night soil, and the sewage and garbage refuse of our large cities are not commercial fertilizers, although having undoubtedly a high agricultural value. Objection has been urged to them that they are "filthy" and liable to contain dangerous pathogenic organisms. Both objections could be met. It seems a more rational explanation that the agricultural methods of this country have not yet become sufficiently intensive to necessitate the conservation of such materials or to justify their commercial exploitation.

New products will come into use from time to time, as in the case of calcium cyanamid and basic calcium nitrate. But it is worthy of note that these substances have become available not so much because of their agricultural value, but incidentally to the efforts of inventors and manufacturers to produce cheap nitric acid for the preparation of high explosives.[1] There seems no reason to doubt that an ample supply of desirable substances will always be available for fertilizer purposes. The immediate practical problem for the future is not the seeking of new fertilizers but the rational use of those at hand.

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[1] In this connection it may be of interest to call attention to the fact that the Twelfth Census shows less than a fifth of the sodium nitrate brought into the United States goes into the fertilizer trade. Moreover, the production of ammonium salts by the extensive coke and gas plants of the country is practically *nil*, not because of any inherent difficulties in making them or because the cost of production is high, but because the market demands in this country are yet too small.

Alkali[1]

In the preceding chapters there have been considered the phenomena which obtain under humid conditions. Under exceptional conditions of prolonged drought there occurs an accumulation of soluble mineral substances at or near the surface of the soil. This phenomenon is pronounced in arid and semi-arid regions,[2] and the accumulations of soluble salts occurring in such regions is known in the United States as "alkali," in India as "reh," in Africa as "brak," and in other countries by various local designations. The study of the extreme conditions producing alkali has added materially to the present knowledge of the processes taking place in soil of humid areas. Moreover, alkali-infested areas are themselves becoming of so much importance with the growing needs for further new lands, that it seems wise to give here an outline of the chemical principles involved in their soil solutions.

Alkali is sometimes a single salt, but usually a mixture of some two or more of the chlorides, sulphates, carbonates, bicarbonates, and occasionally the nitrates, phosphates and borates, of sodium, magnesium, potassium, and calcium, and occasionally strontium and lithium. In the United States, when the carbonate of sodium is present to an appreciable extent, the salt mixture is known as *black alkali*, in contradistinction to *white alkali*, which latter does not contain sodium carbonate.[3] Generally, but not always, soils containing

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[1] Alkali soils of the United States, by Clarence W. Dorsey, Bull. No. 35, Bureau of Soils, U. S. Dept. Agriculture, 1906.

[2] Occasional occurrence of alkali in humid regions, by Frank K. Cameron, Bull. No. 17, Bureau of Soils, U. S. Dept. Agriculture, 1901, p. 36–38. This phenomenon should not be confused with the surface deposition of various kinds of saline material from springs, which is fairly common in both humid and arid regions, the world over.

[3] Black alkali is so called because the caustic solution containing sodium carbonate, in rising to the surface of the soil, dissolves and carries with it organic matter which is subsequently left on the surface in more or less blackish deposits, often ring-like in appearance. It is by no means uncommon, however, to find deposits of "black alkali" which are not black at all, and it is quite common to find "white alkali" so dark in color as to suggest the presence of sodium carbonate, although the latter be absent.

alkali also contain accumulations of the less soluble salts, calcium carbonate, or calcium sulphate, or a mixture of the two. These substances, sometimes cementing the less soluble mineral components of the soil, sometimes almost pure, are found in layers more or less continuous, and from a fraction of an inch to several feet in thickness, in a position approximately parallel to and at a moderate depth below the surface of the soil. In such cases these layers form a "hardpan" and frequently the treatment of this type of hardpan is the most difficult and vexing problem in the management of alkali-bearing soils.

The origin of alkali is often uncertain. In some cases the geological evidences in the area make it certain that the alkali came from the desiccation of former bodies of sea water which had become isolated from the ocean. In other cases the alkali appears to come from the desiccation of lakes which are the depositories of the drainage of a surrounding area, and which have no outlet to the sea. In still other cases it has been supposed that the alkali is derived from wind-borne sea spray. Various explanations of a more or less special character with regard to particular localities or circumstances are to be found in the literature.[1]

The chemical principles involved in the desiccation of a body of sea water are now pretty well understood, owing mainly to the investigations of van't Hoff, Meyerhoffer, and their co-workers.[2] The salts in sea water and those constituting "white alkali" are mainly the chlorides and sulphates of sodium, potassium and magnesium. Calcium is

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[1] An interesting case is the Billings Area, Montana, where the alkali, seems to be derived from the oxidation, solution and subsequent hydrolysis of the pyrites and marcasite of the neighboring Pierre shales. The sulphuric acid thus formed, leaching through shales and sandstones, takes up various bases and the predominating salts in the alkali of this area are the sulphates of sodium and magnesium.

[2] Zur Bildung der ozeanischen Salzablagerungen, von J. H. van't Hoff, Braunschweig, 1905–'09. For a detailed discussion of these results with reference to alkali deposits see: Calcium sulphate in aqueous solutions, by Frank K. Cameron and James M. Bell, Bull. No. 33, Bureau of Soils, U. S. Dept. Agriculture, 1906.

also present, appearing in deep deposits as anhydrite, and at the surface as gypsum.

From the results of this work it is possible to predict the order in which the different salts or minerals will separate from the evaporating solution. At ordinary temperature (25° C) the first salt to be deposited from the dilute solution is *gypsum* ($CaSO_4.2H_2O$) followed by *halite* or *sodium chloride* ($NaCl$) in quantity. Sodium chloride continues to separate at all higher concentrations. Next will be deposited *kainite* ($MgSO_4.KCl.3H_2O$). At the concentration then reached, the stable sulphate of calcium is *anhydrite* ($CaSO_4$), which continues to separate from solution as desiccation proceeds. Consequently, if the gypsum previously deposited is yet in contact with the solution, it tends to be transformed to anhydrite and at all higher concentrations the deposition of anhydrite may be expected. As evaporation proceeds a point is reached where *kainite* and *kieserite* ($MgSO_4.H_2O$) separate. Further evaporation brings a concentration at which *kieserite* and *carnallite* ($MgCl_2.KCl.6H_2O$) are precipitated, and as the process proceeds, finally the point is reached where *kieserite*, *carnallite* and *bischofite* ($MgCl_2.6H_2O$) all three separate with sodium chloride. The final products separating at a higher temperature, 83° C, are the same four solids, sodium chloride, kieserite, carnallite and bischofite.[1] The alternate layers of anhydrite and sodium chloride noticeable in some desiccated sea beds is probably the result of alterations in temperature, anhydrite being less soluble, and sodium chloride somewhat more soluble in hot than in cold water. During

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[1] It will be interesting to compare with the above the following brief description of the Stassfurt salt deposits, taken from Ries's Economic Geology of the United States (1905), p. 127. "At the bottom is the main bed of rock salt which is broken up into layers 2–5 inches thick by layers of anhydrite. Above this come 200 feet of rock salt, with which are mixed layers of magnesium chloride and polyhalite.... Resting on this is 180 feet of rock salt, with alternating layers of sulphates, chiefly kieserite, the sulphate of magnesia. These layers are about 1 foot thick. Lastly, and uppermost, is a 135-foot bed consisting of a series of reddish layers of rock salts of magnesia and potassium, kainite.... kieserite.... carnallite.... tachhydrite....as well as masses of snow-white boracite."

warm weather there would be a greater tendency for anhydrite to separate and in colder weather for sodium chloride to be precipitated. Anhydrite at the surface would gradually absorb water vapor from the atmosphere and be transformed to gypsum.[1]

Besides the principal salts just described, there may separate at one concentration or another other various double salts including *langbeinite* ($2MgSO_4.K_2SO_4$), *polyhalite* ($K_2SO_4.MgSO_4.2CaSO_4.2H_2O$), *glauberite* ($CaSO_4.Na_2SO_4$), *syngenite* ($CaSO_4.K_2SO_4.H_2O$), *potassium pentasulphate* ($K_2SO_4.5CaSO_4.H_2O$), *krugite* ($4CaSO_4.K_2SO_4.MgSO_4.2H_2O$), and possibly others. These are all stable over very restricted ranges of concentration, however, and if formed, probably seldom persist, but pass over to more stable salts as the desiccation proceeds, and have little more than a passing theoretical interest.

The addition of carbonates to the system introduces some further modifications.[2] In this case lime carbonate is the first salt to be precipitated, followed probably by the same order of deposition as outlined above. As the mother liquor becomes more concentrated, it apparently loses its alkaline character, for the addition of an alcoholic solution of phenolphthalein does not produce the characteristic red color. That the solution does actually contain dissolved carbonates is shown by the appearance of the red color on diluting a portion of the mother liquor with distilled water. An interesting example in nature is furnished by the Great Salt Lake, Utah. A test of the water of this lake in 1899 gave no alkaline reaction with phenolphthalein, but the reaction appeared promptly when distilled water was added,

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[1] As examples, some of the gypsum deposits of Kansas may be cited, according to Haworth, Mineral resources of Kansas, 1897, p. 61, and the classical case at Bex, Switzerland, described by J. G. F. Charpentier, Über die Salz-Lagerstätte von Bex, Ann. Phys. Chim., 3, 75–80 (1825), and by G. Bischof, Elements of chemical and physical geology, London, 1854–58, Vol. 1, p. 350–1.

[2] The action of water and aqueous solutions upon soil carbonates, by Frank K. Cameron and James M. Bell, Bull. No. 49, Bureau of Soils, U. S. Dept. Agriculture, 1907.

and further examination showed the water to contain about 0.012 percent sodium carbonate.[1] Slosson has reported similar cases in Wyoming.[2]

One "black alkali" system has been studied with some approach towards completeness.[3] In this case magnesium and potassium salts are not present, the system being composed of water, carbon dioxide, chlorides, sulphates, sodium and calcium salts, with the condition imposed, that the bases are present in amounts more than equivalent to the sulphuric and hydrochloric acids. On desiccation at 25° C calcium carbonate first appears followed by gypsum and then sodium sulphate decahydrate. Next appears a double salt ($2CaSO_4.3Na_2SO_4$) followed by anhydrous sodium sulphate, the Glauber's salt which formerly crystallized being no longer stable. Sodium chloride then precipitates and the concentration finally reaches a point where gypsum is no longer stable, and the final group of salts in contact with the evaporating solution under conditions of stable equilibrium consists of calcium carbonate, the double sulphate of soda and lime, anhydrous sodium sulphate and sodium chloride.

The desiccation of a lake which serves as the final repository of a regional drainage involves essentially the principles just discussed. The constituents involved are the same. A serious problem involved in the consideration of this source of "alkali" is the high ratio of chlorine to the other constituents, in view of its very low ratio in the rocks from which it comes. The explanation undoubtedly involves the fact that the carbonates and sulphates are constantly being removed as calcium salts from a body of water which is more or less continuously receiving the drainage of any considerable watershed, and is at the same time subject to a relatively

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[1] Application of the theory of solutions to study of soils, by Frank K. Cameron, Report No. 64, Field Operations of the Bureau of Soils, 1899, p. 149.

[2] Alkali lakes and deposits, by W. C. Knight and E. E. Slosson, Bull. No. 49, Wyoming Agr. Expt. Station, 1901, p. 108.

[3] The solubility of certain salts present in alkali soils, by F. K. Cameron, J. M. Bell and W. O. Robinson, Jour. Phys. Chem., 11, 396–420 (1907).

high rate of evaporation. The chlorine forming only very soluble salts under such conditions would be segregated and concentrated in the residual mother liquor. More difficult is it to account for the relatively high ratio of sodium to potassium in alkali from such an origin. Some light is thrown on the subject by the progression changes in concentration of a lake water which receives a regional drainage under arid conditions. To this end are given the following results of analyses of the waters of Utah Lake, made at different times[1] over an interval of twenty years, and showing that there is a segregation of chlorine and sodium taking place, although in this case the lake has an outlet in the Jordan River.

ANALYSES OF THE WATER OF UTAH LAKE. RESULTS IN PARTS PER MILLION

	Clarke 1883	Cameron 1899	Brown 1903	Seidell 1904[2]	Brown 1904[3]
Ca	55.8	67.6	80	67.7	67
Sr	—	—	—	1.7	—
Mg	18.6	13.8	92	73.5	86
Na	17.7 }	233.7 }	247	207.2	230
K	? }	? }	30	25.8	22
Li	—	—	—	0.7	—
SO_4	130.6	236.7	365	332.9	378
Cl	12.4	316.5	336	288.5	337
HCO_3	—	—	266	205.5	194
CO_3	60.9	23.7	—	24.0	11
SiO_2	10.0	—	—	22.6	28
Total	306.0	892.0	1416	1250.1	1353

The third general origin of alkali supposes that wind-borne sea-spray carries into the air salts which are left in very fine particles on the evaporation of the water, or are deposited on the ordinary atmospheric dust and carried over the land; and that this dust is precipitated here and there as

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[1] The water of Utah Lake, by F. K. Cameron: Jour. Am. Chem. Soc., 27, 113–116 (1905).

[2] Sample collected May 18. Lake unusually high.

[3] Sample collected Aug. 31. Lake still high for that season of the year.

may be determined by the various meteorological conditions which it encounters. All the land surface is supposed to be receiving more or less of it from time to time, but in arid regions the rainfall and drainage is not sufficient to return to the sea as much as is received therefrom.

It is very probable that wind-borne salts from the sea are being carried over and to some extent being deposited on all the land surfaces of the earth. To what extent this process is taking place, and whether it is sufficient to account for the alkali of any particular region, available data fail to answer satisfactorily. Probably it is always associated with one of the origins of alkali already discussed and is in itself of secondary importance.

An argument frequently advanced against the validity of the hypothesis that wind-borne sea-spray is the origin of alkali is that the relative proportions of the several constituents in "alkali" are seldom if ever those obtaining in sea water. This argument does not take into consideration, however, that the several salts in the spray probably separate into crystals of widely different size and specific gravities, and there may well be taking place a selective or sorting action by the wind. More important, undoubtedly, is the selective action taking place in the soil itself; it can only be an accidental coincidence that the constituents of alkali in any particular occurrence should have the same quantitative relations as in the material from which it originated, no matter what may have been the nature of its origin.

In the field, alkali is found in a bewildering array of forms and types. Quite different combinations of constituents may be found in the same field within a few rods or even a few feet, and each case appears to have a distinct origin, to be in fact a law unto itself. Each alkali deposit represents generally the resultant from a mixture of salt which has been dissolved and reprecipitated a number of times, and which while dissolved has been seeping through the soil under gravitational forces, or has been moving through the soil as film water under capillary stresses. In either event the salt mixture has been subject to the power for selective absorption peculiar to the particular soil mass through which it has been moving. Re-solution is seldom an instantaneous process, and different rates of solution necessarily involve some separation of salts. Finally the alkali deposit is usually so mixed with other soil material that there cannot be recognized the characteristic solid phases (such, for instance, as the double sulphates of calcium and another base) which serve as guides in laboratory studies and in certain salt mines. Even if the characteristic salts are deposited in surface soils, it is very doubtful, owing to their hygroscopicity, if any but gypsum, halite and Glauber's salt can persist for any length of time. The alternations of temperature from night to day characteristic of arid regions, with precipitation of dews, might easily be expected to make noticeable and rapid changes in the characteristics of any given alkali or salt mixture.

It is not surprising, therefore, that attempts to account for the genesis and present appearance of an alkali deposit by comparison with artificial depositions of salt mixtures, as worked out in the laboratory, have generally been disappointing. On the other hand, laboratory studies have been quite fruitful in elucidating the phenomena taking place on the leaching of alkali from a soil, or so-called "alkali reclamation."

Whatever the origin of the alkali, its segregation at or near the surface of the soil is everywhere much the same; that is, there is a translocation and segregation of soluble salts in the below-surface seepage waters, determined mainly by the topographic features, but partly by the texture and structural properties of the soil and subsoil, with a subsequent rise as capillary water consequent upon evaporation at the surface. Precipitation of the solutes may take place at the surface; more commonly it takes place a few inches below, owing to the fact that under conditions of rapid evaporation, there is ordinarily a discontinuance in the capillary columns or the film water at a point below the surface of the soil, the water diffusing thence into the above-surface atmosphere as the vapor phase.

The composition of alkali is varied. In the vast majority of cases, the world over, the predominating compound is sodium chloride. When calcium carbonate is a conspicuous component of the soil, as a hardpan or otherwise, sodium carbonate or black alkali is also generally present, or apt to appear when the land is irrigated. When calcium sulphate or gypsum is likewise present, there is less probability of appreciable amounts of black alkali, and where gypsum predominates or the calcium carbonate is present in relatively inappreciable amounts, black alkali is generally absent, and sodium sulphate is an important constituent of the alkali. Relative rates of diffusion, selective absorption, and sometimes other factors are prominent, however, and the character of the alkali in different spots within a few yards of one another may differ greatly. One of the most interesting manifestations of alkali is the occasional occurrence of a predominating amount of calcium chloride which, as a result of its unusually high hygroscopicity, renders the soil damper, and therefore darker in color than the surrounding soil, and frequently causes even experts to suspect the presence of black alkali. Its true nature can, of course, be determined by a simple chemical examination.

The effect of alkali on the physical properties of the soil is often very marked, aside from the cementing action or hardpan formation of the carbonate or sulphate of lime. Black alkali, by dissolving and segregating the organic matter at the surface, removes from the lower soil layers the "humus" compounds which are of enormous importance to the maintenance of a soil structure favorable to plant growth. Moreover, black alkali is one of the best of deflocculating agents, and consequently soils where it is a noticeable component, frequently puddle with great readiness and are reclaimed with the utmost difficulty. Most of the other constituents of alkali, however, are flocculating or "crumbing" agencies, and if not present in too large amounts tend to increase the readiness with which the soil can be brought into good tilth. In this latter case, by separating in the solid phase, or in forming a viscous soil solution, near the saturation point, they sometimes produce a condition in the soil simulating puddling, and where it occurs below the surface, called an alkali hardpan.

The management of soils infested with alkali is possible in accordance with a few well established principles. Substantial progress has been made in selecting and breeding plants and strains of plants adapted to such soils. Extreme cases are the use of the so-called Australian salt-bushes as forage crops, and the growing of date-palms which through generations of breeding in the oases of the Sahara can thrive in lands so salty as to destroy most of the halophilous plants. More interesting is the unwitting development by the farmers of Utah of strains of wheat and alfalfa which easily withstand three or four times as high a salt content in the soil as do corresponding crops in other alkali regions, such as New Mexico and Arizona.[1] Black alkali, or one in which sodium carbonate is a prominent constituent, is especially destructive to vegetation, not alone on account of a toxic action on plants, but because in any considerable concentration it has a corrosive action on the plant tissue. Not only on this account but also because of its unfortunate effects on the physical properties of the soil, black alkali has received unusual attention from soil investigators. Hilgard[2] has repeatedly urged the use of gypsum as an "antidote" to black alkali, assuming that under conditions of good drainage and aeration a reaction takes place in accordance with the following equation:

$$Na_2CO_3 + CaSO_4 = CaCO_3 + Na_2SO_4$$

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[1] Some mutual relations between alkali soils and vegetation, by Thomas H. Kearney and Frank K. Cameron, Report No. 71, U. S. Dept. Agriculture, 1902; The date palm and its utilization in the southwestern states, by Walter T. Swingle, Bull. 53, Bureau of Plant Industry, U. S. Dept. Agriculture, 1904; The comparative tolerance of various plants for the salts common in alkali soils, by T. H. Kearney and L. L. Harter, Bull. 113, Bureau of Plant Industry, U. S. Dept. Agriculture, 1907; Tolerance of alkali by various cultures, by R. H. Loughridge, Bull. 133, California Agr. Expt. Sta., 1901.

[2] Soils, by E. W. Hilgard, 1906, p. 457–458.

Furthermore, it has been shown that calcium salts and especially calcium sulphate exercise a marked ameliorating effect on the action of other salts upon growing vegetation. On the other hand, the reaction indicated by the equation just given does not run to an end with complete precipitation of the carbonate, and the total amount of alkali is increased in the soil by the addition of the gypsum. Unfortunately, Hilgard's suggestion has not yet acquired the sanction of satisfactory field demonstration, although it would seem to merit more consideration than has been given it. Inasmuch as lime is generally a prominent constituent of soils containing black alkali, it is possible that the maintenance of good drainage and aeration in the soil is itself the best correction of black alkali.

The best use of alkali soils involves irrigation, and it is in the application of irrigation waters that management of alkali soils finds its most highly developed and most important expression. With light sandy soils it has sometimes been found practicable to add sufficient water to carry the alkali down into the soil to such a depth that the crop is well advanced toward maturity before the alkali again rises in sufficient amounts to prove seriously detrimental to the more advanced crops which are generally far more "alkali resistant" than the young seedlings or the germinating seeds. In some cases this procedure can be practiced for a number of years without greatly increasing the seriousness of the alkali conditions, and it may be justified, for a time at least, by economic considerations. Ultimately, however, and more quickly with heavy than with light soils, increasing amounts of alkali must be brought into the surface soil, and this method of irrigating should not be considered as anything more than a temporary expedient. The only procedure which should be seriously considered as a permanent system on an alkali soil, no matter what the texture, is the installation of underground drains, for which purpose, so far, cylindrical tile drains commend themselves as giving the best results. With a well established system of tile drains, the alkali and all excess of soluble salts can be removed from the soil above the drains; and alkali rising from the soil below can, at least, very largely be prevented from rising to the upper soil layers. The reclamation of an alkali tract by underdrainage is not, however, a necessarily quick operation. Generally it must be a matter of several years persistent and careful effort, but once attained should readily be maintained. The reclamation of an alkali tract by flooding and underdrainage involves the reverse process to the crystallization of salt from a brine. If the water in percolating through the soil were long enough in contact with the salts present, to become a saturated solution in equilibrium with them, then the composition of the resulting solution or drainage water would depend upon the particular solid phases or salts which are present in the soil, but not on the amounts of these salts; and the relative proportions of the mineral constituents in the drainage water should remain constant until some one of the solid phases in the soil permanently disappears.

In practice, however, the water passes through the soil at different rates from time to time, the flow from the tiles being copious after a flooding but gradually diminishing as time goes on. One or both of two processes can therefore take place. The water may dissolve some of the salts without at any time or place becoming saturated. As the different salts have different rates of solution as well as different absolute solubilities, it would be expected that not only the concentration of the drainage water, but the composition of the dissolved salts would change from time to time. On the other hand, a part of the water may be imagined to percolate slowly through the finer openings, thus forming a saturated solution with respect to the alkali salts which solution, however, will be diluted on entrance to the drains by a part of the water going through the larger soil openings and dissolving but little salt in its passage. In this case, it would be anticipated that the concentration of the drainage water would increase as the amount of flow diminished but the composition of the dissolved salts would remain practically constant until some one or more of the alkali salts was completely removed. There are, unfortunately, but few experimental data by which these ideas can be tested. In the accompanying table are given the results of an investigation on the reclamation of an alkali tract near Salt Lake City, Utah, where observations on the composition of the drainage water were made at frequent intervals for more than three years.[1]

At first sight these results might appear to show that the composition of the salts was remaining reasonably constant. This conclusion must be received with caution, however. Variations do occur in the constituents which are present in smaller amount, but the variations are not systematic and may plausibly be explained by dilution of saturated solution by unsaturated solution on entering the drains. Confining attention therefore to the constituents occurring in larger proportions, namely, sodium chloride, sodium sulphate and sodium bicarbonate (including the normal carbonate) it should be remembered that the percentage of sodium in these three salts does not vary much, and the "constancy" may be more apparent than real. Indeed a close inspection of the results indicates that while the sodium is remaining practically unchanged, there is some decrease in the chlorine and a corresponding increase in the sulph-ion. From this it would follow that the sodium chloride was being washed out of the soil more rapidly, proportionately, than sodium sulphate; and it would also appear that the solution entering the drains was not in final equilibrium with the salts in the soil.

How long drainage must continue before there is a radical change in the composition of the seepage water cannot be predicted, and unfortunately data regarding this point are not available. It is certain that in time some one or more of the salts in the soil would be removed and the nature of the drainage water would be changed. Alterations in the

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[1] See: Calcium sulphate in aqueous solutions, by Frank K. Cameron and James M. Bell, Bull. No. 33, 1906, p. 10 and 70, and reclamation of alkali land in Salt Lake Valley, Utah, by Clarence W. Dorsey, Bull. No. 43, 1907, p. 13, Bureau of Soils, U. S. Dept. Agriculture.

COMPOSITION OF THE SALTS IN THE DRAINAGE WATER FROM THE SWAN TRACT, UTAH

Date	Ca	Mg	Na	K	SO_4	Cl	HCO_3	CO_3
	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
1902—September	0.38	0.50	33.74	2.04	18.62	37.76	6.49	0.48
October	0.23	0.78	34.73	1.49	19.14	39.52	5.06	0.29
November	0.19	0.74	34.42	1.40	18.61	40.46	3.95	0.23
1903—May	0.38	0.61	34.48	0.84	29.90	38.19	4.30	0.25
June	0.45	0.85	34.18	1.09	17.52	41.00	4.23	0.42
July	0.50	0.80	34.06	1.25	18.24	40.24	4.67	0.30
August	0.35	0.90	34.40	1.12	17.15	42.37	3.48	0.16
September	0.49	0.72	34.54	1.24	17.31	42.02	3.36	0.33
October	0.47	1.02	33.43	1.52	16.08	43.28	3.33	0.30
1904—January	0.15	0.75	33.93	1.26	20.08	36.64	6.94	0.25
February	0.34	0.78	34.59	0.70	18.95	40.15	4.49	—
March	0.29	0.77	34.57	1.28	16.31	42.28	3.81	0.19
April	0.29	0.70	34.28	1.37	20.93	38.04	3.33	1.06
May	0.71	0.74	26.92	4.01	21.26	40.93	4.05	1.38
June	0.37	0.70	32.60	3.55	19.94	37.42	4.05	1.37
August	0.37	0.86	33.85	2.13	17.12	41.31	3.20	1.16
September	0.42	0.79	34.10	1.35	19.01	39.85	4.11	0.37
October	1.04	0.60	33.01	1.86	21.42	36.63	4.68	0.76
December	1.25	0.70	32.62	1.69	19.89	37.44	6.18	0.22
1905—February	0.32	0.67	33.59	0.99	22.30	33.32	8.45	0.36
March	0.31	0.66	33.46	1.30	21.60	33.86	8.46	0.35
April	0.35	0.65	34.20	1.01	20.03	36.99	6.22	0.55
May	0.45	0.86	33.43	1.20	20.59	36.04	6.96	0.47
June	0.40	0.94	34.05	1.32	20.89	35.85	5.71	0.84
July	0.32	0.69	33.67	1.30	21.17	34.94	7.23	0.68
August	0.35	1.04	33.12	1.58	21.58	35.92	5.72	0.90
September	0.42	0.82	33.30	1.26	21.18	34.85	7.41	0.67
1906—January	0.55	0.84	33.12	1.11	21.10	34.35	8.57	0.36

composition of the drainage water furnish the readiest as well as the best guides as to the changes and the nature of the changes taking place in the soil during the process of reclamation. As a practical matter it should be borne in mind that the persistence of the several salts of the alkali mixture does not mean necessarily that they are evenly distributed in the soil; while yet determining the composition of the water entering the drain, they may have disappeared from the upper soil layers which then may hold a solution of quite different character suited to the support of crops. In the case just cited the soil contained, before drainage operations were commenced, upwards of 2.7 percent of readily soluble salts and would not support any growth other than salt bushes and similar halophilous plants. Four years later the soil contained less than 0.3 percent soluble salts and yielded a very satisfactory crop of alfalfa. In such cases, however, the land cannot be considered as finally reclaimed until a material change in the composition of the drainage water shows that there has been a complete removal of some of the solid salts from that portion of the soil feeding the drains.

The rate at which alkali can be leached from a soil is dependent in a large measure upon the absorptive properties of the soil, and to some extent upon the nature of the salts composing the alkali. The leaching is more rapid from sandy than from clay soils, and white alkali is leached more readily than is black. In general, however, the same laws hold here as in any leaching of a solute from an absorbent, and it has been shown that even in the case of black alkali, the rate of removal under a constant leaching follows the law $dx/dt = K(A - x)$.[1] In practice, the water does not percolate through the soil under a constant "head," but the flow is intermittent, so that the value of the above formula is mainly academic. On the other hand, if the drainage between floodings is thorough, this procedure should be more efficient than any other for causing a rapid removal of the alkali salts, if, as is generally the case, a limited quantity of water is available.

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[1] The removal of "black alkali" by leaching, by F. K. Cameron and H. E. Patten, Jour. Am. Chem. Soc., 28, 1639 (1906).

Finally, it remains to be pointed out that the use of excessive amounts of water on alkali tracts is quite as unfortunate in its effects as the use of too little. If water be added to an undrained soil or in excess of the capacity of the drains to remove it, incalculable harm may be done by enormously increasing in the surface soil the amount of salts brought up from the lower layers as the capillary stream rises to the surface in consequence of evaporation there. Should the wetting of the soil proceed so far as to establish good capillary connection with the permanent ground water, the harm may be sufficient to offset in a few weeks or months expensive reclamation efforts of years. The harm to the tract where the water is added may be far less than the harm done to other areas. A large proportion of existing alkali deposits or "spots" results from the evaporation of seepage waters coming sometimes from considerable distances. The overwetting of a soil means the production of seepage waters which are to appear at the surface somewhere else, generally at a lower level, and frequently means the more or less complete ruin of the soils of the lower level. The experience of India, Africa and our own arid states in the increase of alkali spots following the introduction of irrigation, added to our present theoretical knowledge, should make the planning of an irrigation project without adequate drainage provisions, a stupidity, and its accomplishment a public crime. Quite as important is the development of a public opinion that the individual cultivator who deliberately or carelessly uses excessive amounts of water on his tract is a serious enemy to the body politic, and should be treated as such.

THE ATTRACTION PRESSURE

BY J. TRAUBE

In different physiological[1] and physico-chemical[2] papers I have discussed the *attraction pressure* (*Haftdruck*) of a dissolved substance. This expression means the cohesion constant a_{12} of van der Waals. The *attraction pressure* is the *intensity factor* of the solution energy and has been neglected in the theories by van't Hoff and Arrhenius.

If for example we dissolve in water a substance like sugar or alcohol, we change the energy content of the system to a certain extent. This change is proportional, firstly to the *number* of the dissolved particles—that is a capacity factor—and proportional secondly to an intensity factor "the attraction pressure," that is the *pressure*, which corresponds to the union of the substance and the solvent.

There is scarcely a single physical or physiological property of the solutions, which is not intimately connected with the attraction pressure. Though I have already published different memoirs concerning this pressure, my ideas have changed and enlarged in different ways, and therefore I wish to put together in a new paper the *attraction pressures* firstly of the *ions*, secondly of the *non-electrolytes* in their relations to the physical and physiological properties of the substances. I wish to mention here the physiological part of these problems only in a brief manner. That is necessary, because the physiological part of my work is *very important* for the understanding of my theory and therefore I refer to my newest publications in the *Biochem. Zeitschrift* and in *Pflüger's Archiv. f. d. ges. Physiologie.*

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[1] Pflüger's Arch. ges. Physiol., **105**, 541, 559 (1904); **123**, 419 (1908); Arch. exper. Pathol. und Therap., **2**, 117 (1905); Biochem. Zeit., **10**, 371–403 (1908); **16**, 183 (1909); Bickel, Deutsche med. Woch., **1905**, No. 28.

[2] Verh. phys. Ges., **6**, 326 (1904); **10**, 880 (1908); Ber. chem. Ges., Berlin, **42**, 86, 1594, 2185 (1909).

1. The Ions

1. *Surface tension.*[1]—I have chosen the following form for a well-known principle by Gibbs:

The more a substance increases or decreases the surface tension of the pure solvent, the larger or smaller is its attraction pressure. Therefore the order of the surface tensions of molecular solutions is identical with the order of the attraction pressures and thus I calculated from my own experiments with alkali salts[2] the following order of attraction pressures for the best known ions:

Anions: $ClO_4 < CNS < I$; $ClO_3 < CN < NO_2 < NO_3 < Br$; $Cl < OH < F < C_4H_4O_6$ (tartaric acid) $< SiO_3 < SO_4 < CO_3$.
Cations: $H < Tl < Cs < Rb < NH_4 <$ Li(hydr) $< K < Ag < Na$; and $Ba < Sr < Ca$; Mg.

2. *Compressibility.*[3]—With regard to the compressibility Röntgen and Schneider have found that the ions can be arranged in a series which corresponds entirely with the series of capillarity:

Anions: $I > NO_3 > Br > Cl > OH > SO_4 > CO_3$.
Cations: $H > NH_4 >$ Li(hydr.) $> K > Na$.

3. *Diminution in the solubility.*[4]—It is known that salts diminish the solubility of gases, non-electrolytes, colloids and suspensions. As stated by Geffken, there derives from the alkali-salts—in general—the following series:

Anions: $CNS < I$; ClO_3; $NO_3 < Br < Cl < OH < SO_4 < CO_3$.
Cations: $H < Cs < Rb < NH_4 <$ Li(hydr.) $< K < Na$.

As shown, here the series of the ions is like that for surface tension and compressibility, but sometimes the lithium ion has its place at the other side of the sodium. Why that is the case, we may conclude from:

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[1] Comp. Verh. phys. Ges., 10, 888 (1908).

[2] Ibid., 10, 888 (1908), there reference is made to further attraction pressures.

[3] Verh. phys. Ges., 10, 903 (1908).

[4] Loc. cit., p. 895.

4. *The hydrate formation* and the *electrical transference.*[1]—We derive from the hydrate formation of the salts in the solid state as well as in the state of aqueous solutions according to Smirnow, Jones, Garrard and Oppermann, Washburn, Heydweiller and others the following series:

Anions (Garrard and Oppermann): $NO_3 < Br < Cl < SO_4$.
Cations: $H < Cs < Rb < NH_4 < K < Na < Li$; $Ba < Sr < Ca < Mg$.

The investigations on transference show the amount of water, transferred along with the ions by the electric current. They are *especially important,* since probably the attraction pressure can best be measured *as to quantity* by this number of the transferred water molecules. Washburn thus found with the aid of the chlorides:

$$H(H_2O)_{0\cdot3},\ K(H_2O)_{1\cdot3},\ Na(H_2O)_{2\cdot0} \text{ and } Li(H_2O)_{4\cdot7}.$$

According to Garrard and Oppermann the number of the transferred water molecules for the anions NO_3, Br, Cl, SO_4 stood in the ratios of 2.5 : 4 : 5 : 9.

It is highly remarkable that the *lithium ion* in the alkali-series is the most *hydrated.* Therefore its attraction pressure in relation to the water is the *highest.* Since lithium salts considered in the investigations on capillarity, compressibility, influencing of the solubility, etc., were always highly hydrated and since *the attraction pressure of the salt hydrate of course is lower than that of the non-hydrated salt,* it is evident why as regard the capillarity, compressibility and solubility the lithium ion has not in general its place at the end of the series.

5. *Internal friction.*[2]—According to the publications of Reyher, Wagner and Euler the internal friction of the solutions increases in the following order:

Anions: $NO_3 < Br < Cl < OH < SO_4$ and
Cations: $Cs < Rb < NH_4 < K < Ag < H < Na < LiBa < Sr < Ca < Mg$.

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[1] Loc. cit., p. 891 and 911; further Washburn, Jahrbuch. Radioakt., 6, 103 (1909); Jour. Am. Chem. Soc., 31, 322 (1909); see also Heydweiller, Drude's Ann., 30, 873 (1909).

[2] Verh. phys. Ges., 10, 908 (1908).

Only the ion of hydrogen is not in its proper place in the series of attraction pressures.

6. *Diffusion coefficient.*[1]—This coefficient increases in the following manner:

Cations: $H > K > NH_4 > Na > Li$; $Ba > Sr > Mg > Ca$.

7. *Molecular volume, molecular volume of solutions and contraction.*[2]—With the binary potassium salts the molecular volume and the molecular solution volume in water and also the contraction (molecular volume—mol. solution volume) increase as follows:

Anions: $ClO_4 > I > ClO_3 > BrO_3 > NO_3 > Br > Cl > OH > F$.

This conformity with the series of attraction pressures is indeed highly remarkable.

8. *Lowering of the vapor pressure and rise of the boiling point.*[3]—The range of the best known ions is the following:

Anions: $NO_3 < ClO_3 < CNS < Cl < Br < I < SO_4 < OH < CO_3$.
Cations: $Cs < Rb < K < Na < Li$.

9. *Lowering of the freezing point.*[4]

Anions: $NO_3 < CNS < CN < F < Cl < Br < I < OH < SO_4 < CO_3$.
Cations: $Cs < Rb < K < NH_4 < Na < Li < H$; $Ba < Sr < Ca < Mg$.

Though we find essentially the same order of attraction pressures for the freezing point and boiling point, we notice a second influence, which perhaps depends on the weight of the ions. This is shown especially by the place of hydrogen in the freezing point and the inverse range of the halogens as to both properties.

10. *Specific heat.*[5]—The ions *diminish* the specific heat of water. From the investigations by Marignac and J. Thomsen we get the following series, which is nearly the same as the series of attraction pressures:

Anions: $NO_3 < J < Cl < Br < OH < SO_4$, CO_3.
Cations: $NH_4 < Na < K < Ag < H$.

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[1] Verh. phys. Ges., 10, 909 (1908).

[2] Loc. cit., p. 924.

[3] Ibid., 905.

[4] Loc. cit., p. 907 (compare the position of the heavy metals in the publications by Jones).

[5] Verh. phys. Ges., 10, 913 (1908).

It is remarkable that the cation with the lowest attraction pressure has the greatest influence on the specific heat of water, while the anion with the lowest attraction pressure has the least influence with regard to that property.

11. *Heat of solution.*[1]—Though the heats of solution depend also on the internal pressure of the solid salt, nevertheless we obtain a rather good conformity with the series of attraction pressures for salts of the alkali metals:

Anions: $ClO_4 > ClO_3 > NO_3 > CNS > Br > J > Cl$.

12. *Rotation of the plane of polarization.*[2]—From the experiments by Long as to the influence of potassium salts on the rotation of a solution of Seignette-salt, we derive the following sequence of the ions:

Anions: $CNS, J < NO_3 < Cl < Br < SO_4 < MoO_4 < WO_4$.

The attraction pressure in this case is not the single coefficient.

13. *Catalysis, acceleration of reaction and equilibrium constant.*[3]—Here we find in the most different treatises a good *accordance* with the *order* of the *attraction pressures.* The influence of the salts on the velocity of the saponification of ethyl acetate by potassium hydrate leads to the following series of the anions:

Anions: $I; Br < NO_3 < ClO_3 < Cl < C_2H_3O < C_2O_4 < SO_4$.

but the acceleration of the ester-catalysis to the *inverse* series: $Br > Cl > SO_4$ and just so the inversion of cane sugar to the series: $Br > Cl > SO_4$, while the transformation of diacetone-alcohol leads to the series: $SO_4 > Cl > Br$.

From the influence of the acids on the sugar inversion or the decomposition of methyl acetate in presence of salts results the following series:

Cations: $Ca > Sr > Ba > Li > Na > K > NH_4$.

One should notice the antagonism between the order of cations

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[1] Loc. cit., p. 914.

[2] Ibid., 918.

[3] Verh. phys. Ges., 10, 917 (1908) and Washburn's statements in Jahrbuch Radioakt., 6, 122 (1909), and Hoeber's statements in Zeit. phys. Chem., 70, 143 (1909).

and anions with regard to the sugar inversion. Very remarkable is also the series of cations, which results from the influence of alkali nitrates on the *velocity of solution of copper in nitric acids.* This series is the following:

Cations: Li > Na > K > Rb > Cs.

Lithium and sodium nitrate accelerate the reaction. Potassium nitrate is without influence, rubidium and cesium nitrate retard the reaction. This antagonistic effect of the *same* species of ions is very remarkable. We also find it with regard to the swelling or shrinking effect of the same species of ions on gelatine and glutine.

Walden and Centnerszwer[1] have measured the velocity of reaction and the coefficient of equilibrium in the solvents: methyl alcohol and acetone for the reaction:

$$(CH_3)_2SO_4 + MeCNS = CH_3CNS + MeCH_3SO_4,$$

where instead of Me the metals K, Na, NH_4, Cd, Co, Sn and instead of CNS iodine and bromine are to be substituted.

The differences with regard to the velocities of reaction and the coefficients of equilibrium were much less for the cations than for the anions, *which is in general the case for the attraction pressures.*

There resulted for the anions with regard to both coefficients the series: I > CNS > Br. That is the same series as in general for the solubilities of the salts in organic solvents.

14. *Ionic velocities.*[2]

Anions: $ClO_3 < NO_3 < Cl; I; Br < OH$.
Cations: $H; Cs > Rb > NH_4K > Na > Li$.

The attraction pressure is not the sole but the most important coefficient, from which depends the order of the ionic velocity and therefore the electrical conductivity. *The cations with the lowest attraction pressure have the highest velocity and just the inverse is the case with the anions.*

15. *Decomposition voltage.*[3]—From the experiments of

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[1] Walden and Centnerszwer: Zeit. Elektrochemie, 15, 310 (1909).

[2] Verh. phys. Ges., 10, 909 (1908).

[3] Ibid., 10, 911 (1908).

Wilsmore and Nernst we obtain the following series of the decomposition voltages for the anions:

Anions: $I < Br < NO_3 < OH < F < SO_4$.

The decomposition voltage increases in general with the attraction pressure, but there are exceptions.

16. *Diffusion cells.*[1]—According to Nernst and Negbaur the potential differences due to the ions can be arranged in the following series:

Anions: $OH > Cl > Br > NO_3 > ClO_4 > SO_3C_6H_5 > SO_3C_9H_{11}$.
Cations: $Li > Na > NH_4 > K > H$.

The *agreement* with the *attraction pressure series* is *complete.*

17. *Daniell cells.*[2]—From the publications of Neumann, Wright, Thompson and Braun we derive the following series for the anions in more concentrated solutions:

Anions: $CO_3 > SO_4 > C_2H_3O > Cl > NO_3$, $Br > I$.

This is again the series of attraction pressures.

18. *Thermoelectric forces.*[3]—The thermoelectric forces, which appear in solutions of salts of the same acid or base when there is a difference of temperature, may be arranged in the following order:

Anions: $SO_4 > Cl > I$.
Cations: $Li > NH_4 > Na > K > Rb > H$; $Mg > Ca > Ba > Fe$.

With the exception of the ammonia we find once more the series of attraction pressures.

19. *Passivity.*[4]—From Hittorf's researches we get the following series of monobasic anions arranged with reference to the corrosion and passivity (*Passivierung*) of the chromium anode:

Anions: $F > Cl > NO_3 > CN > Br > CNS > I$.

That is again the series of attraction pressures.

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[1] Traube: Ber. chem. Ges., Berlin, 42, 1601 (1909).

[2] Ibid., 42, 1601 (1909).

[3] Podszus: Drude's Ann., 27, 859 (1908).

[4] Traube, Ber. chem. Ges., Berlin, 42, 1600 (1909).

20. *Maximum of surface tension.*[1]—According to the careful measures by Gouy the anions of the alkali salts influence the maximum of surface tension in the electrometer by Lippmann in the following order:[2]

Anions: $P_2O_7 > PO_4 > CO_3; SO_4 > OH > C_2H_3O_2; Cl > NO_3 > Br > CNS > J, S.$

That is exactly the series of the attraction pressures.

21. *Osmotic processes.*—These processes are especially important from the point of van't Hoff's theory. The most simple processes refer to the *swelling* or *shrinking* of gelatine and glue studied by Hofmeister[3] and his scholars. The gelatine *swells* in the chlorides, bromides, nitrates and iodides of the potassium salt solution, but it *shrinks* in the solutions of the sulphates, tartrates, citrates and acetates. This *antagonism* of the *same species of ions*[4] (compare velocity of reaction) exists in the same manner *with regard to the cations*, K, Na, etc., as opposed to the ions Ca, Mg, etc. There are many physiological processes influenced by this antagonism. The order of the anions with regard to the swelling of the gelatine is the following:[5]

$$SCN > J > Br > NO_3 > Cl > C_2H_3O > C_4H_4O_6 > SO_4.$$

There are also the highly remarkable osmotic researches by Brown[6] on the osmosis penetration of water into the covering of barley, when we put a certain quantity of the seed of barley in equivalent solutions of salts. The covering of barley is only permeable for salts of a very low attraction pressure as $HgCl_2$, CdJ_2; the rate at which the water passed into the barley increased from Na : K : NH_4 and from

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[1] Loc. cit., p. 1600.

[2] Compare there further anions. These observations of Gouy seem to be the most important and reliable for the statement of a series of attraction pressures.

[3] Compare Hoeber: Zeit. phys. Chem., 70, 5, 143 (1910).

[4] Hoeber: Phys. Chem. der Zelle and Gewebe, further Traube, Mengarini and Scala, Biochem. Zeit., 17, 443 (1909); Pick and Schwarz: Ibid., 17, 491 (1909); and J. Loeb: Parthenogenese. H. Barth, Leipzig.

[5] Compare Hoeber: Loc. cit.

[6] Brown: Proc. Roy. Soc., 81, (1909) and my latest publications in Biochem. Zeit., March, 1910.

J : Cl : NO_3. Hoeber[1] has found that the velocity of haemolysis increases from SO_4 : Cl : Br; NO_3 : J and Li; Na : Cs; Rb : K. As to the changes in the series of the cations as to physiological processes, compare Hoeber.[2] In the plasmolytic researches of de Vries[3] the order of the alkali ions is the following one: SO_4—Cl—NO_3 and K—NH_4—Na—Li. The swelling of the muscles increases (compare J. Loeb[4]) from Li : Na : K. According to Schwenkenbecher[5] lithium salts do not penetrate into the skin of the frog, but potassium iodide diffuses and Hedin[6] found that the diffusion through dead intestine of beef increases in the order: SO_4 : Cl : NO_3 : Br and Mg : Li : Na : Rb : K. Even for the living intestine there exist only small changes in the series of attraction pressures.[7]

Other important physiological processes.—The capability to precipitate albumen diminishes according to Hofmeister and Pauli[8] in the following order: SO_4 : HPO_4 ; $C_2H_3O_2$: Cl : NO_3 : Br : J : CNS and Li : Na : K : NH_4. The alteration of the melting or freezing point of gelatine[9] also shows the series of attraction pressure and Overton[10] has found with regard to the irritability of the muscles the following order of anions: HPO_4, SO_4, $C_2H_5SO_4$, CH_3COO, $(CHOHCOO)_2$, Cl, Br, NO_3, I, CNS and the order of cations: Li, Na, Cs, Rb, K.

The ions with the lower attraction pressure cause an inflow of water in the muscles, but ions with a higher attraction pressure do not do so.

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[1] Hoeber: Loc. cit.

[2] Loc. cit.

[3] de Vries: Zeit. phys. Chem., 2, 427 (1888); 3, 109 (1889).

[4] Compare Koranyi and Richter: Handbuch. phys. Chem. and Medizin, Vol. 1.

[5] Schwenkenbecher: Compare loc. cit., Vol. 1, p. 344.

[6] Hedin: Pflüger's Arch., 78, 205 (1899).

[7] Compare my publications in Biochem. Zeit.

[8] Hofmeister and Pauli: Compare Hoeber: Phys. Chem. der Zelle and Gewebe, II edit., p. 241.

[9] Hoeber: Phys. Chem. der Zelle and Gewebe, II, p. 255.

[10] Hoeber, loc. cit., 273 and Biochem. Zeit. 14, 210 (1908).

Concerning the irritability[1] of nerves, Mathews, Grützner and Hoeber draw up the following order: $I < Br < Cl < SO_4$; $HPO_4 <$ tartrate; and $K < Rb < NH_4 < Li < Na$. There exists the same inverse action of the cations and anions with regard to the irritability of muscles and nerves as to the precipitation of albumen in acid and basic solutions and as to the velocity of ions and their specific heat. Finally Lillie[2] has stated that as to the irritability of the Flimmer Epithel (?) the alkali-ions can be arranged in the series: I, Br, NO_3, SO_4 and Cl and Li, Na, Cs, NH_4, Rb, K[3], and the same author found the series of anions with regard to the contractibility of the muscles of the medusas:

$$SO_4,\ C_4H_4O_6,\ HPO_4,\ Cl,\ NO_3,\ Br,\ I$$

In my former publications I had calculated the attraction pressures only with the aid of the surface tension.

According as diluted substances increase or decrease the surface tension of water, we distinguished a positive and a negative attraction pressure, but it follows from the preceding material that we can measure the attraction pressure by the most different properties and therefore we ought to consider just those properties that we can determine in the most exact manner. The attraction pressure is *always positive*. However, I might recall my former[4] statements that with regard to substances, which diminish the surface tension of the water, the co-volume of the solution is larger than that of the pure solvent, while with regard to substances, which increase the surface tension of the water, the co-volume is correspondingly smaller. Upon the whole the relations

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[1] Hoeber: Loc. cit., p. 277; compare also Zeit. phys. Chem., 70, 142 (1910) and Koranyi and Richter: Handbuch phys. Chem. and Medizin, I, p. 471.

[2] Hoeber: Biochem. Zeit., 17, 542 (1909) and Chem. Centralblatt, I, 1427 (1909) and II, 1066 (1909).

[3] As to the alteration of the order K, Rb, Cs compare Hoeber's opinion, Zeit. phys. Chem., 70, 144 (1910); there also compare the remarks as to the influence of some organic ions as $N(C_2H_5)_4$, guanidine, piperidine ions on haemolysis, etc.

[4] Verh. phys. Ges., 10, 922 (1908).

of the co-volume to the attraction pressure (l. c.) are very important in their bearing on van't Hoff's theory.

From all these results I conclude that the order of the attraction pressures of the best known anhydrous ions (the anions calculated from the alkali-salts) is the following one:

Anions: ClO_4, CNS, I—ClO_3—NO_3—Br—Cl, C_2H_3O—OH—F—$C_4H_4O_6$—SO_4—CO_3—PO_4—P_2O_7.
Cations: H—Cs—Rb—NH_4—K—Na—Li—Ba—Sr—Ca—Mg—Fe, Al.

Thus we see that *the attraction pressure increases with the valency of the ions.* Further attraction pressures for ions follow from my own measurements on capillarity,[1] from the publications of Gouy[2] concerning the maximum of the surface tension and for the heavy metals from the measurements by Jones[3] concerning the freezing points. These last measurements (compare the curvatures) show especially that the ionization and attraction pressure nearly always run parallel. *The attraction pressure* is the *cause of the ionization.* It will be the most important problem of the future to obtain *quantitative* measures of attraction pressures, and that will best be possible by the *method of electrolytic transference* (compare Garrard, Oppermann, Washburn and others). Another important problem will be the calculation of attraction pressures with reference to other solvents than water. I am now busied with this problem.

2. The Non-electrolytes

1. *Surface tension.*[4]—While salts increase the surface tension of the water, this constant will be diminished in most cases by dissolved non-electrolytes. The differences of the values are here in general much larger than for salts, and therefore we may consider the *surface tensions for equivalent aqueous solutions of non-electrolytes* as a good *measure* of their

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[1] Verh. phys. Ges., 10, 888 (1908).

[2] Gouy: Ann. Chim. Phys. (7) 29, 145 (1903); (8) 8, 291; 9, 75 (1906).

[3] Jones and Getman: Zeit. phys. Chem., 46, 244 (1902); 49, 385 (1904); and Publ. of the Carnegie Institute (1907).

[4] Verh. phys. Ges., 10, 882, 888, 901, 917, 922 (1908) and Ber. chem. Ges., Berlin, 42, 2186 (1909).

attraction pressure as to *water*. From my own researches on a number of well-known non-electrolytes we obtain the following order of the surface tensions and attraction pressures:

Cane sugar, mannit, glycocoll, urea, glycerol, glycol, ammonia, acetamide, formic acid, methyl alcohol, acetonitrile, acetic acid, chloracetic acid, acetaldoxime, ethyl alcohol, acetone, urethane, methyl acetate, propyl alcohol, propylamine, diethylamine, piperidine, pyridine, ethyl ether, phenol, aniline, tertiary amyl alcohol, isoamyl alcohol, peptones and other colloids.[1]

The attraction pressure of the aforementioned substances is diminishing from cane sugar to colloids.

2. *Influencing of solubility.*[2]—From Rothmund's investigations it follows that the solubility of salts as Li_2CO_3, Ag_2SO_4, etc., is diminished by dissolved non-electrolytes more and more in the following order:

Mannit, urea, cane sugar, glycerol, glycol, ammonia, methyl alcohol, acetamide, ethyl alcohol, acetonitrile, urethane, propyl alcohol, acetone, pyridine, piperidine, ethyl ether, diethylamine, tertiary amyl alcohol. There is no doubt that in spite of slight alterations[3] this is the *series of attraction pressures.* I conclude the same from the researches by Armstrong and Eyre,[4] who found that the precipitation of salts such as KCl, NaCl, NH_4Cl from their aqueous solutions by non-electrolytes *increases* with the alcohols from methyl : ethyl : propyl. In the same manner a salt diminishes in a higher degree the solubility of a non-electrolyte as aniline, ethyl acetate, ethyl ether, if the attraction pressure of the non-electrolyte is smaller. Non-electrolytes of a higher

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[1] Verh. phys. Ges., 10, 898 (1908).

[2] Traube: Ber. chem. Ges., Berlin, 42, 2185 (1909) and Rothmund, Zeit. phys. Chem., 69, 523 (1909). It is remarkable that, in my reports in the Ber. chem. Ges., Berlin, I commented on antipyrine as the single important exception; and now Rothmund has just stated, without knowing about my comments, that there is a mistake in the determination of the solubility of antipyrine.

[3] Comp. the numbers: Ber. chem. Ges., Berlin, loc. cit., 2185.

[4] Ref. Chem.-Ztg., 89, 805 (1909).

attraction pressure like ethyl alcohol will be precipitated only by a salt of a higher attraction pressure such as K_2CO_3, while non-electrolytes of a lower attraction pressure such as amyl alcohol will be precipitated even by salts of a lower attraction pressure.[1]

3. *Volume.*[2]—In the case of substances which diminish the surface tension of water very greatly, the attraction pressures and molecular volumes run parallel and so do the molecular contractions (molecular volume minus molecular solution volume). According to my measurements the order of the molecular solution volumes in water is as follows:

Methyl alcohol, acetonitrile, acetic acid, ethyl alcohol, chloracetic acid, acetone, methyl acetate, propyl alcohol, propylamine, pyridine, phenol, diethylamine, ethyl ether, aniline, piperidine, tertiary amyl alcohol, isoamyl alcohol, colloids.

4. *The refraction of light.*[3]—For the molecular refraction according to Lorenz-Lorentz we find the following order:

Methyl alcohol, acetonitrile, ethyl alcohol, acetic acid, acetaldoxime, acetone, propyl alcohol, methyl acetate, propylamine, pyridine, diethylamine, ethyl ether, piperidine, phenol, aniline, tertiary amyl alcohol, isoamyl alcohol.

5. *The number of valences.*[4]—If we consider the close relations between the refraction of light and the number of the valencies existing in the molecule, it is not astonishing that we find for the number of valences the same order as above. Therefore with regard to the non-electrolytes we have a relation between attraction pressures and number of valences just as we have with salts.

6. *Depression of the maximum of the surface tension in Lippmann's electrometer.*—According to Gouy's researches[5] non-electrolytes depress the maximum much more than do

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[1] For further material see Verh. phys. Ges., 10, 895 (1908).

[2] Verh. phys. Ges., 10, 921 (1908); also Liebig's Ann., 290, 46.

[3] Verh. phys. Ges., 10, 924 (1908).

[4] Loc. cit., p. 926.

[5] Comp.: Loc. cit.

salts, a fact which does not quite harmonize with the existing theories.

The depression is small for different kinds of sugar and for glycerol, also for dibasic acids and amido acids. It increases from glycerol : glycol : ethyl alcohol : allyl alcohol : propyl alcohol; from the tertiary alcohols : the iso-alcohols; from methyl: amyl alcohol; from hydroquinone: phenol; it is larger for ethers, esters, nitriles, aldehydes, ketones, halogen alkyls, fatty acids, etc.

All this holds for the series of surface tensions of solutions under normal conditions, and therefore *we also recognize here the series of attraction pressures for the phenomena in the capillary electrometer.*

7. *Electromotive forces.*—There appeared in Bonn in the year 1907 a very interesting inaugural dissertation by R. C. Abt under the title: "Ueber den Einfluss der Nichtelektrolyten auf die elektromotorische Kraft in Ketten." The experiments were made in H-shaped vessels containing an equivalent solution of $CdSO_4$ in water in both tubes and the two electrodes consisting of the same cadmium-amalgam. If there were brought into one of the tubes some percents of different non-electrolytes, there was observed a certain electromotive force, which depended on the nature of the non-electrolyte. The order of the electromotive forces, which was calculated pro mol. of the non-electrolyte, increased from mannit : glycerol : glycol : methyl alcohol : ethyl alcohol : acetone: propyl and isopropyl alcohol: ethyl ether. *We have here just the same order for the electromotive forces as for the surface tensions*[1] *and for the attraction pressures.* I imagine that a future theory of the galvanic elements will be quite different from that of Nernst. We have here and in all the other cases (compare Lippmann and above) to deal with electro-capillary effects.

8. *Acceleration of reaction.*—For the decomposition of

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[1] With regard to allyl alcohol there is surely a mistake, because the statements for the $CdCl_2$ cell and the $CdSO_4$ cell contradict one another. I have therefore omitted this alcohol.

methyl ester or cane sugar by acids in presence of salts with the same anion we found (compare page 456 of this paper) the following order of cations:

$$Ca > Sr > Ba > Li > Na > K > NH_4$$

All these cations accelerated the reaction. On the other hand an addition of *milk sugar* had no effect, *glycerol* had a *retarding* effect, while ethyl alcohol exerted a still more *retarding* effect. Because the influence on the surface tension of the water is in the same direction and decreases from milk sugar : glycerol : ethyl alcohol, I think it highly probable *that the non-electrolytes also influence the velocity of reaction corresponding to the range of attraction pressure.*[1] Therefore we shall be inclined to consider the effects of the *pure solvents* on *different* reactions, studied by Menschutkin,[2] as being *produced by the attraction pressure*; but we shall conclude especially that the well-known affinity series of acids depends on the attraction pressure of the acids. In general the *ionization* and *attraction pressure* run parallel,[3] but there are some exceptions, especially the chloracetic acids. I think the chemical force of the acids and bases depends primarily on the attraction pressure, and we understand, why Goldschmidt and Salcher[4] have found the affinity series of the bases for certain reactions in organic solvents, where an electrolytic dissociation could not occur.

9. *Other physical properties.*—As to other properties we will remember that the *adsorption* and the distribution coefficient[5] are in close relation to the surface tension and therefore to the attraction pressure. In the *Verh. phys. Ges.*, p. 901 I have also shown that the *vapor pressure* of aqueous solutions containing volatile substances, depends on the boiling point of the dissolved body and on the surface tension of the solution. Concerning the freezing point we find that

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[1] I shall undertake further experiments along this line.

[2] Menschutkin: Zeit. phys. Chem., 1, 611 (1887); 6, 41 (1890).

[3] Comp. my statements in Verh. phys. Ges., 10, 916, 929 (1908).

[4] Goldschmidt and Salcher: Zeit. phys. Chem., 29, 89 (1899).

[5] Verh. phys. Ges., 10, 901 (1908).

cryohydrates are only formed by substances with a large attraction pressure, but not by non-electrolytes with a low one.

I do not doubt that *specific heat, heat of solution and dilution of organic substances in water* stand also in a simple relation to the attraction pressure, but we need investigations along that line.[1] Concerning the heat of neutralization[2] I beg to refer to my paper, *Verh. phys. Ges.*, 10, 915 (1908). My views are quite different from those of Professor Ostwald. If acetic acid furnishes a smaller heat of neutralization with sodium hydrate than hydrochloric acid does, I find the reason in the fact that the work to be done in separating the molecules of acetic acid from water is much less than the work which needs to be done in separating the molecules of hydrochloric acid and the corresponding salt ions from the solvent.

As to further electro properties, the tables in my former papers show that also for the organic anions the attraction pressure is the principal factor, on which the *ionic velocity* depends. In Nernst's researches on diffusion cells, his measurements on silver salts enable us to arrange the anions in the order: OH, Cl, Br, NO_3, ClO_4, $SO_3C_6H_5$, $SO_3C_9H_{11}$ (cymolsulphonic acid). Without doubt we have here exactly the order of attraction pressures.

10. *Physiological properties, especially osmotic processes.* —*a. Plasmolysis.*—The important relations which I have stated between the plasmolytic researches of Overton and my measurements of surface tensions[3] were the principal cause of my respective works on this subject.

Overton found that salts do not penetrate into cells of plants. Substances such as cane sugar and amido acids entered into the cells only in very small quantities. There was a little more, but not much more diffusion with such

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[1] It is intended to make such experiments, comp. Bose, Zeit. phys. Chem., 58, 606 (1907). The curvatures of the specific heat of aqueous solvents of methyl, ethyl, and propyl alcohol remind one in a high degree of the curvatures of capillarity.

[2] Comp. Verh. phys. Ges., 10, 915 (1908).

[3] Comp. Traube: Ber. chem. Ges. Berlin, 42, 87 (1909) and Verh. phys. Ges., 10, 882 (1908).

substances as urea and thiourea, glycerol diffused slowly, glycol and acetamide somewhat more rapidly, while solutions, which diffused very rapidly, were the monovalent alcohols, ketones, ethers, esters, amines, nitriles, aldoximes, etc.

The velocity in homologous series increased with increase in the molecular weight.

We have here *complete harmony* with the order of the *capillarity constants* and consequently with the *attraction pressures*.

Osmosis through the covering of barley.—We have already referred to the very valuable paper of Brown on p. 459 of this article. While the covering of barley was impermeable for most salts and mineral acids, and while salts diminished the osmotic velocity of water in comparison with distilled water, the effect of non-electrolytes was quite different, for such substances as ethyl acetate, etc., caused a high *acceleration of the water diffusion* and it was only at the end of 11 days, when the concentration of the non-electrolytes had become equal on both sides of the covering of the barley, that a state of equilibrium was attained, in which the diffused quantities of water were nearly, but not quite the same for different non-electrolytes.[1] The order of the non-electrolytes with regard to the osmotic velocity was: glycerol, glycocoll, urea, glycol, aldehyde, ethyl alcohol, acetone, acetic acid, ethyl acetate. That is exactly the order of the surface tensions. These researches are very important, because in the covering of barley lipoidic substances do not exist, and therefore these researches contradict the well-known theory of Overton.

b. Permeability of the living muscle.[2]—According to Overton's and J. Loeb's investigations the order of the solutions is here *quite the same* as for the plasmolytical osmosis in cells of plants.

c. Haemolysis.—According to the results of my investiga-

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[1] Compare my treatise: Biochem. Zeit., March (1910).

[2] Comp. Handbuch phys. Chem. and Med. Koranyi and Richter, I, p. 431 (1907).

tions[1] the velocity of the haemolysis increases in the following order: methyl alcohol, ethyl alcohol, acetone, propyl alcohol, methyl acetate, urethane, methylethylketone, propionitrile, isoamyl alcohol. We can easily understand the cause of the slight deviations of the order of the surface tensions, for we know that red corpuscles of blood have a covering of lipoids; and therefore the attraction pressure in the lipoids affects the values. Hedin[2] found that neutral salts, sugars, and hexites either do not diffuse or very slightly into the blood cells; that erythrite enters slowly, while the ordinary alcohols, aldehydes, ketones, ethers, diffuse very rapidly.

d. Parthenogenesis.—We can also find[3] the order of attraction pressures for dissolved substances from the diffusion into the eggs of sea urchins. It follows from J. Loeb's researches that strong mineral acids are almost without any effect, but that di- or tri-basic acids such as tartaric acid, or citric acid are somewhat more effective. Still more active are the fatty oxyacids, but the greatest efficiency is shown by the fatty acids, the effectiveness being greater, the higher the molecular weight of the acid. Such substances as the salts of cholic acids, amylene, chloroform, benzol, etc., act in the same way. That is exactly the order of the surface tensions.

e. Nerve cells.—As I have shown already in my first publication[4] the capillary constants run parallel with the narcotic effect of the non-poisonous narcotics, Grützner[5] has stated that when there is a chemical irritation of sensible nerves the velocity of the effect on the nerves increases from glycerol : methyl alcohol : amyl alcohol.

f. The experiments on the *skin* and for *intestine*, on the *dead* as well as on the *living intestine*, also give results in harmony with this series (compare my simultaneous com-

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[1] Traube, Biochem. Zeit., 10, 371 (1908).
[2] Hedin: Pflüger's Arch., 68, 229 (1897); 70, 525 (1898).
[3] Traube: Biochem. Zeit., 16, 182 (1908).
[4] Pflüger's Arch. Ges. Physiol., 105, 556 (1904).
[5] Loc. cit., 58, 69 (1894).

munications in the *Biochemische Zeitschrift* and *Pflüger's Archiv*).

g. *My law of capillarity,*[1] *haemolysis, narcosis, parthenogenesis, heliotropism, and deadly doses of poisons.*—My theory has found the most interesting confirmation in the following way.

In my former papers I stated that equal equivalents of homologous substances (such as alcohols, esters, ketones, etc.) diminish *in diluted solutions* the surface tension of water in the proportion $1 : 3 : 3^2 : 3^3$. One molecular weight of amyl alcohol has the same efficiency as 3^4 molecular weight of methyl alcohol. We find now quite the same law according to the researches of Führer and Neubauer and in my own publications with regard to the haemolysis of the red blood cells, according to the publications of van der Velde for the plasmolysis of plant cells, conformably to Overton's work for the narcosis of tadpoles, in accordance with Führer for the hindrance of the development of the fertilized eggs of sea urchins, according to Geoffroy and Servais for the deadly doses of poisons for rabbits and finally conformably to a new memoir by J. Loeb even with regard to the change of the antiheliotropism of certain crabs into heliotropism. I have tried to explain these very different biological problems in my former publications. (Compare *Pflüger's Archiv., Vol.* 123).

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[1] Comp. Pflüger's Archiv. ges. Physiol., 105, 556 (1904); 123, 430 (1908); further Traube, Biochem. Zeit., 10, 371 (1908) and J. Loeb, loc. cit. (1909).

THEORY OF ATTRACTION PRESSURE

BY J. TRAUBE

It was shown in the preceding paper[1] that the attraction pressure, which is not taken into consideration in the theory of van't Hoff and Arrhenius, is very different for different bodies and depends on the solvent as well as on the dissolved substances. When it is a question of aqueous solutions, the attraction pressure is nothing else but the water-attractive power of the dissolved body. Therefore we conclude that hydrates exist in solutions. This hypothesis, which formerly has been neglected or restricted too much by the adherents of the theories of van't Hoff and Arrhenius, is, as we know, at this time generally accepted. There exist two possibilities with regard to the hydrating effect of the attraction pressure.

1. If we suppose as van der Waals[2] does that the sphere of action (*Wirkungssphäre*) reaches only from molecule to molecule, we reach the conclusion that every dissolved molecule of a non-electrolyte or every ion of a salt is loosely connected only with *one* molecule of water with an intensity, which corresponds to the attraction pressure.

2. The sphere of action is more extended; the *molecules and ions of the dissolved body surround themselves, similarly to the condensation nuclei of the gases, with a water covering, which generally corresponds to the attraction pressure.* We will begin with the discussion of the first hypothesis:

If we suppose with Poynting[3] that one molecule or one ion of the dissolved body is connected with *one* molecule of water, and that this bound water cannot evaporate, and if the solution contains n molecules of the dissolved body to N molecules of the solvent, we get for the vapor pressures

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[1] Jour. Phys. Chem., 14, 452 (1910).

[2] Continuität des gasförmigen flüssigen Zustandes, Leipzig.

[3] Poynting: Phil. Mag., [5] 42, 289 (1896) and my Grundriss phys. Chem., Enke, Stuttgart, 1904, p. 195.

the solution and the solvent f_1 and f_0 respectively, the relation:

$$\frac{f_1}{f_0} = \frac{N-n}{N} \text{ also } \frac{f_0 - f_1}{f_0} = \frac{n}{N}.$$

This simple derivation of Raoult's law was the reason that Poynting's hypothesis formerly appealed to me very strongly, and some time ago I called attention to the papers of A. Werner,[1] who, though guided by quite other ideas, had developed a theory of *monohydrates* which was, in principle, identical with Poynting's theory.

In spite of all that, I do not hesitate to accept the second hypothesis. In the preceding paper I have referred briefly to a number of investigations, among others to the researches of Garrard and Oppermann, Washburn, etc., on the electrolytic transference of ions, to the well-known investigations of Jones on the freezing point, and to the experiments of Kohlrausch on the temperature coefficient of friction and electrical conductivity, all of these show that in general or in most cases the dissolved bodies are surrounded corresponding to their attraction pressure with a more or less extended covering of water. We think that there exist in a *dilute* solution *bound* and *not bound* (or influenced and not influenced) molecules of water, and we suppose a *limit of concentration*, for which the number of *unbound* molecules will be just equal to zero. We think that this limit of concentration is the same as that concentration, for which the *heat of dilution* becomes equal to zero. That concentration separates the *dilute* solutions[2] from the strong ones.

If we consider a *dilute* solution according to van't Hoff, we will understand, why in separating a part of the solvent from the dissolved body by *freezing* or evaporating, the *special nature* of the *dissolved body* either does not appear at all or becomes active in a *secondary* manner only, for it is clear

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[1] Werner: Ber. chem. Ges., Berlin, 40, 4133, 1907 and especially Fortschritte der anorganischen Chemie Vieweg Braunschweig, 1909, p. 218.

[2] It will moreover be an open question, whether the hypotheses 1 and 2 may not be joined together by a kinetic hypothesis, but we will not enter today more fully into these considerations.

that by the more or less extensive hydration the different effects of the ions on the existing surplus of solvent will be equalized, and as long as no bound water is present, the bodies are acting in relation to freezing and boiling point primarily only according to the number of particles.

But things will be quite different, as soon as the above-mentioned, limiting concentration has been exceeded, for then the work necessary to separate the solvent from the dissolved body will depend chiefly on the attraction pressure, and therefore we are not astonished that, according to Biltz, Jones, and others, the ascending of the freezing point curvatures with increasing concentration runs parallel with the attraction pressure. If the solutions become highly concentrated, we observe that bodies with a *great attraction pressure,* such as salts, freeze as *cryohydrates,* while cryohydrates do not exist for *non-electrolytes with a low attraction pressure.*

Further we may recall the well-known osmotic experiment by Pfeffer. In the osmometer a solution of sugar is separated from water by a semipermeable membrane. The water is evidently attracted by the sugar solution corresponding to the difference of pressure brought about by the attraction pressure of sugar. The *velocity* with which salts, sugar, and other bodies with large attraction pressure cause the entrance of water doubtless runs *parallel,* according to the results of the previous paper, with the *attraction pressures* of *molecules* and *ions.* But in proportion as the particles are gradually forming hydrates with increasing dilution, their *specific* influence will diminish by and by, and it may be possible, though it is *not certain,* according to the osmotic researches by Brown, Hoeber, de Vries (compare the previous paper) that the osmotic elevation is just the same after equilibrium is reached. Up to this point it seems that my theory will join very well to the theories of van't Hoff and Arrhenius. My theory would supplement those theories with regard to concentrated solutions. There we have a specific factor, because there is no unbound water, while in the *dilute* solutions we can disregard the specific influence of the hydrated ions. We can not deny that the two theories harmonize up to a certain point, but even in the case of dilute solutions we find *fundamental differences* in the point of view. When we consider simply the separation of the excess solvents from the dissolved body we can disregard the specific intensity factor of the solution energy, that is the attraction pressure, *but only in this case. If, however, there is a question of the separation of the dissolved body from the solvent, if therefore we consider the laws governing changes in solubility, then we are obliged to take account, even in dilute solutions of the specific influence of the attraction pressure.* Salts diminish the attraction pressure of non-electrolytes, of colloids, of red blood cells, and of bacteria (agglutination), and in the same way the non-electrolytes diminish the attraction pressure of salts. This whole inter-relation of the laws of solubility will now be understood, *while the osmotic theory has failed completely to bring this out.* We find quite the same for *osmosis* even in dilute solutions. It is not true that the cause of *semipermeability* is to be found only in the membranes themselves. The membranes which are semipermeable to salts, are not at all semipermeable to aqueous solution of non-electrolytes with a low attraction pressure. *There can never be an osmotic equilibrium between an aqueous solution of alcohol and cane sugar, even if the number of particles on both sides of the membrane is equal. Never do we have equilibrium between a solution of equal equivalents of sodium nitrate and sodium chloride, and even the osmotic equilibrium of molecular solutions of the same salts on both sides of a membrane will be disturbed at once, if a different decrease in the attraction pressure is caused by the addition of other bodies. The attraction pressure is the driving force of osmosis and not van't Hoff's osmotic pressure.*

At once we understand that these quite different views must especially enrich the *physiological* and *biological* sciences the more as just here van't Hoff's theory has failed completely in spite of all attempts to extenuate this fact. I refer once more to my publications, which will appear nearly simultaneously in the *Biochemische Zeitschrift* and especially in *Pflüger's*

Archiv der ges. Physiologie. These papers will bring many other proofs in favor of my theory.

And now to Arrhenius! Since attraction pressure and ionization nearly always run parallel, we may ask the question whether the hypothesis of ionization is necessary at all. I think that we cannot absolutely say no with regard to this question, but in this paper we will leave it aside.

Arrhenius has made, however, the same mistake in the calculation of the coefficients of dissociation, which an electrochemist would make who thought that the electrical energy of a current could only be increased by enlarging the electrical intensity and not the electromotive force of the current. *We must not forget that by increasing the attraction pressure we get the same effect as by augmenting the number of particles.* Therefore *many calculated dissociation factors,* especially those in non-aqueous solvents, *are surely very doubtful.* But the theory of Arrhenius is suffering from yet another fundamental fault. Though according to Faraday and Helmholtz the *electrostatic* and *chemical* forces of the ions are the same, Arrhenius makes them opposed to one another, for according to his views the ions are *electrostatically bound* in dilute solutions, but *chemically unbound.* Even if we assume that in dilute solutions the water-covering of the ions makes the re-association more difficult, we must acknowledge on the other hand that, in view of the powerful electrostatic forces, the re-association is not at all impossible. I think it very probable that the theory of the future will go back to the former idea of Clausius, that even in dilute solutions every dissociation is followed by an association, though the time in which the ions are joined may be very small in comparison with the time, during which they are separated. I think, however, that there are yet other ways of avoiding the difficulties of the Arrhenius theory.

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THE ESTIMATION OF RADIUM

BY STEWART J. LLOYD

In the course of an investigation which involved frequent determinations, by the emanation method, of the amount of radium present in minerals and in solutions, some irregularities were noticed, which led to the examination of the conditions necessary for the accurate determination of radium in this way. The facility with which radium may be estimated by means of its emanation, wherein it is unique among radioactive substances, renders the method of considerable importance. Indeed so simple and convenient is the process that it bids fair to be used as an indirect means of determining substances other than radium, just as the iodine-thiosulphate titration is employed in the estimation of substances ranging from copper to chlorine. At present it undoubtedly furnishes the simplest method of determining uranium in minerals. Unlike most other methods of analysis, too, it has the advantage that the sample is not destroyed in the course of the work, but may be re-examined any number of times. It is quite within the range of possibility, therefore, that the gas-electroscope will take its place in the analytical laboratory along with the polariscope and the refractometer.

The method in question is well known, in outline at least, to all those concerned with measurements in radioactivity. The solution containing radium is boiled to expel all emanation present, sealed up for a definite time, usually several days, to permit the emanation to accumulate, and the emanation then drawn off into a gas-electroscope where its activity is measured. Since in a radium solution which has been freed from emanation the latter grows to half value in 3.75 days, it is possible to calculate the total maximum value of the activity from the formula

$$I = I_0 (1 - e^{-\lambda t})$$

where "I" is the activity observed (the reciprocal of the time of discharge), "I_0" the maximum activity, "λ" the decay constant, and "*t*" the time; and by standardizing the electroscope from time to time with a solution of known radium content, it is possible to determine the actual amount of radium present in any case.

Rutherford appears to have been the first to use this method. After him, Boltwood, McCoy, Joly, and numerous others have practiced it with various modifications. The present article is not concerned with the mode of transferring the emanation from the vessel containing it to the electroscope, which has been the point of difference between them, but with the effect which the state of the solution exercises upon the giving up of the emanation.

It had been noticed that the presence of foreign substances exerted a marked effect on the accuracy of the estimation. To test the extent of this effect and to determine the conditions under which accurate results might be obtained, the following experiments were made.

A dilute radium solution prepared from uraninite residues, and therefore containing barium, was made up, and 10 cc of it placed in each of several 150 cc flasks, 100 cc of water added, the solution boiled vigorously for fifteen minutes, and then small quantities of the following reagents added, one to each flask. The flasks were then tightly stoppered, and allowed to stand for several days. The emanation produced in that time was then measured and the maximum amount calculated. The results are found in the following table.

No.	Reagent	Time of discharge for maximum Sec.
1	H_2SO_4	35.6
2	HCl	18.4
3	HNO_3	18.2
4	Na_2CO_3	27.7
5	$K_2Cr_2O_7$	19.0
6	KOH	19.6
7	MoO_3	18.7
8	HF	19.6
9	Hg	23.3

From this table it is evident that only in the presence of hydrochloric or of nitric acid is the emanation completely evolved. Sulphuric acid and sodium carbonate, which precipitate the sulphates and carbonates of barium and radium, hinder very noticeably the evolution of emanation. The other reagents have but slight effect, mercury more than the rest.

To determine whether other reagents which effected precipitation in the solution had the same effect as sulphuric acid and sodium carbonate, some of the solutions which had been previously used, after boiling to remove emanation, were treated, respectively with the following reagents, sealed up for some days and the emanation measured as before.

						Discharge
To No.	1	was added	$BaCl_2$	producing	$BaSO_4$	27·35
"	2	"	$AgNO_3$	"	$AgCl$	18.2
"	3	"	$CaCO_3$	"	$CaCO_3$	24·9
"	4	"	$BaCl_2$	"	$BaCO_3$	50.2
"	5	"	$Pb(NO_3)_2$	"	$PbCrO_4$	19·1
"	6	"	$AgNO_3$	"	Ag_2O	18.5

It will be seen from the table that the production of a precipitate in a solution does not necessarily mean an impairment of the accuracy of the determination. Only in the case of sulphates and carbonates is the interference with the evolution marked. Further experiments were therefore made to determine if possible the cause of this difference.

Four similar radium solutions were made up, sealed in the usual way, and the emanation measured after an interval.

				Discharge Sec.
No.	1	contained	no H_2SO_4	54
"	2	"	5 cc H_2SO_4 (dilute)	63
"	3	"	" " " plus $BaCl_2$	149
"	4	"	" Na_2CO_3	74

The radium solutions of course contained originally a small amount of $BaCl_2$. It is apparent from the table that the greater the amount of $BaSO_4$, formed the less emanation is given off.

These experiments did not however throw any light upon the mechanism of the retention of emanation, so another series was made. To each of four radium-barium chloride solutions were added equal amounts of $BaCl_2$, and then equal amounts of H_2SO_4 (excess) were run in, with stirring, from a burette, under identical conditions except that No. 2 was precipitated cold, the others hot.

1. The pptd. $BaSO_4$ was filtered immediately, and both the precipitate and the filtrate sealed up at once.

2. As No. 1 except that precipitation was made in cold.

3. Stirred continuously for thirty hours, after precipitation, then treated as 1.

4. Heated continuously for thirty hours after precipitation, then treated as 1.

After a suitable interval the radium contents of filtrates and precipitates were determined.

No.	Residue Sec.	Filtrate Sec.
1	500	12000
2	420	11400
3	144.2	10800
4	133.6	11100

This table indicates that in every case practically the same amount of radium remains unprecipitated by the sulphate, but that the readiness with which the emanation is given off from the part that is precipitated depends very largely upon the treatment to which it is subjected, stirring and heating, especially the latter, facilitating the evolution very markedly.

A similar set of experiments involving the precipitation of $BaCO_3$ instead of $BaSO_4$ was made. Sodium carbonate in excess was added to each of three radium-barium chloride solutions.

No. 1 was filtered at once.

No. 2 was heated for fifty hours and then filtered.
No. 3 was stirred for fifty hours and then filtered
Upon examination for emanation they gave:

No.	Residue Sec.	Filtrate Sec.
1	348	2970
2	144	1200
3	339	2724

The results here are quite analogous to those obtained with $BaSO_4$ except that stirring does not seem to be so efficacious, and the precipitation of radium by the carbonate is not so complete.

A further experiment was made to determine what effect the physical condition of $BaSO_4$ has upon the retention of emanation. A hydrochloric acid solution of radium which gave an emanation content corresponding to a time of discharge of 160 seconds was precipitated with sulphuric acid and barium chloride, and its emanation content measured at intervals of four days. The times of discharge corresponding to the maximum amounts were:

Days	Sec.
4	370
8	175
12	165
16	157
20	163

$BaSO_4$ previously made and heated for some time was then added to the solution and thoroughly shaken with it. The time of discharge was not however affected, remaining 163 seconds.

To ascertain whether or not the total amount of emanation was *finally* obtained from solutions in which sulphates had been precipitated, two solutions containing the same amount of radium, the first acid with hydrochloric acid, the second having a heavy precipitate of $BaSO_4$ produced in it, were measured from time to time.

Days	HCl solution Sec.	$BaSO_4$ solution Sec.
4	57	167
9	58	87
13	56.5	62
17	58	59
22	58.5	58

Conclusion.

For the accurate determination of radium by the emanation method the presence of HCl or HNO_3 is necessary.

If the sulphate or carbonate of barium is present in the solution, prolonged boiling or repeated determinations will be necessary to ensure the extraction of the total emanation.

The retention of emanation by the freshly precipitated $BaSO_4$ is doubtless mechanical only, and is due to the entanglement of the radium chloride or sulphate within the fine almost amorphous precipitate. Recrystallization under the influence of heat releases the radium, and permits the removal of the emanation.

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NEW BOOKS

The Fundamental Principles of Chemistry. *An Introduction to all Text-Books of Chemistry. By Wilhelm Ostwald. Authorized translation by Harry W. Morse. 15 × 21 cm; pp. xii + 349. New York: Longmans, Green and Co., 1909. Price: $2.25.*—This is an admirable book and should be read by everybody who is teaching or studying chemistry. The following extracts from pp. VI, 3, 9, 50, 61, 75, 256, 298, will give some idea of the book.

"The present book has for its object the presentation of the actual fundamental principles of the science of chemistry, their meaning and connection, as free as possible from irrelevant additions. It represents in a sense the carrying out of a thought expressed in the preface to my 'Grundlinien der Anorganischen Chemie.' It was there suggested that it was possible to work out a chemistry in the form of a rational scientific system, without bringing in the properties of individual substances. In order to accomplish this, many exceedingly elementary things must be restated with special reference to the connection between them, and it was also necessary to bring out many new connections in regions hitherto untouched. The difficulties which arise during such a first attempt became very clear to me as the work progressed, and I recognize them fully. They may serve as my excuse for the many irregularities in presentation which will be found in the book. There was no doubt in my mind that the work must be done sooner or later, and this is my justification for undertaking it and carrying it out to the best of my ability.

"The pedagogic importance of the matter is of the same order as its scientific importance. Questions concerning fundamental principles meet the teacher at every step, and the mental character of the developing chemist is frequently determined by the way in which they are answered."

"Not all the properties which we find in a given body have this peculiarity of remaining together. There is no way by which we can change the weight of a body, unless we take away a part of it or add a piece to it, but we can change its temperature, its electrical condition, its motion, etc. We can therefore distinguish between two classes of properties: those which persist with the body and whose sum makes up the concept of the body, and those which can be arbitrarily attached to or taken away from it. The first are called specific properties, the others accidental or arbitrary properties. The distinction is so important that it is the basis for the separation of two of the sciences: chemistry has to do with specific properties, while the arbitrary properties are the province of physics.

"We can, for example, make any body hot or cold, we can electrify it, we can illuminate it with red or blue light, we can magnetize it, etc. In all of these cases we are dealing with arbitrary properties, and their study belongs to physics, and not directly to chemistry. But the metallic nature of silver, its good conductivity for heat and electricity, its stability in air and at high temperatures, its solubility in nitric acid—these we cannot take away singly or change one at a time. The study of such properties belongs to chemistry."

"The result thus stated is an expression of another very important law of nature, that is to say, it is an oft-repeated and invariably confirmed experience. It has been expressed in the concept *matter*; and weight, mass, and volume have accordingly been called the fundamental properties of matter. Such a mode of designation has no disadvantages as long as the experimental origin of the concept is kept clearly in mind. But the idea that there is something more in the concept of matter than the expression of a set of experiences and their reduction to a law of nature has persisted from earlier times. Matter is looked upon as something originally existing, which is at the bottom of all phenomena and in a sense independent of them all. The concept of matter can be shown, however, to be made up of the simpler concepts weight, mass, and volume, and it is certainly less fundamental than these. The law of the invariable connection of these properties has already been expressed in the concepts *body* and *substance*, so there is no necessity for the formation of a new concept to express the same thing. The word 'matter' is so closely connected with the ideas mentioned above that it is not advisable to retain it; we shall therefore not make any use of it whatever."

"Mixtures can also be recognized by the fact that they diffuse light, and therefore appear cloudy. Pure substances, on the other hand, are optically homogeneous, and light is transmitted regularly through homogeneous masses. If a homogeneous substance is reduced to powder, the resulting product is a mixture of the substance with air, and this mixture appears opaque. If a solid body or a liquid is cloudy, it may be concluded with certainty that it is a mixture. Cloudy mixtures of gases have only a temporary existence, for gases form homogeneous solutions in all proportions.

"This means of recognizing mixtures is no longer a valuable one when the particles become small in comparison with the wave length of light. At this point new and remarkable phenomena appear, in which the surface tension, corresponding to the very great surface of separation begins to play an important part. We will therefore for the present omit them in this elementary consideration."

"In agreement with our general definition such a transformation is to be considered as a chemical change, for one substance—a gas—disappears and another—a liquid—having a new set of properties appears. It has been customary to call this change of state a physical change, because it can be so easily reversed. But there are also many chemical processes which can be just as easily reversed; and beside this, the general laws, in accordance with which these changes take place, are precisely the same laws as those which describe undoubted chemical change. It is therefore better to consider a *change of state* as a *chemical change* of the simplest sort."

"The changes of state just described, which are produced in a substance by changes in temperature and pressure, may be considered processes in which mixtures result from homogeneous substances. A mixture of gas and liquid is produced from a homogeneous gas by compression and cooling. If a homogeneous liquid is cooled, there results a mixture of it and a solid substance. If the temperature is still further lowered, the mixture changes into a homogeneous substance again,[1] the constituent corresponding to the first state disappearing and leaving its successor, which corresponds to another state.

"The components of mixtures produced by a transformation of this sort are called *phases*. Phases, therefore, are homogeneous substances which appear in mixtures. They may be either pure substances or solutions. In our general definition of a substance we took no account of shape or quantity. Our definition of a phase is the same in this respect, and all the parts of a mixture which have correspondingly specific properties are included in one phase."

"A formula of this kind suggests an idea which needs careful consideration and one which is very often misunderstood. The symbols for the elements make up the symbols of compounds, and this suggests the thought that the elements are actually physically present in their compounds just as their symbols are present in the symbol of the compound. It is, however, characteristic of a chemical process that substances should disappear, and that others with other properties should take their place. The elements and their properties disappeared when the compound was formed, and it is therefore impossible that an element should persist in its compounds. The idea that the elements have disappeared, but are nevertheless present as such, is an indefinite one, too indefinite for scientific use. The elements can be recovered from their compounds whenever we choose, and this is, as a matter of fact, all that we can say about them. It is somewhat analogous to what happens when an amount of money of various denominations is taken to the bank for safe keeping. The same amount can be obtained from the bank in the same denominations at any time. It by no means follows that the bank has kept the coins paid in during the whole time, but only that the bank has means sufficient to return our deposit. What becomes of the coins in the meantime we do not know, nor is it a matter of importance. A compound can at any time be transformed into its elements again, but we can only conclude from this that the condition for the formation of the elements always exists, and not that the elements persist as individuals in the compound. Certain properties of the elements, their weight, for example, are conserved in the compound, but a given weight cannot be changed by any process whatever, and this fact affords no proof for the persistence of the elements in a compound.

"The question is not, are the elements contained 'as such' in the compound? The answer to this question is decidedly a negative one, for the properties of the elements are not retained in the compound as the properties of the individual gases in a gaseous solution are. A much more important question is the following: Are there other properties of the elements beside weight (and mass) *which are retained in compounds*? Can any connection be traced between the properties of elements and those of their compounds? The answer is a complicated one, and it forms the content of an extended chapter of scientific chemistry. Here we can only say that no property of the elements, except mass and weight, is conserved unchanged in a compound, but approximate agreement in properties

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[1] Mixtures may result from solutions under these circumstances. A salt solution, for example, may form a mixture of solid water and solid salt. The facts as given in the text hold for pure substances and the case of solutions will be taken up later in a special chapter.

is quite common. The properties of the compound can sometimes be represented as the sum of the properties of their elements. These relations are, however, not exact ones, and the degree of their exactness varies with the nature of the properties in question. Many properties of compounds show no apparent relation whatever to those of the elements from which they are made."

"A catalytic effect is, in the majority of cases, an acceleration of a reaction, that is, an increase in reaction velocity. It is not yet completely decided whether or not there are any *negative catalyzers*, or whether the actually observed decrease in reaction velocity is a secondary effect due to small amounts of foreign substances. These would act by destroying the effect of accelerating catalyzers which might be present. However this may be, negative catalyzers are comparatively much rarer than positive ones, of which there are a very great number.

"Catalyzers are all more or less specific in their action, and each special reaction shows its own individual peculiarity with respect to foreign substances which affect its velocity. There are, to be sure, some substances which catalyze many different reactions, but their effect cannot be reduced to two factors, one of which depends only on the catalyzer and the other on the reaction. Influences are active which differ from case to case, and no relation with other properties or factors has as yet been recognized.

"The predominance of positive catalyzers is connected with the fact that very pure substances often react extremely slowly with each other. The active amounts of catalytic substances are often very much smaller than anything we can detect by other means. It would therefore be impossible to refute the statement that pure substances do not react at all with appreciable velocity, and that all our actual reactions are caused by the presence of extremely small amounts of catalytically active, foreign substances. If this statement cannot be refuted it is also, for the same reasons, impossible of proof. It can, however, in general be concluded that an unknown catalyzer is active whenever the velocity of a certain reaction is found to vary under apparently constant conditions, the concentration or some other peculiarity of the catalyzer constituting a variable among conditions which we are assuming constant."

On p. 339 the author says: "Deviation from the phase law only appears when several salts are present in a solution, and the appearance of this deviation is a further reason for considering ions as independent constituents of salt solutions." Of course this is absurd. The phase rule applies equally well to the metathetical reaction between alcohol and acetic acid or to an interchange of ions between sodium bromide and potassium chloride. It also applies without modification to Kahlenberg's experiments with the oleates in benzene solution.

It is interesting to note the change in people's point of view. The title of this book is a perfectly proper one; but the book might equally well have been called "An Elementary Presentation of the Phase Rule."

Wilder D. Bancroft

Recent Advances in Physical and Inorganic Chemistry. *By A. W. Stewart. With an introduction by William Ramsay. 15 × 23 cm; pp. xi + 267. New York: Longmans, Green and Co., 1909. Price: $2.50 net.*—In the introduction Sir William Ramsay says:

"Such essays [as these], I venture to think, will do more to encourage a taste for chemistry than many text-books. They will be followed with pleasure by any one who has mastered the nomenclature and is at home with the simpler conceptions of chemistry. Each may be taken to represent in a readable form the latest work on the subject of which it treats.

"This book, it may be hoped, will have a still further use; it cannot be doubted that some who peruse it will have suggested to them various directions in which they may profitably attempt to increase knowledge. Nothing is so sad as to see much time and labor spent, with patience and devotion, in the investigation of some matter which possesses no real importance. It may be retorted that every true statement is of importance, but this is not so. It is only statements which hold forth some prospect of contributing to an organic whole which can be held valuable. There may, perhaps, be a little more merit in ascertaining to the hundredth of a degree the boiling point of sulphur than of measuring the area of the wings of some particular butterfly; but the difference is barely appreciable. One is as likely to prove useless as the other. It would be well if enthusiasts anxious to carry on research would remember that it is much more stimulating to carry on an interesting research. It is, I believe, not improbable that the reading of such a work as this may aid those embued with the spirit of investigation to make a happy choice of a subject of research. Should this hope be realized, Dr. Stewart will have done a most useful work."

The chapters are entitled: some hydroxylamine derivatives; colloids; reactions in liquid ammonia; the fixation of nitrogen; double salts; the problem of the oceanic salt deposits; the cobaltammines; absorption spectra; the elements of the rare earths; atomic weights; the inactive gases; the radioactive elements; radioactive changes; radioactive emanations. The book covers a wide range and covers it well. He will be a hard man to suit who does not find something to interest him, and most people will be interested in nearly all the chapters.

In the chapter on the cobaltammines the author is on the side of Jörgensen and against Werner, p. 127. "This new view (which of course clashes with the other) has been advanced by Werner in the second edition (1909) of his *Neuere Anschauungen*, p. 211. It furnishes another example of the elasticity of the Wernerian hypothesis, and the ease with which it can be modified to get round a difficulty."

The author believes in Ramsay's preparation of lithium and neon from copper nitrate. After citing the criticisms made by Soddy and Mackenzie, Rutherford and Royds, Mme. Curie and Mlle. Gleditsch, he says, p. 247: "Against this we must set the fact that in the Ramsay and Cameron experiments a copper solution divided into two parts showed the presence of the lithium in the half which was treated with emanation, while the other half, under precisely similar conditions except for the presence of the emanation, showed not a trace of lithium; and that this is not an isolated case, but has been observed on several occasions." The weak point in this reasoning is that it meets an objection which no one has raised. Mme. Curie did not deny the existence of lithium in Ramsay and Cameron's bulbs; but she did bring forward evidence to show that the lithium was not formed from the copper.

On p. 205 the author expresses an interesting, though over-pessimistic, opinion in regard to physical chemistry.

"Within the present generation, we have seen two movements in chemical science which are almost unparalleled in the previous history of the subject. The first of these movements culminated in the decade commencing with 1887. In this year the modern theory of solutions was founded by Arrhenius and van't Hoff, and from this basis the science of physical chemistry began to rise with almost unexampled rapidity. The *Zeitschrift für physikalische Chemie,* first published in 1887, very soon found companions in English and French, and a period of feverish activity in physico-chemical research was opened. To some extent, this wave appears to have spent its force. At the present day, physical chemistry, except in the hands of a few exceptional researchers, has degenerated into a means of attacking the problems of pure chemistry instead of opening up new fields; and consequently there is a certain tendency to decry the subject as a mere means to an end, and not a living branch of science. This is, perhaps, an exaggerated view; but it cannot be denied that physical chemists of the present day are not animated by the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject. It is, therefore, an extremely fortunate coincidence that as the first movement declined, a second and perhaps more powerful one has succeeded it. This second movement rose with even greater rapidity than pure physical chemistry, and yet at the present day we appear to have touched only the fringe of the subject of radioactivity; so that we may look forward to a long career of fruitful investigation still before us in this department of chemistry."

While there is some truth in this criticism, it is due to the fact that many physical chemists are still interested only in "the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject." The difficulty is that most people are still struggling under the limitations imposed deliberately and consciously by Ostwald. Once those are broken through, nobody will have any cause to complain of the wave having spent its force.

In the chapter on absorption spectra, some of the conclusions are of great interest, p. 156.

"At the present time spectroscopic research may be divided into several categories. In the first place, we have a series of investigators who photograph spectra apparently with no idea beyond finding out what the absorption curve looks like. This work is pretty much on a par with that of the organic chemists who apply somebody else's reaction to the iso-propyl derivative when the lower members of the series have already been made; it may eventually be of use to some one, but that will not be the fault of the man who carries it out. Then there is a second class of spectroscopists who apply the Hartley method without seeming to recognize the fact. These, at least, may do work of some practical value, even though it be not very original. Finally, there are two classes of workers whose researches are tending to bring spectroscopy into touch with chemical problems. The first of these concern themselves with the relation between spectroscopic measurements and other physical properties of organic substances, such as refractive index, optical rotatory power, magnetic rotation, and so forth. The second class of investigators endeavor to link their spectroscopic results with their chemical reactions, in order to find out whether there be any connection traceable between the two phenomena. In either of these directions there appears to be a fruitful field awaiting research.

"At the same time, it must be remembered that great care must be taken in the building up of hypotheses. In all the chemical field there is no subject which lends itself more to this than does spectroscopy; but it cannot be too often stated that hypotheses which are not backed by chemical evidence of their correctness are worse than useless. Further, the substitution of vague generalities for definite statements may do considerable harm. It is true in some cases we know so little of the processes which go on within the molecule, that we are forced to express ourselves in general terms; but it should be our aim to come as soon as possible to some definite conclusion in the matter, and put forward something which can be tested—something which is not mere verbiage and an excuse for dodging round a dialectic corner as soon as people begin to look into the subject."

One can endorse all this without reservation; but then it is rather a disappointment to find the author advocating research work on the relation between spectroscopic measurements and other physical properties of organic substances instead of coming out strongly in favor of photochemistry.

Throughout the book there are many instances where the reviewer is not in sympathy with the trend given by the author; but it may be the author who is infallible and not the reviewer. However that may be, the book is a good one and it is to be hoped that we may get many more of the same general type.

Wilder D. Bancroft

Exercises in Physical Chemistry. *By W. A. Roth. Authorized translation by A. T. Cameron. 14 × 22 cm; pp. xii + 196. London: Archibald Constable and Co.; New York: D. Van Nostrand Company, 1909. Price: $2.00 net.*— In the preface the author says that "in this little book I have tried to provide something for the elementary student who is commencing to study the subject, for that purpose assuming as little previous knowledge as possible. I have tried to connect the training in experimental method with the theoretical conclusions derived from the results, and further to train the student to deduce his results correctly, and to comprehend the inner relationships between the data obtained from entirely different experiments."

The first part of the book is devoted to physical chemistry and the second part to electrochemistry. The headings of the chapters are: introductory; the determination of density; determination of molecular weights in solutions; thermochemistry; the determination of optical constants; the thermostat; chemical statics and dynamics; foundations of electrochemistry; electrical conductivity; Faraday's law and transport numbers; measurements of differences of potential; electrostatics.

This seems to be a serviceable book and should be a welcome addition to our laboratories. The only mistake which the reviewer has noticed is on p. 152 where the student is told to use mercuric sulphate as depolarizer in the standard cell. The translation has been fairly well done, though the reviewer objects to "knall gas coulometer," and certainly few people would translate "Praktikum" as "Practical course."

Wilder D. Bancroft

THE VAPOR PRESSURE OF WATER AND AQUEOUS SOLUTIONS OF SODIUM CHLORIDE, POTASSIUM CHLORIDE, AND SUGAR

BY FRANCIS C. KRAUSKOPF

The close relationship between vapor pressure and other physical constants of liquids has kept scientists interested in the subject since the eighteenth century. Aside from its purely scientific importance, an exact knowledge of vapor pressures of liquids, especially of water, is essential for two reasons.

(1) In the exact measurement of the volumes of gases collected over any liquid, a correction must always be made for the vapor pressure of that liquid.

(2) A non-volatile substance dissolved in a liquid will always cause a lowering of the vapor pressure. This lowering was found to be proportional to the weight of solute in a certain weight of solvent, and the same number of particles or molecules of different solutes dissolved in the same weight of solvent seemed to give approximately the same lowering of the vapor pressure of the solvent. At least this was known to be true for chemically similar substances dissolved in the same solvent.

At the present time, the methods of measuring vapor pressure may be divided into the following classes:

(1) Static method. (2) Indirect method. (3) Differential method. (4) Dynamic method.

The static method dates back to the time of James Watt,[1] who introduced water into a Torricellian Vacuum and noted the depression of mercury by comparing it with a normal barometer at the same temperature. This is essentially the same method that has been later perfected and used by Magnus,[2] Wüllner,[3] Raoult[4] and others, and is known today as the static method.

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[1] Anmerk. zu Robinson, Mech. Phil., Vol. II, p. 29.

[2] Pogg. Ann., 61, 225 (1844).

[3] Ibid., 103, 529 (1856); 110, 564 (1860).

[4] Zeit. phys. Chem., 2, 353 (1888).

The indirect method consists in boiling the liquid under different pressures and noting the temperature at which the liquid boils. The method no doubt had its origin in the eighteenth century when the difference in the boiling temperature of water at various altitudes was observed. This method has been perfected in later years by Ramsay and Young[1] and used by them extensively. Within the last year Holborn and Henning[2] have published a paper on vapor pressure. They use the indirect or boiling point method, with a specially standardized thermometer to measure the temperature and a delicate manometer to measure pressures.

Dieterici[3] devised an ingenious method for comparing vapor pressures. He separated the vapor above two different liquids by a flexible metallic membrane and measured the difference in pressure by movements of this membrane. These movements were magnified by means of a long pointer attached to the membrane. The method was ingenious but the apparatus was so complicated that it has not found favor.

The so-called dynamic method was first used by Regnault[4] in 1845 and with it he obtained results for water, which with some corrections are used as standard to-day. The method is based on Dalton's law of partial pressures. This law is as follows: In a mixture of gases each gas exerts the same pressure as it would were it in the same volume alone; or, that the total pressure of a gaseous mixture is equal to the sum of the partial pressures of the constituent gases. It can be expressed by the following equation for a mixture of two gases, A and B.

Volume of A + B : Volume of A : : Pressure of A + B : Pressure of A.

Now if A + B represent a mixture of air and water vapor and if we have the means of determining the total pressure of the mixture and the volume of the air and the volume of

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[1] Phil. Trans. A., 2, 602 (1888).

[2] Drude's Ann., 26, 833 (1908).

[3] Wied. Ann., 50, 47 (1893).

[4] Ann. Chim. Phys. 3, 15, 129 (1845).

the water vapor, then the pressure of the aqueous vapor is easily determined.

In practice a known volume of air is saturated with water vapor. The water is then absorbed and weighed. This weight is then calculated to the volume it would occupy in the form of vapor. This volume is reduced to 0° and 760 mm, as is also the volume of air, and substituted in the above formula.

Derivation of the formula for calculating vapor pressures. Total Pressure: Partial Pressure: : Total Volume: Partial Volume in which

Total Pressure = Barometric Pressure (corrected).

Total Volume = Volume of air observed, corrected to standard conditions and for the expansion of container with temperature, plus the volume of aqueous vapor.

Partial volume or volume of aqueous vapor, is weight of water absorbed multiplied by the volume of 1 gram, in the vapor state = 1.243 liters.

Then: $$\frac{\text{Barometric pressure}}{\text{Vapor pressure of water}} = \frac{\dfrac{\text{Vol. air read} \times (1 + Kt) \times \text{Barometric pressure}}{760 \times (1 + \alpha t)} + \text{wt. of water} \times 1.243}{\text{Weight of water} \times 1.243}$$

and vapor pressure of water =

$$\frac{\text{Barometric pressure}}{1 + \dfrac{\text{Volume air read} \times (1 + Kt) \times \text{Barometric pressure}}{\text{Weight of water} \times 1.243 \times 760 \times (1 + \alpha t)}}$$

K = coefficient of expansion of glass of the aspirators.

α = coefficient of expansion of air = 0.003671.

All the work was done at so near the temperature at which the aspirators were calibrated that in the calculations, K was considered negligible.

Thus it is seen that there are five essential points to a determination by this method.

(1) Exact measure of the volume of air.

(2) Exact measure of the weight of water contained in that volume of air.

(3) Exact measure of the barometric pressure.

(4) Insuring of complete saturation of air by vapor.

(5) Exact measure of the temperature at which the air is saturated.

Most of the experimental difficulties were worked out by Regnault who obtained results that agree very well with those obtained by the static method. But modifications and improvements have been made from time to time by Tammann,[1] Ostwald and Walker,[2] Will and Bredig,[3] Carveth and Fowler,[4] Earl of Berkeley and Hartley,[5] Perman,[6] and others with varying results.

(1) The following general method of measuring the volume of air has been used by all investigators; *i. e.*, to fill an aspirator of known volume with water and draw the air into this, measuring the amount of air, by the amount of water drawn off. This of course necessitates the correction of the volume for the vapor pressure of water, so in the following work it seemed desirable to use some liquid for aspirating that had no appreciable vapor pressure, in order to eliminate the necessity of making this correction. At the suggestion of Professor Kahlenberg a heavy hydrocarbon oil was used in place of water. A very high quality of gas engine cylinder oil was selected.

(2) The weight of water can be easily determined by passing the air, as it is drawn into the aspirator, through a suitable absorption chain, usually sulphuric acid followed by phosphorus pentoxide.

(3) The barometric reading is made from any standard barometer and corrected to zero.

(4) The question of insuring complete saturation of the air with moisture has probably caused most of the dissatisfaction with the dynamic method, consequently most of the

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[1] Wied. Ann., **35**, 322 (1888).

[2] Zeit. phys. Chem., **2**, 602 (1888).

[3] Ber. chem. Ges. Berlin, **22**, 1084 (1889).

[4] Jour. Phys. Chem., **8**, 313 (1904).

[5] Proc. Roy. Soc., **77**, 156 (1906).

[6] Ibid., **72**, 72 (1903).

improvements and modifications of the method have been made with a view of perfecting the method in this particular.

Regnault drew the air to be saturated over a moist sponge and then through screens of silk, which were kept moist. He found that saturation of the air with moisture was very rapidly attained, and that his results agreed closely with those obtained by the static method.

In 1888 Tammann on recalculation of these results found that they did not agree with the results of the static method as closely as Regnault had thought. Tammann also did some experimental work on aqueous solutions, using Regnault's method somewhat modified and concluded that the method is not satisfactory for solutions, largely because the evaporation of the solvent in the current of air causes the concentration of the solution to vary.

Ostwald and Walker modified slightly the apparatus and the principle of the method in applying it to solutions. They drew the air through Liebig bulbs of the solution, and then through a weighed Liebig bulb of water, and then absorbed and weighed the water vapor in the air. The loss in weight of the bulb of pure water divided by the total weight of the water absorbed, equaled the difference between the vapor pressure of pure water and that of the solution. Walker used this modification to determine the molecular weights of substances in dilute solutions.

Will and Bredig, Orndorff and Carrell[1] and others working with this method have used Liebig bulbs as containers for the liquid. Carveth and Fowler used U-tubes in place of the Liebig bulbs but were very much dissatisfied with their results.

Perman seemed to have the best success with this method in his work on the vapor pressure of water at different temperatures. He used, as a means of saturation, what was practically a Liebig bulb with four compartments of about 100 cc each (the last bulb being fitted with a manometer).

The Earl of Berkeley and E. G. J. Hartley were among

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[1] Jour. Phys. Chem., 1, 735 (1897).

the first to think of keeping the liquid stirred as the air was passed over it. In place of Liebig bulbs or U-tubes, they used narrow tubes placed on an oscillating platform, so that the liquid was kept moving back and forth as the air was bubbled through.

In 1905 Professor Kahlenberg[1] devised a simple apparatus for saturating the air, which obviated many of the previous difficulties. This saturating device is shown in Fig. 1, C. This vessel, made wholly of glass, is filled about half full of the liquid whose vapor pressure is desired and then arranged so that it can be shaken laterally as the air is drawn through. This keeps the air on the interior awash with the liquid and insures its complete saturation. The bulb on the outlet tube is sufficient to keep any liquid from being carried over mechanically.

The advantages of this saturating device over others are: (1) It allows the rapid saturation of the air with water vapor, while keeping the pressure the same throughout the whole chain of apparatus. The pressure necessary to draw the air through the apparatus never amounts to more than 1 or 2 mm of mercury. (2) In the case of solutions, it permits the use of a large quantity of solution, and entirely prevents any possibility of local concentration or differently concentrated layers of solution, as the solvent evaporates.

Lincoln and Klein,[2] using this device of Kahlenberg's obtained some very satisfactory results on the vapor pressure of aqueous nitrate solutions at 25°, and made a thorough study of the limitations and sources of error. These have been taken advantage of in this paper.

At the suggestion of Professor Kahlenberg, the author has undertaken the determination of the vapor pressure of water at different temperatures, and also the vapor pressure of certain aqueous solutions at various temperatures and concentrations. These determinations were made using Kahlenberg's shaking device for a saturator and gas engine

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[1] Science, 22, 74 (1905).

[2] Jour. Phys. Chem., 11, 318 (1907).

cylinder oil of negligible vapor pressure for the aspirating liquid.

A brief description of the apparatus and method of operation will be given, followed by the results and the discussion of the results.

The apparatus can be best described by dividing it into three parts:

(1) The thermostat and the shaking and stirring device.

(2) The saturating and absorbing chain.

(3) The aspirator.

The thermostat consisted of a large rectangular galvanized iron tank 24″ × 30″ and 20″ deep; a double paddle for stirring and the shaking device for keeping the saturator in constant motion, were driven by a small electric motor; three layers of asbestos wrapped about the tank, loose enough to allow some air space between, were very effective as heat insulation. At higher temperatures, a sheet iron cover overlaid with asbestos prevented radiation and evaporation from the top. Up to 50° this bath could be easily kept constant to 0.01 of a degree by means of an Ostwald gas regulator. At 60° and 70° the variation was occasionally as much as ±0.02°. At 80° the variation was as much as ±0.04° so a reading on a Beckman was taken every two minutes during the run and the average taken as the correct temperature.

The thermometer used was a normal thermometer graduated to tenths of a degree in large divisions, and standardized by the Reichsanstalt. It permitted readings to $^1/_{100}$ of a degree by means of a lens, this thermometer was further checked against one recently calibrated by the Bureau of Standards. In order to have the thermometer wholly immersed it was surrounded by a glass jacket, into which the water from the thermostat could be drawn to any desired height.

The saturating and absorbing chain is best shown in Fig. 1; C, D, E, and F are immersed in the thermostat. The air was drawn from outside the building and passed first through two large U tubes, one filled with soda lime and the other with pumice stone, moistened with sulphuric acid, to take any carbon dioxide and ammonia out of the air. In passing through the flask G, which was maintained at a temperature 10–20° higher than the thermostat, the air was saturated at the higher temperature. Then in the Wolff bottle F and the block-tin coil E, the air was brought back to the temperature of the bath. In case of solutions the Wolff bottle D, which contained a solution of the same strength as C, was inserted in the chain so as to still further minimize any change in concentration in C.

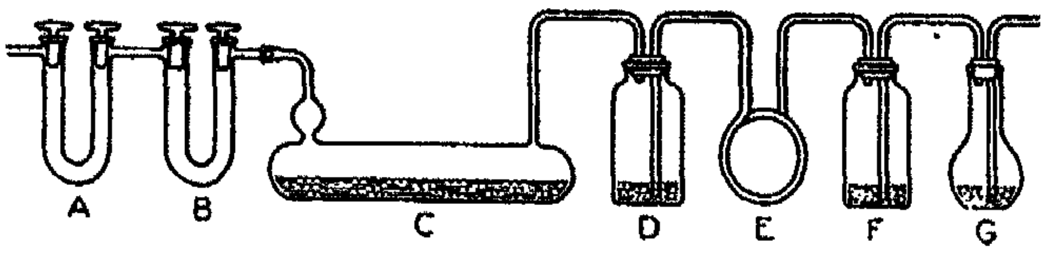

Fig. 1

Final and complete equilibrium was established in the saturator C and the water absorbed by B and A, glass stoppered U-tubes. A was filled with phosphorus pentoxide, and B with sulphuric acid. Joints were made with good rubber tubing wired securely, except the joint between C and B which was a ground glass joint. A and B were arranged in such a manner that they could swing with C, so that the two parts of the joint did not turn on each other as the saturator moved back and forth. This ground joint was held tightly together by a rubber band stretched from a point on the arm of C to a point on B. Such a joint was felt to be much safer for high temperatures than rubber tubing, which necessarily had to be kept hot to prevent condensation. It precluded all possibility of leakage of air or moisture with rubber tubing and was also found more convenient for connecting and disconnecting A and B at the beginning and end of a determination.

The tube connecting the saturator C with the U-tube B could not be kept immersed in the thermostat so it was necessary to heat this tube in some other manner. At low temperatures (up to 40°) this was conveniently done by coiling a platinum wire about the tube and passing an electric current through the wire. At higher temperatures this experimental difficulty proved to be one of the hardest to overcome. Various schemes of jacketing were tried without success. Finally a small lead pipe about $^{1}/_{8}''$ outside and $^{1}/_{16}''$ inside diameter was coiled about the tube with the turns of the coil close together. A current of steam passed through this, heated it uniformly and without danger of cracking the tube or ground glass joint by excessive local heating. At the higher temperatures before starting a determination it was necessary to draw a small volume of air through the apparatus with this tube heated in order to make sure there was no residual water condensed on the sides of the tube.

The aspirators used were exactly similar in size and shape to those used by Lincoln and Klein and need only a brief description here. Their capacity was about 32 liters each. A diagram of one is shown in Fig. 2. The essential improvement in the aspirating device was the use of a heavy gas engine cylinder oil, as the aspirating liquid, instead of water. This oil was carefully tested to see if it had an appreciable vapor pressure at room temperature. A quantity of the oil was placed in a Liebig potash bulb and the bulb carefully weighed. Then a current of dry air was drawn through it, and the bulb weighed at intervals of several hours. The results given in Table I show that the oil had no appreciable vapor pressure at room temperature. As was stated above, this permitted the dispensing with one of the factors in the measurement of the volume of air.

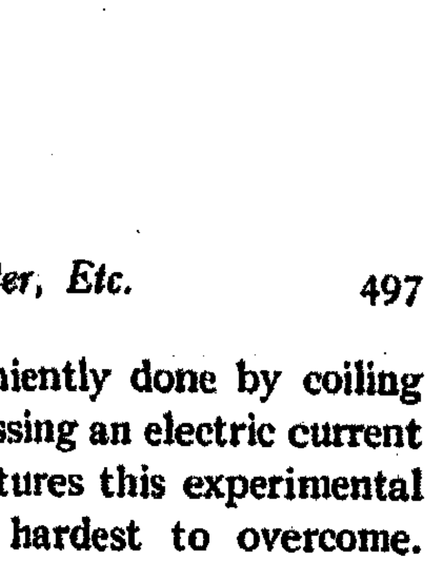

Fig. 2

In Fig. 2, A is a scale, the marks of which were so placed that the space between them represented two liters. This gauge was carefully graduated by means of an accurately

TABLE I

Weight of Liebig bulb No. 1 with oil	46.1085
Weight of Liebig bulb No. 1 alone	21.4320
Weight of oil	24.6765
Weight of Liebig bulb No. 2 with oil	51.0030
Weight of Liebig bulb No. 2 alone	24.1917
Weight of oil	26.8113

Time	Weight of Liebig bulbs and oil	
	No. 1	No. 2
Beginning	46.1085	51.0030
After five hours	46.1070	51.0006
After nine hours	46.1070	51.0006
After fifteen hours	46.1067	50.9998

calibrated two liter flask, using the oil as the liquid. The calibration was checked by weighing on a small platform scale, the total amount of the oil delivered by the aspirator, and was found to agree with the volume measured by the graduations on the gauge. B is the inlet and C the outlet tube for the oil. In making a determination the tube C of aspirator No. 1 was connected to B of No. 2 and *vice versa.* D is a thermometer reading to tenths of a degree and E is an oil manometer. These gave the necessary data for calculating the volume of air to standard conditions. F was attached to the free end of the U-tube A in Fig. 1.

The question as to how fast the air could be drawn through the apparatus and still obtain perfect equilibrium between liquid and vapor has had many and varied answers. Regnault showed that the rate of 25 liters an hour gave results agreeing with those at a slower rate. Tammann used a maximum rate of 10 liters an hour. Ostwald Carveth and Fowler, Berkeley and Hartley, passed the air much more slowly, the latter so slowly as to require several days for a determination. Perman in his work was convinced that air drawn through water is saturated with the vapor very rapidly and Lincoln and Klein tested this point thoroughly, and found no appreciable difference in the results whether the air was drawn through at the rate of 5 liters or 16 liters an hour when working at 25°. This was found to be true in this work also. Since at higher temperatures, only a very small amount of air was required to take up a large quantity of moisture, the speed of the air was so regulated that about one hour was employed to cause an absorption of 0.8–1.0 gram of moisture in the U-tubes A and B.

The two U-tubes A and B were without question sufficient to completely absorb the moisture from the air. The tube A containing phosphorus pentoxide rarely increased in weight more than 1 mg, and could be used for many determinations without refilling. The tube B containing pumice stone moistened with sulphuric acid could be used for two determinations without refilling. To refill it, the dilute acid was poured off and the tube nearly filled with concentrated acid, and this poured off leaving a small amount in the bottom of the tube.

In order to show that the bulb on the outlet tube of C, Fig. 1, was sufficient to prevent any liquid from being carried over mechanically, a strong solution of sodium chloride was put in C and a U-tube of silver nitrate solution put in place of A and B. Then the saturator was shaken very rapidly, and the air drawn through at a much greater rate than usual. The silver nitrate solution remained perfectly clear showing that nothing was carried over mechanically. Although Lincoln and Klein showed that whether equilibrium was approached from a condition of supersaturation or undersaturation made no difference in the results, all the experiments here described were nevertheless performed with the use of a supersaturator.

All glass vessels containing water or solutions through which the air passed were made perfectly clean with dichromate cleaning mixture and then live steam passed through for several hours.

The first determinations made were of the vapor pressure of pure water at temperatures of 24.9°, 25°, 30°, 35°, 40°, 50°, 60°, 70° and 80° C.

The water was purified by twice distilling deep well water from a copper still using a block-tin condenser. In the first distillation the water was acidified with sulphuric acid and chromic acid to oxidize any oily or organic matter and to free the water from ammonia. This water was redistilled over barium hydroxide to free it from carbon dioxide.

When determining the vapor pressure of pure water the saturator was connected to the still in place of the condenser, and the water allowed to condense directly in the saturator. This saved changing the water from one vessel to another and gave it no chance to absorb carbon dioxide from the air.

The results for the vapor pressure of water are given in Table II. They agree well with each other and with the results obtained by other methods and other modifications of this method. In general the results range slightly higher than those given in Landolt and Börnstein as Regnault's corrected results, but are close to Perman's results, and between 50° and 80° are in close agreement with the results obtained very recently by Holborn and Henning, using the boiling point method, as shown in Table III.

The method is perfectly reliable and convenient over the range of temperatures tried. A determination can be made in a short time with assurance that perfect equilibrium has been established between liquid and vapor.

While the use of the oil as an aspirating liquid may make no appreciable showing in the results, it neverthless removes one factor of the equation and reduces the chances for error just that much.

There is no doubt that the apparatus is a somewhat complicated one, but as yet no extremely simple means of measuring vapor pressures accurately has been devised.

This method is especially well suited for determining vapor pressures of solutions between room temperatures and 80° C. Accordingly determinations were made on solutions

TABLE II

Vapor Pressure of Water

Temperature	Volume of air in liters	Barometer reading corrected	Temperature of air in aspirator	Weight of water absorbed	Vapor pressure in mm	Average
24.9	28	729.3	20.8	0.6700	23.50	23.49
24.9	28	720.2	21.1	0.6671	23.49	
24.9	28	725.9	19.0	0.6733	23.48	
25.0	28	730.85	20.6	0.6737	23.70	23.71
25.0	28	735.1	19.2	0.6770	23.71	
25.0	28	742.7	18.5	0.6758	23.67	
25.0	28	741.3	16.4	0.6848	23.74	
30.0	28	736.3	25.3	0.9032	31.90	31.84
30.0	28	734.8	28.5	0.8862	31.67	
30.0	28	737.5	26.2	0.8981	31.88	
30.0	28	735.1	25.8	0.8980	31.80	
30.0	28	729.7	28.0	0.8958	31.93	
35.0	24	732.9	32.1	1.0057	41.77	41.91
35.0	24	732.6	32.5	1.0086	41.98	
35.0	24	734.8	28.5	1.0207	41.94	
35.0	24	733.9	28.6	1.0185	41.86	
35.0	24	735.3	27.7	1.0251	41.99	
35.0	24	734.8	27.0	1.0213	41.75	
35.0	24	735.3	26.6	1.0304	42.09	
40.0	14	735.6	29.0	0.8000	55.22	55.18
40.0	14	734.2	29.0	0.7983	55.12	
40.0	14	742.0	26.3	0.8064	55.21	
40.0	14	741.8	26.4	0.8053	55.16	
40.0	14	736.3	29.1	0.7988	55.17	
50.0	8	730.3	28.8	0.8087	92.24	92.16
50.0	8	730.3	29.0	0.8078	92.22	
50.0	8	730.0	28.7	0.8059	91.98	
50.0	8	730.0	28.2	0.8099	92.21	
60.0	4	730.4	26.1	0.7236	149.04	149.26
60.0	4	730.9	26.4	0.7242	149.28	
60.0	4	731.0	26.3	0.7254	149.43	

TABLE II—(*Continued*)

Temperature	Volume of air in liters	Barometer reading corrected	Temperature of air in aspirator	Weight of water absorbed	Vapor pressure in mm	Average
60.2	4	730.5	26.2	0.7336	150.50	150.65
60.2	4	731.3	26.4	0.7338	150.80	
70.0	2	732.4	22.3	0.6760	234.74	233.99
70.0	2	728.5	22.5	0.6730	233.72	
70.0	2	728.3	22.8	0.6713	233.50	
70.05	2	737.8	19.0	0.6801	234.37	234.46
70.05	2	738.4	19.3	0.6813	234.93	
70.05	2	737.1	19.8	0.6805	234.74	
70.05	2	727.5	21.1	0.6743	233.14	
70.05	2	727.9	22.0	0.6785	234.58	
70.05	2	730.2	22.1	0.6771	234.64	
70.05	2	733.1	19.5	0.6837	235.04	
70.05	2	732.8	19.8	0.6808	234.50	
80.0 — 0.014	2	731.4	19.5	1.3610	354.70	355.08
80.0 — 0.024	2	730.7	20.2	1.3643	355.39	
80.0 — 0.020	2	731.4	22.2	1.3429	354.18	
80.0 — 0.004	2	726.8	24.5	1.3500	355.23	
80.0 + 0.006	2	730.0	25.4	1.3374	355.03	
80.0 + 0.004	2	730.0	25.6	1.3448	355.92	

TABLE III

Comparison of Results

			Results of			
Temperature	Regnault	Tables of Landolt and Börnstein	Perman	Holborn and Henning	Lincoln and Klein	Krauskopf
25°	23.55	23.55	—	23.69	23.76	23.71
30°	31.55	31.55	31.88	31.71	—	31.84
35°	41.83	41.85	—	42.02	—	41.91
40°	54.91	54.97	—	55.13	—	55.18
50°	91.88	92.17	92.39	92.30	—	92.16
60°	148.78	149.21	148.94	149.19	—	149.26
70°	233.09	233.79	233.98	233.53	—	233.99
80°	354.64	355.47	—	355.10	—	355.08

of sodium chloride, potassium chloride and cane sugar in water at different concentrations. For sodium chloride the determinations were made at 40° C and 60° C, and for the potassium chloride and sugar at 40°. The sodium chloride used for the solutions was Kahlbaum's C. P. fused. The potassium chloride was from Merck's and marked highest purity. This was recrystallized twice. The cane sugar used was the purest grade of crystallized rock candy in the market. The water used for the solutions was the same as that used above for the determinations of the vapor pressure of the water.

The results of these determinations are given in Tables IV, V, and VI. The concentrations are expressed as grams of salt per 100 grams of water and in the case of potassium and sodium chloride were determined by evaporating a weighed quantity of the solution to dryness in a platinum dish and weighing the residue. In the case of sugar the water and sugar were weighed out in the proportions desired and then mixed just before a determination was made. This insured the use of a perfectly fresh sugar solution.

To make sure that the concentrations in the saturator remained practically constant determinations of the concentrations were made both before and after a set of runs. It was found that the concentration never changed more than one or two hundredths of a percent. The molecular weights M were calculated according to the formula $M = \frac{f' 18^\circ C}{f - f' 100}$, where C is the concentration of the solution in grams of solute per 100 grams of water, 18 the molecular weight of water, f' the vapor pressure of the solution and f the vapor pressure of pure water. The values given in the column headed μ (Tables IV, V, and VI) represent 1000 times the relative lowering which 1 gram of substance would produce at that concentration. They are calculated according to the formula $\mu = \frac{f - f'}{fC} 1000$. Wüllner's law states that the lowering of the vapor pressure is approximately proportional

Table IV
Sodium chloride solutions

Temperature	Concentration in grams per 100 grams water	Barometer reading corrected	Volume of air in liters	Temperature of air in aspirator	Weight of water absorbed	Vapor pressure in mm	Molecular weight	μ
40.0	5.102	739.6	14	20.5	0.7989	55.71	32.64	5.515
40.0	5.102	737.0	14	25.6	0.7842	55.67		
40.0	5.102	730.9	14	23.4	0.7909	55.62		
40.0	10.40	729.6	14	28.6	0.7475	51.77	28.15	5.994
40.0	10.40	728.4	14	28.4	0.7478	51.74		
40.0	10.40	728.1	14	28.1	0.7480	51.71		
40.0	15.89	733.4	14	29.0	0.7108	49.48	24.73	6.524
40.0	15.89	732.7	14	29.5	0.7101	49.44		
40.0	22.73	734.1	14	28.3	0.6799	47.36	24.78	6.235
40.0	22.73	734.3	14	30.0	0.6760	47.36		
60.0	5.045	733.7	4	30.7	0.6816	143.84	24.96	6.960
60.0	5.045	734.1	4	30.5	0.6820	144.00		
60.0	5.045	734.6	4	31.0	0.6822	144.21		
60.0	10.40	725.4	6	29.9	0.9774	138.19	22.81	7.294
60.0	10.40	726.1	6	29.9	0.9759	138.06		
60.0	10.40	726.2	6	28.2	0.9771	137.58		
60.0	15.89	730.0	6	31.1	0.9208	131.98	21.99	7.245
60.0	15.89	731.3	6	30.6	0.9237	132.48		
60.0	15.89	731.7	6	29.7	0.9223	131.80		
60.0	22.73	732.3	4	28.7	0.5809	125.60	21.48	6.892
60.0	22.73	732.1	4	29.2	0.5809	125.75		
60.0	22.73	732.2	4	30.9	0.5739	125.00		
60.0	22.73	733.1	4	31.1	0.5737	125.17		

TABLE V

Potassium chloride solutions

Temperature	Concentration in grams per 100 grams water	Barometer reading corrected	Volume of air in liters	Temperature of air in aspirator	Weight of water absorbed	Vapor pressure in mm	Molecular weight	μ
40.0	8.674	727.1	14	21.2	0.7848	52.92	36.90	4.878
40.0	8.674	729.4	14	21.8	0.7840	52.97		
40.0	13.313	735.0	14	22.3	0.7630	51.77	36.61	4.917
40.0	13.313	737.7	14	21.7	0.7651	51.81		
40.0	19.585	730.6	14	22.0	0.7394	50.21	35.615	5.054
40.0	19.585	727.3	14	22.4	0.7364	50.07		
40.0	19.585	732.3	14	23.1	0.7389	50.36		
40.0	22.454	734.4	14	21.2	0.7290	49.46	35.57	5.060
40.0	22.454	741.5	14	21.4	0.7311	49.63		
40.0	22.454	740.45	14	21.3	0.7312	49.62		
40.0	22.454	743.6	14	20.4	0.7314	49.51		
40.0	28.54	733.6	14	20.4	0.7097	48.11	34.9	5.158
40.0	28.54	734.8	14	21.0	0.7082	48.09		

TABLE VI

Sugar solutions

Temperature	Concentration in grams per 100 grams water	Barometer reading corrected	Volume of air in liters	Temperature of air in aspirator	Weight of water absorbed	Vapor pressure in mm	Molecular weight	μ
40.0	20	735.5	14	22.3	0.8054	54.43	244.8	7.24
40.0	20	734.2	14	23.1	0.8050	54.38		
40.0	20	733.3	14	22.0	0.8047	54.33		
40.0	40	732.4	14	25.4	0.7865	53.76	272.6	6.43
40.0	40	731.6	14	25.2	0.7870	53.75		
40.0	60	731.3	14	25.9	0.7784	53.34	310.5	5.60
40.0	60	730.7	14	25.8	0.7796	53.37		
40.0	60	730.4	14	27.8	0.7732	53.30		

to the quantity of substance dissolved in a given weight of solvent. According to this the value μ should be constant. For substances that are supposed to dissociate, this value should increase with decrease in concentration. In the results for potassium chloride and sodium chloride at 40° at least, this value is seen to decrease with decrease in concentration. For these same solutions the molecular weight increases with decrease in concentration which is in accord with the results obtained by Kahlenberg,[1] using the freezing point and boiling point methods and opposite to what would be expected according to the Arrhenius Theory of Electrolytic Dissociation. For cane sugar solutions at 40° the value μ increases with decrease in concentration. The molecular weight decreases with decrease in concentration. The result at 40° with a 40 percent solution agrees exactly with a determination made by Walker[2] using a 38 percent solution and working at about 20°.

In all cases the molecular weights calculated from the diminution of the vapor pressure vary greatly from the theoretical.

Summary

(1) In this paper the vapor pressures of water have been determined for temperatures of 24.9°, 25°, 30°, 35°, 40°, 50°, 60°, 70°, and 80°, using Kahlenberg's improved dynamic method. The results obtained agree very closely with the results of other investigators, especially with the more recent results.

(2) The vapor tensions of aqueous sodium chloride solutions were determined for four different concentrations and at temperatures of 40° and 60°; also for potassium chloride solutions at five different concentrations and at 40° C.

The molecular weights calculated from these results increase with decrease in concentration in accord with those obtained by boiling and freezing point methods and opposite

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[1] Jour. Phys. Chem., 5, 339 (1901).

[2] Loc. cit.

to what would be expected according to the Arrhenius Theory of Electrolytic Dissociation.

(3) The vapor pressures of sugar solutions were determined for three concentrations at 40° C. The molecular weights found decrease, with decrease in concentration.

(4) In all cases the molecular weights calculated from the diminution of the vapor pressure differ greatly from the theoretical.

The author takes this opportunity to express his appreciation for the suggestions and help given by Professor Kahlenberg under whose direction this work was carried on.

Laboratory of Physical Chemistry,
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April, 1910

THE BETA ACTIVITY OF URANINITE

BY STEWART J. LLOYD

The percentage of the total α activity of uraninite contributed by each radioactive constituent of that mineral has been made the subject of investigation by Boltwood,[1] by McCoy and Ross,[2] and to a lesser extent by Mme. Curie.[3] Also the absolute maximum ionization current due to the activity of 1 gram uranium in the form of an infinitely thin film has been determined by McCoy and Ashman[4] in connection with their work on uranium oxide as a standard of radioactivity. The present investigation was undertaken, at the suggestion of Prof. McCoy, with a view to ascertaining the percentage of the total β activity to be assigned to each constituent of uraninite, and, if possible, to determine by comparison with the α activity of uranium oxide the total ionization current produced by the β activity of each.

The latter object was however found impossible of realization. It was at first thought that possibly the β rays, like the α, might possess a definite fixed range beyond which they ceased to produce ionization, and that the apparent absorption following the exponential law might be due to scattering alone;[5] that if the latter effect were eliminated, this range might be determined for each substance, and by the use of an electroscope of suitable form and sufficient size the total ionization current obtained, just as in the case of the α activity. With this in mind, a large cylindrical electroscope was constructed, in which the active material emitting the particles could be placed at the centre, by which arrangement the particles "bent out" of an ordinary β ray electroscope by the scattering due to absorbing material would be re-

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[1] Am. Jour. Sci., 25, 269 (1908).

[2] Jour. Am. Chem. Soc., 29, 1697 (1907).

[3] Comptes rendus, 126, 1101.

[4] Am. Jour. Sci., 26, 521 (1908).

[5] Crowther: Proc. Roy. Soc., 80A, 186 (1908).

tained within the ionization chamber, and their ionizing effect included. Upon trial, however, it was discovered, as has recently been shown also by Makower,[1] that actual true absorption as well as scattering of the β rays does take place, so that a determination of the absolute ionization current in a way comparable to that used for the α rays seemed impracticable. The measurements of β activity in this paper are therefore merely relative, and hold accurately only for the particular electroscope used. The order of magnitude will be the same, however, whatever measuring vessel may be employed, and the variations from the numbers here given will not be great, so that the latter may fairly be taken as representing the relative magnitudes of the β activities of the different substances.

The constituents of uraninite known to emit β rays capable of producing appreciable ionization after passing through a sheet of aluminium foil 0.044 mm thick are U X, Ra B, Ra C, and Ra E_2. In order to determine their respective activities with any degree of accuracy it was necessary to devise means of separating them quantitatively not only from the mineral itself, but from any considerable amount of foreign substances introduced during their extraction. Practically no work has been done on the separation of the radioactive substances in a quantitative way, and very little on their general chemical properties, consequently the latter were studied in some detail, especially in the case of U X. In the following pages therefore, after a description of the electroscope used, there will be found measurements of the β activity of uraninite, U X, Ra B, Ra C and Ra E_2, referred to the amounts associated with 1 gram of uranium as a unit; descriptions of the methods found convenient for obtaining these substances in a condition suitable for measurement, and the results of a few other measurements of related interest.

The electroscope used in practically all the measurements is that shown in Fig. 1. It was designed especially

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[1] Phil. Mag., [6] 17, 171 (1909).

for the examination of β activity, and differs from electroscopes commonly used for that purpose in allowing the active material to be placed either at the centre or at the bottom of the ionization chamber, instead of outside. It was made of galvanized iron, had a diameter of 40 cm[1] and the same height. As it was feared that the highest potential difference that could conveniently be used, about 500 volts, would be insufficient, with such an instrument, to give a potential gradient high enough to produce the saturation current, four upright brass rods were attached to the base, each at a distance of 7 cm from the centre, and four similar rods, attached to the central electrode as shown in the figure, were placed between and outside them. In this way there was obtained a potential gradient of not less than 75 volts per cm throughout the ionization chamber, except at a very few points. Separate experiments showed that with this arrangement the saturation current was being obtained with β ray preparations of ordinary strength. The central electrode and the rods attached to it could be rotated at will. A door sliding vertically afforded access to the interior of the electroscope. The central electrode was made up of two sections screwing into each other, so that preparations could be measured, if desirable, at the centre. In most of the measurements, however, the active material was placed on the bottom of the ionization chamber.

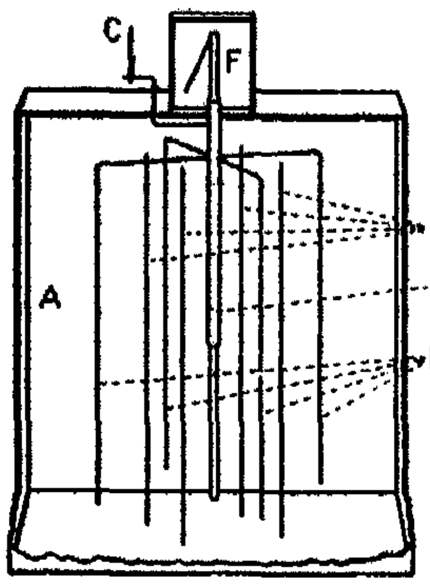

Fig. 1

E. Rods attached to base.
A. Ionization chamber.
F. Gold leaf electroscope.
B. Central electrode.
C. Charging wire.
D. Branches of central electrode.

As a standard of activity, a film of uranium oxide prepared according to the method of McCoy and Ashman[2] was employed. It may be of interest to note that the β activity

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[1] The electroscope was cylindrical instead of square as shown in Fig. 1.

[2] Am Jour. Sci., 26, 521 (1908).

of such a film (weighing 0.753 gram) measured in an ordinary α ray electroscope such as that used in this laboratory by McCoy and Ashman constitutes hardly 4 percent of the whole; in the electroscope just described it amounts to 12 percent. The ratio of the volumes of the two electroscopes is 1–9.5.

Uraninite

In measuring the β activity of uraninite it is necessary of course to take account of the absorption due to the mineral itself, just as in the measurements of the α activity, though the effect is of less magnitude here. Hence three films of each of two samples of uraninite free from thorium, one containing 58.1 percent U, the other 45.1 percent were measured; the ratio of weight to activity plotted against the weight, and this ratio for an infinitely thin film, where no absorption takes place, determined graphically.[1] The activities are given in terms of the standard referred to above, divided by 100 to avoid decimals. As was first pointed out by Boltwood,[2] a small part of the emanation is spontaneously evolved when uraninite is powdered, and hence Ra B and Ra C are present in thin films in less than equilibrium amount. It will be shown later that Ra B and Ra C together contribute 52 percent of the total β activity of uraninite. The amount of emanation and hence the β activity lost was determined essentially as described by McCoy and Ross,[3] namely by boiling off in a mixture of nitric and sulphuric acids the emanation from a weighed quantity of the powdered mineral, sealing up the mixture to allow the emanation to accumulate again, boiling off and measuring once more, and calculating the maximum amount of emanation, using as period 3.75 days. Since the β activity of the immediate emanation products Ra B and Ra C constitutes 52 percent of the whole, evidently the activity found requires to be increased by the activity of 52 percent of

[1] McCoy: Jour. Am. Chem. Soc., **27**, 402 (1905).
[2] Phil. Mag., [6] **9**, 603 (1905).
[3] Jour. Am. Chem. Soc., **29**, 1698 (1907).

the emanation lost in this way. This correction is applied in the following table.

The α activity was excluded by covering the films with sheet of aluminium foil. The amount of β activity cut off by the foil was determined graphically by adding successively 1, 2, 3, and 4 layers of foil, and producing the curve, activity-foils, backwards. It was found that one sheet of aluminium foil 0.044 mm thick cut off 13.65 of the total β activity of uraninite.

Uraninite, 58.1 Percent U

Weight	Activity	Em. lost	Corr. act.	w/a	w/a_0	a_0 per g. uraninite	a_0 per g. U.
0.2175	6.841	4.2 % of total emanation	7.01	0.0312	—	—	—
0.4100	11.42		11.68	0.0352	0.0307	32.6	56.1
0.6934	12.59		12.87	0.0539	—	—	—

Uraninite, 45.1 Percent U

Weight	Activity	Em. lost	Corr. act.	w/a	w/a_0	a_0 per g. uraninite	a_0 per g. U.
0.3398	7.713	3.8 % of total emanation	7.87	0.0431	—	—	—
0.4422	9.365		9.55	0.0463	0.04	25.0	55.4
0.6650	10.23		10.44	0.0637	—	—	—

In the preceding tables w refers to the weight of the film of mineral, a to the activity thereof, and a_0 to the activity of an infinitely thin film, determined graphically as described above.

The average of the two values for a_0 per gram U is 55.75. That is, the β activity of an infinitely thin film of uraninite containing 1 gram uranium and all the successive products of the latter in equilibrium amounts, is, in the electroscope described, 0.5575 times as great as the total activity of the standard film of uranium oxide employed.

Uranium X

As it has repeatedly been shown that uranium X is produced by uranium, and since uranium itself is readily determined quantitatively in uraninite, it seemed much simpler, instead of separating U X from uraninite, to separate it quantitatively from some pure compound of uranium which contained it in equilibrium amount. This separation may be effected to a greater or less extent in several ways; a quantitative separation, however, in which all of the U X is obtained without any uranium, and in addition sensibly free from other impurities, is distinctly difficult.

The compound of uranium most readily obtained is the nitrate. Uranium X has been obtained from it in several different ways:

1. By dissolving uranium nitrate in ether, and separating the aqueous layer, which contains most of the U X and a little U. This separation is not quantitative.[1]

2. By precipitating uranium nitrate with ammonium carbonate and dissolving in excess, whereby the U X remains undissolved. This also is incomplete, and requires the presence of a considerable amount of impurity, such as iron, to make it of any use whatever.[1]

3. By precipitating barium sulphate in the aqueous uranium nitrate solution, whereby U X is carried down mechanically. Three successive operations of this kind remove all the U X. It was found possible also to remove the U X from the sulphate precipitate by boiling with hot concentrated hydrochloric acid, but to obtain a complete extraction acid of such concentration had to be used that appreciable quantities of barium sulphate were also dissolved.[2]

4. By stirring into an acetone solution of uranium nitrate some freshly prepared ferric hydroxide. Results obtained by this method proved very erratic, from 40–90 percent of the U X being removed, never more, even after several operations.[3]

5. By boiling aqueous uranium nitrate with animal charcoal.[4] This method also was not quantitative. A

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[1] Crookes: Proc. Roy. Soc., 66, 409 (1900).

[2] Becquerel: Comptes rendus, 133, 977 (1901).

[3] Moore and Schlundt: Phil. Mag., [6] 12, 393 (1906).

[4] Levin: Phys. Zeit., 8, 585.

modification of it, in which soot was substituted for animal charcoal, and acetone for water proved to be quantitative, however, and entirely satisfactory. It was found, also, more convenient to stir the soot into the acetone than to boil it with the latter.

The complete process employed in the separation was as follows: Five or 10 grams of uranium nitrate, containing about 50 percent U were dissolved in 150 cc of acetone, and stirred for thirty minutes with 1 gram of soot prepared by burning naphthalene. The soot need not be purified before using, as the colored hydrocarbons and other substances in it are removed later, and the fresher the soot the more efficient it appeared to be. The mixture of soot and acetone was then filtered, another gram of soot added to the uranium nitrate-acetone filtrate, and the stirring repeated. Three treatments of this kind suffice. Separate experiments showed that 95 percent of the U X was removed in the first treatment, and practically all in the first and second together. Upon rapid evaporation of the filtrate and measurement of the uranium oxide produced by ignition, scarcely a trace of β activity could be detected. The three portions of soot were then united, and without washing boiled twice with dilute hydrochloric acid for fifteen minutes at a time, the first boiling removing about 95 percent of the U X. This dissolves out from the soot the U X and the small amount of uranium nitrate which had adhered to the soot. The latter can not be removed even by prolonged washing of the soot with ether, alcohol or water. This solution was then evaporated to a volume of 100 cc, 0.05 gram iron wire added, and when the latter had dissolved, ammonium carbonate was added carefully until the uranium had just redissolved. Separate experiments showed that this amount of iron was sufficient to carry down all the U X, and that no uranium remained in the precipitate. Without the iron the separation is quite incomplete. The ferric hydroxide-U X precipitate was then thoroughly washed with water, and dissolved in 10 cc of hydrochloric acid. The resulting solution was shaken three times with ether which had been saturated with gaseous hydrochloric acid, whereby the ferric chloride dissolved in the ethereal layer, and the U X with an inappreciable amount of the iron salt, remained in the aqueous, acid layer. If concentrated acid is used, and the ether is freshly distilled, this separation is quite sharp. The uranium X solution was then evaporated, finally on a gold plate, and its activity measured.

Two samples, each containing 10 grams uranium nitrate, which upon analysis yielded 47.36 percent U, were treated as indicated above, and the resulting activity measured in the electroscope. The residue on the plate weighed in one case 0.0015 gram in the other 0.0027 gram, and had therefore no appreciable absorbing power for β rays. As is well known, U X emits, besides its γ rays, radiation of two kinds, "hard" penetrating rays, and "soft" rays which are unable to pass through 0.044 mm of aluminium foil. Since in the measurement of uranium itself these rays were excluded by the covering of foil, it became necessary to determine here what percentage of the total activity of the U X, as measured in this electroscope, was due to them. The preparation was therefore covered successively by 1, 2, and 3 layers of aluminium foil, and by extrapolation the required value found. It was found that 26.7 percent of the total ionization due to U X was contributed by these soft rays.

Schmidt[1] and others have recently shown that these soft rays are not α rays of short range, as had once been supposed, but β rays of slight penetrating power. The above measurement affords additional evidence of a distinctly different kind in favor of this view, as is shown by the following considerations.

The ratio of the activities due to the two kinds of rays in an ordinary α ray electroscope is approximately as 7-3. Had the weaker radiation been α in character and of short range, its effect would not have increased in magnitude when measured in the larger electroscope, while the activity due to

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[1] Jahrb. für. Rad., 5, 451 (1908).

the penetrating β rays increases about threefold (page 512). Hence in the present electroscope the ratio of the two activities would have been, had the weaker been α in character, about 7-1 instead of 3-1 as it is.

The following table gives the data obtained for two samples of uranium nitrate. Allowance was made of course for the time elapsing between the separation of the U X from the uranium nitrate and the measurements.

Weight of uran. nitrate grams	Weight of uran.	Activity	Activity of hard rays	Activity of hard rays per g. U.
10	4.736	114.6	83.83	17.7
10	4.736	116.9	85.72	18.1

Mean of two values 17.9.

Percentage of total β activity of uraninite due to hard rays of U X, No. 32.1.

The activity of one of these preparations was measured over several months with the object of redetermining the period of U X. Both hard and soft radiations decayed at the same rate, indicating a period of 22.4 days.

The activity of U X was determined in still another way. Three films of uranium oxide were prepared, allowed to stand until they had grown their maximum amounts of U X, and then measured, the absorption due to the oxide itself, and the α radiation, being allowed for as in the case of uraninite. The results were found to agree essentially with those obtained from the measurements on pure U X extracted from pure uranium nitrate.

Weight of U_3O_8	Activity	w/a	w/a_0	Activity per g. U.
0.625	8.941	0.0692	—	—
0.694	9.734	0.0713	0.0675	17.45
0.782	9.731	0.0761	—	—

It was observed also that one layer of aluminium foil 0.044 mm thick cut off 8.7 percent of the β activity of U X (hard rays).

Radio-Uranium

In a recent article Danne[1] has published some measurements which may indicate the existence between uranium and U X of a rayless substance which produces U X, and to which he has given the name radio-uranium. This substance was obtained by him along with U X by precipitating barium sulphate in an aqueous solution of uranium nitrate. As some irregularities and peculiarities had been observed in the course of the present work on U X, it was thought worth while to attempt the detection of this new substance, in an indirect way at least.

If such a substance exists, and has a period at all comparable in length with that of U X, and if the uranium nitrate be freed at once from it and from U X, the rate of growth of the uranium nitrate in β activity should be much different from what it would be if the uranium directly produced U X. Even if the uranium nitrate be only partially freed from this hypothetical substance, the recovery curve of β activity should still be somewhat different from what has been regarded as the normal, the difference depending upon the amount of radio-uranium removed. Danne obtained his radio-uranium by precipitation of aqueous uranium nitrate with barium sulphate, and subsequent *elaborate treatment of the precipitate. In the present* experiment therefore, 10 grams of uranium nitrate were dissolved in water, and barium sulphate precipitated in the solution twenty-five times successively. The uranium nitrate, from which, presumably at least, part of the radio-uranium had been removed, was then precipitated with ammonia, ignited to the oxide and made into a film. Measurements of the growth of β activity extending over seventy days gave a period of 22.7 days, practically the same as that so frequently observed for U X. Hence, if such a

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[1] Le Radium, 6, 42 (1909).

product does exist, and is the parent of U X, it is obviously not removed by barium sulphate. Indeed the phenomena observed by Danne could all be accounted for by the assumption that his uranium nitrate had not been freed entirely from radium.

Chemical Behavior of Uranium X

In the attempt to devise a suitable method for extracting UX from uranium nitrate some new and interesting facts with regard to the chemical behavior of the latter were obtained. As the chemical properties of the less abundant radioactive substances will probably assume considerable importance in the future, especially in the light of the possible position of the latter in the periodic table, these facts are given below.

Uranium X, as has been observed by other investigators, resembles ferric iron very closely in all its reactions. It is precipitated quantitatively from its hot hydrochloric acid solution by the addition of a small amount of ferric chloride and ammonia. This reaction affords a means of determining the amount of U X in a solution which is much more accurate and rapid than the evaporation of the solution and subsequent measurement. The amount of iron added need not be so great as to cause any appreciable absorption of the activity.

When to a hydrochloric acid solution of U X, ferric chloride and aluminium chloride are added, the two metals precipitated by potassium hydroxide and excess of the latter added, the uranium X remains undissolved, with the iron, not a trace following the aluminium.

Ammonium carbonate, when added to a precipitate of ferric hydroxide containing U X, dissolves a small amount of the iron when cold, and quite a considerable amount when hot. The U X is much less soluble in the carbonate than is the iron, being scarcely dissolved at all.

The only way known by which UX can be completely separated from iron is by treatment with ether and hydrochloric acid (page 516). This reaction is of importance, as the most convenient method of obtaining U X from a solution is by precipitation with ferric hydroxide.

Uranium X when precipitated from a solution of uranium nitrate by barium sulphate is not dissolved out by boiling sodium carbonate, but remains with the resulting barium carbonate.

Lead sulphate is not so efficient in carrying down U X as is barium sulphate, the ratio being 7–10. When lead sulphate containing U X is treated with sodium thiosulphate, the U X does not follow the lead, provided there is sufficient impurity present to form a nucleus of undissolved matter.

Ammonium acetate removes from a lead sulphate —U X precipitate about 35 percent of the U X in two extractions.

The precipitation of basic ferric acetate in a solution of U X carried down 70 percent of the activity.

Boiling acetic acid does not remove any of the activity from a barium sulphate-U X precipitate.

Radium B and C

Rutherford's[1] examination of the immediate active deposit from radium led him to the conclusion that radium C alone emitted β rays. Certain irregularities in the decay curves however brought about subsequent investigations by Schmidt,[2] and by Bronson,[3] both of whom demonstrated the existence of β activity in radium B, the latter showing that the β activity of B probably exceeded that of C. The results of their work, so far as the existence of β activity in radium B is concerned were substantiated by Duane,[4] using a very different experimental method. He measured the amount of negative electricity emitted by the active deposit instead of the ionization current due to it. In the present investigation the total β activity due to B and C together was obtained, and by an indirect method the ratio of the two activities, from which data the individual activities themselves were calculated.

To determine the total β activity of the active deposit of radium, that is, the β activity of B and C together, portions

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[1] Phil. Trans., 198 (1904).

[2] Phys. Zeit., 6, 897; 7, 764.

[3] Phil. Mag., [6] 12, 73 (1906).

[4] Le Radium, 5, 65.

of a radium solution were evaporated on platinum plates, allowed to stand for forty days, at the end of which time the activity had reached a maximum, and then measured in the electroscope, interference by the emanation and by the α activity in general being prevented by a closely adhering sheet of aluminium foil. The amount of β activity absorbed by the foil was determined essentially as in previous similar cases. The radium films themselves were so thin that no appreciable absorption took place in them. In order to determine the amount of radium of which the activity was being measured, portions of the same radium solution were compared in a gas electroscope with a weighed amount of uraninite whose uranium and hence radium content was known. Boltwood,[1] however, had previously shown that radium preparations in the form of thin films lose spontaneously quite considerable amount of emanation, and that therefore the maximum activity of a radium preparation was less than it should be, were all the emanation retained. Since a correction for the loss of emanation was made in the case of uraninite, and since in any event the losses for the two materials are by no means proportional, it was necessary to make a similar correction here. To do this, a portion of the same radium solution was evaporated on a small thin copper plate, the activity allowed to reach a maximum, the plate placed bodily in a small flask, and the emanation boiled off and measured in the usual way. The flask was then sealed up, the emanation allowed to grow for a few days, measured again, and the maximum amount calculated. Three determinations of this kind gave 10.7, 11.6, and 11.4 percent of emanation lost, an average of 11.2. The correction is applied in the accompanying tables.

No.	Act.	Corr. act.	Act. per g. U	Average
1	10.61	12.2	28.7	—
2	11.13	12.8	29.9	29.0
3	10.1	11.4	28.5	—

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[1] Phil. Mag., [6] 9, 603 (1905).

Percentage of the total β activity of uraninite contributed by B and C 51.8.

The total β activity due to the active deposit of radium was obtained in still another way, after the method used by McCoy and Ross[1] for obtaining the α activity due to emanation + A + B + C in uraninite. A portion of the uraninite sample containing 58.1 percent uranium was finely ground, treated with nitric acid, evaporated to dryness, and the process repeated three times at intervals of two hours, to free the material from emanation and to allow A, B and C to decay. After the last evaporation the residue was heated strongly enough to decompose all the nitrates present. The resulting residue, mostly oxides, was made into films as quickly as possible, and its activity determined in the usual way. The films were then allowed to stand until the maximum β activity had been attained, about 35 days. The percentage of the total β activity contributed by the active deposit could thus be directly calculated. The results are contained in the following table.

Initial β activity (due to constituents other than B and C)	Final β activity (due to all constituents)	Act. corr. for loss of eman.	Act. of B + C
4.24	8.27	8.8	4.56
5.98	11.72	12.46	6.48

Percentage of β activity of uraninite contributed by B and C therefore 52.0.

The β rays from uranium X, radium B, radium C and radium E_2 are unequally absorbed by the uranium oxide, and as no allowance for absorption was made in these measurements, the close agreement between them and those immediately preceding is fortuitous only.

To determine the individual β activities of Ra B and Ra C advantage was taken of the difference in the temperatures at which they volatilize. A copper plate kept negatively

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[1] Jour. Am. Chem. Soc., 29, 1702 (1907).

charged was placed in a vessel containing emanation, and allowed to remain until the deposit on it had reached a state of radioactive equilibrium. It was then removed, allowed to stand for twenty minutes to ensure the complete decay of Ra A, and the ratio of its α to its β activity measured. The β activity was due to B and C together, the α activity to C alone. Another plate which had been exposed in a similar way was heated for five minutes in an electric furnace to a temperature of 700° C. According to Makower,[1] Ra B volatilizes entirely at this temperature, while Ra C is unaffected The ratio of the α to the β activity was then measured, both activities in this case being due to Ra C. From these two measurements the individual activities were calculated

Let x = β activity of Ra C.
y = β activity of Ra B.
z = α activity of Ra C when all are in radioactive equilibrium.

Then $z/x + y$ = ratio of α to β activity after exposure to emanation and decay of RaA = m_1.
z/x = ratio of α to β activity after heating to volatilize Ra B = m_2,

$$x/y = \frac{m_1 - m_2}{m_2}.$$

The results of several measurements did not agree very closely among themselves, as might be expected from the fact that at the time of measurement, B and C are not present in equilibrium amount. In general, however, it appeared that of the total β activity due to B and C, radium C contributed about 68 percent, Ra B about 32 percent.

Percentage of total activity of uraninite due to B is 15.9
" " " " " " " " C " 35.9

Radium E,

The determination of the β radiation of E_2 was somewhat more difficult than that of any one of the preceding

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[1] Proc. Manch. Phil. Soc., 53, II, 1-8.

substances. Radium B and C depend immediately upon the easily estimated radium emanation, while uranium X may be grown readily from weighable quantities of uranium. Radium E_2 may, indeed, be obtained without trouble from Ra D, but the quantitative extraction of Ra D from uraninite had not been worked out. Possibly the most satisfactory though rather tedious way to obtain the desired result would be to obtain a strong preparation of Ra D, await the growth in it of E_1, E_2 and F, and when equilibrium had been reached, measure the activity of Ra F, the only α ray product present. Since the activity of F in terms of uraninite has been determined,[1] we should know the weight of mineral corresponding to the amount of Ra D in our sample and could then determine E_2 with accuracy. No supply of Ra D with its products was available, however, so that it became necessary to study the quantitative extraction of the latter from uraninite, and to obtain Ra E_2 from it in such a manner as to allow of its activity being measured. A preparation of Ra D was made however, set aside to permit of the growth of Ra F, and will be measured later.

In order to determine the conditions under which Ra D could be extracted quantitatively from uraninite, a study of its chemical behavior was made. As its name radio-lead would indicate, it clings very closely to lead, quite as closely as U X does to ferric iron, following the lead quantitatively everywhere, provided a sufficient amount of the latter is present. In the form of sulphate it dissolves quantitatively in ammonium acetate and in sodium thiosulphate, is precipitated quantitatively by hydrogen sulphide, sulphuric acid, and by sodium carbonate. If the quantity of lead associated with it be small, however, some of the Ra D is lost. The one condition to be fulfilled in order that Ra D may follow quantitatively the reactions of lead appears to be the presence of considerable quantities of that metal.

In obtaining Ra D from uraninite therefore, the following method was used.

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[1] Boltwood: Am. Jour. Sci., 25, 269 (1908).

10 grams uraninite containing 58.1 per cent U were dissolved in dilute nitric acid. The uraninite was practically free from sulphides, so that oxidation of the latter to sulphates was not feared. The residue, mostly silica, showed activity, which disappeared in a few hours. The solution was evaporated to dryness, 100 mg of lead nitrate added, and solution effected by the addition of water and a few drops of nitric acid. Dilute sulphuric acid was then added to precipitate the sulphates of barium and lead. The mixed sulphates were then extracted repeatedly with ammonium acetate, to remove the lead and radio-lead, and the resulting solution precipitated with hydrogen sulphide. The filtrate from the barium-lead sulphates was also treated with hydrogen sulphide, and the resulting precipitate containing lead, bismuth, Ra F, etc., added to the former. The combined precipitate was converted into nitrates, then into carbonates, and then into nitrates again. The nitrates were precipitated by sodium hydroxide, enough of the reagent added to redissolve the lead, and the solution filtered. The lead, all of which was in the filtrate, was converted into a carbonate, then into a nitrate, and the solution evaporated to dryness. At this time it possessed no appreciable activity, and was set aside until Ra E_2 should have grown to maximum amount.

Before measuring the activity of Ra E_2 it was necessary to separate it from the very considerable amount of solid matter, over 125 mg, associated with it, as the absorption of the soft rays of radium E_2 takes place readily. The separation was made in the following manner.

When to a lead nitrate solution containing radium D, E_1, E_2, and F, sodium hydroxide is added, complete precipitation takes place, but upon addition of excess of the reagent only the lead and Ra D redissolve, provided there is sufficient solid matter in the residue to afford a nucleus. The separation becomes quantitative when a drop of ferric chloride solution is added. The solid residue was filtered off, dried, and measured at once, so that no correction needed to be made for decay.

Weight of uraninite	Activity	Act. per g. mineral	Act. per g. Uran.
10	35.4	3.54	6.1

Percentage of total β activity of uraninite due to Ra E_2, 10.9.

The β activity of uraninite per gram uranium was found to be 55.75 in arbitrary units. The activities of the several constituents in the same units, and in percentages are

Uranium X	17.9	32.1%
Radium B	9.0	16.1
Radium C	20.1	36.1
Radium E_2	6.1	10.9
	53.1	95.2%

Whether the missing 4.8 percent is contributed by some constituent as yet unknown, or is due to experimental errors, is hard to say.

It was expected that the total activities as given above would show some intimate relation to the absorbability of the various rays. Such is hardly the case however, as the following table[1] shows. The first column contains the thicknesses, in cm of aluminium foil, required to reduce the activity to half value in each case, the second column the total activities.

Uran X	0.048 0.014	32.1
Ra B	0.053 0.0078	15.9
Ra C	0.0534 0.0131	35.9
Ra E_2	0.016	10.9

Indeed the rays from any one substance do not appear to be homogeneous, so that to obtain comparable numbers for their absorbabilities it would be necessary to know much more accurately than we do at present the relative amounts of the hard and soft rays in each.

It should be noted that account is taken only of those rays which produce appreciable ionization after passing through 0.044 mm of aluminium foil. It is quite possible, indeed probable, that other rays, like the soft rays of U X,

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[1] Le Radium 6, 1 (1909).

exist, and in establishing the numbers of β particles given off by each substance such rays would have to be taken into account. Hahn[1] has recently advanced the hypothesis that a single radioactive substance is capable of emitting rays of one kind only, either homogeneous α or homogeneous β rays. If such is the case, the number of accepted radioactive substances will, obviously, have to be greatly increased, especially the number of those emitting β particles.

Although, as was stated at the beginning of this article, the absolute ionization current due to the β activities of the constituents of uraninite could not be determined with exactness, it is possible, however, from the measurements made, to assign a lower limit to it in each case. According to McCoy and Ross[2] the total activity of 1 gram of uranium is equal to that of 796 square cm of a thick film of U_3O_8. In the electroscope used throughout the present work, the U X associated with 1 gram uranium in radioactive equilibrium was found to possess an activity equal to that of 7.53 sq. cm (α only) of a thick film of U_3O_8. Hence, the hard rays of U X in radioactive equilibrium with 1 gram uranium have an activity equal to that of 0.00946 gram uranium, and hence an ionization current of 4.36 10^{-12} amp. Since U X furnishes 32.1 per cent of the total ionization due to the β activity of uraninite, the β activity of the latter is equal to the α activity of 0.0295 gram of uranium, and gives an ionization current of 1.358 10^{-11} amp. If the soft rays of U X be included, the figures for U X become 0.0129 and 5.95×10^{-12}; for uraninite 0.0329 and 1.516×10^{-11}. If U X is genetically connected with radium, and if the periods of the two be taken as 22 days, and 1760 years respectively, the weight of U X in equilibrium with 1 gram uranium is 1.116×10^{-6} gram. Weight for weight therefore U X (hard rays) is at least 8.48×10^7 as active as uranium. Including the soft rays it is 11.02×10^7 as active as uranium.

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[1] Phys. Zeit., 9, 697.

[2] Jour. Am. Chem. Soc., 29, 1698 (1907)

STUDIES IN THE ELECTROCHEMISTRY OF THE PROTEINS. I. THE DISSOCIATION OF POTASSIUM CASEINATE IN SOLUTIONS OF VARYING ALKALINITY

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I. Introduction

(a) The Object of the Investigation

The investigations of Hardy,[1] Sackur[2] myself[3] and others have shown that the compounds of the proteins with inorganic acids and bases undergo quite extensive electrolytic dissociation when they are dissolved in water. The following investigation was undertaken with the prime object of ascertaining to what extent the protein salts, which are present in solutions of potassium hydroxide to which definite amounts of casein have been added, participate in the conduction of electricity through their solutions—in the hope that the information thus obtained would throw light upon the mode in which the proteins combine with bases and the mode in which these compounds dissociate.

In order to completely determine the share taken in the conduction of a current by the ions, derived from protein salts, which are present in a solution of a protein in alkali or in acid, two measurements are, as a rule, necessary. Thus, suppose we measure the depression of the conductivity of a KOH solution which is brought about by the addition to it of a definite amount of casein—let x_1 denote the conductivity (in reciprocal ohms per cubic centimeter) of the original KOH solution, and x its conductivity after the addition thereto of casein. Let b_1 denote the concentration of the

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[1] W. B. Hardy: Jour. Phys., 33, 251 (1905).

[2] Sackur: Zeit. phys. Chem., 41, 672 (1902).

[3] T. Brailsford Robertson: Jour. Phys. Chem., 11, 437, 542 (1907); 12, 473 and 542 (1908).

original KOH solution and b the amount of KOH which remains unneutralized after the introduction of the casein and c the equivalent-concentration of each of the ions derived from the protein salt. Let U denote the ionic velocity (in cm per sec. per volt-cm potential gradient) of the K^+ ion, V that of the hydroxyl ion and $v_1, v_2, v_3 \ldots\ldots$ those of the ions derived from protein salts, then from familiar electrochemical formulae we have:

$$x_1 = 96.44(U + V)b_1$$
$$x = 96.44(U + V)b + 96.44(v_1 + v_2 + v_3 + \ldots\ldots)c$$
let $x_1 - x \equiv \lambda$, and $b_1 - b \equiv m$.

Then:—

$$\lambda = 96.44(U + V)m - 96.44(v_1 + v_2 + v_3 + \ldots.)c\ldots\ldots(1)$$

In order, therefore, to determine the relative magnitudes of $(v_1 + v_2 + v_3 + \ldots.)c$ in various solutions, it is necessary to measure, not only λ, but also m, the amount of alkali bound by the protein. Of course in cases where, as in Sackur's experiments, alluded to above, and in some of my own previous experiments, the alkali is *completely* neutralized by the protein, no special separate measurement of m is necessary—but in many of the experiments herein described a considerable excess of alkali was present in the solutions, and hence a separate measurement of m was imperative.

In brief, therefore, the investigation herein described consisted in the measurement of the depression in the conductivity of KOH solutions due to the introduction of casein, and in the determination, by means of the gas-chain, of the proportion of the KOH in these solutions which was neutralized by the casein.

(b) The Apparatus Employed

In the gas-chain determinations two platinized platinum electrodes saturated with hydrogen were used—the one being dipped in the solution of unknown hydroxyl-concentration, the other in a solution of known hydroxyl-concentration; the latter being always the original KOH solution and the former the same solution with the addition thereto of a definite amount of casein. The electrodes which were employed were of a design due to Dr. F. G. Cottrell, which has previously been employed by me[1] and has been described in detail by Schmidt and Finger in this journal.[2] They were very kindly prepared for me by Dr. Cottrell himself, to whom I wish to take this opportunity of expressing my thanks.

The hydrogen was generated by the electrolysis of 6 percent (by volume) sulphuric acid, in an apparatus which has previously been described by Schmidt and Finger in the paper cited above. To guard against the possibility of any oxygen, ozone, or hydrogen peroxide being carried over with the hydrogen from the generator, the gas was passed through a heated glass tube which was loosely filled with platinized asbestos and which had, wrapped around it for a distance of about 20 cm, a coil of fine resistance wire, the internal diameter of the tube being about 0.5 cm. The hydrogen was completely cooled before it reached the electrodes, because, after leaving the heater, it was passed through a narrow glass tube about 70 cm long, leading to the water bath. The coil of the heater was heated by a portion of the same current (110 volt University Circuit) which generated the hydrogen, the current being led into the hydrogen-generator through 4 lamps in parallel (three 16 c. p. and one 32 c. p. 110 volt lamp), one of the 16 c. p. lamps being connected in series with the coil. In order to maintain the pressure of hydrogen which was necessary to drive it through the electrodes, the oxygen which came off from the generator was carried off by a tube which dipped into a column of water, the depth of the opening of the tube in the water being adjusted until the levels of the fluid in the inner and outer cylinders of the generator were approximately equal.

The complete chain was arranged as follows. The syphon-tube of the "half-element" containing the fluid into which the electrode dipped was immersed in a beaker filled with the same fluid—thus the "half-element" containing the

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 437 (1907).

[2] C. L. A. Schmidt and C. P. Finger: Jour. Phys. Chem., 12, 406 (1908).

solution of unknown hydroxyl-concentration was in fluid connection with a beaker which contained the same solution, and the "half-element" containing the solution of known hydroxyl-concentration was in fluid connection with a beaker filled with that solution. The two beakers were then connected by a U-tube filled with agar saturated with KCl, thus effectively preventing any mixing of the two solutions and annihilating any contact-difference of potential between them.[1] The gas was passed through the electrode which dipped into the solution containing protein (the solution, that is, of unknown hydroxyl concentration) at the rate of from one to two large bubbles per second, and the excess of gas was permitted to pass through the other electrode. The whole chain was immersed in a small water bath placed inside an incubator which was maintained at a temperature between 31° and 32° (*vide infra*). It was thought necessary, at first, not to permit the hydrogen to escape into the incubator, lest it should be ignited, on opening the door of the incubator, by the flame beneath. Consequently the electrodes were inserted into the half-element through tightly-fitting rubber stoppers, and rubber tubes were attached to the side-tubes of the half-element and carried outside the incubator and the cupboard within which the incubator was set up. For reasons which will shortly be described, however, this procedure was, of necessity, abandoned, and the gas was permitted to escape into the incubator. As no explosion occurred during the progress of these experiments, this procedure was probably safe. The incubator was of the usual double-walled type employed by bacteriologists; its internal dimensions were 45 cm wide by 24 cm deep by 48 cm high. It was provided with two doors, the outer of the usual double-walled type, the inner a glass door through which thermometers, etc., could be read without disturbing the apparatus or causing fluctuations of temperature by currents of air. The inner chamber was provided at the top with two small air-exits.

The potentials between the electrodes of the chain were

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[1] Bjerrum: Zeit. phys. Chem., 53, 428 (1905).

measured on a 100 cm potentiometer bridge-wire, which had previously been standardized in the laboratory of physical chemistry. For the detection of the zero-point on the bridge-wire a D'Arsonval galvanometer provided with a damping-coil was employed, it gave a decided throw with the potential corresponding to 1 mm displacement on the bridge in all of these experiments. The constant fall in potential from end to end of the potentiometer wire was at first supplied by a storage-battery, but since none of the storage-batteries which were immediately available proved of sufficient capacity for the work required of them, this was replaced by an arrangement of four Gladstone-Lalande cells (model G-50), two in parallel and two in series, so as to obtain the voltage of two cells and the internal resistance of one. The potential derived from these was measured against a standard Weston cell, just before and just after every reading. The potential provided by the Gladstone-Lalande cells proved quite sufficiently constant, during the progress of an observation, provided they were always short-circuited across the bridge-wire for 15–20 minutes beforehand—this did not heat the bridge-wire in any degree which could be detected. The Weston cell was checked against another Weston cell which had been prepared in the department of physical chemistry, and the two were found to agree exactly.

The electrodes were platinized with Lummer and Kurlbaum's solution. They were very carefully washed, both within and without, between the observations, first in a stream of distilled water and then in the solution in which they were about to be immersed—every few days they were also washed in chromic and sulphuric acids solution and then, after thorough washing in a stream of distilled water, were allowed to soak for 12 hours in distilled water.

The conductivity-vessel which was employed was of the Kohlrausch-Holborn type, with a thermometer dipping into the fluid between the electrodes. This was immersed in the same water bath as the gas-chain, and the conductivities of the solutions were always measured at exactly 30°. The capacity of the vessel was 0.1305 (measured by determining the resistance of an accurately N/50 KCl-solution). The electrodes were platinized with Lummer and Kurlbaum's solution. The same bridge-wire was employed for determining the conductivities as for determining the potentials of the gas-chain. A telephone was employed to detect the zero-point and the alternating current was supplied by an inductorium of the Ostwald type. The Rheostat was a "five dial bridge," manufactured by Nalder Bros. and certified to read correctly within 0.01 percent at 17° C. Its temperature-coefficient was only 0.025 percent per degree, so that I made no correction for the temperature of the rheostat. The resistance in the rheostat was always adjusted until the zero point was exactly in the middle of the bridge; the resistance in the rheostat was then, of course, exactly equal to that of the conductivity-vessel filled with the fluid under investigation. The arrangement of the wiring is represented in the following diagram.

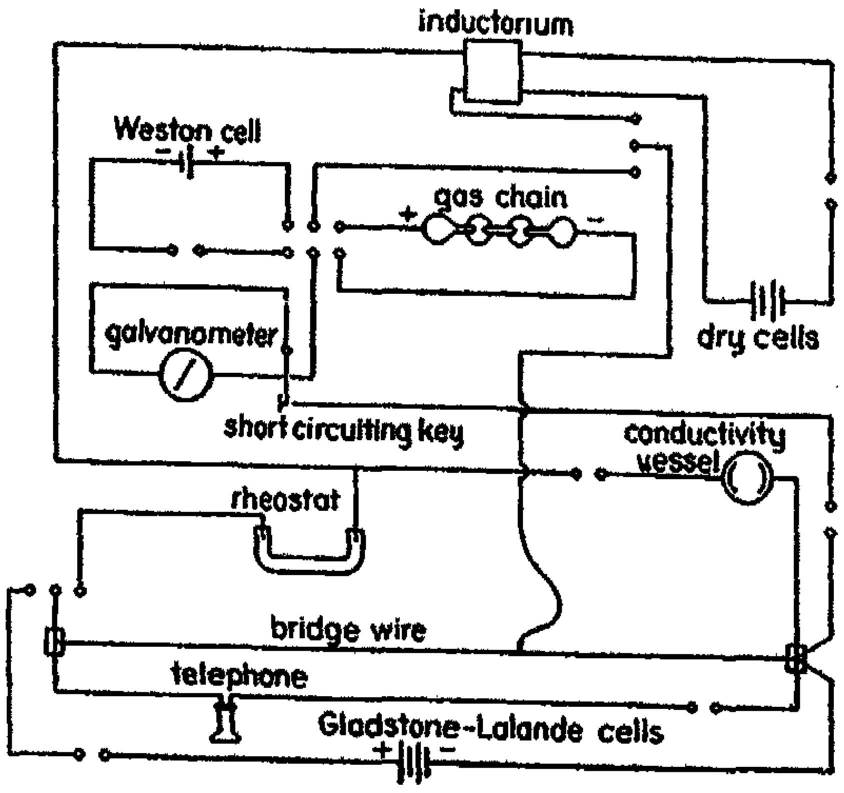

Fig. 1

The wires of the conductivity circuit were all "bell wire," so that their resistance could be neglected. The wires of the potentiometer-circuit were somewhat thinner. All of the wires were insulated and carefully supported on glass, and were never allowed to touch the table. Where it was necessary to carry wires through the table, for example, or through the wall of the cupboard in which the incubator was placed, they were run through glass tubes. The wire connected with the slider on the bridge was encased in rubber tubing.

(c) The Preparation of the Casein

The casein employed was Eimer and Amend's C. P. casein "nach Hammarsten," specially purified in the following manner. Half a pound of the casein was triturated with about 12 liters of distilled water, the water being added in six successive portions. On each addition of water the casein was well stirred up in it in a porcelain mortar and then allowed to settle, then the supernatant water was poured off and fresh water was added. It was then washed in a similar manner in 5 kilos of Kahlbaum's C. P. alcohol, 99.8 percent, and then in 5 kilos of Kahlbaum's C. P. ether, "ueber Natrium distilliert." The mortar, containing the casein drained as free from superfluous ether as possible,[1] was then placed in an incubator over sulphuric acid at 40–50° C, the flame was turned out under the incubator and it was allowed to cool for about 24 hours. The casein is now found, if these operations have been conducted carefully, to be in the form of a dry, pure white powder, still containing, however, a considerable quantity of ether. The casein was now spread out, within the incubator, in a layer not over 1 cm deep, the flame under the incubator was lighted, fresh sulphuric acid was introduced if necessary, and it was allowed to stand for 24 hours at 40–50° C. The casein is then found to be free from appreciable water or ether.

I have previously shown[2] that the casein thus prepared

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[1] At this point it is necessary to avoid exposing the mortar to the moist air of the room a minute longer than is necessary, otherwise the evaporating ether causes the condensation of sufficient moisture to spoil the product unless it is again treated with alcohol and ether.

[2] T. Brailsford Robertson: Jour. Biol. Chem., 2, 317 (1907).

gives every indication of being a pure product—it is insoluble in distilled water, save in traces which adhere to the casein particles, and it neutralizes to phenolphthalein and to litmus exactly the quantities of alkali determined by Söldner,[1] Lacquer and Sackur[2] and van Slyke and Hart.[3]

Casein which has been carefully prepared in the manner outlined above floats upon the top of and is not readily wetted by water or watery solutions of bases; if, however, it contains a mere trace of moisture, it is readily wetted by all save the most alkaline solutions. In order to successfully and completely dissolve perfectly anhydrous casein it is necessary to first add to it a very little of the solution in which it is to be dissolved, rub it up into a paste, and then add, while stirring, the remainder of the solution. This procedure was adopted in all of the experiments described below.

(d) The Experimental Procedure

I have pointed out in previous publications[4] that it is difficult to obtain solutions of caseinates of much higher acidity than neutrality to litmus by merely shaking up casein in solutions of bases—not because casein will not form such solutions, but because, although it dissolves at first with considerable rapidity, after the excess of alkali is neutralized further casein dissolves with extreme slowness. Now it was found at an early stage in this investigation that the conductivities of the solutions containing casein must be measured as soon as possible after complete solution of the casein, for, otherwise, the hydrolysis which casein undergoes, the more rapidly the more alkaline its solution[5] introduces a serious error into the determination. Hence it was imperative, not only that the measurement of the conductivities of these

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[1] Söldner: Landw. Versuchs., 35, 351 (1881).

[2] Lacquer and Sackur: Beitr. Chem. Physiol. u. Path., 3, 196 (1906).

[3] van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905).

[4] T. Brailsford Robertson: Jour. Biol. Chem., 2, 317 (1907); Jour. Phys. Chem., 13, 469; 14, (1910).

[5] T. Brailsford Robertson: Jour. Biol. Chem., 2, 317 (1907). "The Proteins," Univ. of Calif. Publ. Physiol., 3, 174 (1909) and foot-note.

solutions should be determined as soon as possible after complete solution of the casein, but, also, that the preparation of the solution, after the introduction of the casein, should consume as little time as possible. Hence all of the solutions containing casein which were acid to phenolphthalein were prepared by dissolving the casein in excess of alkali and then neutralizing this excess with hydrochloric acid. This procedure was found to have the further advantage that the absolute conductivities of the solutions thus obtained being higher than they would have been had they contained no KCl, the detection of the zero point on the bridge-wire by means of the galvanometer was rendered much easier and a less sensitive galvanometer could be employed than would otherwise have been required. In fact a greater excess of KCl was commonly present in the solution than was absolutely necessary. As a rule, save in the case of the most alkaline solutions, in a series of experiments in which only one concentration of casein was employed, the total concentration of potassium in each solution was kept constant and varying proportions of it were neutralized by HCl.

In this connection it is to be carefully noted that if the solution employed to dissolve the casein be too alkaline little or nothing is gained by the rapidity of its solution, because rapidity of its hydrolysis is also great. On the other hand, as I have said, if too small a proportion of free KOH is present solution is so slow that hydrolysis is extensive. Evidently an avoidance of both of these extremes will yield the most satisfactory results. I have found the proportion 10 cc of N/10 KOH to 1 gram of casein to be about the most satisfactory solvent for the casein. Save in the formation of solutions of higher alkalinity than this, therefore, part of the KOH was neutralized until the portion unneutralized stood in this proportion to the mass of casein undergoing solution, the casein was dissolved therein, and then the desired final proportion of KOH to casein was attained by the further addition of HCl. For example, it was desired to obtain a solution of 1 percent casein in 0.005 N KOH. Accordingly to 75 cc

0.1 N KOH were added 50 cc 0.1 N HCl and in this were dissolved 2.5 grams of casein; upon the attainment of complete solution, and while stirring, 12.5 cc of 0.1 N HCl were added and the whole solution was made up to 250 cc with distilled water; another solution was made up in precisely the same way but without the introduction of the casein; the conductivities of both solutions were then determined and their difference ($\equiv \lambda$) estimated.[1] The two solutions were arranged in the gas-chain in the manner described in (*b*) and the potential between the gas-electrodes immersed in them determined. Hence, of course, the OH concentration of the solution not containing casein being known, that of the solution containing casein was determined. The effect of the presence of KCl upon the dissociation of the KOH was, of course, negligible, since the KOH was always very dilute and even the KCl was always sufficiently dilute to be practically completely dissociated.

The extent of the error which is introduced into the determination of η by dissolving the casein in the first instance in a solution of too high alkalinity may be gauged from the following results:

Final solution 3 percent casein in 0.015 N KOH.

Amount of unneutralized KOH employed to dissolve 7.5 grams casein	$\lambda \times 10^6$
100 cc	305.0
75 cc	296.9

I have mentioned that the desired concentration of the KOH unneutralized by HCl in the solutions containing casein was attained by the addition, to the solutions of the casein in excess of KOH, of HCl *while stirring*. This is a matter of some importance. If acid be poured into a solution of a caseinate which is imperfectly mixed, the casein which is

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[1] Since the concentration of KCl was the same in both solutions it would add the same amount to both conductivities and this would disappear in their difference; that is, assuming that the casein does not combine with or decompose the KCl and that the presence of excess of K^+ ions does not depress the dissociation of the potassium caseinate—as will be seen in the sequel no effects which could be attributed to any of these factors could be detected in these experiments.

precipitated in the acid portions of the fluid forms bulky coagula and is only with difficulty redissolved, even if the quantity of alkali still unneutralized by the acid is more than sufficient to hold in solution all of the casein that may be present. Consequently the solution of the caseinate must be rapidly stirred while the acid is being added. The same procedure, of course, considerably enhances the rapidity with which the casein dissolves in the alkali employed for its solution. I invariably placed the mixed fluid and casein in a beaker of squat form and 400 cc capacity—the mixture was then agitated by a flattened glass rod bent at right angles, so that the horizontal arm was about $2^1/_2$ cm long and as near as possible to the bottom of the beaker; this was rotated at the rate of about 1600 revolutions per minute by a small motor. As soon as the casein was completely dissolved the acid was delivered into the solution, a few drops at a time, from a pipette, the opening of which was held *at some depth below the surface of the liquid.* In some of the earlier experiments the acid was poured upon the surface of the solution, but all of these solutions foam to a certain extent and the foam is not agitated by the stirrer with the same rapidity as the fluid which lies below it, consequently, if the acid is poured upon the surface, casein is precipitated within the foam and is only with great difficulty redissolved, hence solutions prepared in this manner yielded very irregular results both in the gas-chain and conductivity determinations. All of the results reported in this paper were obtained with solutions prepared by delivering the acid into the agitated solution from a pipette dipped below the surface of the fluid. In this operation it is very necessary to avoid holding the opening of the pipette too close to the side of the beaker, as in that case a film of casein is precipitated on the glass and this film redissolves with great difficulty.

Since the conductivities of solutions of the caseinates must be determined as soon as possible after the introduction of casein into the solution employed to dissolve it, for otherwise hydrolysis introduces a considerable error, it is evident that as little time as possible must be consumed in bringing the temperature of the solution to that at which its conductivity is to be determined. This could be achieved in either of two ways: Either a small volume of fluid could be employed, so disposed as to take up the temperature of the water bath very quickly. Or the water bath may be maintained at a somewhat higher temperature than that actually desired, and the conductivity of the fluid can be measured at the moment when it reaches the desired temperature. For reasons which will be sufficiently obvious the latter procedure was found to be the more convenient. The water bath was kept at a temperature lying between 31.5° and 32.5°, a preliminary measurement of the conductivity of the solution was made at a temperature between 29° and 29.5° and this preliminary determination was corrected at precisely 30°. In the first series of experiments upon 1 percent casein solutions this precaution was not taken and, consequently, the conductivity determinations were wholly irregular and unreliable. Of this series (cf. Table III), therefore, only the gas-chain determinations are reported.

Solution of 1 percent casein in 0.03 N KOH.

$\lambda \times 10^5$ determined immediately	348.8
$\lambda \times 10^5$ determined after allowing solution to stand at about 30° for 20 minutes	356.3

It is obvious, however, that in this procedure the gas-chain measurements are made at a temperature some 2° higher than the conductivity measurements, and it may be inquired to what extent this invalidates the comparison of the two sets of determinations. The error which is thus introduced, for the small difference of temperature concerned is, however, negligible, since it was found by actual trial that the difference between the potentials measured at 30° and those measured at 34° could barely, with certainty, be detected upon my potentiometer bridge. Nor is this fact surprising for, exclusive of any possible change in the equilibrium between protein and alkali, the potential, according to the Nernst formula, varies directly as the absolute temperature and therefore only increases by 1/300th per degree centigrade at 30°. It has previously been observed by W. A. Osborne[1] and myself[2] that there is no evidence of an appreciable shift in the equilibrium between casein and alkali, as the temperature rises, until the temperature of 36° is reached. This temperature was never approached in these experiments.

I have mentioned, in describing the apparatus employed, that difficulty was encountered in leading off the hydrogen, after it had bubbled through the fluids, through the exit-tubes of the half-element to the outside of the incubator. The difficulty was this—all of the solutions containing casein foam upon passing the hydrogen through them, and to a greater extent the less the excess of alkali in the solutions. This foam, collecting in the exit and connected rubber tubes, gave rise to a pressure which drove the fluid out of the half-element and thus interrupted the continuity of the chain. Accordingly it was found necessary, not only to abandon the idea of conveying the waste hydrogen out of the incubator, but also to cut off short the exit-tube of the half-element and permit the foam to escape freely into the water bath (the lower end of the exit-tube was, of course, well above the surface of the water in the bath). After this plan had been adopted no further trouble was encountered from this source.

All observers who have endeavored to measure the conductivities of solutions containing proteins have encountered the difficulty involved in the precipitation which occurs at the electrodes, particularly, in the case of casein, in neutral or very faintly acid solutions. Whetham and Hardy,[3] in order to minimize the error arising from this source, adopted the plan of heating the electrode, after platinization, to a dull red, thus clumping the platinum black and reducing the total surface of the electrode. I have hitherto tacitly

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[1] W. A. Osborne: Jour. Phys., 27, 398 (1901).

[2] T. Brailsford Robertson: Jour. Biol. Chem., 5, 147 (1908).

[3] W. B. Hardy: Loc. cit.

assumed this phenomenon to be connected in some way with the passage of the alternating current through the solution. In these experiments, however, I speedily found that in neutral or faintly acid solutions of potassium caseinate marked precipitation of casein occurs at the gas-electrode, without the passage of any current, usually after but sometimes even before the passage of the hydrogen. At first I was inclined to attribute this to gases collected, in the interval between experiments, in the tubes conveying the hydrogen, to impurities in the hydrogen, etc.—but after very careful exclusion of all of these possibilities the precipitation still took place, and it occurred to me that it might be due to the hydrogen ions dissolved in the platinum itself. When hydrogen is passed through a platinized platinum electrode, the potential measured across the chain represents, at first, a higher acidity of this electrode than it does later on, when the electrode has come into equilibrium with the solution; in other words, the hydrogen ions dissolved in the platinum have not yet come into equilibrium with those in the solution, an excess of hydrogen ions is still present in the platinum. It therefore appeared possible that this initial acidity of the platinum itself might be responsible for the precipitation of casein at its surface, and this idea found confirmation in the fact that on prolonged passage of hydrogen the film of protein deposited on the electrode slowly redissolved. It occurred to me that it might be possible to avoid this precipitation altogether by bringing the electrode nearly to equilibrium with a low concentration of hydrogen ions before introducing it into the solution at all; accordingly, before making a gas-chain determination with a caseinate solution of very low hydroxyl concentration (neutral or acid to litmus) the electrode which was to be dipped into the protein solution was immersed in distilled water and gas was passed through it for an hour or more—it was then immediately washed in the protein solution and used. The device was found to work excellently, and in all of the experiments described herein precipitation at the electrodes was avoided entirely, at least so far as the eye could perceive. A similar device was found effective in avoiding precipitation at the electrodes of the conductivity-vessel. The vessel was simply filled with distilled water and allowed to stand in the water bath for some hours before making a determination.

In order to ensure a correct determination of the potential of the chain in these experiments it was always found necessary to pass the gas for three hours, taking a reading every hour, generally for four hours and, in the neutral or faintly acid solutions, for as much as six hours. If two successive readings on the bridge, taken an hour apart, did not differ by more than 1 mm the result was considered correct. Difficulty in obtaining constant readings was, of course, only encountered in the chains yielding the highest potentials, in which, as the apparatus was arranged, 1 mm on the bridge-wire made a difference of only about $^1/_2$ percent to the calculated value of the potential. In the chains of low potential greater accuracy was desired, but no difficulty was encountered in attaining it, since in these, successive readings were nearly always identical, or if they were not, the difference could invariably be traced to some obvious source of error which was eliminated in a repetition of the experiment.

Since, however, prolonged exposure of the protein solution in the gas-chain to the temperature of the water bath was essential, the question arises whether the accuracy of the determinations may not have been invalidated by hydrolysis of the casein. The answer to this question is in the negative, the change in the hydroxyl concentration of a protein solution, due to hydrolysis, is negligible in comparison with the change in its conductivity. Moreover it has been shown[1] that the displacement of the neutral point on the potentiometer-wire, due to hydrolysis of the casein in an alkaline solution of a caseinate is opposite in sense to the displacement due to the coming to equilibrium of the electrode with the solution in which it is dipped. Were appreciable change in

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[1] T. Brailsford Robertson and C. L. A. Schmidt: Jour. Biol. Chem., 5, 31 (1908).

hydroxyl concentration due to hydrolysis occurring, therefore, the position of the neutral point on the bridge should indicate at first a diminishing and later increasing potential. No trace of this was discovered save in one or two of the most alkaline solutions (1 percent casein in 0.03 N KOH; 3 percent casein in 0.05 N KOH), in these the displacement due to hydrolysis was never more than 1 mm and the minimum value of the potential was taken as the true one. It is, however, to be recollected that the hydrolysis was probably most rapid in the period of time preceding the attainment of this minimum, so that even the minimum potential may be considerably in error, especially as in the chains containing these solutions the potential was low and 1 mm displacement on the bridge introduced a considerable error into the determination of the potential. This error is diminished in its percentage magnitude in the calculation therefrom of *m*, the amount of alkali neutralized by the protein, but, nevertheless, the determination of *m*, in the solutions mentioned, is not to be considered trustworthy. In the remainder of the solutions no effect upon the hydroxyl concentration of the caseinate solutions, due to hydrolysis, could be discovered; had such an effect been present to any appreciable extent it would, of course, have been detected in these solutions much more readily than in those in which such an effect was detected, since the potentials of the chains containing these solutions were higher, so that a smaller change in hydroxyl concentration of the solution would have produced a greater (absolute) displacement of the neutral point upon the bridge-wire.

In concluding these prefatory remarks, it may be stated that unless all of the precautions which I have described are observed with the utmost fidelity the results of experiments such as these, and conducted in this manner, will be found to be wholly irregular and, save in a qualitative sense, untrustworthy.

II. The Experimental Results

In the following tables, in which the results of these experiments are shown, the symbols employed have the following significance:

$b_1 \equiv$ The concentration of the KOH solution in which casein was dissolved.

$\pi \equiv$ The potential of the chain in volts $= 0.0601 \log_{10} \frac{b_1}{b}$

$b \equiv$ The hydroxyl concentration of the solution containing casein.

$m \equiv b_1 - b \equiv$ the concentration of alkali neutralized by the casein.

$x_1 \equiv$ The conductivity, in reciprocal ohms, of the solution containing no casein.

$x \equiv$ The conductivity, in reciprocal ohms, of the solution containing casein.

$\lambda \equiv x_1 - x \equiv$ the alteration of the conductivity of the alkaline solution which is brought about by the addition of casein.

$r \equiv$ The total concentration of potassium in the solution.

$z = 96.44\ (U + V)\ m - \lambda =$ the conductivity of the KOH *neutralized* by the casein minus the depression in the conductivity of the alkaline solution due to the presence of the casein = the conductivity of the caseinate itself.

$A \equiv \frac{z}{m} =$ the "apparent" equivalent-molecular conductivity of the caseinate.

Referring to equation 1 (vide introduction) it is evident that z is the portion of the conductivity of its solution which is due to the transport of electricity by the ions of the caseinate itself. The ratio z/m, which we have denoted by A, therefore, is the "apparent" equivalent-molecular conductivity of the caseinate, that is, the equivalent-molecular conductivity which it would possess were, in every solution, the sum of the valencies of the positive ions of the caseinate (mutatis mutandis, the negative ions) equal to the number of KOH molecules bound up in one molecule of the caseinate, or, in other words, were the true equivalent-molecular concentration of the caseinate equal to that of the KOH bound up in it. As this supposition is not necessarily correct for the more and is, as we shall see, very improbably correct for the less alkaline solutions, the values of this ratio cannot be regarded as affording the *true* values of the equivalent-molecular conductivities of the caseinates.

The equivalent-molecular conductivities, at 18° of the KOH neutralized by the casein in the various solutions were computed by interpolation from the results cited in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte" (1898), p. 160. These values were then multiplied by 1.235 in order to obtain the molecular conductivities at 30° (cf. Kohlrausch and Holborn, p. 199). In order to avoid ambiguity the entire table of molecular conductivities which was employed is reproduced here (Table I). The values of the *conductivity* of the KOH neutralized by the casein in any given solution was obtained from this table by multiplying the molecular conductivity lying opposite the concentration nearest to that neutralized by the casein by the concentration of KOH which was actually neutralized by the casein.

It must be recollected that in all except the most alkaline solutions the casein was first dissolved in alkali of such concentration that 10 cc 0.1 N KOH = 1 gram casein, and the desired, final ratio of potassium hydrate to casein was procured by the addition of acid. In the above definitions of my notation such phrases as "concentration of the KOH solution in which the casein was dissolved," "conductivity in reciprocal ohms of the solution containing no casein," etc., refer, not to the solution actually employed to dissolve the casein, but to the solution prepared in exactly the same manner as the *final* solution of potassium caseinate, but with the omission of the casein.

The conductivity of the distilled water is not subtracted from the conductivities of the solutions, because it simply adds the same small amount to each of the quantities x_1 and x and this disappears in their difference ($\equiv \lambda$). It was not, however, above 8×10^{-6} reciprocal ohms.

The value of b and therefore of m was estimated from the

Nernst formula, $\pi = \frac{RT}{F\eta} \log_{nat} \frac{C_1}{C_2}$ where R and T are, respectively, the gas-constant and the absolute temperature, η is the valency of the ion (in this instance I) and F the Faraday constant. This yields the formula $\pi = 0.0601 \log_{10} \frac{b_1}{b}$ at 30°, being the potential of the chain in volts, b_1 the known concentration of alkali in which the casein was (finally) dissolved, and b the hydroxyl concentration of the solution of the caseinate.

TABLE I

Molecular conductivities of KOH solutions at 30°. After Kohlrausch and Holborn

Concentration in G-mols per litre	Molecular conductivity in reciprocal ohms per cc per gramme-mol. per litre × 10³	Concentration in G-mols per litre	Molecular conductivity in reciprocal ohms per cc per gramme-mol. per litre × 10³
0.0010	289	0.0250	276
0.0015	288.5	0.0260	276
0.0020	288	0.0270	275
0.0025	287	0.0280	275
0.0030	286.5	0.0290	274
0.0040	285	0.0300	274
0.0050	284	0.0310	274
0.0060	284	0.0320	273.5
0.0070	283	0.0330	273
0.0080	283	0.0340	273
0.0090	282	0.0350	273
0.0100	282	0.0360	273
0.0110	282	0.0370	272.5
0.0120	281	0.0380	272
0.0130	281	0.0390	272
0.0140	280	0.0400	272
0.0150	280	0.0410	272
0.0160	280	0.0420	271.5
0.0170	279	0.0430	271
0.0180	279	0.0440	271
0.0190	278	0.0450	271
0.0200	278	0.0460	271
0.0210	278	0.0470	271
0.0220	277	0.0480	271
0.0230	277	0.0490	271
0.0240	276	0.0500	270.5

TABLE II

Concentration of the casein 0.5 percent

b_1	π	b	m	$x_1 \cdot 10^5$	$x \cdot 10^5$	$\lambda \cdot 10^5$	r	$z \cdot 10^5$	$A \cdot 10^5$	Remarks
0.02000	0.0160	1.083×10^{-2}	0.00917	—	—	—	0.020	—	—	Hydrolysis too rapid to permit the determination of x.
0.01000	0.0462	1.701×10^{-3}	0.00830	410.4	260.5	149.9	0.020	85.0	102.4	
0.00750	0.0708	4.987×10^{-4}	0.00700	379.4	255.9	123.5	0.020	74.6	106.6	
0.00500	0.1181	5.429×10^{-5}	0.00495	350.8	262.6	88.2	0.020	52.4	105.9	
0.00250	0.2600	1.181×10^{-7}	0.00250	320.6	280.0	40.6	0.020	31.2	124.8	
0.00150	0.2710	4.648×10^{-8}	0.00150	310.7	287.4	23.3	0.020	20.0	133.3	

TABLE III

Concentration of the casein 1.0 percent (first series)

b_1	π	b	m	r	Remarks
0.03028	0.0239	1.213×10^{-2}	0.01815	0.03028	
0.02907	0.0273	1.021×10^{-2}	0.01886	0.03028	
0.02422	0.0320	7.111×10^{-3}	0.01711	0.02422	
0.01817	0.0538	2.314×10^{-3}	0.01586	0.01817	
0.01212	0.0937	3.351×10^{-4}	0.01178	0.01817	
0.01091	0.1042	2.015×10^{-4}	0.01071	0.01817	
0.00970	0.1332	5.907×10^{-5}	0.00964	0.01817	
0.00849	0.1736	1.096×10^{-5}	0.00848	0.01817	
0.00728	0.2276	1.191×10^{-6}	0.00728	0.01817	
0.00607	0.2542	3.583×10^{-7}	0.00607	0.01817	
0.00486	0.2758	1.251×10^{-7}	0.00486	0.01817	Av. value of π = 0.2756
0.00486	0.2753	1.276×10^{-7}	0.00486	0.01817	
0.00365	0.3034	3.265×10^{-8}	0.00365	0.01817	
0.00244	0.3130	1.514×10^{-8}	0.00244	0.01817	

TABLE IV

Concentration of the casein 1.0 percent (second series)

b_1	π	b	m	$x_1 \times 10^5$	$x \times 10^5$	$\lambda \times 10^5$	r	$z \times 10^6$	$\Lambda \times 10^3$
0.03000	0.0231	1.237×10^{-2}	0.01763	795.7	446.9	348.8	0.030	143.1	81.2
0.02500	0.0313	7.523×10^{-3}	0.01748	729.1	386.1	343.0	0.030	144.7	82.2
0.02000	0.0471	3.292×10^{-3}	0.01671	669.2	347.1	322.1	0.030	144.1	86.2
0.01750	0.0603	1.736×10^{-3}	0.01576	641.3	341.6	299.7	0.030	141.6	89.9
0.01500	0.0741	8.782×10^{-4}	0.01412	609.8	341.6	268.2	0.030	127.2	90.1
0.01250	0.0954	3.233×10^{-4}	0.01218	580.0	349.9	230.1	0.030	112.2	92.1
0.01000	0.1299	6.892×10^{-5}	0.00993	548.3	361.5	186.8	0.030	93.2	93.9
0.00750	0.2265	1.276×10^{-6}	0.00750	519.9	378.3	141.6	0.030	70.7	94.3
0.00500	0.2596	2.398×10^{-7}	0.00500	488.8	396.7	92.1	0.030	49.9	99.8
0.00250	0.2903	3.699×10^{-8}	0.00250	459.5	415.6	43.9	0.030	27.9	111.6

TABLE V

Concentration of the casein 1.5 percent

b_1	π	b	m	$x_1 \times 10^5$	$x \times 10^5$	$\lambda \times 10^5$	r	$z \times 10^6$	$\Lambda \times 10^3$
0.03000	0.0439	5.578×10^{-3}	0.02442	790.9	314.5	476.4	0.030	197.6	80.9
0.02000	0.0881	6.842×10^{-4}	0.01932	665.8	299.3	366.5	0.030	170.6	88.3
0.01500	0.1280	1.113×10^{-4}	0.01489	604.1	320.6	283.5	0.030	133.4	89.6
0.01000	0.2523	6.337×10^{-7}	0.01000	546.0	357.5	188.5	0.030	93.5	93.5
0.00750	0.2897	1.136×10^{-7}	0.00750	519.9	374.9	145.0	0.030	67.3	89.7
0.00500	0.3128	3.119×10^{-8}	0.00500	488.8	393.4	95.4	0.030	46.6	93.2

TABLE VI

Concentration of the casein 2.0 percent

b_1	π	b	m	$x_1 \times 10^5$	$x \times 10^5$	$\lambda \times 10^5$	r	$z \times 10^5$	$\Lambda \times 10^3$
0.05000	0.0311	1.522×10^{-2}	0.03478	1254.8	593.2	661.6	0.050	287.9	82.8
0.03000	0.0778	1.525×10^{-3}	0.02847	781.4	242.1	539.3	0.030	243.6	85.6
0.02000	0.1343	1.167×10^{-4}	0.01988	790.9	410.4	380.5	0.040	172.2	81.6
0.01500	0.2425	1.383×10^{-6}	0.01500	733.1	446.9	286.2	0.040	133.8	89.2
0.01000	0.3000	1.020×10^{-7}	0.01000	676.2	486.9	189.3	0.040	92.7	92.7
0.00500	0.3152	2.846×10^{-8}	0.00500	615.6	519.9	95.7	0.040	46.3	92.6

TABLE VII

Concentration of the casein 3.0 percent

b_1	π	b	m	$x_1 \times 10^5$	$x \times 10^5$	$\lambda \times 10^5$	r	$z \times 10^5$	$\Lambda \times 10^3$	Remarks
0.05000	0.0733	3.011×10^{-3}	0.04699	1254.8	381.6	873.2	0.050	401.3	85.33	Average value of m 0.04703
0.05000	0.0739	2.943×10^{-3}	0.04706	—	—	—	0.050			
0.03000	0.1438	1.217×10^{-4}	0.02988	912.6	332.9	579.7	0.040	239.0	67.30	
0.02500	0.2343	3.156×10^{-6}	0.02500	858.6	369.7	488.9	0.040	201.1	80.4	
0.02000	0.2823	4.017×10^{-7}	0.02000	795.7	404.0	391.7	0.040	164.3	82.2	
0.01500	0.3172	7.920×10^{-8}	0.01500	741.5	444.6	296.9	0.040	123.1	82.1	
0.01000	0.3413	2.096×10^{-8}	0.01000	686.8	480.2	206.6	0.040	75.4	75.4	

It will be observed that the "apparent" equivalent-molecular conductivity of the caseinate increases somewhat rapidly (cf. the increase in the equivalent-molecular conductivity of KOH as its concentration diminishes, in Table I) as the combining-capacity of the casein decreases.

Regarding the probable accuracy, unavoidable hydrolysis, etc., apart, of the above determination, the following may be said: In the determination of the potentials of the chains, an error of 1 mm in the determination of the position of the neutral point upon the bridge would result, under the experimental conditions employed, in an error of 0.0015 in the value of π. This error, as a simple calculation serves to show, would lead to an error of 6 percent in the determination of the ratio $\frac{b_1}{b}$. Since the value of b_1 was much more accurately defined than this, we may assume that an error of 1 mm in the determination of the neutral point on the bridge-wire would lead to an error of 6 percent in the estimated value of b. The actual error, due to error in the determination of the position of the neutral point upon the bridge-wire, was certainly not more than half this in the more alkaline solutions, but was possibly two or three times this in the least alkaline solutions. Since b was always less than m, however, and usually very much less, the error in m, arising from this source, may for all practical purposes, be neglected save in one or two of the most alkaline solutions, in which it might possibly amount to 3 percent. The resistance of the conductivity-vessel filled with solution was always determined to within 0.1 of an ohm. The specific resistance-capacity of the vessel employed was 0.1305. A simple calculation shows that an error of 0.1 ohm in the determination of the resistance of the conductivity-vessel filled with fluid would lead to an error of $\frac{x^2}{1.305 + x}$ in the determination of x; since x is always negligible in comparison with 1.305, we may write this $\frac{x^2}{1.305}$, the corresponding error in the determination of

x_1 being, of course, $\frac{x_1^2}{1.305}$. The possible error in the determination of λ will, of course, be the sum of the errors in x_1 and x, that is, $\frac{x^2 + x_1^2}{1.305}$. Thus, in the first experiment cited in Table IV ($b_1 = 0.030$, percent of casein = 1.0) the possible error in the determination of x_1 is 4.87×10^{-5} and in the determination of x is 1.54×10^{-5}, hence the possible error in the determination of λ is 6.4×10^{-5}, or 1.8 percent of its value. In the last experiment cited in Table IV ($b_1 = 0.00250$, percent of casein = 1) the possible error in the determination of x_1 is 1.63×10^{-5}, and in the determination of x it is 1.33×10^{-5}, hence the possible error in the determination of λ is 3.0×10^{-5}, or 6.8 percent of its value. The actual error, due to instrumental sources, was probably not more than half this. Tables of the possible errors in the values of λ, calculated in the above manner, will be found in the theoretical part of the paper.

Theoretical

(1) The Dissociation of Potassium Caseinate Is Not Appreciably Affected by the Presence, in Its Solution, of KCl

As I have already mentioned, in passing, the presence of KCl might be expected to alter the depression of the conductivity of a solution of KOH, which is brought about by the addition of casein, in either of the three following ways:

(*a*) Through decomposition of the KCl by the casein with the liberation of HCl and the binding of potassium. As might be anticipated, under the conditions of the investigation, no evidence of the occurrence of such a reaction was obtained.

(*b*) Through direct combination of the casein with the entire KCl molecule. From the results of Bugarszky and Liebermann[1] and of Hardy[2] it would appear evident that such combination, at such low concentrations of KCl as those employed in these experiments, could only occur to an im-

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[1] Bugarszky and Liebermann: Arch. ges. Physiol., 72, 51 (1898).

[2] W. B. Hardy: Loc. cit.

measurably small extent, and, in fact, as we shall very shortly see, no evidence of the occurrence of such combination was obtained.

(*c*) Through depression of the dissociation of the potassium caseinate owing to the presence of excess of potassium ions. That the value of λ might be affected in this manner by the presence of the KCl appeared very likely, and was fully anticipated when this investigation was undertaken. That it nevertheless does not occur in any appreciable degree is clearly revealed by the following facts:

Two and a half grammes of casein were dissolved in solutions containing varying amounts of KOH of which, in each instance, so much was neutralized by 0.1 N HCl as to leave the equivalent of 25 cc of 0.1 N KOH unneutralized by the acid. These solutions were then each diluted to 250 cc, so that the final solutions consisted of 1 percent casein dissolved in 0.01 N KOH plus varying amounts of KCl. The conductivities of these solutions (at 30°) were then determined, and also the conductivities of solutions similarly made up without the introduction of casein, and from these the values of λ were computed. The capacity of the resistance-vessel employed was 0.1251, so that the possible error in the determination of λ, due to instrumental sources alone, was:

$$\pm \frac{x_1^2 + x^2}{1.251}$$

In the following table are given the results of these experiments. In the first column are given the concentrations of KCl in the solutions, in the second the conductivity, in reciprocal ohms, of the solution containing no casein ($\equiv x_1$), in the third the conductivity, in reciprocal ohms, of the solution containing casein ($\equiv x$), in the fourth the value of λ ($\equiv x_1 - x$), in the fifth the deviation of λ from its average value ($\equiv \Delta$), in the sixth the possible (instrumental) error in the determination of λ ($\equiv \varepsilon$).

It is evident that the values of — thus obtained were appreciably constant, the deviation (Δ) from the average

TABLE VIII

Concentration of KCl	x_1	x	λ	Δ	ϵ
0.00 N	277.4×10^{-5}	81.2×10^{-5}	196.2×10^{-5}	0.5×10^{-5}	0.7×10^{-5}
0.01 N	417.0×10^{-5}	222.6×10^{-5}	194.4×10^{-5}	1.3×10^{-5}	1.8×10^{-5}
0.02 N	548.7×10^{-5}	360.5×10^{-5}	188.2×10^{-5}	7.5×10^{-5}	3.4×10^{-5}
0.03 N	698.4×10^{-5}	494.5×10^{-5}	203.9×10^{-5}	8.2×10^{-5}	5.9×10^{-5}
		Av.	195.7×10^{-5}		

being less or only very slightly greater than the purely metrical error of the determination. I refrain from describing in detail a number of similar experiments which yielded similar results. It will be recollected (Eqn. 1, Introduction) that λ represents the molecular conductivity of the neutralized base plus the share taken by the ions of the caseinate in transporting electricity through its solution. Since in these solutions the KOH was nearly completely neutralized, and the excessively minute concentration of free KOH which was present must have been, in all of the solutions, completely ionized, it is evident that the influence, if any, of increasing the *total* concentration of potassium in the solutions from 0.01 N to 0.04 N upon the dissociation of the potassium caseinate could not have been greater than 5 percent. Now even assuming that an increase in the potassium-concentration of the solutions from 0.01 N to 0.04 N only multiplied the concentration of potassium *ions* four times (which is, of course, probably a gross understatement of the case) then, calling A the concentration of protein-ions in the solution containing 0.01 N potassium, K the dissociation-constant of the potassium caseinate, and X the concentration of the undissociated caseinate, and assuming that the caseinate dissociates into one potassium and one casein ion, we have, for the solution containing 0.01 N potassium:

$$0.01 \times A = KX$$

and for the solution containing 0.04 N potassium:

$$0.04\left(A - \frac{A}{20}\right) = K\left(X + \frac{A}{20}\right)$$

whence $A = 56X$, or the caseinate must, in the first solution, have been $\frac{56}{57}$ths dissociated. If we suppose that the caseinate splits off two or more potassium ions, then the first solution must have been still more highly dissociated. If we assume that only one potassium ion is split off but two or more casein ions, then the degree of dissociation of the first solution would be about $\frac{52}{53}$rds for two casein ions, $\frac{48}{49}$ths for three ions and so forth. Hence, if we assume that the potassium caseinate splits off potassium ions we are forced to the conclusion that it is, at the concentrations employed in this investigation, very completely dissociated. Since, as we shall see, the very definite relation which subsists between λ and the alkalinity of the solution to which the casein was added *is independent of the concentration of KCl in the solutions*, this conclusion applies to all of the solutions dealt with in this investigation. Nor, at first sight, does this conclusion appear to be inconsistent with the physical magnitude of the conductivities observed in these solutions. The velocity of the potassium ion at 18° and 0.01 N concentration is about 61×10^{-5} cm-sec-under 1 volt per cm potential gradient. Assuming that the velocity of the casein ion is about 15×10^{-5} in the same units,[1] the equivalent-molecular conductivity of the potassium caseinate, if it were completely dissociated, would be $\frac{(61 + 15) \times 10^{-5}}{1.037 \times 10^{-2}} = 73.1 \times 10^{-3}$, which, allowing for the difference in the temperatures at which the two estimates are made, approximates very closely to that actually observed (cf. Table IV).

A closer examination of our data, however, reveals a number of facts which are inconsistent with the view that

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[1] Since the velocities of very large ions tend to approach this limit (Bredig: Zeit. phys. Chem., 13, 191 (1894); cf. also W. B. Hardy: Loc. cit., on the velocity of the serum-globulin ion.

potassium caseinate dissociates, in the solution under consideration, practically completely into potassium and casein ions. The value which we have calculated of the theoretical equivalent-molecular conductivity of potassium caseinate upon the supposition that it splits into potassium and casein ions (about 90×10^{-3} at 30° [1]) is the *maximum* value which it could attain at any concentration or combining-capacity of the casein; for in obtaining it we assumed that the caseinate was *completely* dissociated, and the velocity of the casein ion at 18° cannot well be appreciably greater than 15×10^{-5} cm-sec. That is, upon this supposition, it is very improbable that the equivalent-molecular conductivity of a potassium caseinate solution at 30° could ever exceed 90×10^{-5}. Now, as we have seen, the "apparent" equivalent-molecular conductivities of the potassium caseinate solutions, which are given in the tables in the experimental part of the paper, in many cases considerably exceed 90×10^{-3}, reaching, indeed, in solutions in which the combining-capacity of the casein is low, as high a magnitude as 120×10^{-5}, while, as we shall see, extrapolating from the experimental results, it is very probable that could solutions in which casein possesses a still lower combining capacity have been conveniently worked with much higher "apparent" equivalent-molecular conductivities than these would have been observed. This being the case, then potassium caseinate in 1 percent solution in 0.01 N KOH cannot be nearly so highly dissociated as we have concluded it must be ($\frac{56}{57}$ths) on the supposition that it dissociates into potassium and protein ions, for, in that case, its equivalent-molecular conductivity on approaching "saturation" of the alkali, could only increase by 1/57th and, as we have seen, it increases much more than this.

The only hypothesis which would appear to satisfactorily

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[1] I may mention in passing that although I have not made any endeavor to measure it accurately, I have observed that the temperature-coefficient of the conductivity of caseinate solutions is of the normal order of magnitude, that is, the conductivity increases about 2 percent per degree rise in temperature.

reconcile these facts and at the same time harmonize with other features of the behavior of casein and of the proteins in general is that *in its solution in water potassium caseinate does not yield potassium ions, but dissociates into complex ions in which the casein is bound up in a non-dissociable form*—upon which supposition, of course, the presence of KCl might be expected to exert little or no influence upon the dissociation of the caseinate. In this connection it is of interest to note that Bugarszky and Liebermann,[1] by direct measurement with concentration-cells, showed that the depression in the Cl^- ion concentration of an HCl solution, due to the addition of proteins, is almost exactly equal to the depression of the H^+ ion concentration, which would appear to indicate that in the HCl-salts of proteins the Cl^- ion is bound up in a complex ion (since the salts which are formed are presumably, judging by the analogy afforded by casein, quite extensively dissociated). I have pointed out, also, in a previous communication,[2] that although solutions of "neutral" ammonium caseinate obey Ostwald's dilution-formula for a binary electrolyte, yet the sum of the velocities of the two ions into which this salt presumably dissociates, computed by interpolation from the formula, is less than that of the ammonium ion itself, and I have suggested that this phenomenon is due to the formation of complex ions in which the ammonium is bound up in a non-dissociable form.

It is to be noted, however, that should the above assumption turn out to be correct, then *the sum of the valencies of the positive ions which the caseinate yields upon dissociation cannot be equal to or less, but must be greater than the number of KOH molecules bound up in one molecule of caseinate*—for otherwise the apparent equivalent-molecular conductivities given in the tables in the experimental part of the paper would be equal to or less than the true equivalent-molecular conductivities. But the true equivalent-molecular conductivity at 18°, upon the supposition that the caseinate splits

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[1] Loc cit.

[2] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907).

up only into protein ions, cannot well be greater than $\frac{(15 + 15) \times 10^{-5}}{1.037 \times 10^{-2}}$ = about 30×10^{-3}, and at 30° it cannot be much in excess of 40×10^{-3}. In other words, what the ions of the caseinate lose, upon this supposition, in migration-velocity they must gain or more than gain in the number of atomic charges which they transport, for otherwise the observed conductivities could not be attained.

(ii) The Combining Capacity of Casein

A number of investigators have shown,[1] by direct titration to neutrality to litmus, that the combining capacity of casein, at absolute neutrality, is constant, that is, is independent of the total concentration of the system. The potentiometric determinations, cited in the above tables, enable us to confirm these observations. It will be recollected that the OH^- concentration in the solutions containing casein was determined by measuring the potential between two hydrogen electrodes, the one dipped in the solution containing a given concentration of casein, the other in an exactly similar solution to which no casein had been added. Plotting a curve in which the reaction of the solutions containing no casein form the abscissae and the potentials between the two solutions the ordinates, the reaction ($= x$) of the solution to which the given concentration of casein had to be added in order to procure an exactly neutral solution is given by the intersection of this curve with the curve defined by the formula: $y = 0.4107 - 0.0601 \log_{10} x^2$.

The points of intersection of these curves were found in the following way: the values of y in the above curve corresponding to x (alkalinity of solution in which casein was dissolved) = 0.0025, 0.005, 0.0075, 0.010, 0.015 and 0.020 were computed and these points were marked upon 10 × 10 standard

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[1] Soldner: Landw. Versuchs., **35**, 351 (1888). Lacqueur and Sackur: Beitr. chem. Physiol. und Pathol., **3**, 196 (1903). Van Slyke and Hart: Am. Chem. Jour., **33**, 461 (1905).

[2] Taking the H^+ concentration at absolute neutrality at 30° as 1.47×10^{-7}; cf. Kohlrausch and Heydweiller: Wied. Ann., **53**, 209 (1894).

cross-section paper and joined by straight lines. Experimental values of π lying upon each side of its value at neutrality, in each solution, were then also marked off upon the paper and joined by straight lines. The abscissae of the point of intersection of the two straight lines yielded the number of gramme-equivalents of KOH which were bound by the given percentage of casein in the production of an absolutely neutral solution.[1] Dividing the number of gramme-equivalents of KOH neutralized by the casein by the percentage concentration of the casein we obtain the number of gramme-equivalents of KOH neutralized by 1 gramme of casein at absolute neutrality. The following are the results:

Concentration of casein per cent	Gramme-equivalents KOH neutralized by 1 gramme of casein at absolute neutrality at 30°
0.5	52×10^{-5}
1.0 (First series)	50×10^{-5}
1.0 (Second series)	43×10^{-5}
1.5	53×10^{-5}
2.0	54×10^{-5}
3.0	56×10^{-5}
	Av. 51×10^{-5}

The values of the combining-capacities of the casein at neutrality to litmus computed in this manner are seen to be appreciably constant, especially when it is recollected that in solutions so nearly neutral the possible error in the estimation of π is somewhat large (cf. discussion of the experimental errors at the end of the experimental section). The average value is 51×10^{-5} equivalent-gramme-molecules per gramme of casein, which is in excellent agreement with that obtained

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[1] At first it was thought necessary to pass the curve $y = ax^3 + bx^2 + cx + d$ through four of the points of the experimental curve $\pi = f(b_1)$ and to determine algebraically the point of intersection of this curve with the curve $y = 0.4107 - 0.0601 \log_{10}x$; this was, however, found to be an unnecessary refinement, as the results obtained did not differ appreciably from those obtained by the above, simpler, method.

by titration (50×10^{-5} equivalent-gramme-molecules per gramme).

The *maximum* combining capacity of casein, in the presence of considerable excess of alkali, is seen to be surprisingly large— in the neighborhood of 180×10^{-5} equivalent-gramme-molecules per gramme. Were only one —COOH group of the casein molecule concerned, in these solutions, in the neutralization of alkali, the molecular weight of casein would be only 556 which is, of course, having regard to the number of amino-acid groups which must be linked together in the casein molecule, an impossibly low value. Hence, in the presence of excess of alkali, casein must behave as a pluribasic acid.

In this connection it is of interest to refer to the results of Spiro and Pemsel.[1] These observers dissolved casein in excess of alkali, obtaining solutions which, in the light of the results which I have described, must have contained a considerable excess of unneutralized alkali. They then precipitated the caseinate (as they thought, unaltered) by an excess of ammonium sulphate. The precipitate was then filtered off and washed and the quantity of alkali which had been carried down by the casein was determined by titration of the filtrate. The following were their results:

Solution	Mg of NaOH bound by one gramme of casein	Gramme-equivalents of NaOH bound by 1 gramme of casein
1.14 grams casein in 10 cc N/5 NaOH	26.1	65×10^{-5}
1.41 grams casein in 10 cc N/5 NaOH	29.2	73×10^{-5}
1.24 grams casein in 10 cc N/5 NaOH	33.1	82×10^{-5}
1.31 grams casein in 10 cc N/5 NaOH	34.3	86×10^{-5}

Since in all of these solutions the amount of alkali which was actually bound by 1 gram of casein *while* in solution must have been at least 160×10^{-5} gramme equivalents, it is clear that *ammonium sulphate does not precipitate the caseinates*

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[1] Spiro and Pemsel: Zeit. phys. Chem., 26, 233 (1898–9).

in an unaltered condition. The amount of alkali actually carried down by the casein was approximately that which it binds at neutrality to phenolphthalein.

We thus see that while in the presence of excess of alkali 1 gramme of casein will bind about 180×10^{-5} equivalent-gramme-molecules of KOH, in solutions which are neutral to litmus it will only bind 50×10^{-5} equivalent-gramme-molecules of KOH, while, as I have previously shown, in solutions which are "saturated" with casein, that is, solutions which contain only just sufficient alkali to hold the casein in solution, 1 gramme of casein will only bind 11.4×10^{-5} equivalent-gramme-molecules of KOH. This remarkable change in combining-capacity with decreasing alkalinity could only, *since free casein, uncombined with acid or alkali, is insoluble in water,* be achieved in one or both of two ways, namely, (*i*) by a decrease in the number of —COOH groups which are concerned in the neutralization of the KOH as "saturation" is approached and (*ii*) by polymerization of the protein through a series of reactions of the type

$$\mathrm{HXOH} + \mathrm{HXOH} \longrightarrow \mathrm{HXXOH} + \mathrm{H_2O},$$

so that as "saturation" is more and more nearly approached the molecules of casein become heavier and heavier, so that 1 gram of casein necessarily binds less KOH than it could at reactions more distant from that at "saturation."

The relation between m, the amount of alkali neutralized by the casein, and b_1, the alkalinity of the solution in which the casein was dissolved, is shown graphically, for all of the concentrations of casein employed, in Fig. 2. It will be understood, of course, that the curves only represent this relation for alkalinities of the original solution in excess of that necessary to dissolve all of the casein. For an ordinary acid, forming only one salt with the base, which did not undergo hydrolytic dissociation, the curve would, of course, be a straight line parallel with the axis of x. It will be seen that as the proportion of base to casein declines, the combining capacity of the casein tends to become directly proportional to the concentration of the base, but that as the proportion of base to casein (and the excess of unneutralized base) becomes large, the combining capacity of the casein tends towards constancy, *i. e.*, in comparatively strongly alkaline solutions the behavior of casein approximates more and more to that of an ordinary acid.

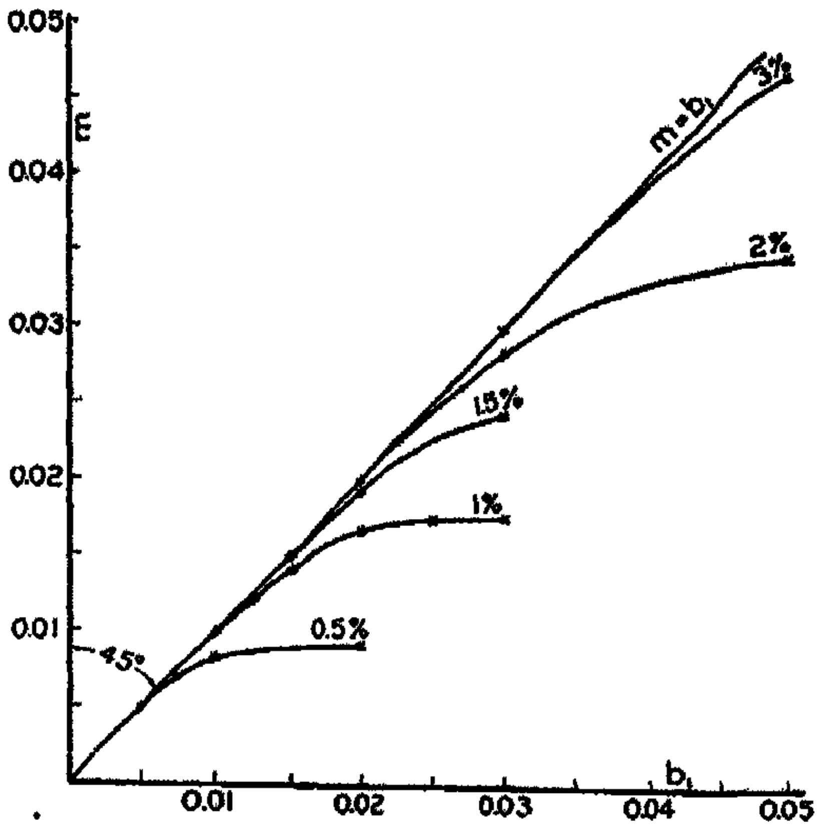

Fig. 2

The ordinates = m = the concentration of KOH neutralized by 0.5%, 1%, 1.5%, 2.0% and 3% casein.
The abscissae = b_1 = the concentration of the KOH solution in which the casein was dissolved.

(iii) The Relation between λ and b₁

An inspection of the tables in the experimental part of the paper reveals a remarkably simple relation between the alkalinity of a solution of KOH and the depression of its conductivity which results from the addition to it of a given amount of casein. This relation is of the form

$$\lambda \times 10^6 = Ab_1 - Bb_1^2 - D,$$

where A, B and D are constants for a given concentration of casein.

Applying this formula to the results cited in Table IV and determining the constants A, B and D from all of the experimental data by the method of least squares, we find:

$$\lambda \times 10^5 = 26880\, b_1 - 475800\, b_1^2 - 28.98$$

In the accompanying table the experimental values of $\lambda \times 10^5$ for 1 percent solutions of casein in KOH of various concentrations ($\equiv b_1$) and those calculated from the above formula are compared. In the first column are given the alkalinities of the solutions to which the casein was added ($\equiv b_1$), in the second are given the values of $\lambda \times 10^5$ experimentally ascertained, in the third the calculated values of $\lambda \times 10^5$, in the fourth the difference ($\equiv \Delta$) between the experimental and the calculated values of $\lambda \times 10^5$, and in the fifth the possible metrical error ($\equiv \varepsilon$) in the experimental determination of $\lambda \times 10^5$.

TABLE IX

b_1	$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Calculated	Δ	ε
0.03000	348.8	349.3	+0.5	±8.0
0.02500	343.0	345.6	+2.6	±6.5
0.02000	322.1	318.3	—3.8	±5.5
0.01750	299.7	295.9	—3.8	±5.1
0.01500	268.2	267.2	—1.0	±4.7
0.01250	230.1	232.8	+2.7	±4.4
0.01000	186.8	192.3	+5.5	±4.1
0.00750	141.6	145.8	+4.2	±4.0
0.00500	92.1	93.5	+1.4	±3.8
0.00250	43.9	35.4	—8.5	±3.7
			$\Sigma\Delta = -0.2$	

It will be seen that the deviation of the calculated from the experimental values of $\lambda \times 10^5$ are nearly always less than the possible error, due to instrumental sources alone, in the experimental determination of $\lambda \times 10^5$, while the algebraic sum of these deviations is negligible. The formula therefore represents, in a highly satisfactory manner, the relation between b_1 and λ for 1 percent solutions of casein in KOH-solutions.

A further inspection of the tables in the experimental part of the paper reveals the fact that the relation between λ and b_1 for *all* of the concentrations of casein investigated can be represented by the more general formula:

$$\lambda \times 10^5 = \alpha b_1 - \frac{\beta}{C} b_1^2 - \gamma C \qquad (2)$$

where C is the percentage concentration of casein and α, β and γ are constants, the values of which we have already determined for 1 percent casein. For a 0.5 percent solution of casein this equation, therefore, becomes:

$$\lambda \times 10^5 = 26880\, b_1 - 951600\, b_1^2 - 14.49$$

in the following table the experimental and calculated values of $\lambda \times 10^5$ are compared—the symbols have the same meaning as in Table IX.

TABLE X

b_1	$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Calculated	Δ	ϵ
0.01000	149.9	159.2	+ 9.3	±2.3
0.00750	123.5	133.6	+10.1	±2.0
0.00500	88.2	96.1	+ 7.9	±1.8
0.00250	40.6	37.6	— 3.0	±1.8
0.00150	23.3	24.2	+ 0.9	±1.8

For a 1.5 percent solution of casein equation (2) becomes:

$$\lambda \times 10^5 = 26880\, b_1 - 317200\, b_1^2 - 43.47$$

in the following table the experimental and calculated values of $\lambda \times 10^5$ are compared:

TABLE XI

b_1	$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Calculated	Δ	ϵ
0.03000	476.4	477.5	+ 1.1	±7.0
0.02000	366.5	367.3	+ 0.8	±5.1
0.01500	283.5	288.4	+ 4.9	±4.5
0.01000	188.5	193.6	+ 5.1	±4.1
0.00750	145.0	140.4	— 4.6	±3.9
0.00500	95.4	83.0	—12.4	±3.8

For a 2 percent solution of casein equation (2) becomes:

$$\lambda \times 10^5 = 26880\,b_1 - 237900\,b_1^2 - 57.96$$

in the following table the experimental and calculated values of $\lambda \times 10^5$ are compared:

TABLE XII

b_1	$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Calculated	Δ	ϵ
0.05000	661.6	691.4	+29.8	±18.5
0.03000	539.3	534.4	− 4.9	±11.5
0.02000	380.5	384.5	+ 4.0	± 7.6
0.01500	286.2	291.7	+ 5.5	± 7.1
0.01000	189.3	187.1	− 2.2	± 6.7
0.00500	95.7	70.5	−25.2	± 6.2

For a 3 percent solution of casein equation (3) becomes:

$$\lambda \times 10^5 = 26880\,b_1 - 158600\,b_1^2 - 86.94$$

in the following table the experimental and calculated values of $\lambda \times 10^5$ are compared:

TABLE XIII

b_1	$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Calculated	Δ	ϵ
0.05000	873.2	860.7	−12.5	±16.4
0.03000	579.7	576.8	− 2.9	± 9.0
0.02500	488.9	486.0	− 2.9	± 8.4
0.02000	391.7	387.3	− 4.4	± 7.6
0.01500	296.9	280.6	−16.3	± 7.2
0.01000	206.6	166.1	−40.5	± 6.8

(iv) The "Apparent" Equivalent-molecular Conductivity of Potassium Caseinate at "Saturation"

We have seen that the relation between λ, b_1 and the concentration of casein ($\equiv$ C) is very accurately represented by the formula:

$$\lambda \times 10^5 = \alpha b_1 - \frac{\beta}{C} b_1^2 - \gamma C$$

Putting, in this equation, $\lambda \times 10^5$ equal to zero we find.

b_1 = 0.00114 C or 0.05536 C. Considering, for the present, only the smaller value of b_1, we see that when λ = 0, that is, when the change in the conductivity of an alkaline solution which is brought about by dissolving a given percentage of casein therein is zero, then the proportion of alkali to casein is such that 1 gram of casein is combined with 11.4×10^6 equivalent-gramme-molecules of alkali. *This is precisely the combining-capacity of casein at "saturation" of the base with casein, that is, when the base has dissolved the maximum amount of casein which it will dissolve.* The exact coincidence of the two numerical values, especially when we consider that the above is computed by least squares from a large number of determinations which are apparently not connected with estimates of the *solubility* of casein, is surprising, and leaves no room for question that the magnitude of the two quantities is determined by identical factors. This result is probably to be interpreted as follows: in order that λ may be negative it will be seen, referring to equation 1 in the introduction, that the amount of electricity transported by the ions of the caseinate through 1 cm in 1 sec under a potential gradient of 1 volt per cm must be greater than that which would be transported, under the same conditions, by the KOH which is neutralized in the formation of the caseinate. It is hardly to be considered possible that this could be accomplished unless free protein, uncombined with KOH, were present in the solution. But free casein is, as is well known, insoluble in water. Hence the point at which λ changes from positive to negative (*i. e.* = 0) marks the point at which further casein cannot go into solution, and the above data may be regarded as affording confirmation of my previous estimate of the alkali-equivalent of casein at "saturation," namely, 11.4×10^{-5} equivalent-gramme-molecules per gramme.[1] Conversely, however, we cannot escape the conclusion that the conductivity (and, of course, the "apparent" equivalent-molecular conductivity) of a solution of caseinate in which

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 13, 469 (1909).

the proportion of casein to base is 1 gramme to 11.4×10^{-5} equivalent-gramme-molecules is equal to that of the KOH neutralized by it, that is, at 30°, to about 280×10^{-3}. But, as we have seen, the true equivalent-molecular conductivity of a solution of potassium caseinate, assuming that it dissociates into potassium and casein ions, could not exceed 90×10^{-3} at 30°. The only mechanism, it would appear, by which so high a conductivity of its solution could be attained is that of dissociation of the caseinate into *two or more polyvalent protein ions*. We cannot, I think, on reviewing the evidence contained in the lack of influence of KCl upon the conductivity of solutions of potassium caseinate, in my previous observation that the sum of the velocities of the ions into which ammonium caseinate dissociates is less than that of the ammonium ion itself, in the high conductivity of solutions of the caseinates which approach "saturation," and in the light of the analogy afforded by the behavior of the salts of the proteins with HCl (cf. the results of Bugarszky and Liebermann, cited above) avoid the conclusion that *potassium caseinate does not dissociate potassium ions as such but that the potassium is bound up in complex, probably polyvalent ions.*

In the light of this conclusion, the rapid increase in the "apparent" equivalent-molecular conductivity of the caseinate as "saturation" of the base is approached finds a simple explanation in the supposition that as the combining capacity of casein diminishes its degree of polymerization increases and, consequently, the number of terminal $-COO^-$ and $-NH_3^+$ groups which may be furnished by 1 molecule is proportionately increased, so that the valencies of the ions into which the salt dissociates also increase. On the assumption, also, that only two such ions are split off by the "neutral" and "basic" caseinates, respectively, my previous results, showing that the Ostwald dilution-law for a binary electrolyte holds good for these solutions are readily understood.

The fact that λ is again zero at high values of b_1 (= 0.05536 C, cf. above) is probably to be interpreted simply as meaning that the addition of a given amount of casein to a solution containing a great excess of alkali does not appreciably affect its conductivity. It is to be observed, however, that this portion of the $\lambda - b_1$ curve was never actually approached in these experiments (since the error in the determination of λ at such high alkalinities is so great as to render the determination of very little value), so that any conclusions concerning it must rest upon a very extended and probably unjustifiable extrapolation from the experimental data.

Conclusions

(1) The "apparent" equivalent-molecular conductivity of potassium caseinate in aqueous solution, that is, the equivalent-molecular conductivity calculated on the assumption that the equivalent-molecular concentration of the caseinate is equal to that of the KOH bound by it, rises somewhat rapidly as the combining capacity of the casein and the alkalinity of its solution decrease.

(2) The numerical value of the "apparent" equivalent-molecular conductivity of potassium caseinate at 30° rises from 80×10^{-5} reciprocal ohms per cc per equivalent-gramme-molecule per liter in solutions containing excess of alkali to that of KOH itself, the latter being determined by extrapolation from the actual observations

(3) The presence of KCl, in the concentrations employed, is without appreciable effect upon the dissociation of potassium caseinate in the solutions investigated.

(4) It is suggested, in explanation of these and previous results, that potassium caseinate does not, when in solution, split off potassium ions, but dissociates into complex polyvalent ions containing the potassium bound up in a non-dissociable form, the sum of the valencies of the positive (or of the negative) ions of the caseinate being greater than the number of molecules of KOH bound up in 1 molecule of caseinate.

(5) The combining capacity of casein (determined by gas-chain measurements) tends to become proportional to the concentration of the alkali in which it is dissolved, at low

alkalinities, but at high alkalinities it tends to approach a constant maximum value.

(6) The maximum value of the combining capacity of casein is about 180 × 10^{-5} equivalent-gramme-molecules per gram.

(7) It is pointed out that ammonium sulphate does not precipitate the caseinates of the alkalies in an unaltered condition.

(8) The combining capacity of casein at neutrality to litmus (*i. e.*, at absolute neutrality) was found to be independent of the total concentration of the system and its average value (6 determinations) was found to be 51 × 10^{-5} equivalent-gramme-molecules per gramme. This agrees well with the value which other observers have found by titration (50 × 10^{-5}).

(9) The depression in the conductivity of a solution of KOH (at 30°) ($\equiv \lambda$) which is brought about by the introduction of a given percentage of casein ($\equiv$ C) is connected with its alkalinity ($\equiv b_1$) by the equation:

$$\lambda \times 10^5 = 2680\, b_1 \quad \frac{475800}{C} b_1^2 - 28.98\, C$$

(10) The depression in the conductivity of a solution of KOH which is brought about by the introduction of a given percentage of casein in zero when the solution contains just sufficient KOH (11.4 × 10^{-5} equivalent-gramme-molecules per gramme) to hold the casein in solution.

THE CONDENSATION OF WATER BY ELECTROLYTES. A CORRECTION

BY F. K. CAMERON AND W. O. ROBINSON

In the January number of this Journal, we published an article under the above title, in which were tabulated the condensations produced in water by some electrolytes together with certain related data. These data were calculated from the density measurements of the solutions and solutes by means of a formula we proposed and by making the explicit assumption that the change in density of the solute was negligible as compared with the change in density of the water, for dilute solutions, that is for N/10 or less concentrated solutions. In how far this assumption is valid, we have no means of determining at the present time. But if the figures in the last column of the table are to be regarded as indicating an actual "hydration" of the solute, it seems altogether improbable that the density of the dissolved solute is the same as for the undissolved state; consequently the fundamental assumption is wrong and the calculations meaningless. The data obtained justified no important general conclusions. The formula used was

$$C = D - s - \left(1 - \frac{s}{d}\right)$$

where C is the concentration to be measured, D the density of the solution, *s* the weight of solute present and *d* the density of the solute.

For a greater part of the tabulated material in the paper the calculations were made incorrectly. To Dr. Samuel C. Lind we are indebted for calling our attention to this and for affording us an opportunity to correct the errors ourselves. Dr. Lind was at the pains to recalculate all the data. Unfortunately, we have found that some of the densities were also given incorrectly, and it has been deemed necessary to again recalculate all the data for this correction instead of giving Dr. Lind's figures. Under the circumstances

Solute, reacting weight and density	Concentration	Density of solution, 25°/25° D/1000	Grams solute per litre s	Volume of solute s/d	Grams water condensed per litre C	Grams water condensed per gram solute	Ratio of mols water condensed to mols solute
H_2SO_4	N/10	1.003420	4.9043	2.666	1.182	0.241	1.22
R. W. = 49.043. d = 1.84,	N/25	1.001411	1.9617	1.066	0.515	0.263	1.43
Landolt u. Börnstein, 3 Auf.,	N/50	1.000726	0.9808	0.533	0.278	0.283	1.54
245.	N/100	1.000396	0.4904	0.267	0.173	0.353	1.92
	N/200	1.000210	0.2452	0.133	0.098	0.400	2.17
HCl	N/10	1.001802	3.6468	4.559	2.714	0.744	1.78
R. W. = 36.468. d = 0.80,	N/25	1.000710	1.4589	1.823	1.074	0.736	1.73
Ansdell, Chem. News, **41**, 75	N/50	1.000335	0.7294	0.912	0.518	0.710	1.58
(1880).	N/100	1.000153	0.3647	0.456	0.244	0.669	1.32
	N/200	1.000069	0.1823	0.228	0.115	0.631	1.06
HNO_3	N/10	1.003365	6.3018	4.146	1.209	0.192	0.67
R. W. = 63.018. d = 1.52,	N/25	1.001329	2.5207	1.658	0.466	0.183	0.65
Landolt u. Börnstein, 3 Auf.,	N/50	1.000651	1.2604	0.829	0.220	0.175	0.61
247.	N/100	1.000312	0.6302	0.415	0.097	0.154	0.54
	N/200	1.000145	0.3151	0.207	0 037	0.117	0.41
N_2O_5	N/10	1.003365	5.4010	3.858	1.822	0.337	2.02
R. W. = 54.01. d = 1.4 (?)	N/25	1.001329	2.1604	1.543	0.712	0.330	1.98
Geuther, Ann. Chem. Pharm.,	N/50	1.000651	1.0802	0.772	0.343	0.318	1.90
Liebig, **245**, 96 (1888).	N/100	1.000312	0.5401	0.386	0.158	0.293	1.75
	N/200	1.000145	0.2701	0.193	0.068	0.252	1.51

Solute, reacting weight and density	Concentration	Density of solution, 25°/25° D/1000	Grams solute per litre s	Volume of solute s/d	Grams water condensed per litre C	Grams water condensed per gram solute	Ratio of mols water condensed to mols solute
H_3PO_4 R. W. = 32.675. d = 1.88, Landolt u. Börnstein, 3 Auf., 244.	N/10	1.002703	3.2675	1.738	1.173	0.359	1.95
	N/25	1.001093	1.3070	0.695	0.481	0.368	2.00
	N/40	1.000701	0.8169	0.435	0.319	0.390	2.12
	N/50	1.000575	0.6535	0.348	0.269	0.412	2.24
	N/100	1.000300	0.3268	0.174	0.147	0.450	2.44
	N/200	1.000170	0.1634	0.087	0.094	0.575	3.13
P_2O_5 R. W. = 23.667. d = 2.39, Landolt u. Börnstein, 3 Auf., 244.	N/10	1.002703	2.3667	0.990	1.326	0.560	4.42
	N/25	1.001093	0.9466	0.396	0.542	0.573	4.51
	N/40	1.000701	0.5915	0.248	0.357	0.604	4.75
	N/50	1.000575	0.4733	0.198	0.300	0.634	4.99
	N/100	1.000300	0.2367	0.099	0.162	0.685	5.40
	N/200	1.000170	0.1183	0.050	0.102	0.795	6.26
CH_3CO_2H R. W. = 60.032. d = 1.04, Landolt u. Börnstein, 3 Auf., 354.	N/10	1.000873	6.0032	5.772	0.642	0.107	0.36
	N/25	1.000348	2.4013	2.309	0.256	0.107	0.36
	N/50	1.000182	1.2006	1.155	0.136	0.114	0.38
	N/100	1.000074	0.6003	0.577	0.051	0.085	0.29
	N/200	1.000048	0.3002	0.289	0.037	0.123	0.41
$(CH_3CO)_2O$ R. W. = 51.024. d = 1.07, Kopp, Ann., **94**, 293 (1855).	N/10	1.000873	5.1024	4.769	0.540	0.106	0.60
	N/25	1.000348	2.0409	1.907	0.214	0.105	0.59
	N/50	1.000182	1.0205	0.954	0.115	0.113	0.64
	N/100	1.000074	0.5103	0.477	0.041	0.080	0.46
	N/200	1.000048	0.2551	0.238	0.031	0.122	0.69

Solute, reacting weight and density	Concentration	Density of solution, 25°/25° D/1000	Grams solute per liter s	Volume of solute s/d	Grams water condensed per litre C	Grams water condensed per gram solute	Ratio of mols water condensed to mols solute
NaOH R. W. = 40.008. d = 2.08, Schiff, Ann. Chem. Pharm., Liebig, **107**, 300 (1858).	N/10	1.004559	4.0008	1.923	2.481	0.620	1.38
	N/25	1.001814	1.6003	0.769	0.983	0.615	1.36
	N/50	1.000901	0.8002	0.385	0.486	0.607	1.35
	N/100	1.000464	0.4001	0.192	0.256	0.640	1.42
	N/200	1.000207	0.2001	0.096	0.103	0.515	1.14
KOH R. W. = 56.108. d = 2.00, Cameron and Robinson.	N/10	1.005155	5.6108	2.805	2.349	0.419	1.30
	N/25	1.002076	2.2443	1.122	0.954	0.425	1.32
	N/50	1.001047	1.1222	0.561	0.486	0.433	1.35
	N/100	1.000524	0.5611	0.281	0.244	0.435	1.35
	N/200	1.000270	0.2805	0.140	0.129	0.460	1.43
NH_3 R. W. = 17.034. d = 0.60, Landolt u. Börnstein, 3 Auf., 253.	N/10	0.999269	1.7034	2.839	0.405	0.238	0.23
	N/25	0.999699	0.6814	1.136	0.154	0.226	0.21
	N/50	0.999845	0.3407	0.568	0.072	0.211	0.20
	N/100	0.999901	0.1704	0.284	0.015	0.088	0.08
	N/200	0.999956	0.0852	0.142	0.013	0.153	0.14
CaO R. W. = 28.045. d = 3.30, Moissan, Comptes Rendus, **134**, 138 (1902).	N/25	1.001948	1.1218	0.340	1.166	1.040	3.24
	N/50	1.000984	0.5609	0.170	0.593	1.057	3.29
	N/100	1.000485	0.2805	0.085	0.290	1.034	3.22
	N/200	1.000247	0.1402	0.042	0.149	1.063	3.31

Solute, reacting weight and density	Concentration	Density of solution, 25°/25° D/1000	Grams solute per litre *s*	Volume of solute *s/d*	Grams water condensed per litre C	Grams water condensed per gram solute	Ratio of mols water condensed to mols solute
$Ca(OH)_2$ R. W. = 37.053. d = 2.08, Landolt u. Börnstein, 3 Auf., 234.	N/25	1.001948	1.4821	0.712	1.178	0.794	3.27
	N/50	1.000984	0.7411	0.356	0.599	0.808	3.32
	N/100	1.000485	0.3705	0.178	0.293	0.791	3.25
	N/200	1.000247	0.1853	0.089	0.151	0.815	3.35
$CaSO_4$ R. W. = 68.08. d = 2.96, Landolt u. Börnstein, 3 Auf., 234.	N/50	1.001338	1.3616	0.460	0.436	0.320	2.42
	N/100	1.000667	0.6808	0.230	0.216	0.318	2.40
	N/200	1.000337	0.3404	0.115	0.112	0.328	2.48
$CaCl_2$ R. W. = 55.505. d = 2.22, Landolt u. Börnstein, 3 Auf., 234.	N/10	1.004581	5.5505	2.500	1.530	0.276	1.70
	N/25	1.001878	2.2202	1.000	0.658	0.296	1.83
	N/50	1.000944	1.1101	0.500	0.334	0.301	1.85
	N/100	1.000506	0.5551	0.250	0.201	0.362	2.23
	N/200	1.000276	0.2775	0.125	0.123	0.443	2.73
Na_2HPO_4 R. W. = 47.336. d = 2.22, Schiff, Ann. Chem. Pharm., Liebig, **109**, 327 (1859).	N/10	1.004625	4.7336	2.132	2,023	0.427	3.37
	N/25	1.001861	1.8934	0.853	0.821	0.434	3.42
	N/50	1.000936	0.9467	0.426	0.415	0.438	3.45
	N/100	1.000464	0.4734	0.213	0.204	0.431	3.39
	N/200	1.000224	0.2367	0.107	0.094	0.397	3.13

Solute, reacting weight and density	Concentration	Density of solution, 25°/25° D/1000	Grams solute per litre s	Volume of solute s/d	Grams water condensed per litre C	Grams water condensed per gram solute	Ratio of mols water condensed to mols solute
Na_2CO_3 R. W. = 53. d = 2.48, Landolt u. Börnstein, 3 Auf., 242.	N/10	1.005519	5.3	2.136	2.355	0.444	2.61
	N/25	1.002204	2.12	0.854	0.938	0.443	2.60
	N/50	1.001102	1.06	0.427	0.469	0.443	2.60
	N/100	1.000550	0.53	0.214	0.234	0.442	2.60
	N/200	1.000257	0.265	0.107	0.099	0.374	2.20
KNO_3 R. W. = 101.11. d = 2.11, Landolt u. Börnstein, 3 Auf., 237.	N/10	1.006212	10.1110	4.793	0.894	0.088	0.50
	N/25	1.002491	4.0444	1.917	0.364	0.090	0.51
	N/50	1.001230	2.0222	0.959	0.167	0.083	0.46
	N/100	1.000612	1.0111	0.479	0.080	0.079	0.44
	N/200	1.000311	0.5056	0.240	0.045	0.089	0.50

we have felt justified in adding some further data which are included in the above table. We believe the densities of solutions given here are reliable to six significant figures, but not to seven, as stated in our former paper. Further, we wish to express to the Journal of Physical Chemistry our appreciation of this opportunity of correcting the errors in our former paper.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.,
March 29, 1910

STUDIES OF OSMOTIC PHENOMENA

BY WENDELL GARRET WILCOX

The direct measurement of the osmotic pressures developed by dilute solutions is of special value in the interpretation of the cause and nature of osmotic phenomena. Various ideas concerning the nature of osmosis have been expressed, the most important ones being briefly as follows:

According to the gas theory of solutions, the membrane is pictured as being "semipermeable" because the openings are too small for the solute, but large enough for the solvent to pass through. According to this theory, the membrane is acting in a purely mechanical manner, and the solvent passes through the membrane because of the tremendous tendency of the solute to expand into an added volume of solvent. In a dilute solution, as in a gas under low pressure, we should expect the closest approach of the osmotic pressure to the pressure calculated according to the gas laws.

Battelli and Stephanini,[1] I. Traube,[2] Bigelow,[3] and others maintain that the effects observed in an osmotic cell are due to the differences in surface tension between the membrane, the solution, and the solvent. Quite recently Bigelow and Bartell[4] have obtained osmotic pressures against membranes consisting of porcelain, and of porcelain whose pores had been clogged with barium sulphate or sulphur. They use this as an argument favorable to the capillary or surface tension theory of osmosis. If osmosis is due to capillary effects, as these investigators believe, and is thus a surface tension phenomenon, we should still find a dilute solution

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[1] Atti. R. Accad. Lincei (V), 14, II, 3 (1905); Atti. R. Accad. Lincei (V), 16, I, 11 (1907).

[2] Zeit. anorg. Chem., 8, 323 (1895); Ann. Phys. Chim. (ii), 62, 490 (1897); Ber. chem. Ges. Berlin, 31, 160 (1898); Chem. Zeit., 26, 1071 (1902); Zeit. phys. Chem., 105, 541 (1904); Phil. Mag. [6], 8, 704 (1904); Pflüger's Archiv, 123, 419 (1908).

[3] Jour. Am. Chem. Soc., 29, 1675 (1907).

[4] Ibid., 31, 1194 (1909).

developing an osmotic pressure which is more or less directly proportional to the concentration of the solution.

Still another explanation has been brought forward as a result of numerous qualitative experiments on dialysis and on the direction of the "main" osmotic current. In this work, which has had for its object the investigation of the activity of the membrane in osmotic experiments, Pickering,[1] Raoult,[2] Flusin,[3] Kahlenberg,[4] and others have been very active. These men have used the numerous experiments in osmosis and dialysis which they have performed to point out activity and selectivity on the part of the membrane. Dialysis experiments point unmistakably to such activity and selectivity on the part of the membrane: indeed, it is difficult to explain the many known cases of dialysis in any other way. The osmotic effects when two different liquids are separated by a membrane permeable to one or both of them, and the possibility of reversing the main osmotic current in such experiments are powerful arguments in favor of this explanation.

Such an explanation carries with it the assumption of loose combinations formed between the membrane and the substance passing through it. As a result of his experiments, Kahlenberg[5] states that "whether osmosis will take place in a given case or not, depends upon the specific nature of the septum and the liquids that bathe it: and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed." According to Kahlenberg it is the activity of the membrane towards the solvent and its inactivity toward the solute that gives rise to a movement of the solvent into the cell. The membrane imbibes solvent on the outside and is robbed of it by the solution on the inside. This goes on until the solution becomes so

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[1] Phil. Mag. [5], 29, 490 (1890); 35, 127 (1893); Nature, 55, 223 (1896).

[2] Comptes rendus, 121, 187 (1895).

[3] *Ibid.*, 126, 1497 (1898); 131, 1308 (1900); 132, 1110 (1901).

[4] Trans. Wis. Acad. Sci., 15, 209 (1906); Jour. Phys. Chem., 10, 141 (1906).

[5] Loc. cit.

diluted, due to the influx of the solvent into the cell, that the attraction of the interior solution for more solvent is the same as the attraction of the membrane for solvent, and an equilibrium is reached. In a closed cell the solvent flows in until the back pressure developed by its entrance, together with the attraction of the membrane for solvent just equals the tendency of the inner solution to take up more solvent, and equilibrium is established. According to this "solution" view of the rôle of the membrane, osmotic experiments are merely experiments in distribution. If this view of the nature of osmosis and the rôle played by the membrane is correct, there must be certain concentrations, small, but not negligible, which exhibit no osmotic pressure. Such concentrations are those at which the tendency of the inner solution to take up more solvent is just equal to the attraction of the membrane for the solvent so that there is no movement across the membrane into the cell.

It is obvious, then, that the direct determination of the osmotic pressures developed by dilute solutions will throw considerable light on the nature of osmotic phenomena by giving strong evidence as to the correctness of the various divergent views held at present.

Historical

In a recent article, Cohen and Commelin[1] have presented a very complete bibliography of the work done on the direct measurement of osmotic pressures. It is, consequently, needless to do more than give here an outline of the work done in measuring directly the osmotic pressures developed by dilute solutions.

R. H. Adie,[2] in his investigation of the osmotic pressures developed by a large number of salts in aqueous solution using a copper ferrocyanide membrane, measured the pressure exhibited by a number of dilute solutions of electrolytes for the purpose of arriving at the value of *i*. The results

[1] Zeit. phys. Chem., 64, 1 (1908).

[2] Jour. Chem. Soc., 89, 344 (1891).

obtained were more or less unsatisfactory and did not agree very well with those calculated.

A. Ponsot[1] used a cell very much like that of Pfeffer to determine the osmotic pressure of dilute aqueous solutions of cane sugar. Two concentrations were investigated, one of 1.235 grams sucrose in a liter of solution, the other of 0.6175 gram in a liter of solution, three determinations being made in the first case and two in the second. These results were in splendid agreement with the theoretical value for these concentrations. The work was carried out at 11.8° C. Later, the same investigator[2] made six determinations of the osmotic pressure of a solution of sodium chloride containing 0.110 gram in a liter. The determinations agreed well with each other and gave a value for *i* ranging from 1.78 to 1.81.

P. S. Barlow,[3] in an article published in 1905, describes the results of some measurements of the osmotic pressure of dilute aqueous solutions, using a copper ferrocyanide membrane. The results obtained were not satisfactory, and they did not agree with those required by the gas theory of solutions. He explained the fact that they were much lower than the theoretical values by showing that the outer liquid gradually took up impurities, thus resulting in a low observed pressure.

The same author[4] using a gutta percha membrane made several determinations of the osmotic pressures given by alcoholic solutions of varying concentrations. On plotting the observed pressures as ordinates and the concentrations as abscissae a curve was obtained which, when extrapolated, cut the axis of the abscissae some distance from the origin. The necessary interpretation was, that there are some concentrations that give no osmotic pressure. Barlow argued from this that osmotic pressures are merely hydrostatic pressures developed incident to the distribution of the solvent between membrane and solute.

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[1] Comptes rendus, **125**, 867 (1898); Bull. Soc. chim. Paris (3), **19**, 9 (1898).

[2] Comptes rendus, **128**, 1447 (1899).

[3] Proc. Cam. Phil. Soc., **13**, (IV), 229 (1905).

[4] Phil. Mag. [6], **11**, 595 (1906).

Barlow[1] found also that dilute solutions of sucrose and dextrose dissolved in a solution consisting of half ethyl alcohol and half water gave osmotic pressures that were far below those calculated from the gas laws. In these experiments he used a copper ferrocyanide membrane.

In an article already quoted, Kahlenberg[2] cites a number of quantitative measurements of the osmotic pressures of dilute pyridine solutions. He found that pyridine solutions of lithium chloride, sucrose, and silver nitrate gave nowhere near the pressure calculated according to the gas laws.

Apparatus

The osmometer used in this work is shown in Fig. 1. The osmometer consisted of a thistle tube, G, the mouth of which was closed with the rubber membrane used. The membrane was fastened by drawing it over the flange, and tying it tightly by winding with strong linen thread. This was done in such a way that the membrane was smooth, taut, and free from wrinkles. This rubber membrane was of unusually fine quality; when unstretched it was 0.15 mm. thick, and when stretched it was about 0.08 mm. thick. The rubber membrane was protected by a piece of strong muslin tied on over it and fastened in the same way that the rubber was fastened. To prevent sagging of the membrane a small perforated steel disk was placed next to the protective muslin. This disk was held in place by another piece of muslin tied on and fastened like the first piece.[3] To the upper end of the stem of the thistle tube, the trap C was fused. This trap was filled with the same solution as that in the osmometer, and was closed by the stopper E, through which passed the tube D, having a very fine capillary. The capillary

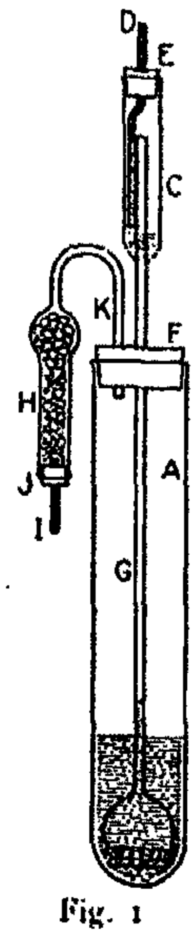

Fig. 1

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[1] Jour. Chem. Soc., 89, 162 (1906).

[2] Loc. cit.

[3] See Kahlenberg, l. c.

tube D extended to a point but slightly above the solution in the trap and opened into the outer air. By means of this trap evaporation was prevented (which was quite necessary, due to the long time that the experiments were run), and the possibility of moisture-laden air coming into contact with the contents of the cell was also obviated. The osmometer was placed in a large test-tube, A, which was 36 cms long and 5.4 cms in diameter. The container A was closed by the cork stopper F, through which passed the stem of the osmometer, and the vent tube K, which in turn was guarded by the large calcium chloride tube H. The calcium chloride tube H was closed by the stopper J, through which passed the fine capillary tube I. To prevent the passage of moisture through the cork stopper F, the latter was heavily coated with collodion solution after the stopper had been forced tightly into position.

A cell of the above construction was necessary in this work for a number of reasons. The pressures studied in this work were small and consequently the ordinary closed cell with a mercury manometer would have been quite unsatisfactory because in many cases the movement of such a manometer would have been so slight as to have approached the error of experiment. Furthermore, the manometer liquid, the solution itself having a far smaller density than mercury, gave a correspondingly greater rise for a given pressure. On the other hand, since the rise in the manometer tube of the cell was due to the influx of solvent with a consequent dilution of the solution, this had to be taken into consideration in determining the true concentration of the solution in the cell at the moment of equilibrium. However, as the solutions investigated were quite dilute, and the rise never very great, the relative change in concentration due to the influx into the cell of 1 or 2 cc. of solvent was not so great as might, at first, be supposed. It is true that there was no way of stirring this cell except by shaking its contents thoroughly from time to time. Kahlenberg[1] has already pointed out the necessity

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[1] Loc. cit. Compare, also, Beltz and Vegesack, Zeit. phys. Chem., 68, 357 (1909).

of thorough stirring, showing that it has an immense influence on the rate of rise of pressure, if not on the apparent equilibrium. Kahlenberg's observations of the effect of stirring on the rate of the rise of the pressure have been confirmed in a qualitative but striking way in the course of this work.

In setting up the cell, the solution was poured rapidly into the osmometer by means of a capillary funnel; more solution was poured into the trap C, and the latter tightly stoppered. Pure solvent was then poured into the outer container after which the stopper F was forced home and immediately heavily coated with collodion solution. Inasmuch as the solution and the solvent were already at the temperature of the thermostat, and as it did not take more than two minutes, at the most to set up a cell, the reading could be taken a few moments after the cell had been placed in the thermostat and before osmosis had begun.

The cells were placed in one or the other of the two thermostats used. These thermostats were of wood, thus giving better heat insulation. They were electrically heated and regulated in the usual way. The thermostats had a capacity of 50 liters, and due to the efficient stirring, and to the fact that they were kept in a room which was itself heated by thermostatic arrangement, the temperature was controlled to one-tenth of a degree or less for long periods of time. No attempt was made to secure finer temperature adjustment than this, as the development of the work showed such small temperature differences to be without effect on the osmotic pressures of the solutions investigated.

Preparation of Materials

E. Cohen and J. W. Commelin[1] as a result of their work on the osmotic pressure of pyridine solutions believe "dass die Gegenwart des Wassers, es sei in der Lösung, es sei in dem reinen Lösungsmittel, einen grossen Einfluss auf den gemessenen osmotischen Druck ausübt. Die Richtung in der sich dieser Einfluss geltend macht, ist abhängig von dem Ver-

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[1] Loc. cit.

hältnis zwischen der Konzentration des Wassers in den Flüssigkeiten zu beiden Seiten der Membran." For this reason it seemed best to use the greatest precautions in preventing the entrance of even traces of water into the cell, and also to use a more rigorous and, if possible, a more efficacious method of drying the pyridine to be used. The method that has been used in the past has been to let it stand for some time over sticks of fused potassium hydroxide. There is no doubt that this removes most, if not all, of the water in the pyridine, but it cannot remove the homologues of the latter.

Cohen and Commelin argue that the wide range in which pyridine boils points to the presence of water not removed by the usual method. In order to settle this point before proceeding with the rest of the work, experiments were tried in which the pyridine was allowed to stand over sticks of good fused potassium hydroxide for periods varying from two to twelve weeks, but even then the pyridine obtained had a boiling point which ranged from 114°.5 to 116°.5 under a pressure of 740 mm. An experiment was next performed in which the pyridine, after standing over fused potassium hydroxide for six weeks, was boiled over Merck's lime for six hours, using a reflux condenser. The result seemed slightly encouraging, and a more rigorous dehydrating agent of the same chemical nature was sought. Barium oxide naturally suggested itself, and some very good barium oxide was made by heating the anhydrous peroxide. Pyridine which had stood over fused potash for four or five weeks was boiled over barium oxide for six hours, using a reflux condenser. The distillate from this treatment was again boiled over fresh barium oxide for a period of six hours as before and then was distilled off. The pyridine obtained from this second treatment had a very constant boiling point. In distilling off 2 liters of pyridine, the boiling point changed from 114.25 to 114.6 under a pressure of 738 mm. It was therefore concluded that this pyridine was free from homologues and free from water. Great care was used to prevent the pyridine thus prepared from taking up water on standing. It was kept in glass-stoppered flasks and these were protected from the water vapor in the air by several layers of sheet rubber drawn over the stopper and tied tightly to the neck of the flask. The pyridine solutions were kept the same way. The pyridine was never allowed to stand long after being dried; it was generally used within a few hours. Before being finally used, the pyridine was again distilled from fresh barium oxide using an all-glass distilling apparatus whose only opening to the air was guarded by a drying tube.

The effect of small amounts of water on the boiling point of pyridine was investigated, using the pyridine prepared by the foregoing method. The pyridine used had a constant boiling point of 114.3° C under a pressure of 738 mm. The 100.33 grams of pyridine used were contained in a large glass test-tube which was jacketed with a large Dewar test tube to reduce radiation. The heating was done by means of a platinum wire resistance in the liquid after the method already described by Richards and Mathews.[1] By carefully regulating the current, superheating could be reduced to a minimum and the liquid boiled at a temperature which did not vary more than 0.015° C. The liquid was then allowed to cool, and a small amount of water was added from a weighed Ostwald-Sprengel pycnometer. The new boiling point was then determined. In this way a total of 1.1713 grams of water were added to the pyridine. The true boiling point was considered to have been attained when the boiling point did not change more than 0.02 of a degree during ten minutes.

The results obtained are given in Table I. Here is shown the effect of various amounts of water ranging from 0.03 to 0.2 gram water in 100.33 grams of pyridine. These results are plotted in the form of a curve in Fig. 2. From this curve it is seen that the lowering of the boiling point of pyridine is directly proportional to the amount of water present. Water has a remarkable effect on the boiling point of pyridine. Traces *lower* the boiling point noticeably and 1 percent of

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[1] Proc. Am. Acad. Arts and Sci., 43, 521 (1908).

TABLE I—THE EFFECT OF WATER ON THE BOILING POINT OF PYRIDINE

(The sample of pyridine weighed 100.33 grams and the barometer was constant throughout at 738 mm)

No of expt.	Total weight water added in grams	Percent water added	Total lowering in degrees
1	0.0000	0.00	0.00
2	0.0300	0.0298	0.10
3	0.0889	0.0886	0.34
4	0.1359	0.135	0.46
5	0.1859	0.185	0.66
6	0.2549	0.253	0.91
7	0.3258	0.323	1.17
8	0.4218	0.418	1.49
9	0.4969	0.492	1.72
10	0.5764	0.571	2.05
11	0.7646	0.756	2.74
12	0.8563	0.846	3.04
13	0.9563	0.954	3.36
14	1.0456	1.031	3.61
15	1.1713	1.153	3.95

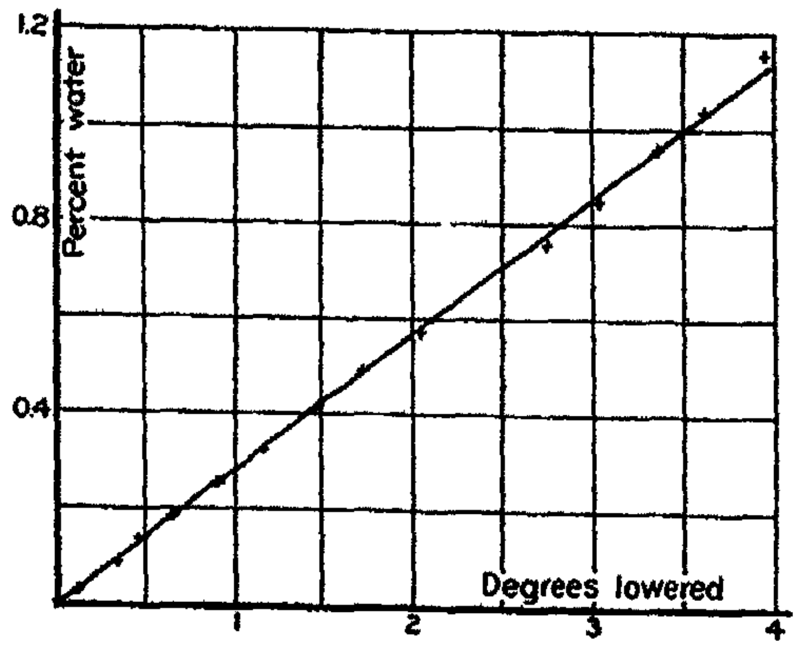

Fig. 2

water causes a lowering of several degrees. The presence of water would thus account for the low boiling pyridine, but it fails absolutely to explain the fact that the pyridine usually obtained in the market boils above the boiling point of pure pyridine, 114.3° C uncorrected. Such a variation in the boiling point of pyridine points unmistakably to the presence of higher homologues, the picolines. The removal of these higher homologues was probably due to undecomposed barium dioxide which oxidized them to the acid; the latter, when acted upon by the barium hydroxide present, would yield barium carbonate and pyridine. Later in the work the picolines were oxidized by boiling with potassium permanganate; the treatment with barium oxide then followed.

In preparing the various solvents used in this work, similar precautions were taken to insure purity of the reagents and freedom from traces of water. Carbon tetrachloride and chloroform were kept standing over phosphorus pentoxide for some time and then distilled from fresh pentoxide. The acetone used was very pure; it was kept standing over calcium chloride for ten weeks, over anhydrous sodium sulphate for one week, and finally it was distilled from anhydrous copper sulphate. The methyl and ethyl alcohols were first dried over lime, then boiled over metallic calcium for five hours using a reflux condenser, and finally distilled from sodium. The isobutyl alcohol was dried by fractionating several times and finally kept over calcium chloride.

The sugar used was the best quality of crystallized sucrose, and has no reducing effect on Fehling's solution. The silver nitrate was recrystallized from Merck's preparation and was fused before being used. The lithium chloride was very pure and was either fused in a current of dry chlorine. or was heated to incipient fusion in the air and cooled over phosphorus pentoxide. The other solutes used were prepared in the usual way, excepting that great precautions were taken to insure freedom from water.

Preliminary Work

About one hundred measurements of the osmotic pressure of various solutes in various solvents against a rubber membrane were made before proceeding with the quantitative work given further on in this paper. These experiments were made for several purposes: first, to find the region of concentration, if such there was, where the solution exhibited but slight osmotic pressure against the membrane; second, to see if this region of concentration varied with the solvent, keeping the membrane and solute the same; third, to test the semipermeability of the membrane toward the solute employed; fourth, to find the time required for complete equilibrium with the cell used in this work; fifth, to determine if this time required for equilibrium varied with the nature and the concentration of the solution employed; and finally to determine the effect of the solute and solvent on the membrane while the cell was running.

In performing these preliminary experiments, while unusual care was taken to secure purity of materials and anhydrous solvents and solutes, the still more elaborate precautions adopted in the quantitative measurements were not followed so rigidly here.

In this preliminary work the following solvents were employed, carbon tetrachloride, chloroform, acetone, methyl-, ethyl-, and isobutylalcohols and pyridine. The solutes used were copper chloride, copper oleate, mercuric chloride, lithium chloride, potassium iodide, sodium iodide, silver nitrate, sucrose, salicylic acid, ammonium bromide, urea, urethane, potassium acetate, and camphor.

Because of the fact that this preliminary work was not strictly quantitative but was merely intended to serve for guidance in the quantitative work which followed, but little emphasis will be put upon it. It will be sufficient to point out the general conclusions that followed from these preliminary experiments. The measurements made in this way showed that there are concentrations, that are by no means negligible, which give slight osmotic pressure against a rubber membrane, and that these concentrations vary with the nature of the solution. In the case of the same solute, they vary with the nature of the solvent. The time required for complete equilibrium with this cell was found to be about fifteen days in most cases, although this also varied with the solution used and the concentration, while in the case of the same solute, it varied with the nature of the solute.

As was found by Kahlenberg[1] previously, solutions of sugar, silver nitrate, and lithium chloride in pyridine proved to be most satisfactory. Of the others, some had to be abandoned because the solute passed through the membrane, as in the case of copper oleate, copper chloride, urethane, urea, mercuric chloride, and also potassium iodide. Others could not be used because of the rapid destructive action that they exerted on the membrane. Such was the action of ammonium bromide, copper chloride, mercuric chloride, and also of a solution of lithium chloride in iso-amyl alcohol.

In determining the time necessary for true and complete equilibrium, a cell like that already described was used. Daily observations were taken of the rise of the liquid in the stem of the cell, and equilibrium was considered to have been reached when the pressure began to drop. It has been previously noticed by others who have worked on osmosis that the pressure in such a cell attains a maximum, and then steadily drops.

Dilute Sucrose Pyridine Solutions

The preliminary experimentation having shown that a concentration of 1 gram molecule of sucrose in 45 liters of solution gave but slight osmotic pressure, a number of quantitative determinations were made of the osmotic pressure that a solution of this concentration gives against a rubber membrane. The sucrose pyridine solution was made by dissolving the necessary amount of sucrose in a little less than a liter of pyridine at 25° C. and then diluting up to 1 liter. The cell was then set up and filled as previously described, and observations were taken daily or oftener until from the behavior of the cell and from a knowledge already gained from the preliminary work, it was found that equilibrium had become established. The cell was then dismantled, the volume of the solution in the cell determined, and also the volume of

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[1] Loc. cit.

the solvent outside of the cell ascertained. The initial volume of the solution in the cell was, of course, already known. The amount of sugar that had passed through the membrane into the outer liquid was obtained by evaporating off the pyridine of the outer liquid, inverting the sugar, and reducing Fehling's solution with it. The cuprous oxide thus obtained was dissolved in nitric acid and the copper determined by the iodine method. The amount of sugar was then calculated from Allihn's tables. The amount of sugar originally in the cell was calculated from the volume of the 45th normal solution originally in the cell. The amount of sugar in the cell at the time of equilibrium was found by subtracting from the amount originally in the cell, the amount that had passed into the outer liquid. From this and the final volume of the cell solution, the concentration of the cell at the time of equilibrium was calculated. The concentration of the sugar in the outer liquid was calculated from the amount of sugar found there, and the volume of the outer liquid. From the final concentration of the cell solution and that of the outer liquid, the differential concentration in favor of the cell was calculated.

The results of twenty measurements made at 25° centigrade are given in Table II. In experiment 20 the amount of sugar that passed into the outer liquid was slight; it was not, however, determined quantitatively. The volume of the outer solution was generally about 60–100 cc. In calculating the pressure found, the density of the pyridine was considered to be unity for all practical purposes. The theoretical pressures are calculated for the concentration in question and on the assumption that there is no "dissociation" of the dissolved molecule, although the lithium chloride and silver nitrate solutions conduct well.

Consideration of these results shows them to be not entirely consistent with themselves, and this is especially so in the case of experiments 6, 14, and 18. These results are not, however, excluded as it is felt that they are as truly representative as the others.

TABLE II—THE OSMOTIC PRESSURES OF PYRIDINE SUCROSE SOLUTIONS AT 25° C

(The original concentration of each solution was 1 gram molecule in 45 liters. In the third and fifth columns the concentrations are given as the number of liters in which 1 gram molecule is contained)

No. of expt.	Rise of osmometer in cms	Final concentration of osmometer	Gram sugar in outer liquid	Differential concentration	Observed pressure in grams per sq cm	Theoretical press. in grams per sq cm	Obs. press. / theor. press. Percent
1	1.5	48.0	0.0185	52.0	16.1	485.0	3.32
2	5.7	49.2	0.0130	52.5	13.2	480.7	2.81
3	0.6	48.1	0.0200	52.5	15.6	480.7	3.25
4	5.2	48.6	0.0280	52.6	13.8	479.8	2.88
5	4.6	48.3	0.0150	53.7	14.6	470.0	3.11
6	4.5	49.3	0.0290	54.8	17.5	460.5	3.80
7	2.6	50.0	0.0300	54.8	15.1	460.5	3.28
8	5.1	49.3	0.0210	55.0	10.7	459.0	2.33
9	0.8	49.5	0.0210	55.0	10.5	459.0	2.28
10	7.8	52.0	0.0314	55.0	12.2	459.0	2.66
11	6.1	51.4	0.0280	55.0	12.6	459.0	2.75
12	2.5	50.0	0.0260	56.0	12.0	450.6	2.66
13	4.3	49.7	0.0180	56.2	8.8	449.0	1.96
14	4.0	50.2	0.0350	56.4	12.0	447.4	2.13
15	4.5	51.0	0.0300	56.6	9.5	446.0	2.18
16	1.5	49.1	0.0180	57.0	6.0	442.8	1.36
17	5.5	53.8	0.0260	58.7	6.0	430.0	1.40
18	4.2	51.1	0.0500	60.1	11.0	419.9	2.62
19	2.5	50.6	0.0350	60.7	7.0	415.7	1.58
20	4.0	not determined	—	—	14.6	—	—

The reasons for lack of better agreement are not far to seek. The membrane, the rubber, having been subject to considerable physical treatment in the manufacturing process, is not likely to be always uniform, and it was to be expected that this would manifest itself in the result obtained. Furthermore, the cells themselves were of somewhat different capacity and a different membrane area was exposed in each experiment with the result that all of the following factors influenced the results obtained: *a*, the amount of sugar that passed the septum, *b*, the dilution of the cell contents, and as a result *c*, the differential concentration.

The results in Table II show a striking divergence from the results calculated according to the gas theory. On the average these cells attained a pressure that was only 2.41 percent of the total pressure required by this theory. Such a discrepancy, a difference of 97.59 percent on the average, between experiment and theory cannot be explained on the basis of any gas theory of solutions. Furthermore, if osmosis is a capillary phenomenon, it is difficult to see how any such results could be expected, for surface tension being a linear function of the concentration, the osmotic pressures, if due to surface tension, should be more or less proportional to the concentration.

Dilute Silver Nitrate-Pyridine Solutions

The preliminary work showed that a concentration of 1 gram-molecule in 40 liters of solution gave but slight osmotic pressure against a rubber membrane, and this concentration was, accordingly, chosen for quantitative investigation. The experiments were carried out as with the pyridine sucrose experiments except that the temperature was 26° C. The silver nitrate in the outer liquid, after removing the pyridine, and dissolving the silver in the residue with nitric acid, was determined by Volhard's method. The seventeen measurements are given in Table III. This table is like Table II, and the same data are given here as in that case. Here experiments 32, 33, and 35 do not agree entirely with the general

TABLE III—THE OSMOTIC PRESSURES OF PYRIDINE SILVER NITRATE SOLUTIONS AT 26° C

(The original concentration of each solution was 1 gram-molecule in 40 liters. In the third and fifth columns the concentrations are given as the number of liters in which 1 gram-molecule is contained)

No. of expt.	Rise of osmometer in cms	Final concentration of osmometer	Gram silver nitrate in outer liquid	Differential concentration	Observed pressure in grams per sq cm	Theoretical press. in grams per sq cm	$\frac{\text{Obs. press.}}{\text{theor. press.}}$ Percent
21	11.5	48.1	0.0578	56.1	16.5	451.5	3.57
22	12.6	48.2	0.0272	57.8	18.3	438.2	4.18
23	10.2	48.4	0.0374	58.0	17.2	436.7	3.95
24	11.5	50.0	0.0306	58.0	18.0	436.7	4.13
25	11.0	48.6	0.0231	58.1	18.0	436.4	4.12
26	4.2	50.7	0.0408	58.6	17.2	432.3	3.98
27	9.2	47.0	0.0272	59.2	14.7	444.8	3.31
28	10.0	50.6	0.0374	59.3	16.5	427.0	3.86
29	8.8	47.7	0.0271	60.0	14.8	422.0	3.51
30	4.8	48.0	0.0340	60.0	12.8	422.0	3.03
31	5.3	49.9	0.0306	60.0	11.3	422.0	2.64
32	5.5	51.2	0.0408	60.1	14.5	421.0	3.44
33	1.5	47.7	0.0340	62.0	14.5	407.0	3.56
34	5.3	51.3	0.0340	63.7	12.3	397.7	3.09
35	10.0	52.0	0.0418	63.8	15.5	397.0	3.90
36	0.0	49.9	0.0408	63.9	12.5	396.4	3.90
37	4.0	50.9	0.0408	64.0	11.0	394.3	3.06

Table IV—The Osmotic Pressures of Pyridine Lithium Chloride Solutions at 26° C

(The original concentration of each solution was 1 gram-molecule in 45 liters. In the third and fifth columns the concentrations are given as the number of liters in which 1 gram-molecule is contained)

No. of expt.	Rise of osmometer in cms	Final concentration of osmometer	Gram lithium chloride in outer liquid	Differential concentration	Observed pressure in grams per sq cm	Theoretical press. in grams per sq cm	Obs. pressure theor. press. Percent
38	0.8	47.0	0.0021	49.5	9.4	511.7	1.83
39	0.4	48.0	0.0025	50.5	10.0	501.6	2.00
40	0.6	48.4	0.0030	51.3	12.6	493.8	2.55
41	0.4	48.0	0.0026	51.3	13.2	493.8	2.64
42	1.2	48.1	0.0030	52.0	13.2	487.0	2.71
43	0.4	49.0	0.0026	52.0	8.4	487.2	1.72
44	0.5	49.5	0.0034	53.0	13.6	478.0	2.85
45	0.9	49.9	0.0047	53.0	15.5	478.0	3.32
46	0.4	49.2	0.0039	53.9	10.7	471.9	2.27
47	1.3	50.8	0.0039	54.6	12.0	464.0	2.59
48	0.5	50.4	0.0039	54.9	10.2	461.4	2.21
49	0.0	49.8	0.0043	55.9	9.0	453.3	1.99
50	0.3	49.7	0.0043	56.0	8.3	452.4	1.84
51	0.4	50.4	0.0043	56.2	14.0	450.8	3.11
52	0.1	50.4	0.0047	56.2	10.2	450.8	2.35
53	0.8	50.0	0.0043	56.7	10.4	446.8	2.33
54	0.1	49.9	0.0039	57.7	11.6	439.4	2.64
55	1.9	54.1	0.0086	58.0	10.0	436.8	2.29
56	0.7	51.7	0.0060	59.0	10.5	429.4	2.45
57	0.3	52.0	0.0064	59.2	10.5	427.0	2.36
58	1.0	51.5	0.0051	59.5	10.0	425.7	2.35

run of the experiments. They are, however, included, for in any series of measurements of this kind results are at times obtained which, like experiments 32, 33, and 35, do not appear to be consistent with the majority of the results obtained.

The reasons for lack of better agreement are those that have already been mentioned in discussing the results obtained with sucrose solutions. Here, also, the enormous divergence between the results actually obtained and those calculated on the basis of the gas laws is apparent. On the average, these silver nitrate cells reached a pressure which was only 3.46 percent of that required by the gas laws. Here, again, is an average discrepancy of 96.54 percent between observation and the requirements of the van't Hoff theory of solutions.

Dilute Lithium Chloride Solutions

The twenty-one measurements of the osmotic pressures of lithium chloride in pyridine, solutions containing 1 gram-molecule of lithium chloride in 45 liters of solution, were made at 26° C in the way already described. The results are given in Table IV. The same data are given as in the preceding tables, II and III. These results show about the same order of agreement as that attained in the cases already considered. These cells developed an average pressure only 2.33 percent of that required by the gas theory of solutions.

Summary and Conclusions

The fifty-eight direct measurements made of the osmotic pressures of dilute pyridine solutions of lithium chloride, silver nitrate and sucrose indicate that experiments in osmosis are merely distribution experiments. For dilute solutions of sucrose, lithium chloride, and silver nitrate the gas laws certainly do not hold. The gas theory of solutions cannot explain such enormous discrepancies, discrepancies which are so great that the theoretical value is about thirty-two times as great as the observed pressures themselves.

In this paper the following results have been obtained:

(1) A new method for purifying and drying pyridine has been described.

(2) The effect of small amounts of water on the boiling point of pyridine has been determined, and this effect has been shown to be directly proportional to the amount of water added.

(3) A simple cell for measuring small osmotic pressures has been described.

(4) Twenty direct measurements of the osmotic pressures of dilute pyridine sucrose solutions have been made.

(5) Seventeen direct measurements of the osmotic pressures of dilute pyridine silver nitrate solutions have been made.

(6) Twenty-one direct measurements of the osmotic pressures of dilute pyridine lithium chloride solutions have been made.

(7) It has been shown that these results are not in harmony with the van't Hoff theory of solutions. The pressures calculated for these solutions according to the gas laws are about thirty-two times as great as those actually found.

The author takes this opportunity of acknowledging the inspiration and help extended him by Professor Louis Kahlenberg at whose suggestion this work was undertaken.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, April, 1910

NEW BOOKS

An Introduction to Physical Science. *By Frederick H. Getman. First edition. 12 × 19 cm; pp. vi + 257. New York: John Wiley and Sons. London: Chapman and Hall, 1909. Price: bound, $1.50 net.*—This is really an elementary physics manual, in which the treatment is essentially qualitative. There are six chapters on mechanics, six on heat, four on light, and five on magnetism and electricity. The author has described many simple experiments and they seem to be very well chosen. Experiment 30 on capillarity, p. 159, is not new of course; but it may be taken as a typical instance of what a qualitative experiment should be.

Whether one approves of this book or not, depends upon one's point of view. This book will seem a step backward to those who believe that no research work can be good which is not accurate at least to one-tenth of one percent. On the other hand, the book will seem pedagogically sound to those who remember that all of our knowledge is qualitative at first and that most of it remains qualitative all our lives.

A student must know that there is such a thing as surface tension before trying to measure it accurately. In fact, if he is wise he will never try to measure it accurately. Much the same thing is true in regard to diffusion. The student can very well learn that when hot, concentrated solutions of almost any salt are cooled, crystals of the salt are likely to separate, long before he determines the actual solubility of any salt. The general facts of sublimation and of boiling are easy enough to learn; but a really accurate determination of vapor pressures takes time. The reviewer believes strongly in the value of qualitative knowledge, though that is not a popular doctrine today; and he is therefore glad to welcome this book.

There are some slips which should be corrected in the next edition, on p. 13 the author speaks of the contraction when alcohol and water are mixed as due to the existence of physical pores. What becomes of the pores when mixtures of alcohol and carbon bisulphide expand?

On p. 30 it is stated that "the work performed by a locomotive in drawing a train of cars from New York to Boston is the same whether it be done in five or six hours." Of course this is not so and equally of course the author does not intend us to take into account the pressure of the air; but he could just as well have selected an illustration which was not so glaringly inaccurate.

On p. 48 the author follows Kohlrausch in giving the same numerical value to density and to specific gravity. Since we always ignore the definition when we are dealing with gases and very often when dealing with liquids, it would be better to make the definition agree with the practice since the former is more easily changed than the latter.

On p. 85 is the statement that the Réaumur scale is but little used. Since it is the one used by most Germans in every-day life, that remark seems a bit exaggerated.

On p. 111 is the statement that the lowest melting alloy of two metals is called the eutectic. If this definition were taken literally, the student would probably conclude that pure cadmium was the eutectic of the silver-cadmium series. Further down on the same page it would be well to qualify the statement that "a block of ice will evaporate slowly if maintained at a temperature below zero."

Wilder D. Bancroft

A Text-Book of Physical Chemistry: Theory and Practice. *By Arthur W. Ewell. 14 × 21 cm; pp. vii + 370. Philadelphia: P. Blakiston's Son and Co., 1909. Price: $2.25 net.*—"This book is intended to serve as a laboratory manual, as a text-book to accompany recitations or lectures, and a convenient book of reference. The laboratory exercises are chosen with the aim of giving the student a clear understanding of the principles involved in the subjects usually included under the title of Physical Chemistry, and also in certain other subjects in advanced physics, which, though not usually included under this title, are of particular importance to chemists."

The subject is treated under the general heads: gases, vapors and liquids; thermodynamics; solutions; thermochemistry; light; chemical kinetics; chemical statics; electrolytic conduction; potential differences; gaseous ions; radioactivity.

The book contains an enormous amount of information and is distinctly valuable. To the reviewer some of the directions seem inadequate. On p. 338 for instance, the student is told to discharge a storage cell down to 1.5 volts at a rate not to exceed 0.01 amp./cm^2. If he discharges at the eight hour rate, he has a pretty long day's work especially since his results are vitiated if he breaks the circuit during the run.

The book is also valuable because Worcester is one of the few places where physical chemistry appears to be taught as a branch of physics rather than of chemistry.

Wilder D. Bancroft

Physical Chemistry for Electrical Engineers. *By J. Livingston R. Morgan. Second edition, revised. 13 × 19 cm; pp. x + 249. New York: John Wiley and Sons. London: Chapman and Hall, 1909. Price: $1.50 net.*—The first edition was reviewed over three years ago (10, 731). The new edition is about ten percent larger than the first one but, except for that, the book has not changed much. There are relatively few misstatements but the reviewer was a little staggered by a sentence on p. 186: "To separate one gram of hydrogen, then, or the equivalent weight in grams of any other metal we require the work

$$\pi \times 96540 \times \text{watt-seconds} = 96540 \times 0.2394\,\pi = 23110\,\pi \text{ cals."}$$

The multiplication sign before watt-seconds is a misprint of course; but it is hardly fair to anybody to define π as the voltage without saying that we have no way of determining π for any single ion.

Wilder D. Bancroft

Photographie. *By H. W. Vogel. Ein kurzes Lehrbuch für Liebhaber und Fachleute. Zweite vermehrte Auflage bearbeitet von Hans Sporl. 10 × 18 cm; pp. ix + 324. Braunschweig: Friedrich Vieweg und Sohn, 1909. Price: bound, 2.50 marks.*—The first ninety pages are devoted to a historical sketch of the development of photochemistry and to an account of photographic apparatus. the rest of the book is given up to the practice of photography, the space being divided about equally between the processes for making negatives and those for making positives. Under the positive processes we find the following headings; Albumen and arrow-root paper; aristo paper; celloidine paper; protalbine paper; transparencies; autochrome plates; bromide prints; printing with chromates; printing with iron salts; landscapes and portraits.

The book is compact and concise but astonishingly complete. There is not much theory but there is a great deal of practice, and good practice is worth more than bad theory. Take it all in all, this is a very useful little book.

Wilder D. Bancroft

Die elektromotorischen Kräfte der Polarization, *und ihre Messung mit Hilfe des Oszillographen. By M. Le Blanc. (Abhandlungen der Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie. No. 3.) 17 × 24 cm; pp. 79. Halle: Wilhelm Knapp, 1910. Price: paper 3.00 marks.*—The author has studied the phenomena of electrolytic polarization by means of an oscillograph. Distinct signs of polarization were found even when the concentration of the ions was apparently sufficient to have prevented this. The amount of polarization depended upon a number of factors, among which perhaps the most interesting was the presence or absence at the electrodes of poisons such as strychnine. The author considers that these effects of polarization are due to reactions taking place relatively slowly at the electrodes. In some cases, it seems probable that we are dealing with hydration and dehydration of the ions.

Wilder D. Bancroft

La Préparation électrolytique des Composés du Plomb. *By Carl Duvivier. 13 × 24 cm; pp. 19. Malines: L. and A. Godenne, 1909.*—It is extremely difficult to see why this pamphlet should have been published. It contains an account of very crude methods of making lead carbonate, lead chromate, red lead and lead peroxide. Although the work is apparently intended to have technical value, no attention is paid to the quality of the precipitate and the use of a porous cup is recommended in nearly every case. The author appears to think that white lead is lead carbonate. *Wilder D. Bancroft*

Handbuch der anorganischen Chemie. *Herausgegeben von R. Abegg und Fr. Auerbach. In vier Bänden. Dritter Band, zweite Abteilung. 18 × 25 cm.; pp. xii + 921. Leipzig: S. Hirzel, 1909. Price: paper, 25 marks; linen, 27 marks.*—The sections have been assigned as follows: carbon to Weigert; silicon to Grossman; glass to Schaller; titanium to Jacoby; germanium to Rudorf; zirconium to R. J. Meyer; tin to Cohen; lead to Pick and Ahrens; the lead accumulator to Mugdan; and thorium to R. J. Meyer. Brauner discusses the atomic weights and Lottermoser the colloid chemistry.

The volume is a great success. To the reviewer the chapters on carbon, tin, and colloids seem rather the most interesting; but that is probably a personal matter. The chapter on the lead accumulator is distinctly the least satisfactory. Here we have a case of mathematics running riot, with an enormous number of mathematical calculations and very few facts.

In the chapter on silicon, Scheid's process is mentioned; but the reviewer did not find a reference to the only commercial process, that of Tone. This is an isolated case and in general the volume is remarkable for completeness and accuracy. In the section on tin, Cohen has reproduced a number of his photographs on the tin sickness. Under thorium we find a very satisfactory account of the luminosity of the Welsbach mantle. It was a very happy thought to include a special section on glass and the data given are of great value.

On p. 174 there seems to be a misprint for we find the remarkable statement that there was fluorine in the lead disulphate which Brauner prepared by letting sulphuric acid react with lead tetra-acetate. This becomes more intelligible and more in harmony with Brauner's experiments if we substitute tetrafluoride for tetra-acetate. *Wilder D. Bancroft*

Über die Erhaltung der Masse bei chemischen Umsetzungen. *By H. Landolt. (Abhandlungen der Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie. No. 1.) 17 × 24 cm; pp. viii + 47. Halle: Wilhelm Knapp, 1909. Price: paper, 1.80 marks.*—In this monograph Landolt presents his three series of investigations on the conservation of mass as a single paper. Fifteen reactions were studied and the final conclusion reached is that if any change of weight takes place it must be less than a thousandth of a milligram. Since the amounts of material varied from about fifty grams to over one hundred grams, we may say that there is no change of weight to exceed one in one hundred million. The investigation is unquestionably a classic and the Bunsen Society is to be congratulated for being able to begin its series of monographs with so admirable a paper. *Wilder D. Bancroft*

Das Radium und die Farben. *Einwirkung des Radiums und ultravioletter Strahlen auf organische und anorganische Stoffe sowie auf Mineralien. By C. Doelter. 14 × 22 cm; pp. viii + 133. Dresden: Theodor Steinkopff, 1910. Price: paper, 4 marks; bound, 5 marks.*—In the preface the author says that "the changes in color caused by radium constitute the essential part of the volume. Since the action of radium, Röntgen and cathode rays varies enormously, it was found necessary to compare the effect of these rays and of ultra-violet light on the same substances. Other experiments on colored substances are also included. The substances studied were organic and inorganic, special stress being laid on the examination of minerals."

The author begins with an introductory chapter on Röntgen rays, cathode rays, ultra-violet light, phosphorescence, and luminescence. After this there comes a chapter on methods. The remaining contents of the book are classified under the headings: color changes of inorganic compounds; coloring of glasses; coloring of rock salt; coloring of gems; organic substances; precipitation of colloidal solutions by radium and by ultra-violet rays; action of radium on gases; coloring action of radium.

The author has brought together a large number of facts and the book is extremely valuable for reference purposes. It is not possible to say much for it as a constructive effort. The author has no very definite theory to bring forward and he is not at all well posted as to the chemical action of light. He does not come out anywhere with the cathode rays though he might reasonably have been expected to discover the same phenomena that Wilkinson did. In no case, does he seem to have considered the question of absorption. One must recognize that it would have been a great deal better if the author had covered less ground and had studied some portion of his subject more thoroughly.

The lack of definite conclusions appears from the following quotations:

"Röntgen rays usually produce less effect than cathode rays. ... With smoky quartz I obtained more effect with Röntgen rays than with cathode rays." "Radium rays appear to be more powerful than Röntgen rays. ... On the other hand, there are cases in which a few hours' exposure to Röntgen rays changes some minerals to an extent which is not equaled by a long exposure to radium. There seems not to be any general rule."

"It is not possible to formulate any general statement in regard to the coloring action of ultra-violet light on mineral glasses and organic dyes." "In many cases, and especially with organic dyes, the action of the two kinds of rays [radium and ultra-violet rays] are the same, both usually causing a bleaching. ... In most cases, however, the two kinds of rays act differently, as with gems and other substances. One might assume different chemical actions, such as reduction with one kind of rays and oxidation with the other. This may well be the true explanation sometimes. We may however have to deal with more purely physical changes (?) such as dissociation, formation of ions, polymerization, changes in colloidal systems, perhaps changes in the degree of dispersion of a solution or in the distance between the particles. It may be that ultra-violet light tends to cause polymerization while radium has a dissociating effect."

"If we take a large number of substances and examine the spectral change due to the coloring, it will be noticed that the direction of the change is not always the same. With most substances the color is displaced from the violet end towards the red end of the spectrum. Colorless substances tend chiefly to become yellowish brown to orange; but the sulphates of barium, strontium and lead behave differently and become blue. ... There is no general rule; blue substances change to yellow and vice-versa."

The criticism is not that the author does not answer all these questions, but that his formulation of the problem is not helpful. He makes no attempt to go back of the obvious fact. In other words he has not mastered his subject.

Wilder D. Bancroft

Physikalische-Chemische Rechenaufgaben. *By R. Abegg and O. Sackur. (Sammlung Göschen.) Leipzig: G. J. Göschensche, Verlagshandlung, 1909. 10 × 15 cm; pp. 104. Price: bound, 80 pfennigs.*—This little volume contains fifty-two questions and answers, one for each week in the year. For anything that the reviewer knows to the contrary, this book satisfies admirably the unspecified demand which it was intended to meet.

Wilder D. Bancroft

STUDIES IN THE ELECTROCHEMISTRY OF THE PROTEINS. II. THE DISSOCIATION OF SOLUTIONS OF THE "BASIC" CASEINATES OF THE ALKALINE EARTHS

BY T. BRAILSFORD ROBERTSON

(From the Rudolph Spreckels Physiological Laboratory of the University of California)

I. Introduction

In previous communications[1] I have shown that the Ostwald dilution-law for a binary electrolyte may be written:

$$m = \frac{1.037 \times 10^{-2}}{v_1 + v_2} x + \frac{1.075 \times 10^{-4}}{G(v_1 + v_2)^2} x^2 \ldots\ldots\ldots\ldots \quad (1)$$

where m is the equivalent-molecular concentration of the electrolyte, x its conductivity in reciprocal ohms per cc,[2] G its dissociation-constant and v_1 and v_2 are the ionic velocities in cm per sec. per potential gradient of 1 volt per cm. In the same communications I have shown that this law holds good for solutions of the "neutral" and "basic" caseinates[3] of sodium and ammonium and, from the values of the constants, upon the assumption that the equivalent-molecular concentration of the caseinate is equal to that of the alkali bound up in it, I computed the values of G and of $v_1 + v_2$ for these salts. It is important to note, however, that the *form* of equation (1) is the same whether the equivalent-molecular concentration of the caseinate is equal to that of the alkali bound up in it or not, provided only, that the *ratio* of

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907); 12, 473 (1908).

[2] In previous articles, cited above, I employed the symbol λ to denote the quantity $1.037 \times 10^{-2}x$, but since, in the first of these "studies," I have employed λ to denote the *depression* in the conductivity of an acid or alkaline solution which is brought about by the introduction of protein, in order to prevent confusion in the notation I refrain from again employing a special symbol to denote the quantity $1.037 \times 10^{-2}x$.

[3] That is, neutral, respectively, to litmus and to phenolphthalein.

the two concentrations is constant for all of the solutions investigated. The fact that for the salts mentioned, in which the proportion of base to casein is constant,[1] the law holds good shows that this condition is fulfilled under the circumstances of the experiments. If, however, not one but ρ equivalent-gram-molecules of caseinate are produced by the neutralization of one equivalent-gram-molecule of base then, calling *m* the equivalent-molecular concentration of the base neutralized, the equivalent-molecular concentration of caseinate in the solution will be ρm and equation (1) becomes:

$$m = \frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)} x + \frac{1.075 \times 10^{-4}}{\rho G(v_1 + v_2)^2} x^2 \ldots\ldots\ldots\ldots \quad (2)$$

and the estimates of $v_1 + v_2$ and of G in my previous papers are, in reality, the values of $\rho(v_1 + v_2)$ and of $\frac{G}{\rho}$ respectively.

In a more recent communication[2] I have shown that in all probability potassium caseinate does not yield potassium ions on solution in water, but, on the contrary, splits up into polyvalent complex ions in which potassium is bound up in a non-dissociable form. The fact that for the neutral and basic caseinates of the alkalies the Ostwald dilution-law for a binary electrolyte holds good shows that the number of these ions which one molecule of caseinate yields is, in all probability, two. The dependence of the conductivity of the caseinates of the *alkaline earths* upon their dilution appeared to afford an opportunity of testing this hypothesis, since, were we to suppose that the caseinates of the metallic bases dissociate into metal and casein ions, since those of the alkalies yield *two* ions per molecule, we should expect that those of the alkaline earths would yield *three* ions per molecule,[3] while if

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[1] = 50×10^{-5} equivalent-gram-molecule per gram for the neutral and 80×10^{-5} equivalent-gram-molecule per gram for the basic caseinates.

[2] Part I of these studies, Jour. Phys. Chem., 14, 528 (1910).

[3] Since it is known that at neutrality to litmus or to phenolphthalein casein neutralizes bases in *equivalent*-molecular proportions. Cf. Soldner: Landw. Versuchs., 35, 351 (1888). Lacqueur and Sackur: Beitr. chem. Physiol. u. Pathol., 3, 196 (1903). Van Slyke and Hart: Am. Chem. Jour., 33, 461 (1905).

we suppose, on the contrary, that the caseinates of the metallic bases dissociate into complex ions containing the metal ion bound up in non-dissociable form, then there is no apparent reason why, if the neutral and basic caseinates of the alkalies yield two ions per molecule, those of the alkaline earths should not do so also. Upon the latter supposition, therefore, we might expect the Ostwald dilution-law for a binary electrolyte to hold good for the basic caseinates of the alkaline earths, but upon the former supposition we should not.

II. Experimental

Casein, purified in the manner described by me in previous articles[1] was dissolved (as rapidly as possible) in solutions of the hydroxides of the alkaline earths $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ in such proportion that 1 gram of casein was introduced into the solution for every 80×10^{-4} gram-equivalents of the hydroxide. The solutions were therefore neutral, or very nearly so, to phenolphthalein. These solutions were then diluted to the various concentrations employed and the conductivity of the solutions measured at each dilution at 30°. The resistance-capacity of the conductivity-vessel employed was 0.1287. The following were the results obtained, the conductivity of the distilled water ($= 4.5 \times 10^{-6}$) having been subtracted from each of the observed conductivities.

TABLE I

Calcium Caseinate

Equivalent-molecular concentration of $Ca(OH)_2$ neutralized by casein	$\varkappa$ = conductivity in reciprocal ohms per cc at 30°
0.032	298×10^{-6}
0.024	254×10^{-6}
0.016	191×10^{-6}
0.012	162×10^{-6}
0.008	130×10^{-6}
0.006	113×10^{-6}
0.004	90×10^{-6}
0.002	57×10^{-6}

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[1] T. Brailsford Robertson: Jour. Biol. Chem., 2, 328 (1907). Part I of these studies: Jour. Phys. Chem., 14, 528 (1910).

TABLE II

Strontium Caseinate

Equivalent-molecular concentration of $Ca(OH)_2$ neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°
0.0224	422×10^{-6}
0.0168	338×10^{-6}
0.0112	238×10^{-6}
0.0084	202×10^{-6}
0.0056	146×10^{-6}
0.0042	121×10^{-6}

TABLE III

Barium Caseinate

Equivalent-molecular concentration of $Ca(OH)_2$ neutralized by casein	x = conductivity in reciprocal ohms per cc at 30°
0.032	326×10^{-6}
0.016	205×10^{-6}
0.008	136×10^{-6}
0.004	91×10^{-6}
0.002	59×10^{-6}

III. Theoretical

Applying equation (2) to the results enumerated in Table I and computing the constants $\frac{1.037 \times 10^{-2}}{\rho(v_1 + v_2)}$ and $\frac{1.075 \times 10^{-4}}{\rho G(v_1 + v_2)^2}$ from all of the observations by the method of least squares we obtain:

$$m = 27.89\,x + 0.267 \times 10^6 x^2$$

inserting, in this equation, the observed values of x, we can compute the "theoretical" values of m, that is, the equivalent-concentration of $Ca(OH)_2$ neutralized by the casein which should, provided that calcium caseinate dissociates into *two* ions, correspond to the observed conductivities. In the following table the observed and calculated values of m are compared.

TABLE IV

Calcium Caseinate

$m \times 10^4$ observed	$m \times 10^4$ calculated
320	320
240	243
160	151
120	115
80	81
60	66
40	47
20	24

Applying equation (2) in the same way to the results enumerated in Table II we obtain:

$$m = 32.65\,x + 0.0493 \times 10^6 x^2$$

the observed values of *m* and those calculated from this formula are compared in the following table:

TABLE V

Strontium Caseinate

$m \times 10^4$ observed	$m \times 10^4$ calculated
224	226
168	167
112	106
84	86
56	58
42	47

Applying equation (2) to the results enumerated in Table III we obtain:

$$m = 23.73\,x + 0.234 \times 10^6 x^2$$

the observed values of *m* and those calculated from this formula are compared in the following table:

TABLE VI

Barium Caseinate

$m \times 10^4$ observed	$m \times 10^4$ calculated
320	326
160	147
80	76
40	41
20	22

It is evident the correspondence between the experimental results and those which are indicated by the Ostwald dilution law for a binary electrolyte is very close—that the dependence of the conductivity of solutions of the basic caseinates of the alkaline earths is such as would be anticipated if they dissociate into only two and not three ions. In other words, these results lend further confirmation to the view that the caseinates of the metallic bases do not dissociate into metal and casein ions, but into complex ions which contain the metal bound up in a non-dissociable form.

If we compute, from the values of the constants in the above equation, the values of $\rho(v_1 + v_2)$ for these caseinates, we obtain:

For calcium caseinate $\rho(v_1 + v_2) = 37.2 \times 10^{-5}$
For strontium caseinate $\rho(v_1 + v_2) = 31.8 \times 10^{-5}$
For barium caseinate $\rho(v_1 + v_2) = 43.7 \times 10^{-5}$

While for the basic caseinates of sodium and ammonium[1] the values of $\rho(v_1 + v_2)$ at 25° are:

For ammonium caseinate $\rho(v_1 + v_2) = 82.3 \times 10^{-5}$
For sodium caseinate $\rho(v_1 + v_2) = 65.8 \times 10^{-5}$

making allowance for the difference between the temperatures at which the two sets of measurements were made, the relation between the values of $\rho(v_1 + v_2)$ for the caseinates of the alkaline earths and of the alkalies forcibly suggests the ratio 1 : 2.

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 12, 473 (1908).

I have previously pointed out[1] that the value of $\rho(v_1 + v_2)$ for neutral ammonium caseinate is somewhat less than the velocity of the ammonium ion itself, but the above values of $\rho(v_1 + v_2)$ for the caseinates of the alkaline earths are very strikingly (nearly 50 percent) less than the velocities of the metal ions themselves. Two explanations of this fact are, at first sight, open to us. Either the caseinates dissociate into metal and casein ions and ρ is 0.5 for the caseinates of the alkaline earths and 1 for the caseinates of the alkalies—or else the caseinates dissociate into two complex protein ions and ρ is twice as great for the caseinates of the alkalies as for the caseinates of the alkaline earths. From the first of these hypotheses, however, it would follow that one equivalent-gram-molecule of $Ca(OH)_2$ gives rise to 0.5 equivalent-gram-molecule of caseinate which, still retaining the view that the caseinates of the alkaline earths yield metal- and casein-ions would lead us to the absurd conclusion that in solutions of these salts the calcium ion is monovalent. On the basis of the alternative hypothesis, however, we must conclude that one equivalent-gram molecule of a hydroxide of an alkali yields twice as many equivalent-gram-molecules of caseinate as one equivalent-gram-molecule of a hydroxide of an alkaline earth. But, since casein neutralizes bases in equivalent-molecular proportions, the molecule of calcium caseinate must be twice as heavy as that of sodium caseinate. Thus, representing the mode of dissociation of basic sodium caseinate by the various possible schematic formulae:

$$NaX^{++} \overset{1}{+} X(OH)''_n; \qquad Na_2X^{++++} \overset{2}{+} X(OH)''''_n;$$

$$Na_3X^{++++++} \overset{3}{+} X(OH)_n''''''$$

according to the number of —COOH groups concerned in the neutralization of bases—then basic calcium caseinate must be represented by the corresponding schematic formulae:

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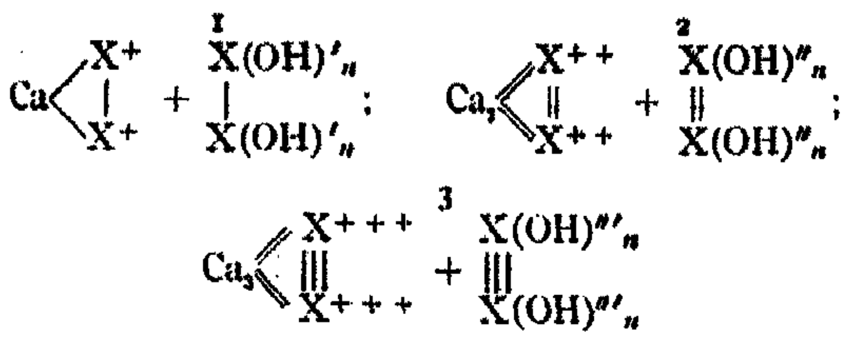
[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 542 (1907).



These schematic formulae clearly correspond with the fact that the caseinates of the alkalies can, while those of the alkaline earths cannot pass through the pores of a clay filter.[1]

Assuming that the value of p for the caseinates of the alkaline earths is 1 while for those of the alkalies it is 2 (corresponding with any of the above pairs of schematic formulae) then the values of $v_1 + v_2$ at 30° for the various "basic" caseinates would be:

For calcium caseinate	37×10^{-5}
For strontium caseinate	32×10^{-5}
For barium caseinate	44×10^{-5}
For ammonium caseinate[1]	45×10^{-5}
For sodium caseinate[2]	36×10^{-5}

It has been pointed out by Bredig[3] that the ionic mobility, with increasing complexity and weight of the ion, tends to approach a constant minimum value which, at 15° lies between 15×10^{-5} and 17×10^{-5}. Hardy has shown by direct observation that the ions of serum globulin have about this migration-velocity.[4] Assuming the lesser value, then at 15° the sum of the migration-velocities of the two protein ions into which the caseinates presumably dissociate would be about 30×10^{-5} and at 30° some 30 percent higher, *i. e.*, about 40×10^{-5}, which obviously corresponds very closely with the above estimates.

Calculating, on the same assumption, the values of G, the dissociation-constant for the basic caseinates we obtain:

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[1] W. A. Osborne: Jour. Physiol., 27, 398 (1901).

[2] The observed values at 25° having been increased by 10 percent to bring them at 30°.

[3] Bredig: Zeit. phys. Chem., 13, 191 (1894).

[4] W. B. Hardy: Jour. Physiol., 33, 251 (1905).

Salt	Temperature	G
Ammonium caseinate	25°	0.1000
Sodium caseinate	25°	0.0810
Calcium caseinate	30°	0.0029
Strontium caseinate	30°	0.0220
Barium caseinate	30°	0.0024

The smaller dissociation-constants of the caseinates of the alkaline earths is not improbably connected with the greater size of their molecules. In order to obtain a definite picture of the relative degrees of dissociation of these salts, it may be pointed out that at 0.01 *N* concentration (= 0.005 *N* concentration of the neutralized alkali or 0.01 *N* concentration of the neutralized alkaline earth) ammonium caseinate would be over 98 percent dissociated, while calcium caseinate would be only about 57 percent dissociated.

We are now in a position to interpret somewhat more fully than was formerly possible, the results obtained by Robertson and Burnett in measuring the depression of the freezing point of water due to dissolved caseinates.[1] In the first place, since there are no metal ions present in solutions of the "basic" and, probably, of the "neutral" caseinates, the observed depressions were entirely due to protein molecules and ions. In the second place, the results which were obtained by them enable us to decide, for the "basic" caseinates, between the possible pairs of schematic formulae for the dissociation of the caseinates, given above, which would satisfy the electrochemical data. If the first pair of schematic formulae represented the true state of affairs, then, since the caseinates of the alkalies are nearly completely dissociated at the dilutions employed, the solution of potassium caseinate which is formed by neutralizing *m*/50 KOH to phenolphthalein with casein should possess the freezing point of an *m*/25 solution, while, since calcium caseinate at 0.01 *N* concentration is only 50 percent dis-

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[1] T. Brailsford Robertson and Theo. C. Burnett: Jour. Biol. Chem., 6, 105 (1909).

sociated the solution of calcium caseinate which is formed by neutralizing $m/90$ $Ca(OH)_2$ to phenolphthalein with casein should possess the freezing point of an $m/60$ solution. If the second pair of schematic formulae were to represent the true state of affairs, that is, if two —COOH groups of the protein take part in the neutralization of bases to form the "basic" caseinates, then the depression of the freezing point in the first of the above-named solutions should be that of an $m/50$ solution, while that of the second should be the depression which would be observed in an $m/111$ solution. If the third pair of schematic formulae were adopted then the depression observed in the first solution should be that of an $m/75$ solution and in the second that of an $m/167$ solution. The depression actually observed in the solution of potassium caseinate was that of an $m/50$ solution, and in the solution of calcium caseinate was that of an $m/120$ solution. Obviously, therefore, we must conclude that the second of the above pairs of schematic formulae represents the true state of affairs—in other words that *in the formation of the "basic" caseinates two equivalents of base are bound up in one molecule of caseinate, and that the salt which is thus formed dissociates into two quadrivalent protein ions.*

Conclusions

1. The caseinates of the alkaline earths obey Ostwald's dilution-law for a binary electrolyte, hence they probably dissociate into two ions.

2. The values of $\rho(v_1 + v_2)$, where ρ is the number of equivalent-gram-molecules of caseinate which is formed by one equivalent-gram-molecule of base and v_1 and v_2 are the velocities in cm/sec. per potential gradient of 1 volt per cm, is twice as great for the caseinates of the alkalies as it is for the caseinates of the alkaline earths.

3. The values of $v_1 + v_2$ calculated upon the supposition that ρ is 2 for the caseinates of the alkalies and 1 for the caseinates of the alkaline earths correspond very closely with the value which would be anticipated.

4. It is concluded that the "basic" caseinates of the alkalies and alkaline earths dissociate into two protein ions each possessed of twice as many valencies as there are molecules of base bound up in one molecule of the caseinate.

5. On the basis of this assumption the dissociation-constants of the various "basic" caseinates are calculated. It appears that at 0.01 *N* concentration (= 0.005 *N* concentration of the neutralized alkali or 0.01 *N* concentration of the neutralized alkaline earth) the caseinates of the alkalies are nearly completely dissociated, while calcium caseinate is only about 57 percent dissociated.

6. Referring to the results which Robertson and Burnett obtained in measuring the depression of the freezing point of water due to dissolved caseinates, it is pointed out that they harmonize with the view that *two* molecules of base are bound up in one molecule of "basic" caseinate and that the ions into which the caseinate dissociates are, consequently, quadrivalent.

ON THE ACTION OF CRUSHED QUARTZ UPON NITRATE SOLUTIONS[1]

BY HARRISON E. PATTEN

Introduction

During a study of the absorption of soluble salts from solution it was found that crushed quartz powder apparently abstracted nitrate from a percolating sodium nitrate solution, but when the quartz was removed from its percolation cylinder and tested for nitrate, it was found that neither nitrate nor caustic soda was held by it. This means that the nitrate is decomposed during its passage through the quartz percolation-bed, and that the products of decomposition are not retained in appreciable amount by the quartz. It is to be expected that denitrifying bacteria would thus break down the nitrate in solution. In addition to this, the question naturally arises as to what part, if any, is taken in this nitrate reduction by the vast surface of quartz in contact with the percolating solution. The experiments described below were made to answer this question.

Experimental

Samples of crushed quartz were treated with C. P. concentrated hydrochloric acid for two days on the steam bath, to remove iron and to kill bacteria; they were then washed by repeated decantation with distilled water fresh from the still, until the washings gave only a faint clouding with silver nitrate, showing removal of practically all chlorine.

Experiment 1.—Twenty grams of coarse quartz powder, having a surface area of some 100 sq. cm per gram,[2] thus treated was shaken with 60 cc of 0.01 N aqueous $AgNO_3$ in a

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[1] Published by permission of the Secretary of Agriculture.

[2] This area is given as 97 sq. cm per gram in Bulletin 59, page 50, Bureau of Soils, U. S. Dept. of Agriculture (1909); this value is calculated from the mechanical analysis on page 20 of the same bulletin. The number 100 is taken here to avoid a refinement of digits unwarranted by the accuracy of both experiment and calculation by which it is derived.

flask blackened to exclude light, allowed to settle, and portions of solution drawn off and analyzed for content of silver and for traces of reduction of nitrate. The 60 cc of silver nitrate used contained 0.0647 gram Ag; of this, 0.007 gram Ag was abstracted from solution by the quartz as shown by titration of the solution before and after contact with the quartz. Further, the quartz was then extracted with distilled water until the decantations gave no cloud with KCl; then concentrated aqueous ammonia was poured upon the quartz, shaken up with it, and decanted. This ammoniacal extract gave a strong cloud of AgCl when it was acidified with HNO_3 and KCl was added. Evidently, $AgNO_3$ or Ag_2O is held on the quartz grains. The titration with 0.001 *N* $KMnO_4$ (with respect to oxygen) showed no reduction, the original silver nitrate solution and the solution removed from contact with quartz required the same quantity of permanganate to produce a coloration. The ammoniacal extract of the quartz gave no test for iron with ammonium sulphocyanate.

The area of 20 grams of this quartz being some 2000 sq. cm, we have the value 0.0000035 gram silver—as nitrate or oxide?—per sq. cm for the absorption effect in this concentration of $AgNO_3$.

Experiment 2.—Fine quartz flour, calculated area 740 sq. cm[1] per gram, HCl— and water-washed, was percolated with 0.01 *N* aqueous $AgNO_3$ containing a few drops of chloroform to maintain sterile conditions. In order to avoid contamination, the percolation apparatus shown in Fig. 1 was used. The percolation tube A expands to a wider tube at B where a perforated platinum plate is sealed in the glass. The tube A is inserted and the wide tube B filled with coarse quartz which is allowed to settle into a filter bed C through distilled water or through the solution to be percolated. The tube A is then placed mouth downward in the large test tube D which is then filled with distilled water (or with the solution to be percolated). The main filter bed of fine quartz

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[1] Bulletin No. 59, Heat Transference in Soils, p. 35 and 50, Bureau of Soils, U. S. Dept. of Agriculture (1909).

(or other absorbent powder to be studied) is now gradually poured into the large test tube and allowed to settle into the filter-bed F. Now when suction is applied at S the liquid gradually passes from E down through F, up through C and over the bend in the tube, down through T into the receiving small test tube H which stands upon the bottom of the pressure flask G.

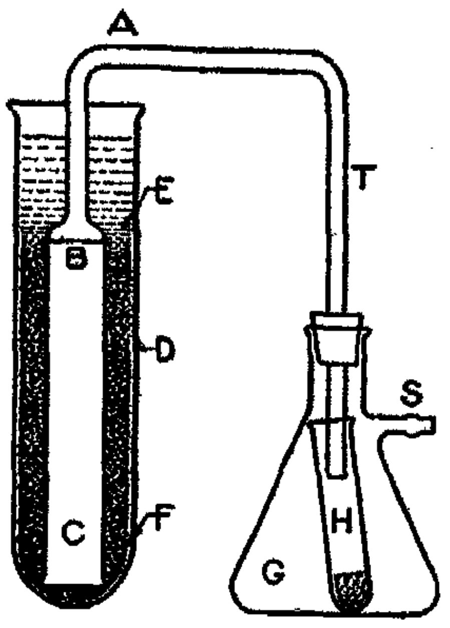

Fig. I

B = perforated platinum plate.
F = filter bed of fine quartz.
Test-tube H contains water.

The percolation apparatus was cased in black paper to avoid reduction of the silver nitrate by action of light.

Blank tests were made upon the quantity of permanganate (0.001 *N*) required to color the distilled water and the silver nitrate solution: 20 cc distilled water required 0.4 cc permanganate for coloration and one drop of chloroform produced no color change. Likewise 20 cc of 0.01 *N* silver nitrate solution required 0.25 cc of 0.001 *N* permanganate to give permanent color, and this was not changed by adding one drop of chloroform.

The first portion of percolate from 0.01 *N* $AgNO_3$ solution through this quartz-flour filter-bed showed an effect of reduction: 20 cc of percolate required 1.15 cc of 0.001 permanganate. It should be noted here that in this experiment the filter bed of quartz flour was formed in distilled water (sterile), consequently the percolating silver nitrate solution had to push ahead of it the distilled water contained in the filter-bed, so that this first portion does not contain all the silver nitrate which a normal percolate should. However, the reduction of nitrate to bodies oxidizable by permanganate is evident.

The second portion of percolate showed still greater reduction: 10 cc of percolate required 1.5 cc of 0.001 *N* permanganate, and by titration with 0.001 *N* KCl was found to contain 0.00638 gram Ag.

The third portion of percolate gave for 10 cc 0.00775 gram Ag, and required 1.2 cc of 0.001 *N* permanganate.

The fourth percolate for 10 cc required 0.7 cc of 0.001 *N* permanganate, and contained 0.00913 gram Ag per 10 cc.

All of the percolates smelled strongly of chloroform. They all held extremely fine quartz particles in suspension. The effect of these suspended quartz particles upon the color produced by permanganate was found by experiment to be either negligible or not above 0.1–0.05 cc of permanganate.

The exact total volume of each of these three percolates was not determined, the purpose here being to establish the presence or absence of surface action rather than to secure a complete quantitative percolation absorption curve.

Experiment 3.—Quartz flour washed with hydrochloric acid and with water—from the same lot used in experiment 2—was percolated with 0.01 *N* silver nitrate using the apparatus shown in Fig. 1, but leaving out the chloroform. The light was of course excluded during percolation. This filter-bed was formed in distilled water, so the first runnings were practically free from silver.

The first 10 cc of percolate (total quantity percolated) required 5.1 cc of 0.001 *N* permanganate, whereas 10 cc of distilled water requires only 0.25 cc of this permanganate solution to color it. Practically no silver was present in solution.

The second percolate (total quantity), 8.5 cc, required 1.3 cc of 0.001 *N* permanganate, and contained 0.0070 gram Ag.

The filter-bed of quartz flour contained some 100 grams of quartz in experiments 2 and 3.

Experiment 4.—Using the same form of apparatus shown in Fig. 1, but with deeper filter-bed of quartz flour—200 grams quartz—distilled water containing chloroform was percolated for some time through the quartz and it was found that only 0.2 cc of 0.001 *N* permanganate was required to color 10 cc of this percolate. The rate of percolation under a water-head of 11.5 inches was one drop in 49 seconds.

The distilled water was removed from the large test tube above the filter-bed and replaced by 0.02 *N* sodium nitrate solution containing chloroform. During 19 hours and 24 minutes 98 cc of solution percolated—part of this being, of course, displaced distilled water—which gives a rate of 0.084 cc per minute. Ten cc of this percolate required only 0.2 cc of 0.001 permanganate for coloration, consequently no reduction of nitrate is indicated. The drops of percolate are coming one every fifty seconds under 11 $^1/_2$ inches water head, so it is evident that the filter-bed has not channeled. The percolate is very slightly opalescent from minute particles of quartz in suspension.

During the next 24 hours 92 cc of solution percolated, and 10 cc of this required 0.2 cc of 0.001 *N* permanganate to color it.

The experiment was stopped at this point.

It appears then that under sterile conditions sodium nitrate is not reduced by contact with quartz to bodies oxidizable permanganate.

Silver nitrate solution under the same conditions shows a reduction, slight but perfectly evident. As would be expected, unsterile conditions show greater reduction of nitrate.

In Table I are given data and calculations which show roughly the magnitude of the effect produced by this surface action of quartz. Using the value 0.000,008 gram of oxygen per cc of 0.001 *N* $KMnO_4$, the actual weight of oxidizing oxygen supplied is calculated. If we assume that the silver nitrate is reduced to nitrite and calculate the quantity of nitrite which the oxidizing oxygen will reconvert to nitrate, a better idea of the importance of this reduction effect is obtained.

Now the quantity of silver nitrate in solution in the percolate is given (very nearly) by calculation from the silver in solution. When the ratio of (hypothetical) $AgNO_3$ to the $AgNO_3$ in solution is obtained, it is seen that the percent of reduction is by no means inconsiderable.

The fact that considerable permanganate is required to color the first portions of percolate, in both experiments 2 and 3, together with the low silver content, suggests that the ratio of silver in solution is not the same in the percolate as in the original solution; the silver being low, this indicates an acid reaction in the solution. The acidity was not tested for in these experiments, as the bearing of it on this question had not been entirely appreciated then, and it was thought sufficient to titrate with permanganate to see whether reduction had taken place.

Another aspect of this reduction is, that for every 8 grams of oxygen required to oxidize the percolate 107.88 grams of silver may have been deposited from solution—13.5 times the weight of oxygen. Consequently any experiment employing silver nitrate solution in contact with silica, or silicates or bodies capable of producing adsorption or absorption effects should be most rigidly scrutinized to insure the absence of this effect, or to determine the degree to which it enters as a disturbing factor.

Further, the fact that in experiment No. 1 a coarse quartz powder was found to retain silver—in some form—not washed out by water, but given up to ammonia-water, suggests that part, at least, of the reduction observed in these solutions takes the form of deposition of a compound of silver.

The negative result obtained with sodium nitrate indi-

TABLE I

Action of quartz powder on silver nitrate

1 Experiment No	2 Percolate No	3 Volume of percolate	4 Volume of $\frac{N}{1000}$ $KMnO_4$ cc	5 $4 \rightleftharpoons O_2$ grams	6 $4 \rightleftharpoons AgNO_3$ grams	7 Silver in solution in percolate grams	8 $7 \rightleftharpoons AgNO_3$	9 $AgNO_3$ in original solution per 10 cc grams	10 $\frac{AgNO_3}{AgNO_3}$ per cent
2	1	20	0.9	0.0000072	0.000069	?			?
	2	10	1.25	0.000010	0.000096	0.00638	0.00996	0.01433	0.96
	3	10	0.95	0.0000076	0.000073	0.00775	0.01221	0.01433	0.59
	4	10	0.45	0.0000036	0.000035	0.00913	0.01433	0.01433	0.24
3	1	10	4.85	0.0000388	0.000373	trace			
	2	8.5	1.05	0.0000084	0.000809	0.007	0.01102	0.0122	0.73

cates that the reduction of nitrate in the soil is probably due to bacterial agencies and to reduction by inorganic and organic chemical reactions rather than due to a catalytic surface effect of the soil grains. It may be that the looser combination of the heavy metal nitrates and their greater degree of hydrolysis facilitate this reduction observed for silver nitrate. The results of Graham[1] with silver nitrate solution and charcoal, giving metallic silver, support this view. Likewise of Esprit,[2] Moride,[3] Heintz,[4] Oechsner de Coninck,[5] and Liebermann.[6] The decrease in the quantity of oxidizable bodies in the silver nitrate solution and the increase of silver in solution as percolation proceeds (see Table I), gives further indication that the observed reduction of nitrate is due to an absorption which decreases as the absorptive capacity of the quartz surface is satisfied. Whether this absorption process is in part due to a purely chemical reaction of quartz upon silver nitrate, is an open question.

Bureau of Soils
U. S. Department of Agriculture
April 15, 1910

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[1] Pogg. Ann., 19, 139 (1830).
[2] Jour. Pharm., 16, 192 (1849).
[3] Comptes rendus, 41, 605 (1855).
[4] Liebig's Ann., 187, 227 (1877).
[5] Comptes rendus, 130, 1627 (1900).
[6] Wien. Akad. Ber., 74, 331 (1877).

THE PHOTOGRAPHIC PLATE. IV

BY WILDER D. BANCROFT

THE EMULSION. PART IV

The passages quoted[1] from the papers of Lüppo-Cramer, Lobry de Bruyn, Sheppard and Mees, and Eder make it quite evident that the ripening of silver bromide is not due to a reduction. It seems equally clear[2] that we are not dealing with a series of allotropic modifications. Sheppard and Mees[3] have pointed out that a mere increase in the size of the grain for the same mass of material will not account for the increased opacity and resultant increase in sensitiveness. We have thus eliminated: changes in the composition of the silver bromide itself; changes in the chemical state of the silver bromide; and changes in the physical state of the silver bromide alone. That eliminates everything in case we are dealing with pure silver bromide and consequently we are forced to conclude that the so-called silver bromide grain is not pure silver bromide but is a complex of silver bromide, gelatine, and water. The ripening of silver bromide must therefore consist in a change in the composition of the complex. In so far as we can predict these changes in composition, we can predict the changes in sensitiveness. This is really a simplified form of Quincke's hypothesis.[4] It is rather interesting to note that, at one time or another, nearly everybody comes round to some form of Quincke's hypothesis, Ostwald, Lüppo-Cramer, Sheppard and Mees, Lottermoser, Eder, Schaum.[5] The objections to Quincke's point of view are that it is unnecessarily complicated and that he did not apply it to any concrete case.

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[1] Bancroft: Jour. Phys. Chem., 14, 56, 68, 71, 73 (1910).

[2] Cf. Lobry de Bruyn: Ibid., 14, 66 (1910); Sheppard and Mees: "The Theory of the Photographic Process," p. 203 (1907).

[3] Jour. Phys. Chem., 14, 71 (1910).

[4] Ibid., 14, 73 (1910).

[5] Bancroft: Jour. Phys. Chem., 14, 60, 63, 72, 117, 118, 246 (1910).

Before showing what can be done with a simple form of the same hypothesis, it will be desirable to clear up the matter of a possible crystallization in the silver bromide grain.

Schaum[1] says that any spontaneous change to another modification, such as the crystallizing of the silver bromide must be accompanied by a decrease in the free energy and consequently a decrease in the sensitiveness to light. This is an instance of a half-truth which is much more harmful than a deliberate mis-statement. Schaum is entirely right if one grants his premises, which are that he is dealing with pure silver bromide as a one-component system. While his conclusion holds absolutely for the hypothetical case for which it is deduced, it has no bearing at all upon the actual case of a silver bromide emulsion. During a spontaneous change, the free energy of the whole system must decrease; but it does not follow that the free energy of each component decreases during that change. If we have an unsaturated solution which evaporates spontaneously, the chemical potential, and therefore the free energy of the dissolved substance increases until the solution is saturated with respect to it. If we have a supersaturated solution which then crystallizes spontaneously, the chemical potential of the solvent increases. There is therefore no *a priori* reason why the formation of crystalline silver bromide or a crystalline complex of silver bromide, gelatine and water should not be accompanied by an increased sensitiveness to light. When we are once freed from the tyranny of bad thermodynamics, it may be possible for us to find out what the facts really are instead of throwing over our observations[2] because they do not agree with some other fellow's theory.

Not having any analyses of the silver bromide grain as yet, it is impossible to say whether the ratio of gelatine to water is an important factor or not. That point can wait perfectly well till some later date when satisfactory methods

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[1] Jour. Phys. Chem., 14, 64 (1910).

[2] Cf. Bancroft: Jour. Phys. Chem., 14, 71, 102–108, 237 (1910). Sheppard and Mees: "The Theory of the Photographic Process," p. 70 (1907).

of analysis shall have been worked out. We can state definitely however that we get the maximum sensitiveness when we have a definite but small amount of gelatine in the grain, and when we have a definite but small amount of water in the grain. The sensitiveness decreases when the amount of gelatine or of water becomes greater or less than the corresponding, unknown, optimum value. We deduce this from the following facts.

A silver bromide which contains no gelatine or extremely little gelatine[1] is not as sensitive as a silver bromide containing more gelatine. The plate is also not especially sensitive if the silver bromide grain is rich in gelatine,[2] while it is much more sensitive if the silver bromide is precipitated from a solution containing only an extremely moderate amount of gelatine.[3] Since drying a plate increases its sensitiveness up to a certain point,[4] we see that there is a limiting value for which we get a maximum sensitiveness, everything else remaining the same. As further evidence, we have the fact that the original emulsion is more sensitive if a silver-rich solution is used.[5] Incidentally this explains some of the effects due to pressure.[6] It has always seemed absurd to assume that either silver or bromine could be squeezed out of silver bromide by pressures which did not rupture the gelatine film. It takes very little pressure, however, to squeeze water out of a sponge and not much to displace it in a jelly. What we do when we draw lines on an unexposed plate with a smooth glass rod, is to ripen some of the grain to the fogging point. One could probably make a slow plate more sensitive by putting it for a while under a suitable, uniform pressure; but the method does not seem to be one which promises much in the way of results.

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[1] Eder, Schumann: Jour. Phys. Chem., 14, 41, 252 (1910).

[2] Lobry de Bruyn, Eder: Ibid., 14, 69, 122 (1910).

[3] Henderson: Jour. Phys. Chem., 14, 122, 233 (1910).

[4] Baekeland, Eder, Farmer, Schaum: Jour. Phys. Chem., 14, 35, 126, 127, 128 (1910).

[5] Monckhoven, Schumann: Jour. Phys. Chem., 14, 121, 249 (1910).

[6] Eder's Handbuch der Photographie, 2nd Ed., 2, 41 (1897); 5th Ed., 3, I, 80 (1902); Baekeland: Jour. Phys. Chem., 14, 34, 38 (1910).

Since ripening, by hypothesis, consists in a change in the gelatine and water concentrations of the silver bromide grain, it follows that there is no necessary connection between sensitiveness and coarseness of grain. While it is pretty generally true that the sensitiveness of a commercial plate increases with increased coarseness of grain, this must be looked upon as purely accidental. It is due to the fact that as yet we do not know any method of obtaining the desired concentrations within the grain without at the same time causing an agglomeration. If it were possible to take a very sensitive plate and to chop up the coarse grains with so sharp a knife that there was no pressure exerted upon them, I do not believe for a moment that such a hypothetical plate would show a decrease in sensitiveness. When we are dealing with silver bromide and water only, the finest grains are the most sensitive.[1] Here we are dealing with a two-component system with one volatile component and it is therefore easy to get any desired composition of the grain. With a three-component system, silver bromide, gelatine, and water, the adjustment of the concentrations is not so simple. Since we have not known that we were trying to adjust concentrations, it is perhaps not surprising that only one type of ripening has been worked out and that people have therefore been led to false conclusions.[2] It should be possible to make a plate which would come nearer to satisfying the astronomers[3] than anything now on the market. It is interesting to note a comparatively recent statement by Wallace:[4] "Messrs. Lumière have introduced a special 'Σ' emulsion, which from measurements by the writer gives a special increase of 2.3 times that of the 'Seed 27 Gilt Edge.' This Σ plate, however, cannot be used generally in astronomical work, as the grain is 1.7 larger than that of the '27.' The Σ plate also fogs badly in development."

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[1] Cf. Weisz: Jour. Phys. Chem., 14, 248 (1910).

[2] Cf. Bancroft: Jour. Phys. Chem., 14, 98, 99, 102, 106, 109, 115 (1910).

[3] Wallace: Jour. Phys. Chem., 14, 120 (1910).

[4] Astrophys. Jour., 28, 42 (1908).

Now that we know what constitutes ripening, we can draw some interesting conclusions in regard to the limits of ripening. Under ordinary conditions the limit of ripening is reached when the unexposed plate fogs in the developer.[1] Since the plate is never uniform,[2] we may easily have a small portion of the emulsion in an over-ripened state while the bulk of it is not up to standard pitch. I have not been able to find any published accounts of anyone having taken special precautions to obtain an exceptionally uniform product, though it is probable that something of this sort is done by some manufacturers.

Van Bemmelen[3] has already shown that a silicic acid gel contains more water when precipitated from a dilute solution than when precipitated from a concentrated solution. These gels change in composition with time, temperature, partial pressure of water vapor, and concentration of other substances. This is exactly what the photographic emulsion does except that we measure the change of concentration indirectly by means of the sensitiveness. The silicic acid gel changes slowly on standing under ordinary conditions, much more rapidly when heated. The silver bromide emulsion ripens slowly in the cold and very much more rapidly when heated. If the silicic acid gel is precipitated from a concentrated alkaline solution of silicic acid, it comes down in a form similar to that obtained by aging a gel precipitated from a more dilute solution. This is very like what happens with a silver bromide emulsion.

In all matters affecting the emulsification and ripening of silver bromide we are dealing with phenomena which are not really photochemical at all. We make use of photochemistry to show that the emulsion has ripened; but the phenomena of ripening are common to all emulsions whether sensitive to light or not. Until we have a fairly satisfactory theory for emulsification and ripening in general we cannot

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[1] Bancroft: Jour. Phys. Chem., 14, 41, 42 (1910).

[2] Eder: Ibid., 14, 45 (1910).

[3] Zeit. anorg. Chemie, 13, 233 (1897).

hope to clear up all the details of the special case. It is worth while however to consider what we know about the general theory of emulsification and of ripening. We can then see in how far we can apply this knowledge to the particular case of silver bromide emulsions.

Wolfgang Ostwald[1] discusses the phenomena of emulsification but comes to the conclusion[2] that we are still far from a satisfactory theory of the emulsifying action of certain ions. Freundlich[3] gives us more facts and makes us think that we are getting ahead.

"We may picture to ourselves the action of a protecting colloid somewhat as follows: The formation of an outer film when the particles have the same charge depends chiefly on straight adsorption; when the particles have different charges, it depends also on the electrical adsorption. If the film is once formed, it protects to the extent that the sol can now be considered as an emulsion colloid and is therefore less sensitive to electrolytes, for instance. If this film is tough, the uniting of two particles of the suspension colloid is of course made very much more difficult thereby. *But even though the film is not especially tough and merely consists of substances which lower the surface tension very much*—which is necessarily the case since they are adsorbed—*this alone must check agglomeration very markedly.*

"Donnan[4] has shown that when there is a contact between two particles, each surrounded by a film, there is necessarily an increase in the concentration of the adsorbed substance at the surface of contact. The surface tension will therefore be decreased still more at that point and the higher surface tension at the other portions of the surface will not favor a fusion at that point but will rather tend to tear the particles apart because the substances in the surface film will always

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[1] Grundriss der Kolloidchemie, 289–309 (1909).
[2] Ibid., p. 308 (1909).
[3] Kapillarchemie, 456, 459, 473 (1909).
[4] Zeit. phys. Chem., 31, 42 (1899).

tend to pass from the place of lower surface tension to that of higher surface tension.

"These changes make it intelligible that the protecting colloids, previously mentioned, are able to preserve an already existing or just formed mass of very fine particles and *are also able to emulsify a solution in mass.* The emulsifying action of alkali on oils has long been known. If one pours a layer of dilute alkali over a commercial oil such a olive oil, a very slight shaking is enough to form a milky liquid. After Gad[1] had made a number of qualitative experiments, Quincke[2] increased our knowledge of the phenomena very considerably by showing that oil is emulsified only by such dissolved substances as lower very much the surface tension between oil and water." "The reason why colloidal solutions of soaps, albumen, starch, and glue are so effective in forming emulsions, seems to be that, with these substances which diffuse so slowly, the adsorption and the equalizing of the concentrations does not take place rapidly. Consequently, the differences in the surface tension are maintained long enough to enable the mechanical effect to take place.

"The mechanism of the conditions for stability with emulsion colloids was previously referred generally to the solubility of the colloid phase; but it is now very probable that it may be due to the mutual reaction with the dispersing medium, in that the *liquid, dispersed phase is separated from the dispersing medium by an adsorption film containing a substance or substances formed by inter-action with the dispersing medium.* Thus the stability of an oil emulsion depends on the soap solution due to the action of alkali on oleic acid. This is the explanation which Quincke has given for the stability of colloidal solutions because the 'oily liquid' which he mentions so often is merely the adsorption film."

"We have already described how we are to picture to ourselves the emulsifying action of soap on oil. In the ex-

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[1] Du Bois-Reymond's Archiv. anat. Physiol., 1878, 181.

[2] Wied. Ann., 35, 380 (1888).

periments then under consideration, there was an external pressure driving the oil into the dispersing medium. We must now consider how the emulsification takes place under ordinary conditions. From the experiments of Quincke[1] we know that oleic acid is not emulsified in pure water and that soap must be present. The tendency of the oleic acid to emulsify is especially marked if the acid is brought in contact with an alkaline solution and this solution then diluted with, or replaced by, water. From the oleic acid there protrude globular and worm-like growths—the myelin forms—which show a tendency to split off drops of oil, so that finally the oil is emulsified in the water. Similar phenomena are obtained by adding a solution of an alkali oleate to oil and water. The following sequence of events is quite probable. The alkali oleate tends to distribute between the oleic acid and the water. An alkali oleate is soluble in a good deal of water; but with oleic acid it forms masses which are sparingly soluble in water. At the surface between oleic acid and water, there is formed a film of an acid oleate, this film being permeable to water. Just as in Traube's experiments, some water will tend to pass into the oleic acid phase in order to dissolve more alkali oleate, and consequently we have an arching of the oleic acid phase. This then becomes more marked because the surface tension is lowered by the adsorption of the alkali oleate dissolved in the water. This does not take place entirely regularly and the surface tension consequently varies from point to point. These differences of surface tension set in motion the outgrowths from the oleic acid phase and cause the formation of drops.

"The behavior of the oleic acid has been taken as typical. It seems probable that we have similar conditions whenever amorphous substances or gels are emulsified in liquids, as for instance when albuminoids are dissolved in alkali or stannic acid in ammonia. A part of the phase which is to be emulsified dissolves in the dispersing medium as a substance which is adsorbed very gently. Protuberances arise from swelling

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[1] Pflüger's Archiv., 19, 129 (1879); Wied. Ann., 53, 593 (1894).

or from liquid passing through a semipermeable wall and the rest of the emulsification is caused by movements due to differences in adsorption and resulting differences in surface tension. In other cases it seems to be essential that the natural gel shall be freed from a protecting film before the dispersing medium can act. After a dilute solution of permanganate or any other oxidizing agent has acted on a starch, this substance dissolves more readily in water than it did before the treatment."[1]

There are some specific facts in regard to the reversible coagulation of gelatine solutions which we need and which I therefore quote.[2]

"Electrolytes and other foreign substances affect the reversible change of sol to gel to a great extent and in a very complex way for we have to distinguish between two fundamentally different things. The equilibrium between sol and gel may actually be displaced and the rate of gelatinization may be changed. This is easily seen from the following considerations: At higher temperatures a pure gelatine sol is practically a stable sol and its viscosity does not increase. If cooled, a range of temperatures is reached where the viscosity is not constant. It increases rapidly or slowly until the sol has solidified to a gel. The foreign substances may not only displace the critical range of temperatures; they may also alter the rate of change. Since we have not been able to separate these two effects, it is not surprising that the action of foreign substances seems complex. It is pretty certain that both must be taken into account, because otherwise one must postulate enormous retarding effects, since many substances (sulphocyanates for instance) are able to keep a gelatine solution containing fifty grains to the liter, liquid for an indefinite time at temperatures well below that of the 'point of modification.'

"We can however say that, with electrolytes, the effects

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[1] Wolff: Comptes rendus, 141, 1046 (1905).

[2] Freundlich: Kapillarchemie, 418, 420, 423 (1909).

are always lyotropic.[1] Sulphates, tartrates, etc., raise the point of solidification, decrease the period of solidification, and increase the rate of change of the viscosity with the time. They therefore help the solidification. Chlorides, nitrates, bromides, iodides, sulphocyanates act in the opposite way and in that order. We therefore have again the series

$SO_4 > CH_3CO_2 > Cl > NO_3 > Br > I > SCN$ ($>$ benzoates, salicylates).

"The effect of the cations is very limited and counts only in the neutral region. Hydrogen and hydroxyl ions act like chlorides and nitrates; they check gelatinization."

"The electrolytes show another peculiarity beside that of affecting the gelatinization. They may precipitate the gelatine or salt it out. When the concentration of the electrolyte is high, the gelatine precipitates in clots which do not form a sol spontaneously when the solution is diluted. This precipitation can be brought about both by electrolytes which increase gelatinization and by those which check it. This is a proof that we are dealing with a phenomenon quite distinct from the one affecting the reversible change of sol to gel. . . . Although potassium chloride lowers and sodium sulphate raises the temperature of solidification, concentrated solutions of both salts cause the precipitation of flocks. . . . If we arrange the salts according to the strength of their precipitating powers we get again a lyotropic series.

$SO_4 >$ Citrate $>$ Tartrate $>$ Acetate $>$ Chloride.

That salt is said to have the highest precipitating power which precipitates with the lowest concentration.

"The precipitation differs from the change in the gelatinization because non-electrolytes do not precipitate gelatine. They often prevent the precipitation and, sometimes, change the flocks back into a colloidal solution. The action

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[1] (Affecting the internal pressure. Freundlich: Kapillarchemie, p. 54 (1909)).

of several electrolytes is not additive and in such solutions a number of complications arise.[1]

"There is still a third phenomena which complicates the properties of a gelatine sol. A pure sol is not stable even at the higher temperatures at which it does not gelatinize. The viscosity decreases continuously until it reaches a definite, final value. At the same time the sol loses the power to gelatinize. It changes from the α form to the β form; it becomes saponified.[2] Hydrogen and hydroxyl ions accelerate this irreversible change very much and this must always be kept in mind in experiments in which the sol is heated, no matter for how short a time.

"Although the multiplicity of these properties is very perplexing, the transfer of water must be the important factor in all cases. If this were not so, the lyotropic influences would not be so prominent. From the experiments on viscosity, we concluded that gelatine sols contain a very viscous phase which is rich in gelatine and poor in water. This phase preserves to a great extent the viscous and solid properties of the amorphous gelatine. Gelatinization must be due to the fact that these finely divided masses, which are chiefly in the form of drops at high temperatures, coalesce as the temperature falls and become ever more viscous. This is certainly due in part, if not entirely, to a decrease in solubility. These viscous masses finally form the skeleton throughout which the drops of the solution are distributed; in other words, a gel is formed. The effect of the foreign substances must be due to the fact that they change the solubility of gelatine in water and to the fact that by dissolving in the gelatine phase they change its viscosity. Since the effects of the foreign substances are largely additive, it looks as though it were more a case of solubility than of a surface condensation."

"A large number of other emulsion colloids behave like the gelatine sol. The best known of these is the sol

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[1] Pauli and Rona: Beiträge chem. Physiol. und Pathol. 2, 25 (1902)

[2] v. Schroder: Zeit. phys. Chem., 45, 94 (1903).

of agar-agar, a substance whose chief constituent is a polyose, *∂*-galactone. Its power of gelatinizing is much greater than that of gelatine since a sol containing only one gram to the liter gelatinizes at 0°. Foreign substances affect the agar-agar sol much as they do the gelatine sol. Nitrates, iodides, sulphocyanates, benzoates, urea, thio-urea, increase the time of gelatinization while salts of polybasic acids, acetates, bromides and chlorides decrease it."

Freundlich[1] also gives some special facts with regard to silver salts which are of distinct interest to us.

"Lottermoser and Rothe[2] have shown clearly that there is always adsorption of the salt present in excess when the silver iodide sol is formed; and that this salt can be displaced by others. Thus, silver iodide, precipitated from an ammoniacal solution contains ammonia which can be displaced by nitric acid, whereby some ammonium nitrate remains in the surface. This was finally removed by careful washing. The adsorption of silver nitrate by this precipitated silver iodide is described by an exponential formula. Within certain ranges of concentration a similar formula holds good for the adsorption of potassium iodide, although at the higher concentrations there is a surprising decrease in the amount adsorbed. This last is probably to be accounted for by the assumption that silver iodide changes its structure and consequently its adsorbing power."

"Lottermoser prepared sols of silver halides by letting a dilute solution of a silver salt flow into a dilute solution of an alkali chloride. *The silver halide remained if there were a slight excess of alkali halide in the solution.* The sol precipitated in flocks, however, if the two solutions were exactly equivalent, so that the whole of the halide reacted with the silver. When the sol was dialyzed, a trace of alkali halide always remained adsorbed, just as happens with other electrolytes and other sols. These sols were negative and the halogen ion was therefore adsorbed more strongly than the

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[1] Kapillarchemie, 323, 360, 361 (1909).

[2] Zeit. phys. Chem., 62, 359 (1905).

alkali ions. The experiments were made chiefly with iodides.

"With the silver halide it was also possible to prepare a positive sol. If Lottermoser let a dilute solution of an alkali halide flow into a dilute solution of a silver salt, he obtained a positive sol, so long as there was an excess of silver salt, owing to the greater adsorption of the silver ion. Here too there was flocculation when the solutions were equivalent."

"If the disperse-phase is precipitated as flocks, the suspension is not so simple a matter, while one may consider the submicrons as loose groups of amicrons in which the Brownian movements help out the disintegrating action of a charge. The stationary, precipitated flocks are not in a state of equilibrium. As we shall later describe more in detail, they change from the amorphous, finely-divided form into even coarser and more crystalline forms and, with the smaller surface, offer ever fewer points of attack to each disintegrating influence. Freshly precipitated flocks are therefore easily brought into colloidal solution again under certain conditions, whereas it is more difficult with older ones and requires the use of mechanical means, fine grinding, powerful stirring and the like. Such a behavior has been observed by many different investigators[1] during the formation of colloidal sulphides, hydroxides, etc."

We can now discuss some of the facts in regards to the peptonizing of silver halides.[2] Silver bromide can be precipitated in aqueous solution and subsequently emulsified by a hot solution. Since we know that gelatine is adsorbed by silver bromide, this is right in line with the general facts in regard to emulsification. The silver iodide hydrogel is converted into a hydrosol by potassium iodide and there is an optimum concentration of the iodide. Since the iodide is adsorbed, it should tend to peptonize the gel. While we

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[1] For instance, Spring: Ber. chem Ges. Berlin, 16, 1142 (1883); Linder and Picton: Jour. Chem. Soc., 61, 114 (1892); Wissinger: Bull. Soc. chim. Paris, 49, 452 (1888).

[2] Bancroft: Jour. Phys. Chem., 14, 15-23 (1910).

do not know in this case just what determines the optimum concentration, it seems to depend on a balance between the peptonizing action and the precipitating action. We get a similar phenomenon with salts, gelatine and water. We have another form of the same thing in Lüppo-Cramer's experiments, where a hydrosol is obtained if silver halides are precipitated with a slight excess of halide, whereas no hydrosol is obtained when there is no excess or when there is a very large excess of the halide. We must keep in mind, however, that the balance here is not between the peptonizing and the precipitating actions; but between the peptonizing and the solvent actions, because the silver halides form true solutions with an excess of the alkali halide. Since gelatine will emulsify a silver halide, it is not surprising that gelatine and potassium bromide should emulsify silver chloride. What does not seem clear, however, is Lüppo-Cramer's statement that silver chloride, formed by precipitation from aqueous solution, shows no tendency to emulsify in gelatine under the influence of chlorine ions. It looks as though this experiment would have to be repeated. It is quite natural that the gelatine should decrease the pectizing effect of an excess of bromide. Since gelatine is a much more efficient protecting colloid than dextrine, gum arabic, or albumen in the case of colloidal gold,[1] it is not surprising that Lüppo-Cramer should also have found it more effective with respect to silver bromide. I do not at present know how we could have predicted the great emulsifying power of collodion in presence of potassium bromide, nor why it should not emulsify silver bromide in presence of ammonia. That a heated silver bromide or iodide should not peptonize readily with gelatine and bromide is not surprising because heating in that way ages the gel and it is an entirely general fact that a gel, which has aged, is not readily converted back into a sol. One must be permitted to doubt the absolute accuracy of Lüppo-Cramer's statement. It seems probable that he has not paid sufficient attention to the time factor though,

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[1] Freundlich: Kapillarchemie, 451 (1909).

of course, irreversible changes are not out of the question. However this may be, it is clear that the failure to peptonize a ripened Schleussner plate with bromide comes under the same head. Lüppo-Cramer was dealing with a silver bromide gel which had been aged or ripened. Carey Lea's experiments with colloidal silver are in harmony with this. When his reducing agent gave him a silver containing little or no water, a gray silver, it could not be peptonized. When he obtained a silver with more water in it, the silver could be converted into a sol.

In view of the fact that ammonia ripens silver bromide and therefore removes water and probably gelatine from it, the silver bromide from an ammoniacal solution is probably in a higher stage of ripening than a silver bromide precipitated from a neutral solution. If this proves to be the case the following paragraph contains nothing surprising.[1]

"If the silver bromide is formed from ammoniacal silver oxide instead of from silver nitrate, it differs in shape and color from that precipitated from a neutral solution and it cannot be peptonized in presence of gelatine. Even when not precipitated in presence of ammonia, it only requires a few minutes shaking of the silver bromide with a very dilute solution of ammonia to bring the silver bromide into such a state that ammonia does not cause an emulsification in presence of gelatine. Bromides cannot peptonize a silver bromide precipitated from an ammoniacal silver oxide solution."

Under conditions of precipitation we must consider the statement[2] that a moderate excess of potassium bromide is desirable. An excess of silver nitrate would not be possible because it would react with the gelatine during ripening and cause fogging. A moderate excess of potassium bromide would make the silver bromide less soluble and would, there-

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[1] Lüppo-Cramer: Jour. Phys. Chem., 14, 23 (1910). Through an inadvertence the words "silver nitrate" and "ammoniacal silver oxide" have been transposed in the original paragraph.

[2] Jour. Phys. Chem., 14, 14, 15, 44, 106 (1910).

fore, presumably make it precipitate with less water and therefore in a more sensitive form. When we come to the effects of an excess of bromide, the matter is not so simple. The bromide will make the silver bromide more soluble, which would accelerate crystallization and would therefore make the silver bromide more sensitive. The potassium bromide may also lower the setting-point of the gelatine which would presumably be bad for the plate. It therefore seems possible only to predict that a large excess of bromide will be beneficial or will be deleterious, depending on which of two unknown factors one assumes to be the more important. This harmonizes only too well with the experimental data. The following two sentences will illustrate my meaning: "A very finely divided, extremely satisfactory silver bromide is obtained by dissolving this salt hot in potassium bromide and then causing it to separate either by cooling the solution of by diluting it with a gelatine solution." "When an emulsion contains too large an excess of potassium bromide it is apt to be flat or even fogged after ripening by cooking." It is quite clear that these experiments must be repeated by the same man so that we may have comparable data. It is quite possible that the sentences quoted are both correct; but that does not help us until we know what the other conditions were.

Since ripening, by hypothesis, consists in bringing the composition of the silver bromide grain toward certain values of silver bromide, gelatine and water, there are at least three different ways in which this can be done. For lack of better names we will call these processes: recrystallization, dehydration, and degelatinization. We may add something which will first dissolve the silver bromide and then let it separate in a more nearly crystalline form. Abney's explanation[1] for the advantage in using an excess of potassium bromide when precipitating silver bromide is that "silver bromide is soluble in potassium bromide and crystallizes, on cooling, in yellowish crystals which yield a green, highly

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[1] Jour. Phys. Chem., 14, 14 (1910).

sensitive silver bromide when washed." Lüppo-Cramer[1] notes that "an excess of halide salt causes a crystallization of the grain more readily with silver bromide than with silver chloride, while ammonia changes silver chloride to the crystalline state more readily than it does silver bromide. Silver iodide is extraordinarily readily soluble as a complex salt and we shall see in the following paper that it becomes crystalline especially easily when a large excess of iodide is used, while ammonia seems to have no effect of that sort at all." Everybody knows that the solubility in ammonia decreases from silver chloride to silver iodide and it is this property which determines the rate of ripening.

A beautiful instance of the same thing occurs in the case of silver nitrate and silver iodide.[2] "Silver nitrate also has a marked ripening action on grainless silver iodide gelatine. The greenish yellow, opalescent emulsion becomes at once intensely yellow. If it is heated it soon becomes entirely opaque and the grain even coarsens until the plate lets grayish blue light through whereas a pure silver iodide emulsion scarcely changes at all. The ripening, or grain-coarsening action, of an excess of an iodide is much less than that of an excess of silver nitrate when the emulsion is hot, while the reverse is the case when the emulsion is cold. With the grainless silver bromide gelatine, silver nitrate checks the ripening process as I have already pointed out, and the same effect is produced with silver chloride gelatine." In Dammer's Handbuch there is no reference to the solubility of silver iodide in silver nitrate and one might easily suppose that some other explanation would have to be found.[3] Fortunately Hellwig[4] has shown not only that silver iodide is soluble in silver nitrate but that it is much more soluble than either silver bromide or silver chloride. At 25° silver iodide is less soluble in a given silver nitrate solution than it is in

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[1] Jour. Phys. Chem., 14, 105 (1910).

[2] Lüppo-Cramer: Jour. Phys. Chem., 14, 119 (1910).

[3] Cf., however, Comey: Dictionary of Chemical Solubilities, 374 (1896).

[4] Zeit. anorg. Chem., 25, 157 (1900).

an equivalent solution of potassium iodide. While Hellwig does not give solubilities at higher temperatures, the following passage makes it probable that the solvent action of silver nitrate increases more rapidly with the temperature thand does that of potassium iodide.[1]

"If silver iodide is added to a hot concentrated solution of silver nitrate, the silver iodide clots to a compact mass, the surface of which is covered with a film of whitish crystals. These crystals are probably the double salt $Ag_3I(NO_3)_2$. If the mass is stirred thoroughly with a glass rod, the silver iodide and the adhering crystals dissolve slowly, and there is formed a colorless liquid with a high refractive index. If still more silver iodide is added, there comes a point where the iodide melts at the bottom of the vessel to a pale yellow oily liquid. This oily liquid and the supernatant aqueous solution form two clearly-marked liquid layers. If these two phases are shaken together vigorously, a dirty yellow emulsion is formed which soon separates into the two clearly marked liquid layers. If the upper colorless layer is poured off quickly and carefully, and is allowed to cool slowly, colorless, pointed needles crystallize. The oily layer solidifies to a dirty yellow crystalline mass. The oily phase is certainly to be considered as a solution of silver nitrate, water and complex salt in silver iodide, the melting point of which has been lowered from 527° to below 100°."

We can remove water from the emulsified silver bromide grains by dehydration and when we do so we increase the sensitiveness.[2] This loss of water is very possibly also accompanied by an extrusion of gelatine; but we have no direct proof of this as yet. In any event the elimination of gelatine does not keep pace with the elimination of water because there seems to be a limit to the sensitiveness which can be obtained by merely drying a plate.

There is also the possibility of degelatinization, in other

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[1] Hellwig: Zeit. anorg. Chem., 25, 166 (1900).

[2] Baekeland, Eder, Farmer, Schaum: Jour. Phys. Chem., 14, 35, 126, 127, 128 (1910).

words that our ripening agent may remove gelatine from the silver bromide grain either directly, by acting as a solvent for the gelatine, or indirectly, by changing the temperature of solidification of the gelatine or something of that sort. Since we invariably get an agglomeration during ripening, it is clear that every ripening agent must either act as a solvent for silver bromide or must remove from the surface of the silver bromide grain substances which lower the surface tension, in other words, gelatine and water. This last conclusion may be considered a strong argument in favor of the theory under discussion or it may be looked upon as an ingenious case of reasoning in a circle. Personally, I am a little doubtful how to classify it.

So far as one can judge from the paragraphs quoted,[1] the hard gelatine is not so readily adsorbed as the soft gelatine and consequently it is easy to overdo the ripening and to get plates which fog. With the soft gelatine this difficulty is eliminated to a certain extent but we then get a film which does not adhere so well to the glass. When plates are made on a commercial scale, it may be safer, as Eder says, to have the soft gelatine constitute one-third to one-half the mixture. If one wishes to make a special plate for a special purpose, it would seem wiser to take no chances and to use the hard gelatine. As against that, we have Schumann's statement[2] that the best gelatine to use is soft gelatine, Nelson's No. 1. This apparent contradiction seems to be due to two things. The statement that "a hard gelatine fogs readily" is very vague and does not mean much of anything until one knows the conditions. In the second place Schumann was not ripening his plates and he was working under such conditions that the danger from frilling was reduced to a minimum. Consequently, what holds good in this case does not necessarily apply in other cases.

Since we are maintaining that there is no necessary connection between the coarsening of the grain and the in-

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[1] Bancroft: Jour. Phys. Chem., 14, 52 (1910).

[2] Jour. Phys. Chem., 14, 257 (1910).

crease in sensitiveness, it will be wiser to consider these two phenomena separately and we will therefore take up first Lüppo-Cramer's[1] experiments on the coarsening of the grain in so-called grainless emulsions. Lüppo-Cramer found that ammonia, ethylene diamine, ammonium sulphocyanate, sodium sulphite,[2] sodium amino-acetate, potassium cyanide, the thiocarbamides, bromides, chlorides, and hydrochloric acid "coarsen the grain of a so-called Lippmann emulsion quickly and visibly when the latter is heated in presence of one of them." He refers this very properly to the solvent action on silver bromide. He finds however that soda and also sulphuric acid increase the size of the grain fairly rapidly, and he says:[3]

"The acceleration of the coarsening of the grain by soda, bisulphite, and sulphuric acid cannot be accounted for in the same way because these substances have no solvent action at all upon silver bromide, as is easily shown by the fact that they do not prevent the precipitation of silver bromide. Since the growth of the grain is obviously affected by the greater or lesser viscosity of the colloidal medium, we might account for the effect of these reagents, and especially of sulphuric acid, by postulating that they increase the rate of growth indirectly by decreasing the cohesive action of the glue and by thus permitting the grains to coalesce more readily."

Since there is no solvent action on silver bromide, we must be dealing with a degelatinization. It is interesting to note that sulphates head one of Freundlich's lyotropic series;[4] but I fear that this is merely a coincidence. While sulphates act one way on gelatine, acids act the other way and consequently we could only have a differential effect with sulphuric acid at best. If the coarsening of the grain is due to the acid, nitric acid should be more effective than sulphuric acid,

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[1] Jour. Phys. Chem., 14, 110–116 (1910).

[2] On p. 110, eighth line from top, read sulphite instead of bisulphite.

[3] Lüppo-Cramer: Jour. Phys. Chem., 14, 112 (1910).

[4] Kapillarchemie, p. 418 (1909).

which is not the case. If the coarsening of the grain is due to the sulphate, then nitric acid should have no effect. The results are therefore inconsistent and more experiments will have to be done before this matter is settled.

The experiments with bathed plates are identical in principle with those on recrystallization, p. 636. Lüppo-Cramer[1] added silver nitrate solution or ammoniacal silver oxide solution to gelatine films containing potassium iodide, potassium bromide or sodium chloride. He found that when silver nitrate is added, the iodide plate becomes opaque more rapidly than the bromide plate or the chloride plate, while the reverse is true in case of an ammoniacal silver solution. Silver nitrate dissolves silver iodide more readily than it does silver bromide or chloride, while ammonia dissolves silver chloride and bromide more readily than it does silver iodide. Since the composition of the silver bromide grain changes during ripening and since the change in composition consists in an elimination of gelatine and water, there is no longer any difficulty in accounting for the increasing opacity.[2]

The effect of different substances in changing the sensitiveness of a photographic plate has been summed up by Sheppard and Mees[3] in the following words: "Generally silver solvents facilitate ripening. Oxidizing agents retard it, but this has been dealt with under desensitizers, while reducing agents are said to have a favorable influence. But this may be merely due to a destruction of a desensitizer."

While this summing is not complete and is not entirely correct, it will do admirably as a starting point. Everybody is agreed that substances which dissolve silver bromide promote ripening, provided no other reaction takes place. Not having any theory to guide them, Sheppard and Mees have overlooked the possibility of dehydration and of degelatiniza-

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[1] Jour. Phys. Chem., 14, 77 (1910).

[2] Sheppard and Mees, Gaedicke: Jour. Phys. Chem., 14, 71, 98 (1910).

[3] Jour. Phys. Chem., 14, 70 (1910).

tion. Sheppard and Mees[1] consider oxidizing agents as desensitizers and they show that the action of such substances as cupric,[2] ferric, mercuric, and uranic salts "occurs *during exposure by reversal of the photochemical action*, and not by any modification of the sensitive salt." "From all these results it appears justifiable to conclude that a definite quantity of the metallic salt is irreversibly absorbed by the silver halide, and that this subsequently counteracts the photochemical action during exposure. It is probable that something of the nature of a solid solution is formed, the maximum effect with any salt being the quantity which forms a saturated solution of the halide."

If one is to call these oxidizing agents desensitizers, it would seem the natural thing to call reducing agents sensitizers instead of considering their effect as limited to the destruction of a desensitizer. In so far as a substance acts as an oxidizing agent or a reducing agent, it is a depolarizer and consequently has an effect on the sensitiveness. Before this point of view can be accepted, it is necessary to discuss some of Lüppo-Cramer's objections[3] to the theory of sensitizers.

Lüppo-Cramer bathed collodion plates in specified solutions for one minute and then washed the plate thoroughly. He found that there was a marked decrease in apparent sensitiveness when the bath contained ferric chloride, acidified ammonium persulphate, potassium permanganate, acidified bichromate, cupric chloride, or potassium ferricyanide. Since these are all oxidizing agents, the results are exactly what they should be, though that is not the conclusion that Lüppo-Cramer draws.

He next tried substances which absorb halogen. "If a collodion plate is bathed for one minute in a one percent aqueous solution of aqueous hydroquinone and the plate is then washed thoroughly, the sensitiveness is doubled and

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[1] "The Theory of the Photographic Process," 247, 254, 257, 260 (1909).

[2] Cf. Eder: Jour. Phys. Chem., 14, 215 (1910).

[3] Jour. Phys. Chem., 14, 129–145, 147–149 (1910).

there is not the slightest formation of fog. Adurol, the halogen-substituted product of hydroquinone, behaves just like the latter; but no increase of sensitiveness is to be noted when the plate is bathed in pyrogallol, metol, gallic acid or iron vitriol. On the other hand, it seems as though these substances behave like hydroquinone if the plates are left in the solutions for a longer time. An effect is obtained with pyrogallol by allowing the emulsion to stand in an alcoholic pyrogallol solution for several hours. Exactly the same thing happens with narcotine, in regard to which von Hübl[1] also established that its action as a sensitizer only appears after a long time."

This again is exactly what should happen provided we supplement the theory of sensitizers by the very probable assumption that some substances take longer than others to diffuse into, or be adsorbed by, the silver bromide grain. Lüppo-Cramer considers these results as fatal to the theory of sensitizers because "the increase in sensitiveness caused by the sensitizers occurs when the sensitizer has been in contact with the unexposed silver bromide for a greater or lesser time but has been removed completely from the film." The whole difficulty lies in the last half a dozen words. Lüppo-Cramer believes that the sensitizer has been removed completely from the film while most people doubt it.

The following quotation from Sheppard and Mees[2] seems to have a bearing on this point: "Lumière and Seyewetz have shown the tenacity with which this 'hypo' is retained. A parallel experiment with potassium bromide showed that the film retained sufficient bromide after five minutes' washing to influence considerably the *subsequent development*. However, increased washing only slightly affected the result with thiosulphate. Experiments on the characteristic curve showed that it was impossible to wash out the hypo completely. Treatment with hypo destroyers lessened the effect partially, but not entirely. It appears

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[1] Die Collodiumemulsion, 35, 52.

[2] "The Theory of the Photographic Process," 135 (1907).

probable that the thiosulphate is strongly absorbed by the silver bromide, possibly forming to some extent a solid solution, or traces of a solid double thiosulphate.

In another place Sheppard and Mees[1] point out that "freshly precipitated silver bromide treated with bichromate or chromic acid takes a yellow coloration, which is not removed by long washing." Since the results obtained by Lüppo-Cramer are exactly those which would be obtained in case the sensitizers were not washed out of the silver bromide and since Lüppo-Cramer offers no proof that he did wash the sensitizers out completely, the simplest assumption is that they were not removed completely. This assumption has the further advantage of expediency because otherwise we are left without any explanation of the phenomena since Lüppo-Cramer offers none.

Lüppo-Cramer is even less fortunate in his statement that "ammonia, hydroquinone, the ready mixed developers, and the bromine absorbers decrease the sensitiveness of silver to light when they are present during the exposure." It did not seem possible that bathing a plate in a metol solution should reduce the sensitiveness to one-half and we therefore repeated the experiment. Instead of decreasing the sensitiveness, this treatment increases the sensitiveness to such an extent that Lüppo-Cramer evidently over-exposed his plates badly. I had suspected this from the start;[2] but it was rather a comfort to have it confirmed.

Lüppo-Cramer makes a good deal of the fact that an intimate mixture of silver chloride and silver citrate is blackened by light a good deal more rapidly than either one alone. From the point of view of the Grotthuss theory, this is precisely what should happen. The citrate is a depolarizer for chlorine. We have had analogous cases before. Ferric chloride is not readily decomposed by light but ferric citrate is.

While these experiments of Lüppo-Cramer are just what

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[1] "The Theory of the Photographic Process," 238 (1907).

[2] Bancroft: Jour. Phys. Chem., 14, 150 (1910).

one would have predicted, this is not at all the case in the experiment[1] with nitrite solutions and silver chloride. Lüppo-Cramer found that precipitated silver chloride or a silver chloride gelatine plate blackened less rapidly when immersed in a five percent solution than when immersed in pure water. On the other hand, a sensitizing action was obtained when a silver chloride plate was bathed in a nitrite solution and then dried. With the dried plate the concentration of the nitrite was high and its sensitizing action correspondingly great. That would not account for a retarding effect of the five percent solution. Since the retarding action does not occur to any great extent when the silver chloride plates are merely moistened with the nitrite solution, Lüppo-Cramer attributes the difference in result to the difference in the absolute amount of the solution, though he does not explain why this should produce such a result. We do know cases of this sort. If filter paper is moistened with a potassium iodide solution, a small current will set free visible amounts of iodine while this will not happen if the electrodes are placed in a beaker of solution. The reason for this is that the iodine dissolves in the large mass of the iodide solution, while the diffusion is so slow in the pores of the filter paper that there is a local excess of iodine. This cannot be the explanation of Lüppo-Cramer's experiment because we should not then get a sensitizing action with the so-called dried plate containing the high concentration of nitrite. If we bar diffusion phenomena, it seems quite impossible for the absolute mass of the solution to have an effect if the conditions at the surface of the silver chloride layer are the same in both experiments. I see only one way in which these conditions could vary and that is that the nitrite solution absorbs certain rays which are active in changing silver chloride. If this proves to be the case, the difficulties disappear, because the experiments are not comparable if the intensity and quality of the lights also varied.

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[1] Lüppo-Cramer: Jour. Phys. Chem., 14, 149 (1910).

The sensitiveness[1] of different silver bromide emulsions to the solar spectrum is quite in harmony with the view that ripening consists in a change in the amount of gelatine and water in the silver bromide grains. There is always a maximum sensitiveness for silver bromide gelatine about wavelengths 420–460, regardless whether "the bromide is precipitated hot or cold, whether the emulsion is boiled or not boiled, digested or not digested. Boiling, digesting or treating silver bromide gelatine with ammonia, has the effect only of increasing the sensitiveness for the other colors, violet, ultraviolet, green, and red, the increase being less for the less refrangible rays." Of course we might have different modifications of silver bromide in gelatine, each with the maximum absorption at the same place; but it is not very probable and it certainly is not the simplest assumption. With increasing opacity we get a broadening of the absorption band, which is what one would expect. The differences between a long exposure and a short exposure are also qualitatively what they should be. With a very short exposure, we get only an effect at the point of maximum sensitiveness whereas a longer exposure gives us a developable effect due to the less active rays.

When silver bromide and silver iodide emulsions are mixed together or silver chloride and silver iodide emulsions, we should expect to recognize an effect due to each salt, which is just what happens. If the mixed emulsions are ripened or if the two salts are precipitated together, we should expect to get results approximating equilibrium conditions whatever they might be. Now Küster[2] has shown that silver chloride and silver bromide form a continuous series of solid solutions. Consequently this pair of salts would show a double maximum if mixed after precipitation and a single maximum if precipitated together or if ripened together after having been mixed. Unfortunately, the cases cited by

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[1] Vogel, Eder: Jour. Phys. Chem., 14, 228–236 (1910).

[2] Zeit. anorg. Chem., 19, 81 (1899); 23, 25 (1900).

Eder[1] do not include this particular pair; but the results given by him are just what they should be if we assume that silver iodide forms a continuous series of solid solutions with silver chloride and with silver bromide. If this is true, we can go one step further. If silver chloride and silver iodide are precipitated together in varying proportions, the position of maximum sensitiveness can be made to shift continuously from the position corresponding to silver chloride to the one corresponding to silver iodide. The assumption of a continuous series of solid solutions between silver bromide and silver iodide accounts for the peculiarities in the behavior of brom-iodide plates,[2] whereas if we assume the existence of a double salt as Eder does, we should then have silver bromide plus double salt in the emulsion and we should not get the continuous variation in properties which we seem to have. If silver iodide formed a double salt with silver bromide, it would be possible to sensitize the excess of silver bromide with dyes such as eosine, whereas we find[3] that "brom-iodide emulsions with more than two percent iodide are much less readily sensitized than pure silver bromide emulsions. It is practicable, however, to sensitize emulsions containing up to five percent of silver iodide." The fact that silver bromide and silver iodide affect silver chloride in the same way[4] is another reason for believing that silver iodide and silver chloride form a continuous series of solid solutions just as silver bromide and silver chloride do. I must admit, however, that I do not see why the addition of potassium iodide to the developer should have a beneficial effect on ultraviolet plates.[5] As this may be a question of development, we can ignore this difficulty for the present.

There are some points about staining plates with optical sensitizers which call for more experiments. It seems as

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[1] Jour. Phys. Chem., 14, 232 (1910).
[2] Eder: Jour. Phys. Chem., 14, 79–82 (1910).
[3] Eder: Ibid., 14, 240 (1910).
[4] Eder: Ibid., 14, 82 (1910).
[5] Schumann: Jour. Phys. Chem., 14, 258 (1910).

though the best way to get the dye into the silver bromide grains would be to add it to the melted emulsion; but that is apparently not the case. Schumann[1] says that "finished plates, when bathed in an eosine solution are four times as sensitive to yellow green as is the case when the dye is added to the melted emulsion. The same thing is true for erythrosine and for the colors of the eosine and cyanine groups." If this is really a fact, there seems to be only one explanation possible, that the melted gelatine takes up more dye than the solid gelatine and that this dye cannot be washed out readily from the solidified gelatine. In other words, the difference in the two cases must be due to a screening action of the dye in the gelatine, though, in that case, it is surprising that neither Schumann nor Eder should have given this explanation.

The theory that the silver bromide grains in a dry plate consist of silver bromide, gelatine and water in varying amounts is enough to account for the effect of developers on the exposed and unexposed plates.[2] We also get differences between silver bromide with one content of water and silver bromide with another water content, as is shown by Schaum's experiments on silver bromide containing no binder.[3]

We have now merely to consider the question of the medium in which the silver bromide is emulsified.[4] The medium can act in two ways, as an emulsifier and as a sensitizer. Gelatine is one of the best of the protecting colloids[5] and it is partly to this that it owes its superiority over caseine, gum arabic, dextrine, starch, etc. Collodion has high emulsifying powers; but it is not a sensitizer and therefore collodion plates are not as sensitive as the best dry plates. Schumann's

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[1] Jour. Phys. Chem., 14, 241 (1910).

[2] Lüppo-Cramer, Schaum: Jour. Phys. Chem., 14, 119, 243–248 (1910).

[3] Schaum: Ibid., 14, 247 (1910).

[4] Eder, Lüppo-Cramer, Lobry de Bruyn, Schloemann, Cooper and Nuttall, Schumann: Jour. Phys. Chem., 14, 12, 19, 20, 26, 69, 113, 202, 204–209, 211–227, 252–254 (1910).

[5] Freundlich: Kapillarchemie, 451 (1909).

experiments[1] with ultra-violet plates are conclusive proof that gelatine acts as a sensitizer and I cannot see that Lüppo-Cramer's[2] experiment with a gelatine film superposed on a collodion plate is of any value. "Collodion plates were washed thoroughly with water, were then covered with a film of a one percent gelatine solution, and were exposed with a check-plate. When the plates were developed, the one covered with gelatine developed somewhat more slowly than the other, but when allowance was made for this it was found that the gelatine layer had not increased the sensitiveness in any way." Since a sensitizer must be incorporated in the silver bromide grain to work, and since such substances as pyrogallol and metol are only adsorbed slowly[3] it is not surprising that no effect was obtained with a superposed film of gelatine.

In some ways, agar-agar is more promising than gelatine. It has a much higher jellying power.[4] "The viscosity of agar is much greater than that of gelatine with the same percentage of solid. We have estimated that a solution of gelatine of definite strength is about as 'thick' as a solution of agar containing 1/8 percent of the amount present, this agreeing with the figures given by Stanford."

"A solution of 3 percent is difficult to use, as it is too thick. We find a 1 percent solution is most convenient, though a 2 percent solution is quite easily worked. A 1 percent solution is about as thick as an 8 percent solution of gelatine. If two emulsions contain the same amounts of chemicals, except that the medium in the one is gelatine and in the other is agar, and if the solutions are of the same 'thickness,' then the amount of agar will be one-eighth the amount of gelatine; in coating a plate or paper with these solutions and drying, one will get the same amount of silver per square foot, but only one-eighth the amount of medium

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[1] Jour. Phys. Chem., 14, 252 (1910).

[2] Ibid., 14, 145 (1910).

[3] Lüppo-Cramer: Jour. Phys. Chem., 14, 130 (1910).

[4] Cooper and Nuttall: Jour. Phys. Chem., 14, 215, 216 (1910).

when using agar. In the case of paper this would not matter so much perhaps but with plates it means that the pellicle will be extremely thin. It will be of great interest to ascertain what influence this has on the sensitiveness of the emulsion and on the development. If the pellicle is so much thinner, the light will be able to act more rapidly on the sensitive salt and should give increased rapidity. One would expect that in development, the developer would penetrate more rapidly and therefore develop more energetically; on that account also less exposure should suffice.[1] In that case, one should be able to obtain plates of extreme rapidity, great latitude, and with a fine grain."

As yet no agar plates have been made which are anything like as fast as the best gelatine plates; but we do not know whether this is because agar is a less effective sensitizer than gelatine or because the possibilities of the agar plate have not yet been realized experimentally. For that matter, there is no reason to suppose that the last word has been said in regard to fast gelatine plates. If a suitable depolarizer is incorporated with the silver bromide grain and if a suitable developer is used, there seems to be no *a priori* reason why we should not have an infinitely fast plate with as fine a grain as one pleases. It is possible that gelatine is the ideal protecting colloid for silver bromide, though I doubt it; but it certainly is not the ideal sensitizer. Instead of trying to combine the two properties of the protective colloid and the sensitizer in one substance, it will be more rational to add the ideal sensitizer, when found, to gelatine or agar or whatever may prove to be the best, protecting colloid. By working along these lines, with a clear understanding of the factors on which sensitiveness depends, it seems to me quite probable that photographic plates can be made which will be enormously superior to anything which can now be obtained.

The general results of this paper may be summed up as follows:

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[1] [This conclusion seems to be based on faulty reasoning. W. D. B.]

1. The silver bromide grain is a complex of silver bromide, gelatine and water.

2. The process of ripening consists in changing the composition of the silver bromide grain towards an unknown, optimum concentration.

3. There is no necessary connection between sensitiveness and coarseness of grain.

4. Chemical and optical sensitizers are depolarizers.

5. Gelatine acts as an emulsifying agent and as a sensitizer, whereas collodion apparently acts only as an emulsifying agent.

6. The peptonization of silver bromide is merely a particular case of the general problem of the peptonization of any precipitate.

7. The peculiarities of mixtures of silver chloride, silver bromide and silver iodide can all be explained on the assumption that each of these salts can form a continuous series of solid solutions with either of the two. This is known to be the case for silver chloride and silver bromide.

8. It seems theoretically possible to make an almost infinitely fast plate having a very fine grain.

Cornell University,
March, 1910

ON THE RELATION OF OSMOTIC PRESSURE TO THE INTRINSIC PRESSURE OF LIQUIDS

BY M. M. GARVER

The term "Intrinsic Pressure" was introduced by Lord Rayleigh[1] to represent an internal pressure in liquids arising from molecular attractions. The existence of such a pressure, together with estimates of its probable value had previously been shown by Young and by Laplace who represented it by the symbol K. The symbol K has been generally retained by later writers, but the term "intrinsic" has not been so generally accepted and retained. Careful examination will show that there are two distinct kinds of internal pressure in liquids, to one of which the term intrinsic seems particularly appropriate in contrast with extrinsic. The pressure exerted by an ideally perfect gas upon the walls of the containing vessel may appropriately be termed extrinsic pressure, but there is also in the interior of a body of gas what we may call an intrinsic pressure which is numerically equal to the extrinsic pressure. If we define the intrinsic pressure of a gas as the rate of change of momentum per unit area of the gas impinging on one side of an element of a plane area within the gas, the resultant change of momentum per unit time of all the molecular impacts resolved normal to the plane being regarded as the total pressure, the definition would make the intrinsic pressure numerically equal to the outwardly directed pressure on the containing walls. We may assume that the intrinsic and extrinsic pressures are numerically equal only in the absence of molecular attractions between the molecules, and that when the substance has reached such a degree of condensation that the molecular attractions are appreciable, the extrinsic pressure becomes less than the intrinsic, gradually diminishing as the liquid state is approached, becoming zero only in the case of a vaporless liquid. But from the fact that in the interior of

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[1] Phil. Mag., 30, 288 (1890).

liquids, the molecular attractions on any given molecule during any appreciable interval of time will be equal in all directions, the freedom of motion, except as to the length of the mean free path, should not be interfered with; consequently the molecules should be capable of exerting a pressure within the liquid in any direction in which their freedom of motion is opposed. In that case the definition just given of intrinsic pressure should apply to liquids as well as to gases. It will be noticed that such a pressure, just as in a gas, must be proportional to the absolute temperature and density conjointly; consequently cannot be simply a change function of a gravitating force. Laplace's K is always assumed to be a function of the masses and distances of the molecules. Inasmuch, however, as the molecular attractions affect the densities, intrinsic pressure may be regarded as indirectly a function of the molecular attractions; but, as previously indicated, it does not vanish when the molecular attractions become zero.

That the general line of reasoning made use of in deducing the law of gas pressure from the molecular kinetic theory is applicable to the interior of liquids will be evident to anyone who will read carefully Maxwell's deduction of the law of gas pressure given in his Theory of Heat (10th ed., p. 319). The only additional hypothesis required will be that necessary to explain the absence of pressure on the walls of the containing vessel, and the approximate definiteness of volume of a liquid. This characteristic difference between a liquid and a gas is fully accounted for by the generally accepted theory of the unbalanced molecular attractions which cause the superficial tension in liquids. This unbalanced molecular attraction in and near the surface of liquids is sufficient to retain all the molecules having a translational energy below a certain definite value,—the escaping molecules constituting the vapor. Since the vapor is composed of those molecules which escape from the liquid in consequence of possessing, in the liquid, exceptionally high energy of translation it is not evident, without careful analysis, how the average energy of translation per molecule can be the same in the liquid and vapor states. This conclusion, however, seems to be amply verified by experimental evidence and is an essential postulate in the deduction of the intrinsic pressure and intrinsic energy of liquids. The results of the assumption amply justify the hypothesis by enabling us to predict and compute results which are verified by experiment. The apparent improbability of the hypothesis may be made to disappear entirely by restating it in a different form as follows: The work which must be done by the molecules in passing from the liquid to the vapor state is just sufficient to deprive them of their excess of translational energy over the average in the liquid state.

The foregoing considerations would seem to indicate that we may be warranted in assuming that the interior of a liquid differs from the interior of a gas mainly in three different ways: (a) In the length of the mean free path; (b) In the degree of curvature in the path; (c) In density, or, in the number of molecules per unit volume. If, in addition we borrow a notion from astronomy, we may form a concrete conception of a liquid and of the critical state as a transition state lying between the liquid and gaseous conditions. In a planetary system of bodies satellites can exist only when the velocity of translation of the satellite is less than a certain definite maximum which gives a parabolic orbit. Less velocity than this maximum yields elliptical orbits, higher velocities lead to hyperbolic paths. Thus a comet may visit the solar system and then leave it never to return if its speed is sufficiently great, just as a molecule of vapor may leave a liquid mass never to return. Applying this notion to a molecular system with the understanding that the absolute temperature represents the mean square of the translational velocity of the molecules, we see that at a definite temperature the molecular attractions cease to be the controlling influence and the substance becomes essentially a gas irrespective of volume or proximity of molecules. In all cases, however, what is called the externally applied pressure is supplementary to the molecular attractions which in the ideal gas is zero. On the other hand, we might define an ideal liquid as a vaporless liquid exerting no extrinsic pressure, the molecules being held within the given volume solely by molecular attractions. The term *ideal* may be understood as a state approached but never actually reached.

These preliminary remarks have been deemed necessary because the writer knows of no simple exposition covering the above ground, or of any generally accepted canon to which he could refer as to the relation of a vapor to its liquid. In order not to be misunderstood in what follows, it was considered necessary to state the point of view as to what constitutes a liquid so as to bring out clearly the meaning to be attached to the term intrinsic pressure of a liquid. In previous papers the writer has insisted, and offered evidence to show, that the experimental facts do not permit of introducing any special hypothetical forces of attraction or repulsion between solute and solvent, or of expansive force on the part of the solute, in our efforts to explain the dynamics of osmotic phenomena. And since it has been shown that the depression of the vapor-pressure of a solution is directly proportional to a corresponding depressed normal activity of a solvent, it is important to bring out definitely and define clearly just what constitutes this normal activity of a solvent before endeavoring to establish a definite relationship between it and osmotic phenomena.

Suppose we assume that the characteristic normal activity of a liquid at any temperature is due to its intrinsic pressure which may be obtained from its vapor-pressure at that temperature by simply multiplying the vapor-pressure by the ratio of the densities of the substance in the liquid and vapor phases. It will be found that what is known as the osmotic pressure bears a very simple relation to the intrinsic pressure as thus defined.

In a recent paper,[1] in discussing the conditions neces-

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[1] Jour. Phys. Chem., 14, 260 (1910).

sary to produce osmotic equilibrium, I was led to the equation:

$$pv = PV = RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (A)$$

where pv represented the product of the pressure and volume of a vapor and PV the product of the corresponding values for its liquid phase. At first sight the result seems absurd. The P representing pressure in the liquid phase cannot be interpreted in the same sense as that in which we interpret the p as applied to the vapor phase. In order to distinguish between the two pressures, I called the former the intrinsic pressure of the liquid, having in mind the intrinsic pressure of Lord Rayleigh and other writers, but stated that it did not necessarily represent an actual molecular pressure and at the same time briefly otherwise indicated an interpretation. Further examination of the matter has led me to the interpretation indicated above which confirms, but extends, the first impression. The name intrinsic is also retained as it seems particularly appropriate when its derivation is considered.

The equation (A) may also be interpreted simply as expressing an energy relation, since

$$p_1 = \frac{1}{3} n_1 m u^2 = \frac{2}{3} \frac{n_1 m u^2}{2}$$

On the assumption that the average molecular energy of translation is the same for the liquid and vapor phases, the intrinsic pressure $P_1 = \frac{2}{3} \frac{n_2 m u^2}{2}$, whence

$$P_1 = p_1 \frac{n_2}{n_1} = p_1 \frac{\rho_2}{\rho_1}$$

if the molecular weight is the same in the two phases.

The equation (A) was derived from the proportion

$$\frac{p_1 - p_2}{p_1} = \frac{P_1 - P_2}{P_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (B)$$

on the assumption that a difference in vapor-pressure due to a difference in elevation, $h_2 - h_1$, is proportional to the difference in pressure of the liquid columns due to the same difference in level. In consequence of the variation of density of the vapor with pressure this is not strictly true, but is approximately too small by about 1/2 percent for each hundredth, for values lying between 0 and $\frac{1}{10}$. Or, in symbols

$$\frac{p_1 - p_2}{p_1} < \log_e p_1 - \log_e p_2$$

by about the amount indicated above, for values not greater than $\frac{1}{10}$. For the ordinary differences encountered in actual measurements of depressed vapor-tensions the simpler expression introduces no appreciable error.

The intrinsic pressure of a liquid solvent was defined as $P_1 = p_1 \frac{\rho}{\rho'}$, where p_1 is the pressure and ρ' the density of the vapor of the solvent at some chosen temperature, ρ the density of the liquid phase of the solvent at the same temperature. For gram-molecules at the absolute temperature T, the above becomes, on writing RT for $p_1 v_1$, since $\frac{M}{v_1} = \rho'$, $P_1 = \frac{\rho RT}{M}$ where M is the molecular weight of the solvent. Therefore from formula (B)

$$P_1 - P_2 = \frac{p_1 - p_2}{p_1} \frac{\rho RT}{M}, \text{ or } \frac{\rho RT}{M} \log_e \frac{p_1}{p_2}$$

one of the standard forms of the equation for the osmotic pressure, the only symbols having any reference to a dissolved substance being p_2 the depressed vapor-tension of the solution, and P_2 its intrinsic pressure.

Boynton,[1] working from purely molecular kinetic assumptions, derives the same equation for the osmotic pressure as the difference between two molecular pressures, but gives no estimate of their numerical values or otherwise suggests their physical significance. The above deduction is based

[1] Kinetic theory, p. 222 (1904).

upon a simple fundamental assumption involving the ratios of the pressures required to produce simultaneous equilibrium between vapors and liquids at different levels. The condition that the assumptions made should satisfy the necessary conditions of equilibrium, involving no contradiction of accepted dynamical laws is easily shown. The fundamental assumption made was that the ratio of the pressures of the vapor and liquid phases is the same for both solution and pure solvent. In the recent paper previously referred to, I assumed that

$$\frac{p_1}{p_2} = \frac{P_1}{P_2}, \text{ or } \frac{p_1}{P_1} = \frac{p_2}{P_2}$$

and independently, from conditions of equilibrium, derived the equations

$$p_1 - p_2 = \rho' gh \text{ and } P_1 - P_2 = \rho gh \ldots. (C)$$

The fact that the two sets are derived independently leaves the possibility that they may not be simultaneous. The two equations (C) are really equations of condition which must be satisfied simultaneously in order to prevent a possible assumption of a perpetual cycle. The ratios must satisfy the equations (C) or they are not simultaneous with the two equations.

From the equations (C) by division,

$$\frac{p_1 - p_2}{P_1 - P_2} = \frac{\rho'}{\rho}$$

In order to satisfy the condition that the equations of equilibrium (C) and the ratios shall be simultaneously satisfied it is sufficient to assume that

$$\frac{p_1}{P_1} = \frac{p_2}{P_2} = \frac{\rho'}{\rho}$$

then either set includes the other and the ratios satisfy the conditions of equilibrium. But this condition gives at once the definition of intrinsic pressure

$$P_1 = p_1 \frac{\rho}{\rho'}$$

previously given, or, on substituting volumes for densities

$$p_1v_1 = P_1V_1 = RT \ldots\ldots\ldots\ldots\ldots\ldots (D)$$

as before, but more simply, without the process of integration.

The derivation of equation (D) by different processes of reasoning and the fact that it enables us to derive well-known equations by exceedingly simple methods ought to convince us that the general gas equation may be applied also to liquids if we give to the symbol P_1 a proper interpretation. Perhaps intrinsic energy would be a better specification, but since it may be deduced by similar reasoning to that employed in deducing gas pressure, intrinsic pressure seems not inappropriate. When we consider its intimate relation to osmotic pressure it seems necessary to specify it in terms of pressure. Again when we consider the light, active molecule of water vapor and the enormous intrinsic pressure molecular aggregates may exert when condensed to a liquid, we receive a new insight into the significance and importance of water in the process of Nature. No other liquid is so generally a solvent, has so light and active a moleclue and can consequently pentrate and exert its great pressure through so many septa throughout so wide a range of conditions.

In equation (D) P_1 represents what I have called the intrinsic pressure of the liquid solvent. But the osmotic pressure $P_1 - P_2 = P'$ (say) also satisfies the equation $PV = RT$; or, $P'V' = RT$ must also be satisfied. Since the second members of the equations are identical

$$\frac{P'}{P_1} = \frac{V_1}{V'}$$

If we assume the intrinsic pressure of the pure solvent to be due to N molecules and the intrinsic pressure of the solution to be due to $N - n$ molecules, we have

$$\frac{P_2}{P_1} = \frac{N - n}{N}, \text{ whence } \frac{P_1 - P_2}{P_1} = \frac{n}{N} = \frac{P'}{P_1} = \frac{V_1}{V'}$$

Therefore

$$V' = V_1 \frac{N}{n} \text{ and } P' = P_1 \frac{n}{N}, \text{ or } P'V' = P_1V_1$$

That is, the volume concerned in osmotic pressure is the volume of the solvent increased in the ratio $\frac{N}{n}$ while the pressure is diminished in the ratio $\frac{n}{N}$. This is equivalent to ascribing to the one-*n*th part of the solvent a volume *n* times as large as it actually occupies with a corresponding diminution in pressure. This fact explains the dual relation of osmotic pressure to the gas laws and to the volume of the pure solvent. The relation of osmotic pressure to the volume of the pure solvent was amply demonstrated by the extensive experiments of Morse and Frazer[1] who showed that for aqueous solutions of sugar the osmotic pressure was inversely proportional to the *volume of the solvent* containing the sugar and *not* to that of the volume occupied by the sugar.

This experimental fact is important and should not be ignored. The concentrations were carried up to 30 percent and showed conclusively that the volume in the equation $PV = RT$ *does not* relate to the volume occupied by the solute but to the volume of the solvent; and that therefore the pressure phenomena arose from the number of molecules of the solvent replaced by the non-volatile solid. *The general gas equation does not then apply to a dissolved solid but to the liquid solvent.* If each molecule of a liquid solvent has an average intrinsic energy, or pressure, equal to and just like that of a gas, except as to mean free path, then the presence of a foreign substance that dilutes the solvent or in any way interferes with its normal activity so as to depress it, causes the pure solvent to exhibit a greater activity than the solution just in proportion as the activity of the solvent in a unit volume of solution is lowered. It seems to me that the experimental evidence compels us to conclude that osmotic

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[1] Am. Chem. Jour., 10, 141 (1906).

pressure enables us to measure the degree of depression of the normal activity of a liquid due to the presence of a foreign substance in solution and not the pressure exerted by the foreign substance itself.

To illustrate: The intrinsic pressure of water at 0° C is 1235 atmospheres. A normal solution of sugar contains 1 mol of sugar to 55.6 mols of water. Therefore the osmotic pressure of such solution at 0° C is $1235/55.6 = 22.2$ atmos. If, at the same temperature, 46 grams of alcohol be substituted for the 342 grams of sugar, the osmotic pressure remains 22.2 atmos., if the membrane is not permeable to the alcohol molecule, and so on. In simple cases like these, the result is as if one molecule of solvent were removed, or replaced by, one molecule of the non-migratory solute. *The ultimate effect of the presence of the foreign substance is to bring about, and determine the direction of, certain energy transfers.* In this respect these comparatively simple phenomena are similar in their final result to those more obscure actions known as catalytic—a substance induces actions by its presence but seems otherwise to take no part and to suffer no change.

In dealing with the intrinsic pressure of liquids it is necessary to bear in mind the characteristic difference between it and pressure in gases and vapors. If this be done we can at once place the dissolved solid substance as belonging distinctly to the liquid state or phase; for while the molecules of the non-volatile solute may possess the average energy of translation and be distributed in space so as to give the requisite number of molecules per unit volume, they must lack the characteristic mean free path of a vapor. The great and distinct difference between a substance in dilute solution and a rarefied gas or vapor is found in the mean free path,—a quantity inversely proportional to the number of molecules in unit volume. Nernst's[1] equation showing the resistance to diffusion proves the extreme improbability of his theory of diffusion. It is impossible to suppose that

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[1] Theoretische Chemie, 6th Ed., p. 158 (1909).

the mean free path of a non-volatile substance in dilute solution can increase with dilution to the extent it would have to do to occupy the volume and at the same time exhibit the pressure attributed to it. Those molecules at a distance greater than the free path could not exert any pressure, or have any influence in producing a pressure, on a dividing wall or membrane. But the number of molecules taking part in, or contributing to, the pressure in dilute solution cannot be the same as in the corresponding vapor unless the mean free path be the same in both. This is extremely doubtful, as shown by Nernst's equation.

Again, this peculiarity of intrinsic pressure,—its narrow range in consequence of the extremely limited mean free path,—throws light on a characteristic of osmotic pressure that has been insisted upon by some writers.[1] Osmotic phenomena through membranes are manifested only when the membranes are wetted by the liquid. For if not wetted by the liquid they are outside the liquid, and the molecules will be confined by the unbalanced pressure due to the superficial layer through which only the molecules, constituting a small percentage to form the vapor, can escape. That the semipermeable membrane be *within the liquid* is evidently a *sine qua non.* There must be no unbalanced molecular attractions preventing free and untrammelled motion of the liquid. Therefore if the attractive force between the substance of the membrane and the liquid is equal to, or greater than, that of the liquid for itself, the superficial boundary confining the activity of the liquid extends into the substance of the membrane itself. Only under such conditions can a substance be said to be truly within a liquid.

In conclusion, it will be of interest to have a résumé of results with a complete separation of experimental facts and their dynamic interpretation from the hypothetical explanation of them.

(1) The maximum work obtainable by diluting a dilute solution is equal to a sum of elements each of which is just

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[1] Kahlenberg: Jour. Phys. Chem., 10, 141 (1906).

sufficient to lift each element of mass of the solvent added, to a height which will equalize the difference in the vapor-pressures of the pure solvent and solution. This proves that the solute takes no active part in the production of the work,—the liquid solvent is the active agent.

(2) The requirements of dynamic equilibrium between the vapors and the liquids, (simultaneously), through a semi-permeable septum, impose the conditions (if the membrane be actually semi-permeable) that where the differences in vapor-pressures ($p_1 - p_2$ or Δp_1) be small, we must have

$$\frac{p_1 - p_2}{P_1 - P_2} = \frac{\Delta p_1}{\Delta P_1} = \frac{\rho'}{\rho} \cdots\cdots\cdots\cdots \text{(E)}$$

where ΔP_1 represents the excess of pressure exerted through a semi-permeable septum by the pure solvent over that of the solvent in the solution, and ρ'/ρ represents the ratio of the density of the vapor of the pure solvent to the density of its liquid phase at the same temperature. In other words: The presence of the solute depresses both the vapor and liquid phases in exactly the same ratio. This is a dynamic requirement on the supposition that a semi-permeable septum is obtainable. Its validity may be confirmed as follows:

Recurring to the arrangement of an osmotic cell with an open top and semi-permeable bottom immersed to a depth, *d*, in the pure solvent,—the open top being at such height, *h*, as to equilibrate the vapors,—the depth to which the semi-permeable bottom is immersed in the pure solvent cannot affect the equilibrium. For suppose it does; then the pure solvent alone being able to pass in or out, a change in the concentration of the solution, in either case, will be produced at the bottom which will be opposed by the isothermal distillation at the open top thus setting up a never-ending cycle, so that no state of equilibrium, for a given concentration, is possible except one depending on the equilibrium of the vapors alone. But this requirement is entirely independent of the depth and consequent hydrostatic pressure on the semi-permeable bottom. Hence it follows as a corollary that *what-*

ever may be the pressure exerted by the dissolved substance it has no definite numercial relation to what is known as the osmotic pressure, which is a differential function of the solvent alone.

(3) The equation (E) may be stated in a more striking way by substituting words for the symbols of the effects.

$$\frac{\text{Depressed vapor activity}}{\text{Depressed liquid activity}} = \frac{\text{Depressed vapor tension}}{\text{Osmotic pressure}} = \frac{\text{vapor density}}{\text{liquid density}}$$

the temperature of liquid and vapor being the same and the liquids separated by a semi-permeable septum.

It should be noted that the dynamic requirement is entirely independent of the number of molecules or their nature, whether simple or complex, neutral or electrolyte, or whether dissociation occurs or not, the only essential requirement being semi-permeability. Measuremnts of osmotic pressure can then really determine little more than whether the septum is permeable or not to certain constituents of a solution. Depressed vapor-tension and osmotic pressure have a fixed definite ratio provided a semi-permeable septum can be secured. The depression of the vapor, the lowering of the freezing point, the elevation of the boiling point,—each gives us otherwise as much information as could the osmotic pressure.

(4) The above points, (1), (2), (3), relate to experimental facts and their dynamic interpretation. We may now be permitted, perhaps, to offer a hypothetical explanation of the observed facts.

The point requiring elucidation and one that would, if explained, throw light on a wide range of other facts is the equation (E) above. How can we explain the equality of action of the solute on both the vapor and liquid phases?

It was mentioned previously that the effect produced by the presence of the solute in certain simple cases was as if each molecule of solute had withdrawn from action one molecule of solvent. Perhaps this is the real explanation.

If solution is a chemical rather than a physical fact there must be some sort of chemical union when a substance dissolves. We have the analogous case of water of crystallization,—a loose but definite sort of chemical union between a salt and *n* molecules of water. Therefore when a substance is dissolved it may unite more intimately with one or more molecules of the solvent than with the remainder. The result would be to take out of action the molecules of solvent held by union with the solute with the result that both the vapor and liquid phases of a solution are less active in the same proportion than equal volumes of the two phases of the pure solvent. The facts discovered in connection with liquid crystals seem to point in the same direction.

It must also be evident that the dynamical facts are in opposition to the hypothesis of dissociation as an explanation of the abnormal depression of the vapor-tension of solutions of electrolytes unless we introduce the additional hypothesis that the solvent is also dissociated to the same extent by the formation of the ions. This latter form of the hypothesis seems to be unnecesssary, for it has been shown by Prof. Poynting[1] that electrolytic conductivity may be accounted for by association rather than by dissociation. Taken all in all, the dynamic interpretation of experimental facts seems to indicate that the part played by the solvent in any tenable theory of solutions is of greater importance than the present dominant theory, in any adequate way sufficiently recognizes. This latter conclusion was also drawn by van der Waals[2] as a deduction from his analysis of certain experimental results.

State College, Pa.
April 6, 1910

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[1] Phil. Mag., 42, 289 (1896).

[2] Zeit. phys. Chem., 8, 215 (1891).

THE POTENTIAL OF THE OXYGEN ELECTRODE: A REPORT OF PROGRESS

BY E. P. SCHOCH

It is well known that the oxygen-hydrogen (Grove) cell shows great irregularity in its e. m. f.: a day or two after its preparation, it usually attains to a voltage of approximately 1.08 volts in nearly all electrolytes, but higher voltages have been observed by Wilsmore, Bose and others; and a few days later the voltage usually sinks below 1.08 volts, so that this voltage may be more or less accidental. Theory requires such a perfectly constant potential difference between the hydrogen and the oxygen poles in all electrolytes; but the maximum amount of this potential difference (1)*, as recently ascertained by indirect methods, is 1.231 (±0.001) volts at 17° C. Hence the value 1.08 volts cannot be due to the (maximum) electromotive force of the gases—or, in other words, it cannot be the potential with which the action of the poles is reversible. If we reverse, experimentally, the action of the cell—*i. e.*, discharge oxygen and hydrogen by electrolysis—even then the reversible potential does not show itself by allowing these gases to be evolved at a potential difference slightly greater than 1.231 volts. Instead, we find that a potential difference exceeding 1.5 volts must be applied before any currents greater than mere diffusion currents will pass, and the evolution of gases will show itself.

Since we know that the hydrogen electrode is perfectly reversible in its action, that its potential is independent of the metal used in its construction (2), and that its value is accurately reproducible in all sorts of electrolytes, it follows that all the observed irregularities are due to the oxygen electrode. It is now known that the irregularities of the platinum-oxygen electrode are due to the fact that the electrode metal is oxidized, and that its potentials are due to

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* The numbers in parentheses refer to the list of references given at the end.

the oxides and not to any oxygen gas that may be present. For this recent advance in our knowledge of the subject we are mainly indebted to Foerster (17), E. Mueller (8), Lorenz (13), Woehler (12) and Ruer (14), and on account of its general importance a brief account of this work is here given.

Since the study of the oxygen electrode involves a consideration of the discharge of the "oxygen-forming" anions, it is desirable to present here at the beginning a summary of what appears to the writer to be our present knowledge of these actions. The recent developments in our knowledge of the platinum electrode have been chiefly instrumental in clarifying our view of these actions.

The potential required for the electrolytic discharge of an ion at any particular moment is determined by the opposing potential of the electrode—irrespective of the nature of the ion. Thus, to discharge hydrogen or oxygen into an electrode absolutely devoid of any electrochemically-active material requires the application of an exceedingly small e. m. f. only, while their discharge into an electrode charged with these gases requires an e. m. f. above 1 volt. Apart from the opposing potential of the electrode *there is no such force* as "intensity of fixation," or "holding power" (3) which might have to be overcome in the discharge of ions.

With continued electrolysis the discharge potential naturally depends upon the product formed, *i. e.*, as it is commonly expressed, upon the particular process that takes place. The *process* is considered as being determined by the original substances and the final product, irrespective of the details of the transformation. Thus the discharge of the chlorine ion upon an indifferent electrode (graphite, platinum, etc.) which results in free chlorine takes place at a different potential than upon a silver electrode with which it forms silver chloride. The difference in these potentials, however, is directly due to the difference in the electromotive forces of the *products*. To illustrate again: silver, when deposited together with mercury with which it forms an amalgam of a lower potential than pure silver, is actually deposited at this lower potential; again, oxygen gas is liberated at a lower potential on platinum than on lead with which it forms lead dioxide.

However, in actual operations, the (main) process does not necessarily determine the potential. The amount of a substance which is necessary to impart a definite potential is exceedingly small, and such a small amount of a high-potential product is frequently formed and remains, although the main product is of a nature which would impart a lower potential to the electrode; under these conditions the (main) process does not determine the potential, because its operation can be continued only by overcoming the higher potential of the portion formed in small amount. Two striking illustrations of this state of affairs are at hand. Luther and Brislee (4) found that during the electrolytic discharge of chlorine from hydrochloric acid on polished platinum electrodes, the latter are affected in such a way as to exert a greater opposing potential than that due to the chlorine, and hence the whole discharge of chlorine requires this high potential. The authors think that in this case the chlorine may be produced as a secondary product: this is not necessarily the case, since all that is required is that the reaction between the chlorine and the high potential product is so slow that enough of the latter constantly remains to impart its high potential. The second example is found in the discharge of nickel (or iron) which in its deposition always forms, wholly or partly, a hydride of a potential much above that exerted by pure nickel (5). Hence for the continued deposition of nickel this higher potential must be exceeded.

Of course, this state of affairs makes the main process an irreversible process: the extra potential to be overcome entails a loss of free energy. Since the discharge of "oxygen producing anions" always takes place at potentials above 1.23 volts, it is an irreversible process, and hence the potential of the discharge of these anions has not, in general, any relation to the process. The term "discharge potential" even when used in its proper sense as the potential with which certain electrolytes produce certain products[1] should not, in general—perhaps never—be applied to irreversible changes. We are confirmed in this conclusion when we consider that an electrode discharge probably takes place simultaneously through several *series* of changes, and that these changes are, in general, differently *catalyzed* by any of the substances temporarily or permanently present in the solution or on the electrode (including the electrode material), and it is difficult, if not impossible, to ascertain which of these different processes produces the "highest potential product." Thus it appears that all conclusions as to the process that has taken place which are based mainly on a "turn" in the "current-voltage" curve obtained in an irreversible operation are questionable, if not absolutely wrong. In this class belong the well-known explanations of the "turns" in the "current-voltage" curve obtained in the electrolysis of acids and bases, which ascribes each of the different "turns" to the setting-in of the discharge of another class of anions. It is thus seen that the cause of all abnormal pole potentials is to be found primarily in the pole itself; and specific considerations of the process should not be made until something definite is known about the pole. The following report gives the advance in our knowledge of the platinum pole itself.

We will now proceed to the main topic of this paper, and we shall present next the essential points observed in the behavior of the oxygen (platinum) electrode.

When small electromotive forces are applied to platinized platinum electrodes in dilute sulphuric acid or sodium hydroxide solution, the potential of the anode increases rapidly—though nothing but extremely small currents, of the order of "diffusion" currents pass until the potential of an anode

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[1] Note that the use of this term, or any other term such as "holding power," in the sense that a certain potential is required for every kind of ion to have its electric charge separated from it, is never admissable—there is no such force.

passes 1.50 volts;* then bubbles of oxygen gas begin to appear. From this point on the rise in anode potential is less rapid than before, yet much more rapid than that shown by a reversibly acting gas electrode. In other words, the current-voltage curve turns from its first direction, which is almost parallel to the voltage axis, to a direction which makes quite a large angle with this axis but does not turn as much as would make it almost parallel to the current axis: if it were a reversible electrode which had turned its "reversible point" at approximately 1.50 volts then its final direction would have been nearly parallel to the current axis. The polarization potential also increases steadily with the time during which the current continues uninterruptedly; but there is no indication that a definite maximum value for any particular current density exists.

This extensive polarization can not be due to a specific surface attraction exerted by the platinum upon the gas (adsorption) such as has been assumed for hydrogen and practically proven for this gas by Moeller (6), because the range of potential produced by this influence is too great (it extends to nearly three volts). Furthermore, Foerster (17) has pointed out that platinum is able to functionate definitely at either a lower or a higher potential, which would require a change in the adsorptive power without any apparent reason for such a change. Thus he observed that in an alkaline solution of sodium acetate at 75° a platinum anode showed a potential of 1.8 volts for 45 minutes, while it oxidized the action with a low efficiency—10 to 20 percent—then it seemed to undergo a transformation almost abruptly: the potential rose steadily to 2.50 volts, and the oxidizing efficiency of the current immediately increased to 80 percent and over. This fact can not be harmonized with the conception of a gas layer—neither with the conception that the potential difference might be caused by a resistance film.

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* All potentials in this paper refer to a constant hydrogen electrode in the same electrolyte: the algebraic sign is that observed in the experimental arrangement, as recommended by Luther (see LeBlanc, Text-book, page 245).

These are the ideas that have been advanced heretofore in explanation of this phenomenon.

The continuity of the potential rise requires that the electromotively active substance formed on the anode shall be of a physical form which can change its concentration continuously: it can not be a single *solid* which is formed, because this would exhibit a constant potential irrespective of its quantity, or in other words, during its formation the potential would remain practically constant. In contradistinction to this, the material formed should be one which is dissolved, in a sense, by the remainder of the electrode, or the substance from which it is formed, so that, corresponding to its constant increase of concentration, it would exhibit an increase of potential. We shall see that the facts indicate the actual existence of such a state of affairs.

When the oxygen electrode is left at rest after it has been polarized, it shows a *steady* decrease in electromotive force (self discharge!) until a potential of 1.08 volts is approximately attained. However, this "resting place" is not the end of the self-discharge; it is merely a point at which the potential commonly lingers for sometime, after which it drops to still lower potentials. These facts which had been more or less accurately determined by earlier investigators were carefully tested by Foerster and found as given above.

Lorenz (7), who has made a special study recently of the discharge of these anodes, and who has devised a special method for this purpose, has found that the discharge of a polished platinum electrode, in contra-distinction to the platinized electrode investigated by Foerster, exhibits a large number of distinct steps—or points at which the potential remains constant for some time during the discharge. This behavior indicates the presence of distinct oxides with different potentials. However, these steps are observable only with special manipulation, and there appears to be a distinct tendency in the action of the electrode to obliterate these steps and to exhibit a continuous drop in potential during discharge. It is on this account that these different steps are ordinarily not observed. Their obliteration may be due to a variety of causes, but argues nothing against the interpretation of the existence of the steps.

The points at which the potentials remained constant in Lorenz's discharge of polished platinum electrodes are the following: 1.3, 1.05, 0.97 (?), 0.94, 0.74, 0.64, 0.57, 0.43, 0.27, 0.12, 0.05, 0.008 volts.

The behavior of the platinum anode can not be interpreted without considering the behavior of other metal anodes. Foerster[1] has shown that the behavior of the iridium anode is quite similar to that of the platinum anode, except that in its course of self-discharge it drops steadily to a much lower value than that shown by platinum—namely to 0.865 volts—and the drop is much more rapid then with platinum. Westhaver has shown that an oxygen iridium electrode shows a potential of 1.06 volts in place of 1.08 volts shown by platinum. Platinum and iridium are the only two metals that were considered heretofore as not oxidized by gaseous oxygen, and hence they were the only metals with which it was attempted to obtain the potential of this gas; as it is seen, both metals exert a specific influence in their electrochemical action with oxygen, which is difficult to explain except by the fact that it is their oxides that are active and not the free oxygen gas.

The behavior of lead as an oxygen anode is well known through the storage cell. Recently the alkaline accumulator has made the behavior of the nickel oxide anode also fairly well known. An extensive study of the behavior of copper anode in a solution of sodium hydroxide was made by E. Mueller (8): this has again clearly revealed the connection between the existence of oxides, the anode potential, and the potential at which oxygen is evolved. Lorenz (9) showed that oxygen gas electrodes constructed with such oxidizable metals as lead, silver, nickel, copper, iron, zinc, exhibit potentials which are identical with those shown by their oxides. These observations together with many others

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[1] Loc cit.

obtained in the study of passivity and "valve action" of metals may be summarized somewhat as follows:

(1) During the discharge of "oxygen yielding" anions all metal electrodes are oxidized.

(2) The potential of the electrode is that of the oxide irrespective of any (adsorbed) oxygen gas also present.

(3) The oxides specifically determine the potentials with which oxygen is evolved.

(4) The amount of an oxide that must be actually present to give all characteristic effects may be less than is optically preceptible.

(5) Oxygen gas does not appear to be directly electromotively active.

The proof that the platinum anode is actually oxidized and that it owes its potential to the presence of oxides was recently brought by the work of Woehler, Lorenz, and Ruer, not to mention several others who assisted in an indirect way. The essential parts of their work are here given.

Woehler (10) found that platinum black exposed to oxygen or air increased slowly in weight. It does this even at the ordinary temperature, and somewhat more rapidly at higher temperatures—up to 300°. In one case an increase of 2.3 percent was observed. Most of this oxidized portion is readily soluble in hydrochloric acid—in one case 18 percent of the platinum was dissolved. Besides this soluble oxide, which according to the determinations must be PtO, another oxide is undoubtedly present—perhaps PtO_2, which is readily formed by oxidation of PtO. Woehler prepared some platinum monoxide, and showed that the general behavior of this substance towards reagents is identical with that of the oxidized platinum black. Platinum sponge and thin platinum foil showed the same behavior, although in a lesser degree, as might be expected from their relative degree of fineness. He has also studied critically the preparation and properties of the oxides of platinum, (11) and has reached the conclusion that the above-mentioned two oxides exist in the form of several hydrates. Just after preparation, these compounds are readily soluble in concentrated hydrochloric acid; but only slightly soluble in sulphuric or nitric acids. They dehydrate on standing, and the dehydrated products are markedly less soluble in acids: the compound PtO_2, H_2O is absolutely insoluble in hydrochloric acid.

Recently (12) Woehler has succeeded in preparing the oxide PtO_3 by the anodic oxidation of an alkaline solution of PtO_2. Of course the first direct result was a salt of the oxide from which he obtained the oxide itself by treatment with acetic acid. This oxide is insoluble in dilute sulphuric or nitric acids and dissolves but slowly in hydrochloric acid with the evolution of chlorine. The oxide is exceedingly unstable, and decomposes into PtO_2 and free oxygen. The rate of decomposition becomes markedly less as the percent of PtO_3 in the mixture decreases, and this indicates that the two oxides form a solid solution in which the concentration of the higher oxide and hence its oxygen pressure becomes gradually less.

This oxide, PtO_3, is probably the oxide the formation of which on platinum anodes has been frequently observed. The slow rate of interaction with acids which characterize particularly the higher oxides of platinum probably accounts for the relatively slight loss of platinum in electrolytic operations.

Lorenz (13) undertook to determine potentials of the different oxides which Woehler had identified. He found he could not do this by the ordinary *compensation* method, on account of the ease of decomposition (dehydration, etc.), which characterizes these compounds[1] but his special "anode discharge" method gave him satisfactory results, and these are here given together with the corresponding "resting points" of the potential during the discharge of a platinum anode:

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[1] Different hydrates exhibit different potentials as Streintz has shown in connection with the oxides of lead.

Resting points	Oxide potentials	Formulae
0.94	0.93	$PtO_2, 4H_2O$
—	0.86	$PtO_2, 3H_2O$
0.74	0.74	$PtO_2, 2H_2O$
0.64	0.63	PtO_2, H_2O
0.57	0.53	PtO_2
0.43	0.45	$PtO, 2H_2O$
—	0.34	PtO, H_2O
0.27	0.25	PtO.

The potential shown by the oxide PtO_3 has not been measured so far—possibly it is not measurable because the oxide decomposes so rapidly—but judging from the fact that it is prepared by the anodic oxidation of PtO_2 it should exhibit a potential above 0.93 volts, and hence it is probably the oxide to which all higher potentials are due.

Mention should be made here of the work of Ruer (14) on the dissolution of platinum during alternating current electrolysis. Ruer showed that platinum is dissolved if it is exposed first to strong oxidizing agencies, *e. g.*, extensive anodic polarization—which is followed by an exposure to reducing agencies of a sort which would produce only a partial reversal of the previous oxidation, *e. g.*, limited depolarization. Either agency or both could be exercised by ordinary chemical agents just as well as electrolytic operations. The dissolution takes place during the operation of the reducing agency. One of the ways in which he produced these conditions was by superposing a direct current electrolysis upon an alternating current electrolysis of sulphuric acid between platinum poles: under these conditions the anode was dissolved extensively. He reached the conclusion that metallic platinum is first oxidized to a high oxide which is insoluble; that the latter is then reduced to a lower oxide which is readily acted upon by the electrolyte (sulphuric acid). It is interesting to note that the properties of the oxides of platinum as recently ascertained by Woehler fully bear out this explanation.

The proofs that the behavior of the "platinum-oxygen" electrode is due to the presence of one or more oxides is practically complete. Yet, concerning the details for the potentials above one volt, two different views may be entertained. The different potentials may be due to a number of distinct oxides—including perhaps some unknown oxides, or perhaps a series of unknown hydrates of the known oxides. This is Lorenz's view. Again the potentials may be due to a *solution* of a higher oxide in the material of the electrode: this is Foerster's view.

Before the appearance of Woehler's discovery of PtO_3, Foerster predicted that such a high oxide should exist, that it would decompose spontaneously into its elements and that its rate of decomposition would be slower as its concentration in the solid solution which it forms with the electrode metal becomes less. We note that Woehler found the properties of PtO_3 to conform to this prediction with the exception that the decomposition products are oxygen and a hydrate of PtO_2 in place of oxygen and the metal, as Foerster had predicted. This property of PtO_3 unites the views of Foerster and Lorenz: the lower potentials are probably due to different oxides as shown by Lorenz, while the higher potentials are due to different concentrations of PtO_3 in PtO_2. Whether the potential, 1.08 volts, of the platinum-oxygen gas electrode is due to a certain oxide, or whether according to Foerster's view it is due to a balance between the rate of formation and the rate of decomposition of the high oxide which results in such a concentration of the latter that it shows this potential—this is still an open question.

A word may be added here on the details of the evolution of oxygen. Foerster[1] and E. Mueller (8) consider that the evolution of oxygen results secondarily through the formation and decomposition of a high oxide. Although they do not express themselves further, yet we may infer that they believe that oxygen is not evolved except through such an action. It seems to the writer that such a view is not tenable. G. Schulze (16) has shown in his investigation on "valve action" that the formation of oxygen takes place also while

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[1] Loc cit.

other oxides are present which are not capable of such decomposition (aluminium oxide, magnesium oxide, etc.). Again the view in question would limit the possible mode of reaction to *one*, which is contrary to our general experience in electrode actions. However, this review is scarce the proper place to argue this question.

After this paper had been finished, there appeared an article by K. Bennewitz (18) which deals with the potential of the anode during the electrolysis of dilute sulphuric acid. Although the theoretical considerations and the experimental procedure present much that is both new and valuable, yet, with the exception of the influence of electric waves which will be mentioned below, he presents no new observations, and hence his results do not help to decide the question in what form the oxygen is present just prior to its evolution. He observed irregularities in the current voltage curve at 0.76, 1.08, and 1.50–1.63 volts respectively, *i. e.*, at points previously observed by other investigators. The irregularities observed at 0.76 and 1.08 volts, Bennewitz ascribes to the formation of oxides, but the potentials 1.50–1.63 volts he ascribes to overvoltage; however, it does not appear that he has considered the possibility of the formation of PtO_3, which, as we have seen, accounts very well for this potential.

The new item in the fundamental considerations and method of procedure of this paper is the rotation of the pole with the view of producing a constant "diffusion layer," and the separation of polarization effects due to diffusion from all other effects. In this the author succeeds very well, and he makes a particularly valuable contribution in showing that critical "turns" in the current voltage curve may be ascertained by calculation from *any* of the points in the curve. By this means he located the "turn" at 1.50–1.63 volts (the different values depending upon the surface of the electrode, etc.), and he showed that there is only one such "turn" obtained above 1.08 volts in the electrolysis of dilute sulphuric acid.

When the anode is connected with the antenna of a

Hertzian oscillator, the "turn" in the "current-voltage" curve shows itself just above 1.23 volts—*i. e.*, just above the theoretical reversible potential. This is a very interesting result, but so far it proves or disproves nothing because it has not been shown that under *all* conditions electric waves place the "turn" at this point. And finally, should this prove to be the case, it would not prove that we are dealing with the phenomenon of over-voltage because at this potential the rate of decomposition of PtO_3—which according to the oxide theory, is increased by the electric oscillations—may have reached its maximum value, possibly because its formation *begins* at this potential. In this connection we should recall that Lorenz observed a "resting point" at 1.30 volts in his study of anodic discharges.

LIST OF REFERENCES.

The numbers in parenthesis refer to the following list:

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2. This has been tested with Pt and Pd by Neumann: Zeit. phys. Chem., **14**, 203 (1894) and with Ir by Westhaver: Ibid., **51**, 65 (1905).
3. See LeBlanc: "Textbook of Electrochemistry," translated by Whitney, p. 292.
4. Zeit. phys. Chem., **45**, 216 (1903) or see Foerster: "Elektrochemie wässeriger Lösungen," p. 344.
5. Schoch: Am. Chem. Jour., **41**, 226 (1909).
6. Zeit. phys. Chem., **65**, 226 (1908).
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8. Ibid., **13**, 133 (1907).
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NEW BOOKS

Thermodynamique et Chimie. *Leçons élémentaires. By Pierre Duhem. Seconde Édition entièrement refondue et considérablement augmentée. 16 × 25 cm: pp. xii + 579. Paris: A. Hermann. 1910. Price: paper, 16 francs.*— The first edition was reviewed eight years ago (6, 192); and the author has done well to limit the growth in the second edition to some eighty pages. The arrangement of the material has not been changed radically and consequently the most interesting part of the book is the author's attitude in regard to "false equilibrium" so-called. Duhem maintains his belief in the theory and he quotes the experiments of Pélabon, Hélier and others at length. He has a definite answer to the criticism of Bodenstein, namely that Bodenstein did not repeat Pélabon's work at all and that Bodenstein's work has no real bearing on the theory of false equilibrium, p. 462.

"In Pélabon's experiments the liquid sulphur or selenium was present as a single drop, exposing only a small surface to the hydrogen. On the other hand, when Bodenstein wished to study the formation of hydrogen sulphide, he began by spreading the sulphur in very fine drops over the walls of the flask. When he wished to study the formation of hydrogen selenide, he covered the walls with a thin film of selenium by sublimation in a vacuum. Bodenstein's experiments therefore differ from Pélabon's in that *one of the substances occurs in capillary dimensions. Under these conditions Bodenstein found no false equilibria.*

"In the preceding chapter we have seen how much the laws of reversible equilibrium are changed when a phase of capillary dimensions takes part in the equilibrium. We have seen how the study of capillarity enabled us in certain cases to establish a general law of which the simplified law holding for macroscopic substances is a special case."

"It seems that all the known facts may be summed up in this statement. *In capillary spaces changes take place which do not occur when these spaces are absent, because the system then remains in a state of false equilibrium.* This statement takes account of the discrepancy between Bodenstein's results and those of Pélabon. It takes account, also, of a number of other facts. It explains the action of porous or pulverulent substances, so often made use of in chemistry. We know that platinum sponge or platinum black causes an immediate reaction between hydrogen and oxygen while the system remains in false equilibrium when no platinum is present. People have recognized for a long time that this phenomenon is not due to any chemical reaction between platinum and oxygen or hydrogen and that it is due to the very fine pores of the platinum sponge or the minute interstices between the grains of platinum black."

Duhem does not admit that carbon is always burning in the air and he makes no reference to extrapolated values of reaction velocity. He raises the following point, however, p. 464:

"The first diamond which was cut in Bruges in 1476 for Charles the Bold is now in the Spanish crown. For four hundred and thirty-three years this diamond has been in contact with the oxygen of the air. If there is an equilibrium it must be a false equilibrium because, at low temperatures, the reversible equilibrium between carbon and oxygen is represented by carbonic acid. If one denies the existence of false equilibria, one must admit that the diamond has been burning continuously since 1476 but that the amount of combustion has been so slight that the change has not tarnished the brilliancy of the facets."

Duhem states, p. 465, that experiment will never allow us to distinguish between the hypothesis of false equilibrium and that of an infinitely slow reaction velocity. "The physicist will always be free to hold either one of these doctrines; but the uncertainty has no practical disadvantage because it comes to the same thing experimentally whether we say that the reaction velocity is absolutely null or that it is so low that there is no way of detecting it."

Wilder D. Bancroft

Theoretical Principles of the Methods of Analytical Chemistry. *Based upon Chemical Reactions. By G. Chesneau. Authorized translation by Azariah Thomas Lincoln and David Hobart Carnahan. 15 × 23 cm; pp. x + 184. New York: The Macmillan Company, 1910. Price: $1.75, net.*—On p. 3 the author says:

"In my instruction in the School of Mines, I endeavored to apply these new theories to the critical examination of the processes of analytical chemistry, thus following the example of the illustrious leads of the German School of Physical Chemistry, but in advancing in this study, I have been led to adopt a method different from that which is advocated by that school. The fundamental principle of the theory of Ostwald, based upon the phenomena of Electrolysis, consists in attributing to salt solutions a hypothetical composition of elements, or groups of elements, termed 'ions,' which are the sole active agents in the double decomposition of salts. This purely electrolytic theory appeared to me in contradiction to a number of continually increasing facts, firmly established by experiment, and it seemed to me preferable in the discussion of the processes of analytical chemistry to employ a method, which I will call 'calorimetric,' depending only on the calorific phenomena involved in the occurring reactions, and on the laws deduced from the principles of Thermodynamics."

On p. 53 he says:

"The study of these conditions may be carried on by two different methods:

"1. A method which I shall call *Calorimetric*, consisting in considering exclusively the reacting masses and the heat change in the double decompositions, and in utilizing the data of the calorimeter in order to interpret the direction of the displacement of the equilibrium by the aid of the principles of thermodynamics. This method will permit us to explain the processes of analysis based upon double decompositions without forming any hypotheses upon the constitution of the salt molecules in aqueous solutions. It admits the fact alone that heat is the only mode of energy capable of variation in the system in which the chemical reaction is produced, realized in the calorimeter at an obviously constant temperature. The energies corresponding to the electric state, luminous state, etc., of the system, are then supposed to be constant or, at least, to occasion variations of a magnitude negligible in comparison to the calorific effects, which represent well the conditions realized in the practice of inorganic analysis.

"2. A method which we can call *Electrolytic*, which attributes to salt solutions a hypothetical molecular constitution based upon the manner in which they act under the influence of an electric current produced by a source outside of the solution and dividing the dissolved molecules into two elements or groups of elements called ions, set free at the electrodes: H and Cl for HCl, 2K and SO_4 for K_2SO_4, Na and OH for NaOH, etc. In this method, we admit (and this is what constitutes the hypothesis), that, in salt solutions *not subjected to an electric current*, and whose electric charge is consequently constant, the molecules are more or less dissociated into free ions which alone play the active rôle in double decompositions. We extend, moreover, to the masses of the ions and the undissociated molecules, the laws of equilibrium drawn from the principles of thermodynamics, but without specifically incorporating the heat effect of the reactions, which, in this method, is replaced by the *electrical conductivity*, corresponding to the degree of dissociation of the chemical molecules into free ions. The electrolytic method, which is that adopted by Ostwald in *Scientific Foundations of Analytical Chemistry*, is certainly more attractive, *a priori*, than the calorimetric method, in that it is attached to the general theory of Arrhenius, permitting coördination of a large group of phenomena, abnormal in appearance, in the most varied domains; osmotic pressures, freezing points, boiling points, electrical conductivities, etc. But, as we will see later, numerous facts have been established in these later years, notably by Professor Kahlenberg of the University of Wisconsin, which cast a certain doubt upon the legitimacy of the extension of the electrolytic theory to the concentrated salt solutions which are commonly employed in inorganic analysis, and under these conditions, it appears to us preferable in order to explain the processes of analysis, to have recourse to the calorimetric method, which is surely free from hypotheses and appeals only to the reaction taking place. Moreover, the two methods will be successively described and, in the theories which I will present in the course of this work upon a few of the operations of inorganic analysis founded upon double decomposition, I will take care to indicate the electrolytic explanation of Ostwald beside the calorimetric explanation, giving the reasons which seem to me to militate in favor of the latter."

The subject is presented under the headings: influence of the physical state of precipitates upon their purification by washing; theoretical principles of the methods of analysis based upon irreversible reactions; study of double decomposition of salts by the calorimetric method; electrolytic theory of double decomposition of salts; objections to the ionic theory; general processes of analysis based upon double decomposition of salts; study of some methods based upon double decomposition of salts.

Some of the sections are very good, notably the one on colloidal amorphous precipitates and pseudo solutions. The author brings out clearly, p. 48, the important fact that the ratio of permanganate to ferrous sulphate varies considerably when the titration is made by different men. In too many cases, however, he merely translates Ostwald's statements into terms of the so-called calorimetric method. On p. 170 the author states that methyl orange is a medium strong acid which is just what Ostwald says, whereas everybody ought to know that the color changes are independent of the sulphonic acid group. In its capacity as an indicator methyl orange is a weak base.

The translators usually come out second-best in their struggles with "will" and "shall." *Wilder D. Bancroft*

Experimentelle Untersuchungen über Atomgewichte. *By Theodore William Richards. Deutsche Ausgabe besorgt von J. Koppel. 16 × 24 cm; pp. viii + 886. Hamburg and Leipzig: Leopold Voss, 1909. Price: paper, 35 marks.* —This portly volume contains the papers on atomic weight determinations published from the Harvard laboratory during the twenty years from 1887 to 1908. The elements studied are: barium, bromine, cadimum, calcium, cesium, chlorine, cobalt, copper, hydrogen, iodine, iron, magnesium, manganese, nickel, nitrogen, oxygen, potassium, silver, strontium, sulphur, uranium, and zinc.

Everybody knews that this work of Richards is the most accurate of its kind that has ever been done. For those who are interested in something more than the final numerical values, it is a great help to have this volume of collected papers. In view of the increased momentum, we may hope for a second volume of equal size at the end of a decade. *Wilder D. Bancroft*

Radiochemistry. *By A. T. Cameron. 13 × 19 cm; pp. viii + 170. London: J. M. Dent & Sons, 1910. Price: bound, 2 shillings, 6 pence.*—The subject is treated under the following headings: radioactive methods illustrated by the thorium series of elements; the radiations from radioactive elements; life of a radioactive element; classification of the radioactive elements—their physical and chemical properties; methods of work with radium emanation—the life period of radium; the atomic weight of the emanations—liquid and solid radium emanation; the chemical effects produced by the radiations; the production of helium during radioactive changes and its identity with the α particle; recent attempts at transmutation; chemical evidences of transformation; recent results and speculations; radiogeology; the medical application of the radiations; bibliography.

In the preface the author says: "The title of this book has been chosen deliberately; the science of radioactivity has developed to such an extent as to make it justifiable and convenient to divide it. Here it is treated from a chemical standpoint; the physical side is introduced only so far as is necessary to explain the special experimental methods."

The following quotations from pp. 34, 84, 94, 140 and 151 will give some idea of the scope and style of the book:

"No fewer than twenty-six new elements have been discovered by radioactive methods; uranium and thorium were known long before their activity was observed. Of these twenty-eight elements, five are said to be rayless; in them no activity has been detected by the instruments in use at present. The others emit one or more kinds of ray; nine or ten give α particles alone. An appreciable life-period is possessed by nine only—uranium, ionium, radium, radio-lead, polonium, mesothorium, thorium, and radio-thorium and actinium. The remainder are none the less true elements, although their short life may never permit them to be examined by other than radioactive means.

"These twenty-six elements fall naturally into three large groups, namely, the elements uranium, thorium, and actinium, and their respective disintegration products. Using Rutherford's method of classification (from Radioactivity, pp. 449–50) in a slightly modified form, the elements can be grouped as shown below. Only the atomic weights of three—uranium, radium, and thorium—are known with any certainty. The α particle is a helium atom (of atomic weight 4), and the atomic weights of the other elements, calculated by deducting 4 for each α particle evolved, may approximate to those given in brackets. The present state of our knowledge does not allow great stress to be placed on this hypothesis."

"There is reason to believe that the chemical effects produced by radioactive elements are all due to the radiations which they emit, and that the difference in the effects produced by α and β rays is quantitative only. Most of the experiments have been made with radium or its emanation, but it must be remembered that it is probable that all the elements which emit rays would produce the same effect if the action of these rays could be concentrated sufficiently.

"Ultraviolet light (*i. e.*, electrons) decomposes water to produce hydrogen and hydrogen peroxide, while Kernbaum's quantitative results with the β rays from radium suggest that the reaction is represented by the equation

$$2H_2O = H_2 + H_2O_2.$$

Again Herchfinkel has just shown that the decomposition of carbon dioxide can be effected either by ultraviolet or by β rays, and Cameron has proved that hydrogen and oxygen are recombined by β rays.

"It seems, therefore, that most of the reactions which can be brought about by α and β rays together (as in the cases where emanation is mixed with gases or dissolved in liquids), are also produced by the β rays alone. It is consequently of interest to see what is the relative chemical effect of the two kinds of radiations. Some preliminary measurements with water by Cameron point to the conclusion that α and β rays produce ray for ray in liquids a quantitative effect of the same order.

"Two possible mechanisms of these chemical effects suggest themselves. One, a theory of collision, would be similar to that of the production of ions in a gas. We should then expect that the relative chemical effects of the two rays be proportional to the relative ionizing effect, about 100 : 1 (α rays greater). This cannot be the case in liquids, although it is not disproved for gases. The other apparent possibility is an effect of the nature of electrolysis, and here the similarity observed in the magnitudes of the effects might possibly prove more easy of explanation."

"Accepting in the meantime the general truth of the theory of disintegration, it is of some interest to speculate as to how these numerous new elements fit into the periodic table. Many arrangements have been proposed, in nearly all of which the attempt has been made to fit each element into a *separate* place in the table.

"There seem to be numerous grounds for regarding any such attempt as a mistake. The number of spaces vacant for elements of weight less than uranium are too few for the number in the uranium and thorium groups alone.

The atomic weights of uranium, thorium and radium may be regarded as definitely fixed within one unit. There is very strong evidence for the belief that the atomic weights of the emanations of thorium and radium differ by only one or two units. Their coefficients of diffusion are practically the same. Under the same pressures they condense at nearly the same temperature. Again, intermediate between thorium and its emanation comes the element radiothorium, which resembles radium in every respect. Unless the theory of Rutherford and Soddy is wrong *ab initio*, we must suppose that radiothorium and radium occupy the same place in the periodic table. On similar grounds it seems probable that in most cases at least two of these radioactive elements occupy the same space. With regard to the actinium series nothing definite can be stated until the atomic weight of actinium has been determined. But the actinium series resembles those of the two others strongly and seems to fit into the same groove.

"Cameron has recently suggested a form of the periodic table which fits all the known facts and makes only three assumptions:

"1. More than one element can occupy the same space.

"2. The emission of an α particle necessitates transference to a space of lower atomic weight.

"3. The emission of a β particle, or the occurrence of a rayless change, may, or may not, be accompanied by such a transference."

"Kelvin has shown that an immense length of time must pass before the earth's interior can cool appreciably by heat radiation to the surface. He calculated that if the specific heat and thermal conditions are the same as with surface rocks, even after a thousand million years there would have occurred no sensible loss from an interior core equal to one-half of the earth's volume. Similarly we can argue that a tremendous length of time would occur before a heating effect became perceptible. Under all ordinary conditions we should expect that any element existing at the earth's surface also existed in some greater or smaller quantity throughout; there appears to exist no reason that uranium should be an exception.

"Therefore, Joly concludes, the earth's interior temperature is rising. If the supply of heat is large enough the effects must *ultimately* be felt at the surface; but if very low, then the decay of the uranium itself may intervene and a surface effect become apparent.

"Wonderful possibilities are brought before us. Peaceful cooling may await the earth, or catastrophic heating may lead in a new era of life. Our geological age may have been preceded by other ages, every trace of which has perished in the regeneration which has heralded our own.

"Whatever be the future or the past of our world, we have the untrammelled regions of space in which such varied destinies must surely find their accomplishment. The planets may now be in varying phases of such great events. And when a star appears in the heavens, where before we knew of none, may not this be a manifestation of the power of the infinitely little over the infinitely great—the unending flow of energy from the unstable atoms wrecking the stability of a world?"

The author gives up the claim that lithium has been prepared from copper. He admits that Ramsay's experiments can be accounted for on the assumption that lithium dissolves from the containing vessel under the influence of radium when copper nitrate is present. He also accepts Rutherford's view that the alleged synthesis of neon was merely a case of leakage.

Wilder D. Bancroft

Introduction to Physical Chemistry. *By Harry C. Jones. 13 × 19 cm; pp. xv + 279. New York: The Macmillan Company, 1910. Price: $1.60, net.*—The first two hundred pages of this book have evidently flowed from the pen of the writer with perfect ease:—the style has all the vigor and freshness that naturally characterizes the utterances of the enthusiastic investigator as he speaks about his own field of labor. The presentation is strictly modern, as might be expected, since Professor Jones is a prominent worker on the subject.

The best part of the book is the chapter on solutions. Here we find no remnant of other text-book presentations, and all points of merit show to their best advantage.

The latter part of the book—from pages 200 to the end—is decidedly inferior to the first part—possibly because the author has no interest or special experience in this part of the subject. The treatment of electromotive force, polarization, chemical dynamics and equilibrium appears to be merely restatements of old text-book information, not even supplemented with modern references. However, this should not argue against the value of the book as a whole because a part of it is a real contribution—and in so far, it is ahead of many other texts. Besides, is is rare that an active investigator can keep up with the whole field.

The reviewer is aware that even in the first part there are many questionable points. With no interest to quibble it may be pointed out that it is misleading to attempt to derive atomic weights from molecular weights by division, p. 7; that we do not believe that the "law of Avogadro" has been placed "among the laws of nature," p. 27; that we do not share the opinion that "the above experiments" (on dry ammonia gas with dry hydrochloric acid gas etc.) "*show conclusively* that molecules have little or no chemical activity and that ions are the chief agents causing chemical action," p. 199. While we do not believe that there is a difference of opinion allowable on some of these points, yet we believe that the many points of excellence of the book allow us to overlook them.

E. P. Schoch

EXPERIMENTS ON SOLARIZATION. II

BY G. A. PERLEY

The following work was undertaken in order to account for the remaining doubtful points in regard to the whole subject of solarization. This represents a continuation of the previous work and the same stock developer was utilized.

Solution A	Solution B
1000 grams water	1000 grams water
126 grams Na_2SO_3	252 grams Na_2CO_3
21 grams hydroquinone	

Homolka[1] cites a very interesting case where an exposed plate previously immersed in a dilute solution of stannous chloride yielded only a black silver image upon development with indoxyl, and no indigo image. With an ordinary exposure to light he was able to develop the latent image on the silver bromide gelatine by means of indoxyl. Both a silver and an indigo image were obtained. Such a difference between the action of stannous chloride and that of light seemed to warrant a more careful study.

Accordingly a solution of indoxyl was made by the method of Heumann and Bachofen,[2] fusing indigo at 110° C with pure caustic potash in an atmosphere of nitrogen. The fusion was prolonged until the blue indigo color had disappeared and the melt had assumed an orange red color. The crystals thus obtained dissolve in water forming a yellow green solution. During the whole operation much care must be taken in order to exclude air. An indoxyl developer of the following type was made:

2.0 grams indoxyl
8.0 grams Na_2SO_3
0.5 grams KBr
100.0 grams water.

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[1] Eder's Jahrbuch der Photographie, 21, 58 (1907).

[2] Ber. chem. Ges. Berlin, 26, 225 (1893).

Plates were immersed in a solution of stannous chloride for varying intervals of time and after a thorough washing were developed in the indoxyl developer. In Table I are tabulated the best data:

TABLE I

Number	Stannous chloride solution	Immersion	After treatment with KCN
1	25 g. in 100 cc H_2O	4 hours	blackish
2	"	1 hour	bright pink
3	"	30 min.	light pink
4	"	10 min.	blackish
5	"	1 min.	dark pink
6	"	10 sec.	pinkish blue

After development with indoxyl the plates were fixed, and then treated with potassium cyanide solution for the same length of time. Due to the excess of silver in numbers 1 and 4 the image remained black; however if all the silver was dissolved by means of the cyanide in sufficient quantities, a pink rather than blue image was found to be present. It is now easy to explain why Homolka failed to obtain anything but a dark silver image with his experiments on stannous chloride. The effect of a solution of varying concentrations of stannous chloride upon a photographic plate is analogous to that of light. With increasing concentration of stannous chloride the silver bromide is reduced to a substance lower in bromine. Upon development with indoxyl, less indoxyl is oxidized for the higher concentration of stannous chloride and accordingly there is a silver image much more dense than the indigo one. This excess of silver then masked the indigo image. When the latent image is developed by indoxyl we have a reduction to metallic silver, but at the same time, the indoxyl is oxidized to the blue indigo. Hence it is perfectly easy to see the error caused by the masking effect.

It seemed advisable to determine the effect of some of our weaker reducing agents upon a silver bromide plate. A standard solution containing 0.6 gram of stannous chloride per liter was first employed. Bromide plates were immersed in varying concentrations of the above solution, taking care to maintain the time of immersion constant. Table II gives the results:

TABLE II

Number	Stannous chloride in cc	Water in cc	Immersion	After development	Type
1	1	100	22 min.	1 min.	dark
2	5	100	22 min.	1 min.	↓
3	10	100	22 min.	1 min.	
4	25	100	22 min.	1 min.	graded slightly
5	50	100	22 min.	1 min.	towards a
6	100	100	22 min.	1 min.	darker tone
7	150	100	22 min.	1 min.	↓
8	200	100	22 min.	1 min.	

Only a slight gradation in the densities of the developed and fixed plates was noticeable in Table II. In other words, we had only the first analogy to light action. No maxima (or minima) in the density degree of exposure curve could be detected. The whole experiment was unsatisfactory. As no reduced silver could be observed from the action of the stannous chloride alone upon the plate the possibility of using too dilute solutions was considered as a cause for the failure of the analogy of this solutions to that of light action. A more concentrated solution of stannous chloride was then tried with more fruitful results. The initial data are given in Table III:

TABLE III

Number	Stannous chloride in grams	Water in cc	Immersion	After development	Type
1	0.06	100	22 min.	1 min.	black
2	10	100	22 min.	1 min.	white

With just these few measurements it was perfectly evident that under the proper conditions a very close analogy to the action of light on the plate could be obtained by proper treatment with stannous chloride. Number 1 represents the action of a weak light in producing the first negative, while number 2 is analogous to the solarizing action of light.

In order to gain better control of this work a new method of attack was attempted. A new solution was made as a standard, containing 250 grams of stannous chloride per liter. A silver bromide plate was immersed a certain depth in this solution, and kept there for a suitable length of time. It was then immersed still farther in the solution for another period of time. By continuing this process one end of the plate received the longest exposure and the gradation could be followed from one end of the plate to the other. Utilizing such a scheme Tables IV and V give the data obtained.

TABLE IV

No.	Grams of stannous chloride in 100 cc water	Immersion	After development	Type
1	25	32 min.	1 min.	white
2	25	7 min.	1 min.	medium black
3	25	30 sec.	1 min.	slightly black

Another run which yielded far better results was the following:

TABLE V

No.	Grams of stannous chloride in 100 cc water	Immersion	After development	Type
1	25	8 hours	1 min.	slightly dark
2	25	1 hour	1 min.	lighter
3	25	30 min.	1 min.	white
4	25	10 min.	1 min.	black
5	25	1 min.	1 min.	slightly dark
6	25	10 sec.	1 min.	slightly dark
7	25	None	2 min.	white

Hence we see that maintaining all our variable factors constant, by aid of stannous chloride we may obtain a perfect analogy to light action on a bromide plate. A plate after undergoing these steps was fixed and mounted to use as a lantern slide. At the same time another plate was exposed by sections to outdoor light in such a manner that the stages from the initial negative to the final reduced negative would be produced. These two slides were retained in order to show the close analogy. With stannous chloride the various stages were far from being perfect analogies, but the general principle was distinctly evident. The only really imperfect feature is that of the final reduced negative. This is not as dense as that obtained by the action of light for an extremely long period. The second negative produced by the stannous chloride is more of a brown than a black. This is undoubtedly due to some action of the stannous chloride on the gelatine. A better black for the final negative can be obtained by substituting a dilute developer solution for the stannous chloride.

In order to verify this analogy, the study of the action of sodium arsenite upon an unexposed bromide plate was taken up. A solution of ten grams of sodium arsenite in a hundred grams of water was made. In the absence of light, unexposed bromide plates were treated in a similar manner to those in Table V. The data are given in Table VI:

TABLE VI

No.	Grams sodium arsenite in 100 cc water	Immersion	After development	Type
1	10	8 hours	1 min.	black
2	10	30 min.	1 min.	white
3	10	5 min.	1 min.	dark
4	10	1 min.	1 min.	slightly dark
5	None	None	1 min.	white

The gradations obtained in Table VI were decidedly better than those obtained with stannous chloride. The second negative was black rather than brown as in the case with stannous chloride. In the data of Table VI, number 1 gives the time required to obtain a dense negative. Darkening really begins very rapidly after passing through the white stage of number 2. This white stage, for the concentration used, existed only for a short interval. It was very interesting to note that in both cases the change from the first negative through the solarization zone to the final reduced negative is much more abrupt than that produced by light. The densities of the initial negatives were nowhere near as deep as those produced by light action. This was deceptive in the first work and the complete stages were not obtained. By careful regulation of the time of immersion the whole thing comes out splendidly, especially with sodium arsenite.

In order to increase the range of chemical solarizers the ferrous oxalate developer was next taken up. At first sight it seemed possible to gain any gradation desired by utilizing the proper mixture of ferrous and ferric oxalates. The oxalate developer as given by Eder was employed and the ferric oxalate solution was made in the same ratio.

Solution A		Solution B	
Neutral potassium oxalate	100 grams	Ferrous sulphate	100 grams
Water	300 grams	Water	300 grams
		H_2SO_4	5 drops

With these solutions the results as given in Table VII were obtained with an after development of 1 minute and then fixing:

TABLE VII

No.	Ferrous oxalate solution cc	Ferric oxalate solution cc	H_2O cc	Immersion			Gradation
				hrs	min	sec	
1	20	0	60	1½	30	1	Dark to slightly lighter
2	20	2	58	1½	30	1	Dark to slightly lighter
3	20	5	55	1½	30	1	Dark to slightly lighter
4	20	10	50	1½	30	1	Dark to slightly lighter
5	20	15	45	1½	30	1	slightly dark
6	20	20	40	1½	30	1	slightly dark

Separate plates were immersed in each of the above solutions for variable times; the first portion of the plate was in the solution 1 ½ hours, the next 30 minutes, and the next one minute. Under these conditions only a slight gradation from dark to light was perceptible. As far as verifying the previous analogies was concerned the whole was very unsatisfactory. By much work it should be possible to control this method. As better results might be obtained with fewer variables, only the regular ferrous oxalate developer was used and the strength varied by diluting. In this method the time of immersion is the only variable, and it makes the matter of manipulation much easier to control. Table VIII represents the results obtained under such conditions:

TABLE VIII

No.	Ferrous oxalate solution	Water	Immersion	After development	Type
1	40 cc	60 cc	1 hour	1 min.	black
2	40 cc	60 cc	30 min.	1 min.	black
3	40 cc	60 cc	5 min.	1 min.	black
4	40 cc	60 cc	1 min.	1 min.	black
5	40 cc	60 cc	15 sec.	1 min.	white
6	40 cc	60 cc	2 sec.	1 min.	black
7	None	None	None	1 min.	white

In the work as represented in Tables VII and VIII the final development was with the regular hydroquinone developer after washing the oxalate out thoroughly. The changes in gradation here were very abrupt but could be seen with perfect ease. The final black was especially good, while the initial negative was of a medium density as compared with the final. The detail was much poorer than was obtained in the case of the sodium arsenite, yet the analogy is the same. We have the same thing occurring with different colored lights and those of different intensities; the blue rays yielding a final reduced negative much more rapidly than the green, and the steps in the gradations are much more difficult to control.

The action of stand developers is well known and the fact that negatives are always the resultant led us to expect that we were dealing with a phenomenon similar to the above weak reducing agents rather than with one depending on rate of development.

A stand developer[1] was made up of the following composition:

Metol	5 grams
Citric acid	0.5 grams
Pyrogallol	4 grams
Acetone	16 cc
Na_2SO_3	20 grams
Water	4800 grams

Exposed plates of the same emulsion were immersed in the same amounts of the above developer for varying degrees of time. The plates were then removed and developed with the usual stock developer. If there was a continual pushing over of the image, as would necessarily follow from our first assumption, we should expect during some stage of the various immersions to be able to develop partial negatives and positives. Table IX gives the condensed results of many trials:

TABLE IX

No.	Stand developer	Immersion	After development	Type
1	50 cc	1½ hours	None	negative
2	50 cc	1 hour	1 min.	negative
3	50 cc	40 min.	1 min.	flat negative
4	50 cc	20 min.	1 min.	flat negative
5	50 cc	10 min.	1 min.	flat negative
6	50 cc	5 min.	1 min.	negative
7	50 cc	3 min.	1 min.	negative
8	50 cc	1 min.	1 min.	negative
9	50 cc	30 sec.	1 min.	negative
10	50 cc	5 sec.	1 min.	negative

In no case could there be detected the formation of a positive or any signs of a jumble effect. It follows then that

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[1] Eder: Eder's Jahrbuch der Photographie, 21, 475 (1907).

the stand developer at that specific concentration acts upon an exposed bromide plate simply as a slow developer, and that the resultant negative is the first negative and not the second. Farther verification of this was shown by exposing a plate for varying degrees of time to external light such that a negative, positive and final negative effect were obtained on various sections of the same plate. One-half of the plate was developed in the regular stock developer, while the other half was allowed to remain in the stand developer. Upon comparing the final relative densities no marked pushing over could be detected with the stand developer. Both portions of the plate seemed to maintain consistent gradations.

The above facts then suggested the question within what limits a developer acted analogous to light and where the action was one of rapid reduction. Accordingly solutions of the above Eder stand developer were made containing 25 cc. of the developer and 75 cc. of water. Unexposed plates were immersed in the solution for varying intervals of time. The method was the same as that adopted for the stannous chloride and sodium arsenite experiments. In Table X are given some of the results obtained:

TABLE X

No.	Stand developer	H_2O	Immersion	After development	Type
1	25 cc	75 cc	5 hours	1 min.	Faint black
2	25 cc	75 cc	3 hours	1 min.	Faint black
3	25 cc	75 cc	1 hour	1 min.	White
4	25 cc	75 cc	20 min.	1 min.	Dark
5	25 cc		5 min.	1 min.	Faint black
6	None	None	None	1 min.	White

The gradations in Table X were not of the best type and far inferior to any of the previous solutions. The results would not always check. The possibility of an error arising through the different rates of diffusion of this and the substances previously used gave us a new clue as to the failure. If the developer diffused very slowly there would only be a surface effect and this would prevent the complete stages appearing on final development. Accordingly, the stand developer was divided into two portions as the following:

Solution A		Solution B	
Acetone	16 cc	Metol	5 grams
Na_2SO_3	20 grams	Citric acid	0.5 gram
H_2O	2400 grams	Pyrogallol	4 grams
		H_2O	2400 grams

After many trials the data as given in Table XI yielded perfectly satisfactory results. A plate was completely immersed in Solution B for a long time and then for a certain time to one depth in Solution A. The plate was pushed down farther and farther into the solution and kept there for varying lengths of time. The final development was accomplished with the regular stock developer after the plate had been washed thoroughly:

TABLE XI

No.	Developer				Immersion in Sol. A	After development	Type
	A	H_2O	B	H_2O			
1	40 cc	40 cc	50 cc	50 cc	18 hours	1 min.	dark
2	40 cc	40 cc	50 cc	50 cc	9 hours	1 min.	faint dark
3	40 cc	40 cc	50 cc	50 cc	2 hours	1 min.	white
4	40 cc	40 cc	50 cc	50 cc	30 min.	1 min.	dark
5	40 cc	40 cc	50 cc	50 cc	5 min.	1 min.	faint dark

Hence we see that the stand developer at a proper dilution duplicates the action of light, but for the usual work this dilution is not practical and is never used.

A case of the above was called to the writer's attention quite recently. Mr. V. Skillman, of Cornell, had taken several photographs, using a film pack. In accordance with the exposure given a very dilute developer was employed and this required a long time for development. The consequence was that all the films turned out as partial positives and with mongrel effects. The real explanation of this is that, due to the very low concentration of the developer, it has aided in pushing the negative over close to the solarizing point, and the action was perfectly analogous to all the previous experiments. Still more recently the writer has received two plates that were partially solarized under the same conditions with a very old developer.

There is one suggestion in connection with all experiments on this particular line of work which might prove an aid to persons unfamiliar with such. When dealing with ordinary white light our density-time curve in its stage towards the point of solarization evidently has a very gradual slope. From merely qualitative observations the curves with most of the weak reducing agents employed are very abrupt, as would be the case if only violet rays were used in the light exposure. Accordingly, unless sufficient care is exercised the point of solarization may easily be passed without any knowledge of it. By slow steps there will be no danger of falling into this error.

In a previous article[1] the work of Carey Lea had been discussed and the errors of the work explained. Since that time our attention has been called to the fact that with certain grades of sodium hypophosphite there was no evident solvent action on silver bromide. Accordingly the previous experiments were repeated and the same grade of hypophosphite was used as in the previous case. The results checked perfectly. In order to be absolutely certain of such results the sodium hypophosphite was analyzed qualitatively for impurities. Barium chloride gave a decided white precipitate, which upon treatment with hydrochloric acid gave a white precipitate of sulphur. This seemed to show the presence of sodium thiosulphate. Of course the presence of this substance would explain the solvent action as previously observed. The particular brand of hypo-

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[1] Perley: Jour. Phys. Chem., 13, 648 (1909).

phosphite was obtained from the chemical stock room from a bottle labeled C. P. and placed on the American market by a reputable firm. At present we are unable to say whether sodium thiosulphate occurs as a common impurity, but it is easy to see how such might be the case. Of course the material might have been contaminated by accident. Our previous explanations as regards the action of Carey Lea's solution apply, provided his specific brand of hypophosphite contained the same impurities as those used in our first experiments, and such explanations account for all the observed facts. Pure sodium hypophosphite was prepared by the action of phosphorus on hot caustic and then by recrystallization. The pure hypophosphite solution had no apparent solvent action on silver bromide.

It then seemed advisable to try the action of this pure hypophosphite on a bromide plate. A solution of 50 grams in 100 cc. of water was prepared and the plate was immersed in it for varying intervals of time. After washing thoroughly and developing with the stock developer the results given in Table XII were obtained:

TABLE XII

No.	Grams hypophosphite in 100 cc H_2O	Immersion	After development	Type
1	50	48 hours	1 min.	black
2	50	25 hours	1 min.	black
3	50	2½ hours	1 min.	lighter
4	50	2 hours	1 min.	medium dark
5	50	30 min.	1 min.	less dark
6	50	5 min.	1 min.	light

Thus by dipping a plate by degrees into a nearly saturated solution of hypophosphite the final development yields a plate quite analogous to that produced by the action of light.

A closer observation of the results obtained by Carey Lea showed that "marking a bromide paper with a concentrated hypophosphite solution and then *throwing* it into a developer yielded a negative, but by continually weakening the hypophosphite a point is reached where the marks appear reversely, or lighter marks on a dark background." He leaves the matter at this point without explanation. It was noticed that marks were made on the bromide with hypophosphite solution, so his experiments were duplicated exactly. Strange to say, in the knowledge of our previous experiments, the results checked beautifully. A plate was then marked with clear water and placed in the developer and here also we obtained light marks on a dark background, provided the plate was not extremely overdeveloped. In the light of this, all of Lea's results become perfectly clear even though a pure hypophosphite was used. With high concentrations of hypophosphite and throwing into the developer he has at his marking points an extremely concentrated developer. As he dilutes he comes to a point where the reducing action of the aqueous hypophosphite and developer is just the same as that of the developer on the dry section of the plate. For still increased dilution the action of the developer on the marked section is diluted in respect to that on the dry portion. This section of the plate is then entirely different from the dry portion, hence white marks on a dark background. It could not be otherwise. Another curious feature is that Carey Lea cites the action of time as often producing the same effect as dilution. He observed that a paper yielding in 24 hours a negative, after that time gave a positive (the dilution was not specified) but that the effect was uncertain. Our last results show a method of making this a certainty and show that Lea's results on this are in perfect harmony with our present theory. In case the hypophosphite contained impurities our first explanation likewise accounts for the facts, but the effect of time as mentioned by Lea seems to favor the second explanation.

Former work[1] on the presence of a depolarizer in the film during an exposure had presented many undesirable complications. With a knowledge of the many factors which

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[1] Perley: Jour. Phys. Chem., 13, 643 (1909).

could influence the previous results a more systematic outline was followed. Using a standard lantern slide plate, contact printing was resorted to. An arc lamp was used as the source of illumination. In order to eliminate any light differences an automatic shutter, in principle like that of a camera shutter, was placed in front of the arc lantern lens. By aid of this, exposures to a fifth of a second could be controlled. The light was emitted from the lens through a 1/4 inch aperture. As these few pencils of rays were too active for the distance available, a rotating sector was placed in front of the aperture. By aid of this the light was cut down to one twenty-fifth of its original intensity. With such a device the quality of light remains constant while the intensity can be varied by changing the distance of the plate from the source of light or by altering the time of exposure. In all the experiments the plates were exposed at a distance of nine yards from the source of light. As a type of hydroquinone developer the stock one was used with A 10 parts, B 10 parts and water 200 parts. The metol and oxalate developers were used in the ratio of 1 : 10 : 10 : 200 (metol : sulphate : potash : water).

Plates were immersed in the above developers before exposure. Check plates were likewise immersed in water for the same length of time. All plates were then exposed to the same light at a constant distance from the arc and then developed immediately. The check plate and the plate containing the developer were always developed together in the same developer for the same time. The data according to Table XIII show the results:

TABLE XIII

No.	Developer in film	Exposure	Resulting density
1	Hydroquinone	5 sec.	decidedly dark
2	Water	5 sec.	faint image
3	Metol	5 sec.	medium dark
4	Water	5 sec.	faint image
5	Ferrous oxalate	5 sec.	faint image
6	Water	5 sec.	faint image

The above plates were developed with the regular stock developer (the oxalate excepted) and development continued until the plate containing developer began to fog. The hydroquinone plate was much more dense than the water check plate. The metol plate was not as dense as the corresponding hydroquinone plate; but there was a decided difference between the metol and its check water plate. The difference between the metol and hydroquinone could be explained as due to the relative rates of diffusion of the two substances into the plate. However the amazing feature of the above work came with the presence of ferrous oxalate in the film during exposure. As this solution has a high rate of diffusion we should obtain the most dense plate of the three, other conditions being equal. As a matter of fact the density was less than that of the check water plate. Of course this plate was given an after development in the regular ferrous oxalate developer. When the absorption spectrum of a very thin layer of this developer was examined it was seen that a greater portion of the blue and all the violet were cut out. Accordingly a very thin tube of the oxalate developer was placed in front of the water check plate during the exposure, while a tube of water of corresponding thickness was placed in front of the plate containing the axalate developer. Under these conditions the oxalate plate yielded a more dense image than its check plate. Thus we see that such a detail as light absorption introduces decided errors in this case.

Another particular case of the above absorption error was noticed when a two weeks' old metol developer was used to check up some of the previous work. It was observed that the developer had assumed a brown color. Nevertheless, but little attention was given this, since it developed a plate perfectly. With such a developer in the film, the first results could not be checked. Upon examining the absorption spectrum of even a very thin film of this developer a decided absorption in the violet was evident. Thus the greater portion of the really active rays of light were taken away, causing an extremely large error. This would occur very infrequently with a metol developer as it is usually made up fresh; but the error with the oxalate must always be a great factor.

Another striking example of the effect of absorption is given in connection with Lüppo-Cramer's[1] work on the theory of sensitizers. He found that precipitated silver chloride blackened less rapidly when immersed in a 5 percent solution of sodium nitrite than when in water. On the other hand, a sensitizing action was obtained when a silver chloride plate was bathed in a nitrite solution and then dried. However, a retarding action does not occur when the plates are merely moistened with the nitrite solution. Lüppo-Cramer considers the difference as due to the relative amounts of nitrite present. As this seemed rather unsatisfactory, the absorption spectrum of a nitrite solution was examined. There is a decided absorption in the blue with even a dilute solution of nitrite. Accordingly experiments with silver chloride were undertaken in order to show the effect of this absorption. A precipitated silver chloride was placed in two glass tubes which allowed light to enter at one point. The silver chloride in both tubes was covered with equal layers of a 5 percent solution. In one tube above the mixture of silver chloride and nitrite solution was placed a separate tube of a 5 percent nitrite, while over the other was placed a separate tube containing an equal height of water. Only the rays of light which passed through the tubes of nitrite and water were incident upon the silver chloride. Exposures were then made in duplicate to sunlight for the same length of time. The silver chloride, in the tube permitting light to enter through the water, blackened many times more rapidly than that in the tube where light entered through the nitrite solution.

The silver chloride blackened more slowly in the nitrite solution than in water in the experiments as conducted by

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[1] Jour. Phys. Chem., 14, 149 (1910).

Lüppo-Cramer, but as absorption of light by the nitrite readily takes place, these experiments are faulty.

In order to determine whether the nitrite solution had any sensitizing action on the silver chloride two glass tubes similar to the above were employed. In one was placed silver chloride immersed in a thin layer of a 5 percent nitrite solution. Light was allowed to enter this tube through a separate tube containing water. In the other was placed silver chloride immersed in a layer of water of the same height as that in the first tube. Light was allowed to enter this tube through a separate tube containing a nitrite solution equivalent to that in the first. The two tubes were exposed to the same source of light for the same length of time. Under such conditions the silver chloride immersed in the nitrite solution darkened more rapidly than the silver chloride immersed in water.

These experiments only increase the number where absorption of light by various solutions has caused erroneous conclusions.

Previous to the above experiments much labor had been expended in an attempt to use daylight as the source of light. An interior of a lecture room with very constant outside illumination had been selected and many plates were exposed to the same object at the same distance, but consistent results could never be obtained. One hour of the day would yield a much brighter light than the next, with the consequence that we could never vouch for the exactness of our results. With the apparatus employed such a variable factor was eliminated. All differences in density were of such a nature that they could be judged qualitatively. Especially with hydroquinone the plate seemed at least two times as fast as the check water plate and under the best conditions all were twice as good where they contained the developer. Of course such estimates are not exact, but great differences from the water check plate were easy to observe provided error due to absorption was eliminated.

These results are at great variance to those obtained by Lüppo-Cramer,[1] who found the sensitiveness in most cases to be decreased by presence of a depolarizer in the film during exposure. It seems probable that the source or quality of light as well as absorption must have altered the results, for our experience showed already that no reliance could be placed upon outdoor exposures. Accordingly the methods were improved in order to eliminate the many variable factors in other experiments.

With the above concentrations of hydroquinone in the film the problem of quality or effect of various colored rays was undertaken. In order to obtain definite colors, various solutions of brilliant green, acid rhodamine dyes, fluoresceine and permanganate of definite absorption factors established by aid of the spectroscope were made. Table XIV gives a good generalization of the effect of quality of light under these conditions:

TABLE XIV

No.	Color of light	Exposures	After development	Relative types
1	yellow	3 min.	1 min.	faint dark, badly fogged
2	water	3 min.	1 min.	lighter
3	yellow-green	2 min.	1 min.	faint dark, badly fogged
4	water	2 min.	1 min.	lighter
5	green-blue	30 sec.	1 min.	medium dark
6	water	30 sec.	1 min.	lighter
7	blue	5 sec.	1 min.	dark
8	water	5 sec.	1 min.	much lighter

In the case of the rays from the yellow to the green an exposure sufficient to cause final development yielded a badly fogged plate. This disturbing feature tends to obscure the real outlines. This is undoubtedly due to the very slow action of the rays of low actinic value. In consequence there is a tendency for a gradual development over the whole surface and accordingly a lack of contrast. For all the rays

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[1] Bancroft: Jour. Phys. Chem., 14, 134 (1910).

that do not cause a uniform fogging (or a long exposure) the effect of the presence of a depolarizer in the film was, not to decrease the sensitiveness, but to increase it as compared with the water check plate. In the experimental work all other factors were maintained constant as in the previous case. The little ray filter was placed in front of the lens and the distance of the plates was maintained constant, while the times of exposures were varied.

We have considered the major portion of the field of solarization and have brought the discordant facts into a general system. From the action of several of our reducing agents it is perfectly evident that the latent image is a reduction product of silver bromide. In other words the ratio of bromine to silver is less than in the normal silver bromide.

There are still one or two minor details to be straightened out. One of these is the antagonistic effect of different lights, or the Herschel effect. Abney[1] has given us only the major details as to his method of showing the effect of red light upon a plate exposed at the same time to a source of white light, and as Lüppo-Cramer[2] denies the existence of the phenomena observed by Abney, it seemed advisable to duplicate exactly the former work in order to give a full explanation.

An apparatus was so arranged that the light from an incandescent lamp might fall on the whole surface of a bromide plate. From another source a small bundle of brilliant red rays were allowed to fall upon a section of the already illuminated plate. With such the data in Table XV were obtained:

TABLE XV—EXPOSURE TO WHITE LIGHT ALWAYS CONSTANT

No.	Exposure to red	Development	Type of red spot portions
1	10 sec.	1 min.	Darker than surrounding plate
2	30 sec.	1 min.	Much darker than surrounding plate
3	1 min.	1 min.	All of plate same intensity
4	2 min.	1 min.	Little lighter than surrounding
5	5 min.	1 min.	White surrounded by black.

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[1] Phot. Jour., 32, 318 (1908).

[2] Phot. Correspondenz, 39, 134 (1902); 43, 432 (1906); 46, 344 (1909)

The plates were developed with the regular stock developer and the results hardly need explanation. What actually occurred when Abney found that red light destroyed the action of white light upon a bromide plate was that the red light was undoubtedly very intense. Very possibly it was not composed solely of pure red rays, but may have contained a few more powerful actinic rays. When an exposure was made under these conditions the portion where the red was incident was much more strongly illuminated. The result was a solarization phenomenon at this point. When obtaining the data of Table XV only a very intense pure red light was employed. The filter was made of acid rhodamine (dye). By continued exposure we have the negative first, and next the positive formed. All this is due only to the excessive exposure received at this particular point. Thus we see that the so-called antagonistic effect of various lights on the photographic plate is only one type of solarization. If Abney had given more specific details as regards his source of light, or if we could have learned more in detail as regards Lüppo-Cramer's methods wherein he failed to confirm Abney's results, the whole matter could have been interpreted without experimental corroboration.

In the Clayden effect a very short exposure to an intense light followed by a short exposure to diffused light yields a reversal, but if the original exposure is too long only a negative results. The mechanical strain theory, as well as the other theories advanced to explain this phenomenon have been given[1] rather completely and accordingly will not be repeated. The fact of the reversals seems perfectly logical and can be explained simply as a solarization phenomenon. In order to verify this statement, a medium induction coil was employed. Thin sparks of about four inches in length were photographed Under such conditions only negatives were obtained when the plate was developed in the regular stock developer. By aid of condensers a very dense and brilliant spark was produced. Exposures to such yielded three

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[1] Bancroft: Jour. Phys. Chem., 13, 269 (1909).

classes of images; the initial negative, the positive and the second negative, when the spark was least bright, of medium illumination or most intense, respectively. Several photographs of the uncondensed sparks were taken. By fogging these plates for a short time, positives were readily produced. Thus we see that with varying intensities of the sparks, negatives or positives may be obtained. If the spark is not sufficiently intense a positive may be produced by merely fogging with diffused light (this is simply one method of producing positives from would-be negatives). There seems to be nothing exceptional about this so soon as one follows out the different stages. When flashes of lightning are photographed, almost any type may result. When the lightning is distant and not intense, the usual negative is obtained, but if the flash is quite intense a positive would result. When the lightning is extremely bright and in close proximity it would be possible to obtain the second negative. The stages are merely those observed when the ordinary action of light on a silver bromide plate is studied. The explanations for the latter apply to the same extent as to the former.

In all this work Seed's lantern slide plates were used. However, it seemed advisable to try the effect of a solarizing exposure on several grades of plates. It was found that Seed, Cramer, and Lumière plates solarized with the proper exposure. The rapid 'Sigma' Lumière plate was the easiest to control in the production of direct positives. Lüppo-Cramer[1] states that the silver bromide gelatine plates with an extraordinary fine grain, such as the Lippmann plates, show no normal solarization at all. This seemed interesting if true, and accordingly experiments were made with Lumière's 'Red Label' plates. These plates are supposed to be unsurpassed for fineness of grain. Using a constant source of light, plates were exposed under a lantern slide plate by contact for varying degrees of time. The first experiments yielded no solarizing effect even under conditions which pro-

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[1] Photographische Probleme, 138 (1907).

duced beautiful results with the Sigma plate. A more careful study was made and very slow stages were employed as the variable factor was altered. For a given distance from the source of light an exposure was then found which yielded positives consistently. Under these conditions the plate assumed an appreciable fog. When too long an exposure was given, the final reduced silver masked everything. Previous failure to obtain positives with very fine-grained bromide plates is due to the fact that the change from that portion of the degree of exposure-density curve where solarization occurs to the final reduced silver is very abrupt. Under such circumstances the solarizing portion of the curve is easily passed and only the initial or final negatives are obtained. By very moderate steps in varying the degree of exposure the phenomenon of solarization becomes perfectly evident in the finest of bromide plates.

Another method of producing positives from the fine grained 'Red Label' plate is by exposure during development to a green-blue light. This yielded far better results than the previous method as the uniform fog is not so troublesome. By this method failure to obtain positives from even a very fine grained bromide plate should never result.

A general summary of our results show that the two assumptions made by Professor Bancroft account for all the facts and bring many theories into one general system. The assumptions were based on the theory of Grotthuss, and on the experimental facts that silver bromide which had been slightly decomposed by light is reduced faster by a developer than either unexposed or completely exposed silver bromide.

(*1a*) The action of light on a silver halide compound corresponds to that of a direct current or of a fairly weak reducing agent. It causes the silver halide to pass through all the possible stages.

(*1b*) A fairly strong reducing agent (a developer) does not cause the silver halide to pass through all the possible stages and does reduce certain silver halogen solid solutions or sub-halides faster than others which contain less halogen.

(2) Oxidizing agents do not increase the tendency towards solarization, but regard the formation of the weak normal image with a better positive resulting.

(3) Reducing agents do not retard solarization, but tend to mask it by excessive reduction.

(4) In the production of positives splendid control of Nipher's method may be obtained by aid of green-blue rays; positives may be obtained by slow reduction using a weak developer, but this requires a very long time; positives may be obtained by aid of a weak depolarizer in the film for a much shorter exposure than is otherwise demanded. This wet process is very impracticable, and is very messy to handle.

(5) The Waterhouse reversal is due to a sensitizing action of the thiocarbamide. Better control is obtained by a preliminary sensitizing in the thiocarbamide solution, and the development with the usual developer. For under exposures this is the ideal manner in which to produce a fine dense positive.

(6) In Kogelmann's work negatives could only have been obtained after treatment of over-exposed plates with thiocarbamide by use of a too dilute or old developer, or by too short a development.

(7) Carey Lea's reversals were due undoubtedly to the difference in the action of the developer on the surrounding dry film instead of a wetted film. The dry film developed first in cases of low concentration of hypophosphite. Pure hypophosphite acts like a weak developer.

(8) By the use of chemical reducing agents as stannous chloride, sodium arsenite, or very weak developers, it has been shown that the latent image is a reduction product, or that the ratio of bromine to silver is less than in the normal silver bromide. By such agents we find a verification of the second assumption.

(9) A chemical which dissolves silver from the latent

image will check solarization, while any which dissolves silver bromide will increase the tendency to solarize.

(10) In Homolka's indoxyl development the excess silver masked the positives. The stannous chloride acted analogous to light and caused the excessive reduction.

(11) The presence of depolarizers in a film during exposure increases the sensitiveness.

(12) The stand developer acts as a slow developer rather than as a weak reducing agent.

(13) The antagonistic action of light on a photographic plate is due only to the effect of excess exposure and is only a phenomenon of solarization.

(14) The disintegrating action of light as brought forth by Lüppo-Cramer is not necessary for the explanation of the Clayden effect. The effect is produced by the normal action of light of high intensity. It is only another instance of solarization.

(15) Extremely fine-grained plates will solarize provided the proper precautions are observed.

This work was suggested by Professor Bancroft and the writer desires to express the greatest gratitude for the interest and many suggestions always at hand in this work.

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STUDIES IN THE ELECTROCHEMISTRY OF THE PROTEINS. III. THE DISSOCIATION OF THE SALTS OF OVO-MUCOID IN SOLUTIONS OF VARYING ALKALINITY AND ACIDITY

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I. EXPERIMENTAL

(a) The Preparation of the Ovo-mucoid

The whites of eggs were beaten up to a froth and allowed to stand in shallow vessels overnight. The subnatant fluid was then poured off, the froth being rejected. This fluid was diluted to five times its volume with distilled water, and to every liter of the diluted fluid was added 130 cc of approximately N/10 acetic acid (made up by diluting 10 cc of glacial acetic acid to 1750 cc). This mixture was heated slowly to boiling-point, being rapidly and uniformly stirred meanwhile, and, after being allowed to boil for about 3 to 5 minutes, was put aside in rather shallow vessels for about 12 hours. At the end of this time most of the coagulum had floated to the top, and the subnatant fluid was filtered through hardened filter-paper. Filtration was very rapid, and the filtered fluid, when boiled, either with or without the further addition of acetic acid, remained perfectly clear. The fluid which was thus obtained was now slowly evaporated to 1/5 of its volume; the temperature of the fluid never being allowed to rise above 55° C. After allowing this fluid to cool, the protein was precipitated from it by the addition of ten volumes of 99.8 percent alcohol (Kahlbaum's) and was allowed to settle in tall glass cylinders. The supernatant fluid was then syphoned off and the precipitate was washed in the same volume of alcohol as that employed in the precipitation. This washing was repeated, again employing the same volume of alcohol, and the precipitate was allowed to steep in this alcohol for about 24 hours, in order, if possible, to remove all adherent or combined acetic acid. The alcohol was then siphoned off and the precipitate was washed in the same volume of ether (Kahlbaum's ueber Natrium destilliert). This washing was repeated. The ether was then siphoned off and the thick suspension of protein in ether which was thus obtained was rapidly poured into a hardened filter, the filter and the contained suspension of protein in ether being at once transferred to an incubator and the filtration continued over H_2SO_4 at 40° (to avoid condensation of atmospheric moisture on the filter. It goes without saying that throughout the processes of washing, settling, etc., possible introduction of atmospheric moisture was avoided by keeping the glass cylinders closed with ground glass-stoppers).

After the completion of filtration, the ether which had filtered off was removed from the incubator and the precipitate allowed to dry for 24 hours. The protein is then obtained in the form of chalky cakes which are very readily broken up into fine, impalpable powder. This powder was passed through a fine sieve and kept in a glass-stoppered bottle. It was found not advisable to work with fewer than 6 dozen eggs at one time as, otherwise, the amount of precipitate which is finally obtained is so small that the danger of excessive caking and partial decomposition, in drying, due to the deposition of moisture upon the filter, is very great. Not quite 40 grams of the powder were obtained from 24 dozen eggs.

The protein which is thus obtained has been identified by Mörner[1] as a mucoid and is termed by him ovo-mucoid.

About a gram of the ovo-mucoid thus obtained was dissolved in about 100 cc of N/2 HCl and this solution was boiled until 30 cc of fluid had distilled over. This distillate was

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[1] C. Th. Mörner: Zeit. phys. Chem., 18, 525 (1894). Cf. Hammarsten: "A Text-book of Physiological Chemistry," Translated by Mandel, New York, 1904, p. 431.

then tested for acetic acid. It contained a trace of an acid of the fatty series, sufficient to yield a slight coloration with ferric chloride, but insufficient to yield a precipitate of ferric hydrate on boiling or to yield the ethyl acetate test.

(b) The Experimental Procedure

The experimental procedure was, with the simplifications which were rendered possible by the fact that ovo-mucoid dissolves readily and rapidly in solutions of all reactions, identical with that employed in a previous investigation, upon the dissociation of potassium caseinate.[1] To each of the solutions introduced into the gas-chain 0.01 KCl was added in order to attain a favorable conductivity in the chain. This KCl-solution was itself very faintly acid; its acidity was estimated by determining the potential between it and 0.01 *N* KOH (dissolved in 0.01 KCl) and was found to be $6.95 \times 10^{-6} NH^+$. The solutions which were employed in the conductivity determinations did not, however, contain added KCl, but were simply prepared by dissolving the ovo-mucoid in solutions of known HCl or KOH concentration. Hence λ ($\equiv$ the depression in the conductivity of the acid or alkaline solution resulting from the addition of the protein) was estimated by subtracting the observed conductivity of the ovo-mucoid solutions from that of the HCl or KOH solution in which it was dissolved—the latter being estimated by interpolation from the tables of Kohlrausch and Holborn.[2]

It may be mentioned, in passing, that none of the difficulties which are encountered in casein solutions, arising from precipitation at the electrodes are met with in solutions of ovo-mucoid. Ovo-mucoid would also appear to be much less readily hydrolyzable than casein.

In the accompanying tables the symbols employed have the following significance:

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[1] Part I of these "Studies:" Jour. Phys. Chem., 14, 528 (1910).

[2] Kohlrausch and Holborn: "Leitvermögen der Elektrolyte," Leipzig, Pp. 160 and 199 (1898). For the mode of employing these tables, cf. Part of I these "Studies."

b_1 ≡ The concentration of the KOH solution in which the ovo-mucoid was dissolved.

a_1 ≡ The concentration of the HCl solution in which the ovo-mucoid was dissolved.

π ≡ The potential of the chain in volts. In solutions of ovo-mucoid in alkali $= 0.0601 \log_{10}\frac{b}{b_1}$; in solutions in acid $= 0.0601 \log_{10}\frac{a_1}{a}$.

b ≡ The hydroxyl concentration of the solution (in alkali) of ovo-mucoid.

a ≡ The hydrogen ion concentration of the solution (in acid) of the ovo-mucoid.

m ≡ The concentration of alkali (or of acid) neutralized by the ovo-mucoid.

x_1 ≡ The conductivity, in reciprocal ohms per cc of the solution containing no ovo-mucoid. (At 30° C).

x ≡ The conductivity in reciprocal ohms, of the solution containing ovo-mucoid. (At 30° C).

λ ≡ $x_1 - x$ ≡ The alteration of the conductivity of the alkaline or acid solution which is brought about by the addition of ovo-mucoid.

It should be observed that since free, uncombined ovo mucoid is soluble in water it is not possible, without additional data, to evaluate the "apparent" molecular conductivity of the ovo-mucoid salt as it is in solutions of the caseinates. (Cf. Part I of these "Studies.")

TABLE I

1 percent ovo-mucoid dissolved in KOH solution

b_1	π	b	m	$x_1 \times 10^5$	$x \times 10^5$	$\lambda \times 10^4$
0.0005	0.0755	2.77×10^{-5}	0.00047	14.5	41.2	−26.8
0.0010	0.0475	1.62×10^{-4}	0.00084	28.9	44.9	−16.0
0.0020	0.0500	2.95×10^{-4}	0.00171	57.6	56.5	+ 1.1
0.0030	0.0367	7.34×10^{-4}	0.00227	86.0	70.3	+15.7
0.0050	0.0356	1.28×10^{-3}	0.00372	142.0	103.8	+38.2
0.0100	0.0185	4.92×10^{-3}	0.00508	—	—	—

TABLE II

1 percent ovo-mucoid dissolved in HCl solution

a_1	π	a	m	$x_1 \times 10^5$	$x \times 10^5$	$\lambda \times 10^5$
6.95×10^{-6}	0.1087	1.08×10^{-7}	6.84×10^{-6}	—	—	—
0.0005	0.2261	8.65×10^{-8}	0.00050	22.6	40.3	− 17.7
0.0010	0.2107	3.12×10^{-7}	0.00100	45.1	43.2	+ 2.0
0.0020	0.1726	2.69×10^{-6}	0.00198	90.2	52.5	+ 37.7
0.0030	0.1492	9.88×10^{-6}	0.00299	135.0	60.6	+ 74.4
0.0040	—	—	—	179.5	68.4	+111.1
0.0050	0.1190	5.24×10^{-5}	0.00495	223.8	77.6	+146.2
0.0075	—	—	—	334.8	105.9	+228.9
0.0100	0.0610	9.66×10^{-4}	0.00903	444.0	152.2	+291.8

It will be observed that in many of the least alkaline and acid solutions λ is negative, in other words, that the addition of ovo-mucoid to the solution actually *raises* the conductivity instead of depressing it. This is undoubtedly because, in these solutions, the conductivity of the free ovo-mucoid itself more than makes up for the depression in the conductivity due to the neutralization of the small amount of acid or alkali which is present.

II. THEORETICAL

The combining capacity for acid of ovo-mucoid at absolute neutrality (neutrality to litmus) can be estimated (cf. part I of these "Studies") by determining the abscissa of the point of intersection of the experimental curve:

$$\pi = f(a_1)$$

with the curve:

$$\pi = 0.4107 + 0.0601 \log_{10} a_1$$

The point of intersection of these curves was determined by the graphic method described in a previous paper and found to be at:

$$a_1 = 0.0007$$

hence 1 gram of ovo-mucoid neutralizes 7.0×10^{-5} equivalent-gram-molecules of acid in forming an absolutely neutral solution. It will be observed that ovo-mucoid is more *basic* than it is *acid*. The contrary is the case with the proteins, the electrochemistry of which has hitherto been studied. Thus 1 gram of casein, at absolute neutrality, binds 50×10^{-5} equivalent-gram-molecules of *base*[1] and 1 gram of "insoluble" serum globulin neutralizes, at neutrality to litmus, 10×10^{-5} equivalent-gram-molecules of base.[2]

The relation between *m*, the amount of acid or of alkali neutralized by the ovo-mucoid, and the acidity or alkalinity of the solution in which it is dissolved is shown graphically in the accompanying figure. It will be seen as the proportion of acid or of base to ovo-mucoid declines, the combining-capacity of the ovo-mucoid tends to become directly proportional to the concentration of the base, but that as the proportion of acid or of base to ovo-mucoid (and the excess of unneutralized acid or base) becomes large, the combining capacity of the ovo-mucoid tends to attain a maximum. The behavior of ovo-mucoid is therefore strictly analogous to that of casein (cf. Part I of these "Studies").

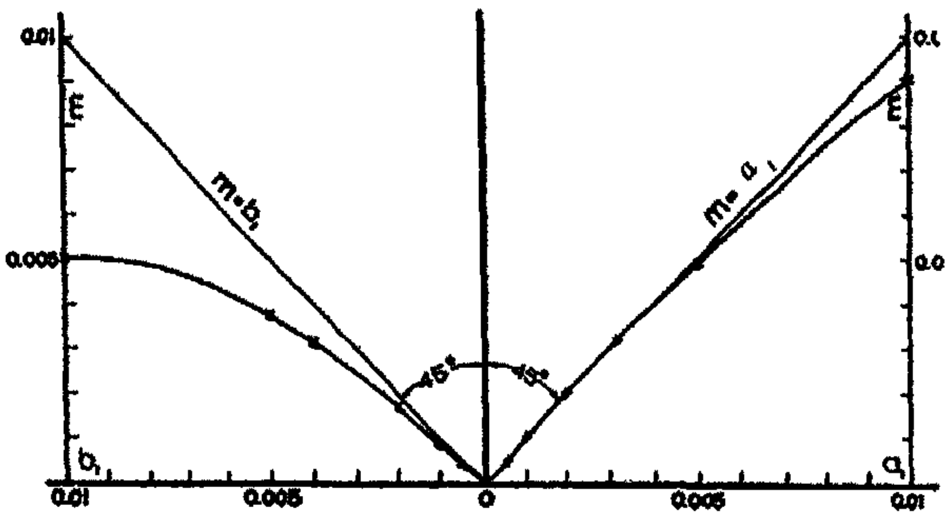

Fig. 1

b_1 is the concentration of KOH in which 1 percent ovomucoid is dissolved; *m* is the number of gram-equivalents of KOH which is neutralized per litre.

a_1 is the concentration of HCl in which 1 percent ovomucoid is dissolved; *m* is the number of gram-equivalents of HCl which is neutralized per litre.

The *maximum* combining capacity of ovo-mucoid for

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[1] Soldner: Landw. Versuchs., **35**, 351 (1888). Lacqueur and Sackur: Beitr. chem. Physiol. und Pathol., **3**, 196 (1903). Van Slyke and Hart: Am. Chem. Jour., **33**, 461 (1905). T. Brailsford Robertson: Part I of these "Studies," Jour. Phys. Chem., **14**, 528 (1910).

[2] W. B. Hardy: Jour. Physiol., **33**, 251 (1905–6).

acid was evidently not attained in any of the solutions investigated—but it is obviously in excess of 90×10^{-5} gram-molecules per gram, probably in excess of 100×10^{-5} equivalent-gram-molecules per gram. The maximum combining-capacity of ovo-mucoid for alkali would appear to be in the neighborhood of 50×10^{-5} equivalent-gram-molecules per gram. For purposes of comparison it may be recalled that the maximum combining capacity of *casein* for alkali is about 180×10^{-5} equivalent-gram-molecules per gram.

It is an interesting fact, which a glance at Table II reveals, that when 1 percent ovo-mucoid is dissolved in 6.95×10^{-6} N acid, although the protein is still acting as a *base*, yet this solution is actually *more* acid than the solution which is obtained by dissolving 1 percent ovo-mucoid in 0.0005 *N* HCl. A similar phenomenon was observed by W. B. Hardy in solutions of serum globulin.[1] The interpretation of this phenomenon is probably as follows. The acid-capacity of the protein *increases* with the acidity of its solution and that very rapidly in the neighborhood of the neutral point where a proportion of the amphoteric molecules are probably behaving as *acid* molecules, although the majority are behaving as *basic* molecules. With decreasing acidity of the solution in which the protein is dissolved, therefore, the acid-combining capacity of the protein may actually diminish so rapidly as to leave uncombined a greater quantity of acid in a less than in a more acid solvent.

In a previous communication (Part I of these "Studies") I have shown that the relation between the depression of the conductivity of an alkaline solution which is brought about by the introduction of casein and the alkalinity of the solution to which the casein is added may be expressed by the equation

$$\lambda \times 10^5 = \alpha b_1 - \frac{\beta}{C} b_1^2 - \gamma C,$$

where λ is the depression of the conductivity of the solution, b_1 its alkalinity, C the percentage concentration of the

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[1] Loc. cit.

casein and α, β and γ are constants. For 1 percent solutions this becomes

$$\lambda \times 10^5 = \alpha b_1 - \beta b_1{}^2 - \gamma.$$

I find that the same law holds both for solutions of ovo-mucoid in acid and for solutions in alkali, save that in the *acid* solutions we must replace b_1 by a_1, the *acidity* of the solution to which the ovo-mucoid is added. Applying this equation to the results enumerated in Table I we obtain

$$\lambda \times 10^5 = 20850\, b_1 - 1250000\, b_1^2 - 35.6;$$

in the accompanying table the values of $\lambda \times 10^5$ calculated from this formula are compared with those which were obtained experimentally.

TABLE III

$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Calculated
—26.8	—25.5
—16.0	—16.0
+ 1.1	+ 1.1
+15.7	+15.7
+38.2	+38.4

Applying the corresponding equation to the results enumerated in Table II and evaluating the constants from all of the observations by the method of least squares we obtain

$$\lambda \times 10^5 = 41990\, a_1 - 852700\, a_1^2 - 41.4;$$

in the following table the calculated and observed values of $\lambda \times 10^5$ are compared.

TABLE IV

$\lambda \times 10^5$ Experimental	$\lambda \times 10^5$ Calculated
— 17.7	— 20.6
+ 2.0	— 0.3
+ 37.7	+ 39.2
+ 74.5	+ 76.9
+111.1	+113.0
+146.2	+147.2
+228.9	+225.5
+291.8	+293.2

The agreement between the observed and calculated values is all that could be desired and it is evident that the equation $\lambda \times 10^5 = \alpha b_1 - \beta b_1^2 - \gamma$ expresses a general relation (for a given concentration of the protein) which subsists between the alkalinity or acidity of a solution to which protein is added and the depression (or increase) of its conductivity which results. Unfortunately lack of material has prevented me, for the present, from ascertaining the influence of the *concentration* of the ovo-mucoid upon the values of the constants which define this relation for ovo-mucoid.

Regarding the theoretical significance of this relation the following may be tentatively suggested. In my previous communication referred to above I have pointed out that

$$\lambda = (U + V)m - (v_1 + v_2 + v_3 + \ldots.)c,$$

where U + V is the molecular conductivity of the neutralized acid or base v_1, v_2, v_3, etc., are the velocities in cm per sec per cm potential gradient and c is the equivalent-molecular concentration of the ions derived from the protein and its salts. Comparing the equations

$$\lambda = (U + V)m - (v_1 + v_2 + v_3 \ldots..)c$$

and

$$\lambda = \frac{\alpha}{10^5} b_1 - \frac{\beta}{10^5 C} b_1^2 - \frac{\gamma C}{10^5},$$

and recollecting that in the less alkaline solutions m^1 very nearly equal to b_1, it would appear probable, from considerations of symmetry, that *in solutions of low alkalinity:*

$$\frac{\alpha}{10^5} = U + V \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

and

$$(v_1 + v_2 + v_3 \ldots.)c = \frac{\beta}{10^5 C} b_1^2 + \frac{\gamma C}{10^5} \ldots\ldots\ldots \quad (2).$$

Equations exactly similar in form would of course be obtained for solutions of the protein in *acid*. The first of these relations is obviously very nearly satisfied by the numerical values of the constant α ascertained above. For solutions of ovo-mucoid in HCl-solutions $\frac{\alpha}{10^5}$ is 0.420, while U + V for HCl at infinite dilution is 0.384. For solutions of ovo-mucoid in KOH-solutions $\frac{\alpha}{10^5}$ is 0.209, and U + V for KOH at infinite dilution is 0.218 .[1] The second of the above relations expresses the equivalent-molecular-concentration of the protein ions in terms of the concentration of the protein and of the concentration of acid or base in which it is dissolved.

Conclusions

(1) Ovo-mucoid is more strongly basic than acid.

(2) The acid-combining capacity of ovo-mucoid at absolute neutrality at 30° C is 7×10^{-5} gram-equivalents per gram. (Hydrochloric acid.)

(3) The combining capacity of ovo-mucoid for acids and bases tends to become equal to the concentration of acid or alkali in which it is dissolved at low acidities and alkalinities—but at higher acidities and alkalinities it tends to attain a constant maximum value.

(4) The maximum combining capacity of ovo-mucoid for HCl was not attained in any of the solutions investigated, but it is certainly in excess of 90×10^{-5} gram-equivalents per gram—probably in excess of 100×10^{-5} gram equivalents per gram..

(5) The maximum combining capacity of ovo-mucoid for KOH is about 50×10^{-5} gram-equivalents per gram.

(6) The depression in the conductivity of a solution of KOH (at 30°) ($\equiv \lambda$) which is brought about by the introduction of 1 percent ovo-mucoid is connected with its alkalinity ($\equiv b_1$) by the equation

$$\lambda \times 10^5 = 20850\, b_1 - 1250000\, b_1^2 - 35.6.$$

(7) The depression in the conductivity of a solution of HCl at 30° ($\equiv \lambda$) which is brought about by the introduction of 1 percent ovo-mucoid is connected with its acidity ($\equiv \alpha_1$) by the equation

$$\lambda \times 10^5 = 41990\alpha_1 - 852700\alpha_1^2 - 41.4.$$

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[1] Cf. Kohlrausch and Holborn: Loc. cit., p. 200.

THE BEHAVIOR OF IRON AND NICKEL ANOS DEIN VARIOUS ELECTROLYTES

Review of Theory and General Results

BY E. P. SCHOCH AND C. P. RANDOLPH

In a previous communication by one of us (1)* it was shown that the nickel anode in sulphate electrolytes exhibits a behavior which practically proves the suggestion previously made by LeBlanc that the process of metal dissolution is a velocity phenomenon. It was also shown that when the current density is large enough to produce anodic polarization exceeding a few millivolts, then another process may take place simultaneously—namely, the "oxidizing" discharge of anions.

About the same time as the time of appearance of this article, LeBlanc published his study of polarization with the aid of the oscillograph (2) as a result of which he sets forth essentially the same view of the details of anodic actions. He produces experimental evidence that polarization due to concentration effects alone does not exceed a few millivolts, and he considers that greater anodic polarization is due to the (simultaneous) discharge of oxygen producing anions. The latter he distinguishes as *chemical* polarization. This view, thus arrived at independently from different observations, may hence be considered to be fairly well established.

LeBlanc did not study the effect of the discharge of oxygen producing anions upon the surface of the electrode, nor the peculiar relation of conditions that brings about the marked change in the rate of dissolution of the metal, which characterizes more particularly the phenomenon of passivity; but he is of the opinion that passivity phenomena involve no actions other than those set forth above. One of us (1) had definitely established this view through the study of

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* The numbers in parenthesis given throughout the article refer to the list of references given at the end.

experiments directed to this end. The theoretical view then proposed has been further confirmed and extended through the experimental work in this paper and is here given in its present form.

The relative tendency to produce either one of the two possible modes of anodic action—*i. e.*, metal dissolution or oxidation—depends on (*a*) the specific metal; (*b*) the electrolyte, or more particularly, the specific anions; and (*c*) their manner of contact as influenced by diffusion, etc. With any particular metal and anion—*e. g.*, nickel with sulphation—the diffusion influence is naturally largely dependent on the current density, or the potential gradient in the layer of electrolyte adjacent to the anode surface. With current densities that produce a polarization of only a few millivolts, no noticeable change is produced on the anode, but with larger current densities portions of the surface are oxidized, and thus rendered *inactive* as far as metal dissolution is concerned. The oxidized and the unchanged surface spots exert different opposing electromotive forces, hence the current density is no longer uniform all over the surface, but greater over the active spots. This produces here a steeper potential gradient and sets up an unstable, special or "accidental" diffusion relation which favors the tendency toward metal dissolution, so that this action may even take place exclusively. Though this stationary condition may maintain itself fairly indefinitely yet any uncontrollable or unknown influence may easily disturb it so that the oxidizing action may set in again. The interruption of the current, even for a moment, destroys any such particular diffusion relation. If a current of the same density is then reapplied as soon as possible, the oxidizing discharge will be found to be relatively prominent—*i. e.*, the extent of the active surface is reduced—and this continues until another special diffusion relation such as the one above establishes itself. With *extensive* anodic polarization these special diffusion relations cannot, in general, maintain themselves, and hence the oxidizing discharge finally continues until practically the whole surface has been rendered inactive, and the evolution of oxygen sets in.

The two different kinds of surface spots—the active and the oxidized or inactive—may serve as the poles of a short-circuited cell: by the action of this cell, the oxidized spots are discharged whenever the current is cut off or whenever its density is diminished so that the relation of the electromotive forces permits this local current to pass.

In (1) the conclusion was reached that the particular effect wrought upon the surface of the anode by the oxidizing discharge could be either a film of free oxygen gas or a cover of metal oxide. The remarkable progress recently made in our knowledge of the potential of the oxygen electrode has thrown much light on this point, but as the whole subject will be found reviewed elsewhere in THIS JOURNAL (3) it is sufficient here to present a summary of the general results as follows:

(*a*) During the discharge of oxygen yielding anions all metal electrodes are oxidized.

(*b*) The potential of the electrode is that of the oxide irrespective of any (adsorbed) oxygen gas also present.

(*c*) The oxides specifically determine the potentials with which oxygen is evolved.

(*d*) The amount of an oxide that must be actually present to give all characteristic effects may be less than is optically perceptible.

(*e*) Oxygen gas does not appear to be directly electromotively active.

The formation of an oxide layer on a passivized metal electrode may be considered to be pretty well established—at least all the arguments based upon optical observations, and the argument that passivity with acid or alkaline electrolytes respectively should be due to different causes—all these drop to the bottom because there are positive indications of the formation of oxides when optical means fail, and the anodic formation of oxides in the presence of acids is also known to be a fact. However, there is one point that possibly needs some further consideration; *i. e.*, the faculty of some anodes to become soluble again at nobler potentials after they have become passivized. The example that is before us in this connection is that of chromium, which Hittorf has demonstrated so carefully (4). This example is cited particularly by the adherents of the "special metal surface" theory, or the "electron density" theory. W. J. Mueller (5) has recently published a study of the anodic behavior of thallium in which the author considers that he has found an example similar to chromium. When we examine carefully into the details of these examples and eliminate what appears to us as doubtful cases—namely, the direct formation from the metal of trivalent chromium ions or of bivalent thallium ions (see below)—then we reach the general conclusion that after an anode has become passivized with reference to metal dissolution, the second stage of solubility entails the removal, by reaction, of oxygen together with the metal, usually in the form of a complex ion. Thus a chromium anode that has become passive with reference to the formation of bivalent ions, does not in general become active again to form trivalent ions, but becomes active in forming chromations, in the formation of which oxygen also enters. Hence it is likely that these actions consume a part of the oxidized surface, somewhat as illustrated by E. Mueller (6) in his study of the anodic behavior of copper in sodium hydroxide solutions.

The "special metal surface" theory or the "electron density" theory lead us to expect that the direct formation of ferric ion would take place on an iron pole after it has become passive with reference to the formation of ferro ion, yet this direct formation has never been observed and in our experiments we were particularly careful to watch this point. Upon examination we also find that the dissolution of chromium as a trivalent ion has never appeared as an intermediate stage of activity between that of the formation of the bivalent ion and of the chromation. Whenever the formation of trivalent chromion takes place it is under conditions which make it possible for the formation to be indirect—either through the reduction of the chromation by alcohol, or the oxidation of the bivalent ion by a layer of oxide which had been previously formed by heating. The observations of W. J. Mueller on thallium which lead him to consider that a state of activity exists corresponding to the dissolution of the thallium anode as bivalent ion—intermediate between the state of formation of monovalent thallium and of thallic oxide respectively—this observation should not be interpreted as he has because bivalent thallium is otherwise not known to exist, and the voltage and amperage relations observed may be due just as well to an entirely different cause than that which the author considers. Thus there is no example left of the second stage of activity of an anode which does not involve the consumption of some of the oxygen of the protective oxide cover.

A phenomenon that is fundamentally identical with the one just described is presented by the electrolysis of alkaline solutions of acetates with iron or nickel anodes and this example supports our contention admirably. In its specific influence upon anode actions, the acet-ion appears to be similar to the sulphation. The iron or nickel anodes passivize in this electrolyte with relatively small current densities, but at lower potentials the anodes become active again: the increase in current density at these low potentials is not surprising, because oxidation of the acet-ion takes place, but the extensive metal dissolution which takes place here and which has also been observed and commented upon by other investigators (7) requires special consideration. In alkaline solutions the acet-ion is extensively oxidized to methyl alcohol, particularly on iron and nickel anodes (8) and this action uses more oxygen than that corresponding to the discharge of the acet-ion. Hence portions of the oxide surface are probably reduced, the metal surface is temporarily laid bare and a part is dissolved before the oxide cover is reformed over it.

Many essential elements of our theoretical view have been previously advanced by other investigators, notably by Haber (9) in his theory of "mobile pores" and again by Sackur and Alvarez who suggest that the formation of the oxide may be a velocity phenomenon of the reaction between the anions and the anode. Since these publications together with those previously referred to represent the latest views of the subject of passivity (except one—see below) we believe that our view extends the theory in the right direction.

Foerster (11) looks upon the function of oxygen in this connection as a *negative* catalyzer of the process of metal dissolution and thus was led to consider hydrogen as a *positive* catalyzer of this process. Inasmuch as the quantities (concentrations) of hydrogen and oxygen theoretically present on the electrode are reciprocally related, the facts will fit his theory as well as the oxide theory; but we believe that the relation of the facts as presented by Foerster's view is less direct than that presented according to our view.

The experimental work in this paper was primarily directed to test further the theoretical views which so far had been established with nickel in sulphate and chloride electrolytes only. Experiments were made (*a*) with neutral solutions of potassium sulphate, nitrate, perchlorate, chlorate, bromate, iodate, chromate, and hydroxide, and with sodium acetate; (*b*) with acidified and alkaline solutions of the sulphates, nitrates, and acetates respectively; and finally (*c*) with mixtures of sulphate with chromate and sulphate with fluoride. Many of these solutions were tried on both nickel and iron anodes. The results of these experiments not only confirmed the theoretical view held by us but led us to extend our view in so far as we realized that *both* modes of anodic action—*i. e.*, metal dissolution and oxidizing action—are specifically influenced by the particular anions present.

According to the prevailing theory of metal dissolution, which assumes that the metal changes direct to cations, this particular process does not appear to be necessarily influenced by the anions present; hence we held at first that the specific influence of the anion was limited to the oxidizing action, and the fact that halides prevent the attainment of passivity was ascribed to their reaction with oxygen. However, fluorides have the same effect as anode actions in chlorides, etc., and their effect cannot possibly be due to any reaction with oxygen. This and other considerations forced us to the conclusions that the nature of the anion also asserts a specific effect upon metal dissolution.

When arranged in the decreasing order of their tendency to effect metal dissolution (or the increasing order of tendency to effect oxidation—which is naturally the reciprocal of the former) the anions present the following list: (*a*) Halogens, (*b*) sulphates, (*c*) acetates, (*d*) perchlorates, (*e*) nitrates, and (*f*) chromates, chlorates, bromates, iodates, hydroxides—the latter all practically in one class. Of all anions, iodation seems to have the greatest tendency to anodic oxidizing action.

The actions of the mixtures of two anions indicate that the specific influence of an anion shows itself irrespective of the presence or absence of other anions. The mixture will show a relative tendency toward metal dissolution as contrasted with oxidizing action which is just what we would expect if every anion would react individually with the electrode. The total effect is somewhat proportional to the concentrations of the different anions, although it is modified by the action of the cell formed between the active and inactive spots.* Sackur and Alvarez (10) have also found in a similar experiment that mixtures of chlorion with sulphation give results that vary as the relative concentrations of these ingredients vary.

Although no attempt is to be made here to formulate any details of the mechanism of the two modes of anodic change, yet we feel that we should point out that the marked specific influence shown by every anion in a mixture indicates that some individual interaction takes place between the anions

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* In this connection it should be remembered that the electromotive force of this cell—and hence its rate of action—depends directly on the concentration of the hydroxylion (respectively, hydrion) in the electrolyte.

and the anode (or with the metal ions when they are first formed). Of this we are particularly impressed when we stop to realize that the free energy difference of either mode of anodic change is the same irrespective of the intermediate steps or of the anions that take part in the change; and furthermore, that there is no difference in the ease of electrical discharge of one anion as compared with another, because strictly speaking there is no such force as intensity of fixation of the electron upon the ion.

In concluding this discussion of general results we wish to point out that the results here attained are of importance in the problem of the corrosion of iron, because fundamentally considered the latter is an electrolytic phenomenon and hence involves the same facts as those here considered. With the conclusions reached in this paper it is readily seen that the corrosive character of an aqueous solution could not be extensively lessened by additions of certain electrolytes such as chromates, hydroxides, etc., as was once hoped for; again it is seen that any previous passivizing or "chromating," etc., of an iron surface would not protect it appreciably against the action of a natural water containing sulphates or chlorides, etc.

Experimental Details

The immediate object of the following experiments is to ascertain the potentials exhibited by an iron or a nickel anode as the latter is subjected to various current densities in different electrolytes. In designing the apparatus the following points were considered—the reasons for which are self-evident from the theoretical view advanced for the phenomena to be studied:

(*a*) To remove and exclude oxygen from both the electrolyte and the surface of the anode.

(*b*) To prepare the surface of the anode in a definitely reproducible manner.

(*c*) To stir the liquid next to the anode effectively.

(*d*) To keep the composition of the electrolyte around the anode constant—above all to prevent the accumulation of ferrous ions, since their oxidation would complicate the phenomena.

(*e*) To prevent access of hydrogen to the anode.

The apparatus designed to meet the above requirements and which was used in the experiments with iron anodes is shown in Fig. 1. *h* is a three-liter flask, *g* a glass tube which acts as a siphon and conducts the solution to the U-tube *n*; *c* is a "return" condenser, *b* a cooling-jacket, and *i* a vessel containing ice. *a* is a three-way stop-cock, whereby any air that enters the tube *g* may be allowed to escape; and *s* is a glass tube which connects the capillary *f* with the calomel electrode, not shown, and which is filled through the thistle tube *d*.

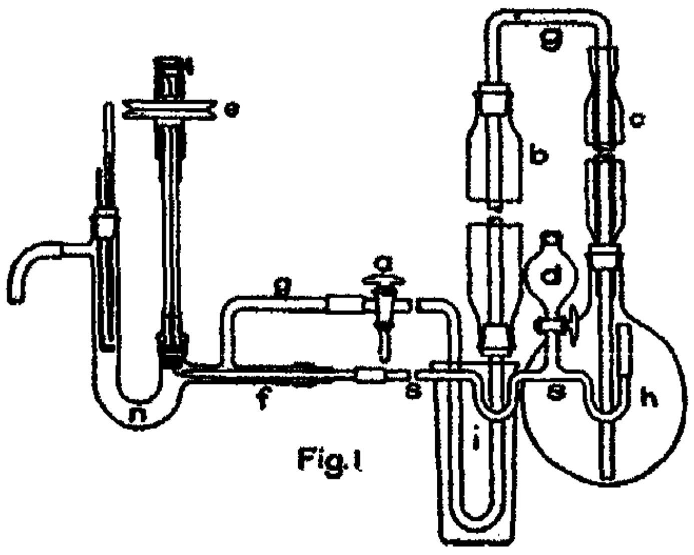

Fig. 1

In Fig. 2, *n* is the U-tube 12 mm. inner diameter, and of thin glass, in which the electrolysis takes place, *q* is the anode, with an exposed area of 0.57 sq. cm., the vertical surface being covered by the rubber tubing *i*; *p* is a very small rubber stopper; *c*, a copper wire soldered to the iron which makes the electrical connection for the electrolyzing current (through a brass sleeve, *d*, and a brush); *e* is a pulley; *m*, a brass tube; and *d*, a piece of rubber tubing. In the left arm of the U-tube, the thermometer *l* and the cathode (a platinum wire) *k* are held in position by the stopper *o*.

The operation for making a series of measurements was the following: The U-tube was filled with dilute hydrochloric acid, and this was allowed to remain long enough to clean the surface of the anode thoroughly. The acid was then displaced with water which had been boiled in the flask *a* to free it from air; and the latter in turn was displaced by the boiled electrolyte. The electrolyte then in the U-tube was boiled for several minutes and cooled to 23°–27°, the temperature at which all the measurements were made. During electrolysis the electrolyte was passed through the U-tube at a rate of 10 to 20 cc per minute, depending upon the current, and the anode was rotated at the rate of 200 revolutions per minute. The potential was read as soon as it had become approximately constant after increasing the current, which in most cases was within two to three minutes after changing the electromotive force.

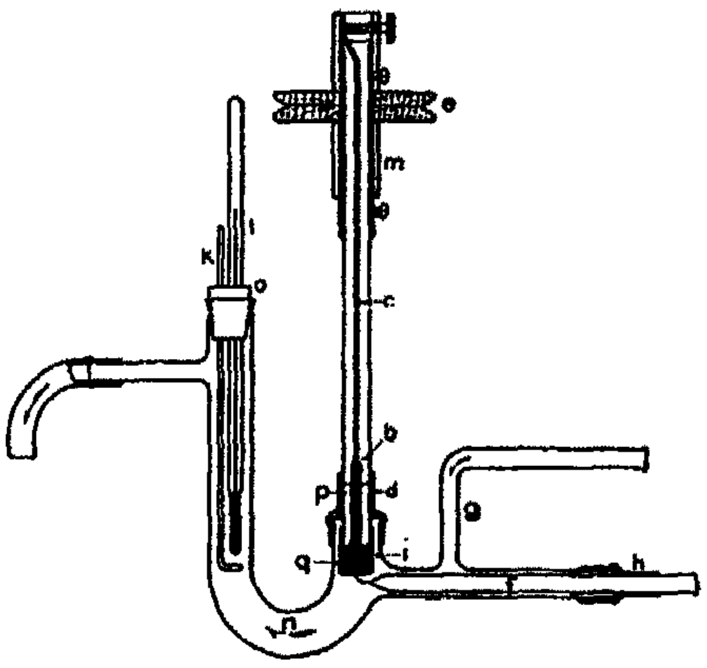

Fig. 2

The apparatus and the method of measurement used in the experiments with nickel is essentially the same as the above except that a larger anode, 3.47 sq. cm. in area, was used.

The concentrations of all solutions are given in gram-equivalents (1 equivalent = 1 N). The table of polarization values for potassium permanganate, for ammonium persulphate and for ferric sulphate were not determined because these solutions react extensively on contact with these metals.

Ferrous sulphate was not used because it is oxidized at the anode.

All current densities in the following tables are given in milli-amperes per 1 sq. cm., and all potentials are measured against the normal calomel electrode in international volts, and no correction is applied for diffusion potentials. The algebraic signs prefixed to the potentials are those shown by the anode in the experimental arrangements—in accordance with the suggestion of Luther (13). The potentials are said to decrease or fall when they become more noble and vice versa.

For nickel, all preliminary experiments concerning the potentials shown without current in various electrolytes and their relation to the reversible potential in nickel salt solutions, as well as for the reproducibility of the surface condition, are found in (1). For iron, we made the following experiments: The potential of ordinary sheet iron in N/1 $FeSO_4$ solution was found to agree with that given by Richards and Behr (14). The precautions taken to prevent oxidation in making up the solution were as suggested in the above-mentioned article, *i. e.*, the flask was thoroughly washed out with hydrogen, then freshly boiled water was run in upon the salt which had previously been put into the flask, and hydrogen was passed through the solution. The potential of sheet iron in this solution rose in 4 hours to —0.714 volt which was the maximum value attained. The potentials of different samples of ordinary wrought iron in N/1 K_2SO_4 were found to be practically the same, —0.795 volt and these different samples also gave coinciding "current-voltage" curves. Cast iron and steel, however, showed potentials slightly higher than wrought iron, —0.828 and —0.830 volt respectively, yet they gave current-voltage curves that coincide practically with those of wrought iron. Commercial wrought iron was used in all the following experiments.

The numerical results obtained are presented in Table A (experiments with iron anodes) and Table B (experiments with nickel anodes). The "current-voltage" curves plotted

TABLE A

Potentials of iron anodes, referred to the normal calomel electrode. In each column, the potentials above the heavy horizontal line are negative; below, positive. An asterisk marks the beginning of a rapid passivizing drop. The electrolytes with which these potentials were obtained are indicated by the roman numerals at the head of these columns

Current density mil-amp. per sq. cm	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
0.0	0.795	0.929	1.05	0.702	0.673	0.766	0.735	0.828	0.536	1.06	0.456	0.437	*0.534*	0.447	0.764	0.397
0.09	—	0.857	0.963	0.699	—	0.766	0.675	0.60	—	0.973	0.35	0.226	1.10	0.406	0.725	0.389
0.18	—	0.772	0.927	0.693	—	—	0.648	—	—	0.935	*0.017*	0.211	1.47	0.377	—	0.373
0.35	—	0.729	0.851	0.683	—	—	0.631	0.525	0.534	0.913	0.334	*0.049*	1.51	0.33	0.704	0.35
0.88	—	0.696	0.636	0.673	0.590	0.725	0.59	0.45	0.529	*0.45*	0.768	0.06	1.57	0.28	0.665	0.29
1.233	—	—	—	—	0.580	—	0.56	0.40	0.526	0.100	—	0.22	—	—	—	—
1.75	0.668	0.649	0.426	0.650	—	0.694	0.54	0.33	—	0.58	1.53	0.43	—	0.18	0.642	*0.012*
3.51	—	0.618	0.268	0.631	0.528	—	0.487	0.144	0.502	0.60	1.56	0.86	—	0.08	—	0.228
5.3	—	0.550	0.216	—	0.487	—	0.455	*0.021*	0.496	0.64	—	1.43	—	0.043	—	0.414
8.8	0.622	0.521	*0.017*	0.582	0.460	0.642	0.42	0.144	0.470	0.66	1.61	—	—	*0.012*	0.559	0.290
17.5	0.587	0.474	0.628	0.548	0.43	0.621	0.336	1.06	0.44	0.706	1.69	1.45	—	0.023	0.497	0.39
35.1	0.569	0.470	0.53	—	0.325	0.584	*0.228*	1.62	0.346	0.797	—	—	—	0.030	0.393	0.41
87.7	0.520	0.443	—	0.498	0.23	0.538	1.90*	—	0.121	—	—	—	—	0.018	0.248	0.62
140.0	0.475	0.425	—	0.430	*0.15**	0.497	—	—	*0.010**	—	—	1.60	—	—	*0.101*	—
175.0	0.450	*0.420*	1.97	0.387	*1.75*	0.476	—	—	0.22	—	—	—	—	—	—	—
264.0	*0.427*	1.90	—	—	—	0.433	—	—	—	—	—	—	—	—	0.104	—
350.0	*2.2**	—	—	*0.196*	—	—	—	—	—	—	—	—	—	—	0.248	—
482.0	—	—	—	2.07*	—	0.320	—	—	—	—	—	—	—	—	0.501	—

from this data appear in the two accompanying figures. The list of the electrolytes employed, together with special observations, is given below; and the Roman numerals in the tables and in the plots of the curves refer to this list of electrolytes. Experiments I to XVI inclusive were carried out with iron anodes; the rest, XVII to XXII, with nickel anodes.

TABLE B

Current density mil-amps per sq. cm	Potentials of nickel anodes, referred to the normal calomel electrode. In each column, the potentials above the heavy horizontal line are negative; below, positive. An asterisk marks the beginning of a rapid passivizing drop. The electrolytes with which these potentials were obtained are indicated by the roman numerals at the head of these columns (see list in experimental part)					
	XVII	XVIII	XIX	XX	XXI	XXII
0.0	0.428	0.428	0.489	0.489	0.263	0.163
0.0029	—	—	0.428	0.408	0.240	—
0.0058	0.326	0.380	—	0.290	0.230	0.075
0.0115	0.280	—	—	0.240	0.184	0.040
0.023	0.250	0.300	*0.347*	0.170	0.126	0.030
0.0346	0.224	0.265	*	*0.05**	*0.021*	*0 020*
0.058	*0.224*	*0.244*	0.75	0.34	0.104	—
0.086	*	0.100	—	0.42	0.205	0.147
0.144	1.18	1.1	0.91	0.54	0.402	0.363
0.202	1.18	—	—	—	0.538	0.58
0.288	1.20	—	—	—	0.66	0.662
0.432	—	—	—	—	0.787	—
0.576	—	—	—	—	0.911	0.745
0.864	—	—	—	—	1.14	0.859
1.44	1.30	—	—	—	1.35	0.948
2.88	—	—	—	—	1.55	1.30
5.76	—	—	—	—	1.57	—

I. N/1 K_2SO_4. When the current is interrupted after the anode has been passivized, the potential of the anode rises slowly, but boiling brings it promptly to the initial potential, —0.795 volt, and the surface is then in the original condition again. If the solution around the anode is not renewed, *i. e.*, if it is not passed through the apparatus, the potential of the anode rises much more slowly than when the electrolyte passes through the apparatus. After oxygen has once been evolved, the current can be decreased to a density of 0.11 mil-amps. without stopping the evolution of oxygen, provided the circuit is not broken.

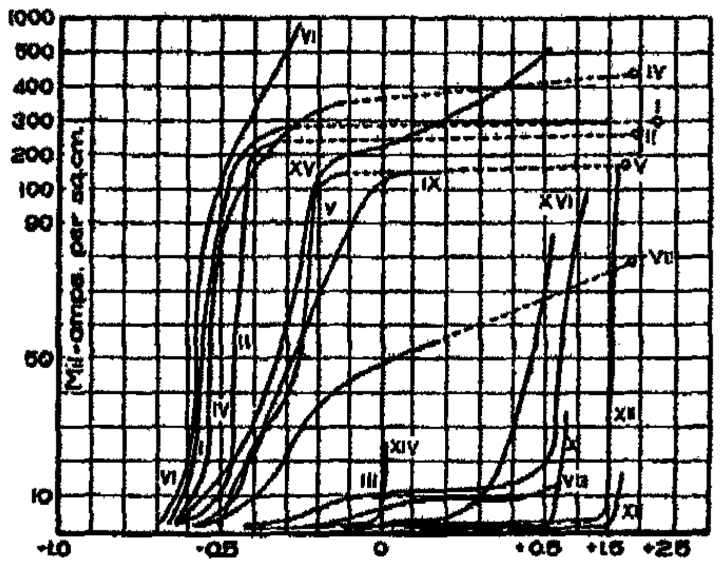

Fig. 3

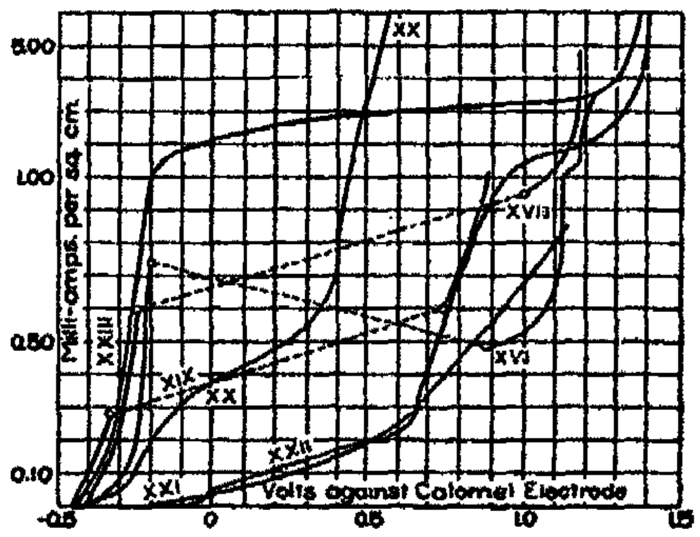

Fig. 4

II. N/1 K_2SO_4, N/100 KOH. As soon as the circuit is opened the potential of the anode rises slowly. On boiling, the original condition of the surface is restored. With a current density of 17.5 mil-amps. a white precipitate (probably ferrous hydroxide) forms in the electrolyte. As soon as oxygen is evolved this precipitate is oxidized as shown by the dark green color it assumes.

III. N/1 K_2SO_4, N/10 KOH. On opening the circuit the potential of the anode rises slowly and even on boiling it does not rise higher than —0.845 volt. Furthermore when the current is turned on again the behavior of the anode shows that the surface has not recovered its original condition.

IV. N/1 K_2SO_4, N/100 H_2SO_4. On opening the circuit the potential rises immediately to —0.691 volt and on boiling it rises to —0.704, which is slightly higher than the initial potential. Of course the surface recovers its original condition immediately after opening the circuit.

The behavior of iron with these four electrolytes is strictly similar to that of nickel with the exception of the specific tendency of iron toward metal dissolution, which is much greater than that of nickel. Hence in general the return from the passive to the active condition is much more rapid with iron than with nickel.

V. N/1 K_2SO_4, with 1/60 gram mol $K_2Cr_2O_7$ per liter. The anode does not regain its initial potential after polarization as quickly as it does with potassium sulphate alone; yet its potential begins to rise as soon as the current is cut off, and in five to ten minutes it reaches 0.67 to —0.68 volt, which shows that in spite of the presence of the bichromate the surface rapidly attains its unimpaired, active condition. A comparison of Curves, I, V and XV, shows that the specific oxidizing tendency of the chromate is certainly interfered with by the sulphate, which is best understood by considering that both actions—metal dissolution and oxidation—are specifically influenced by both kinds of ions present, but that the sulphation has a greater tendency to effect metal dissolution than it has a tendency to oxidize, while for chromation the reverse is the case.

VI. N/1 K_2SO_4, N/10 KF. On opening the circuit the potential arises immediately to —0.749 volt, and the surface soon becomes as effective as before. Evidently this mixture of electrolytes has a greater tendency toward metal dissolution than the pure sulphate solution.

VII. N/10 KNO_3. When the circuit is open the potential of the anode begins to rise slowly. Boiling hastens the rise, but does not restore the original condition of the surface.

VIII. N/10 KNO_3, N/100 KOH. As usual, on opening the circuit, the potential rises, but it is evident that the tendency for the surface to regain the active state is much less than with No. VII. This experiment together with IX were designed to ascertain whether or no the influence of an addition of hydroxylion or of hydrion to nitrate electrolytes would have the same relative effect as when added to sulphate electrolytes. On comparing the relative positions of the curves it is seen that the influence is in strict accord with the theory advanced.

Since it is a matter of common experience that the nitrate ion is a better oxidizing agent in the presence of hydrion than in its absence, one might have expected the addition of nitric acid to favor the attainment of passivity. However, a careful consideration shows that ordinary oxidizing actions are accompanied by the formation of water, the free energy of which formation is increased by an increase in the concentration of hydrion; but these anodic actions are not accompanied by the formation of water, and hence it is not surprising to find that the addition of nitric acid lessens the tendency toward attainment of passivity.

IX. N/10 KNO_3, N/100 HNO_3. In this electrolyte the anode does not exhibit as high a potential without current as in the neutral nitrate, which is probably due to a small amount of direct oxidation. The relative position of the curves shows that the surface is not extensively impaired by such oxidation. When after polarization the circuit is open the potential of the anode rises rapidly and the original condition of the surface is soon restored.

X. N/10 KOH. The values between —0.725 and +0.58 volts are unsteady. After opening the circuit the potential of the anode rises immediately; on boiling it rose to —0.845 immediately, and afterwards continued to rise slowly.

It is remarkable that even with hydroxides, chromates, chlorates, bromates, and iodates the anode potentials return—

when the circuit is open—fairly readily to the initial potential. This indicates that the tendency, to metal dissolution, of these anions is still appreciable.

XI. N/30 $K_2Cr_2O_7$ (1/60 gram mol per liter). The potentials of the anode down to 0.197 volt are not constant. When the circuit is open the potential begins to rise slowly. On boiling it reaches 0.039 volt immediately and then continues to rise slowly.

The results obtained with N/15 K_2CrO_4 (1/30 gram mol per liter) are approximately identical with the results in XI.

XII. 2N/3 $K_2Cr_2O_7$ (1/3 gram mol per liter). On breaking the circuit the potential rose to 0.087 volt immediately, and at the end of forty hours it was at —0.416 volt, which is practically the initial potential.

XIII. N/3 KIO_3. On opening the circuit the potential rose immediately to 0.29 volt, and in 2 hours more, to —0.331 volt. On boiling it rose to —0.455 volt which is not quite as high as the initial potential. With this electrolyte the oxidation to periodate, corresponding to the oxidation of chlorate to perchlorate does not take place, for the well-known reason that this oxidation requires a higher potential than the evolution of oxygen on iron or nickel anodes.

The curve of these values has not been plotted. It would run close to the horizontal axis up to 1.5 volts where it would turn so as to run almost parallel to the vertical axis.

XIV. N/3 $KClO_3$. When the potential of the anode reached 0.023 volt, the formation of perchlorate began, and hence the increase of current density and the unsteady potential observed.

XV. N/8 $KClO_4$. After breaking the circuit the potential of the anode rose in five minutes to —0.725 volt. The anode soon regained the original unimpaired state of the surface. This electrolyte gives a behavior very much similar to that of sulphates.

XVI. N/3 $KBrO_3$. The most notable thing about this electrolyte is the irregularity introduced through the formation of perbromate; this begins at 0.4 volt. Since the formation of perchlorate takes place at 0.02 volt and the evolution of oxygen on an iron anode takes place at 1.5 volts, it is readily seen why the oxidation of iodates does not take place with iron anodes.

The behavior of nickel in acetate solutions was studied very carefully because the complications arising from the variable oxidation of the acet-ion and its dependence upon the concentration of hydroxylion had made this case a very interesting one: this is so, particularly because extensive metal dissolution can take place even at anodic potentials which otherwise characterize passivity—a point that has already been commented upon in the first part of this paper.

Realizing that the current-voltage curve might change extensively with the concentration of hydroxylion, we made a number of trials with solutions which were just slightly on one or the other side of neutrality. All of these experiments were carried out with nickel anodes.

XVII. N/1 $Na_2CH_3O_2$ slightly acidified (0.047 N beyond the "phenolphthalein neutral point").

XVIII. N/1 $NaC_2H_3O_2$ neutral toward litmus, which is still 0.015 N acid toward phenolphthalein.

XIX. N/1 $NaC_2H_3O_2$ neutral towards phenolphthalein, which is slightly alkaline toward litmus.

XX. N/1 $NaC_2H_3O_2$, N/10 KOH.

The general run and the relative positions of the Curves XVII to XX is just what is theoretically to be expected on the assumption that in the main the acet-ion has the same relative tendency toward the two kinds of anodic action as the sulphation. In this connection it must be noted that on nickel anodes—just as on iron anodes—the evolution of oxygen is the predominating action with neutral solutions (see also (8)). The oxidation of the acet-ion, to methyl alcohol becomes extensive only as the solution becomes alkaline. Hence in XX currents of much greater density than may be obtained with sulphate electrolytes under the same conditions may be maintained here at potentials less noble than those with which oxygen is evolved, which would be impossible if the oxidation of the acetion did not take place.

XXI. N/3 KIO_3, nickel anode. On breaking the circuit the potential of the anode rose immediately to 0.455 volt; in two hours more it rose to —0.165 volt. Beyond this point the rise in potential was inappreciable even on boiling. On account of the extremely small current densities obtained with this electrolyte it was impossible to ascertain with certainty whether the surface had attained its original state.

XXII. 2N/3 $K_2Cr_2O_7$ (or 1/3 gram mol per liter) nickel anode. The potential rises very slowly after breaking a circuit.

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EXPERIMENTAL DETERMINATION OF BINODAL CURVES, PLAIT POINTS, AND TIE LINES, IN FIFTY SYSTEMS, EACH CONSISTING OF WATER AND TWO ORGANIC LIQUIDS

BY WALTER D. BONNER

Comparatively little is known of the compositions of the two coexistent liquid phases which are often formed when three liquids are mixed together. The earliest determinations seem to have been made by Tuchschmidt and Follenius in 1871, but the only considerable experimental research on the subject is that published by W. D. Bancroft in 1895. Now that the graphic methods of the Phase Rule have been applied to problems of this sort, more particularly by van Rijn van Alkemade, Schreinemakers, and Roozeboom, it seemed desirable to add to the stock of experimental data, and accordingly the present investigation was undertaken.

When alcohol, for example, is gradually added to a mixture of ether and water, at some constant temperature, the compositions and quantities of the two layers of liquid gradually change, and finally a homogenous solution is obtained. The points of the "Binodal Curve" give the quantity of alcohol which must be added to any given quantities of ether and water in order to bring about homogeneity, and the extremities of the "tie lines" give the compositions of the various pairs of liquids which may exist in equilibrium. When the two layers are practically of the same composition, the tie line is reduced to a point, the "plait point," on the binodal curve.

The experimental researches hitherto published have dealt mainly with the data for the binodal curve; the positions of tie lines, that is the compositions of the various pairs of coexistent liquids, have been determined in but few cases.[1]

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[1] By Waddell, Schreinemakers, Roozeboom, Wright. See Bibliography, p. 787. The paper by Duclaux contains data enough for the calculation of the tie lines.

As I wished to study as many different systems as was possible, and as organic liquids are in general costly, it was necessary to develop a method of working which would not necessitate the use of more than a few grams of material in each experiment. The difficulties of analysis were avoided by adopting a modification of the method of "quantitative synthesis" employed by Bancroft,[1] and the positions of the tie lines and plait points were determined by the graphic method described by W. Lash Miller and R. H. McPherson,[2] and applied by them in a few cases.

Method of Working

My method of working may best be described by reference to a particular case. Three Ostwald-Sprengel pyknometers with long capillary discharge tubes[3] were filled with ether, water, and alcohol, respectively, and from these 0.354 gram ether and 0.501 gram water were weighed into a cylindrical glass tube about 12 cm long and 1 cm in diameter, to the upper part of which a tube of larger bore (1.5 cm diameter and 3 cm long) had been sealed for convenience of corking. This tube was at once corked and immersed in a well stirred mixture of ice and water contained in a covered rectangular glass "aquarium" (such as is often used for gold fish) the sides of which were jacketed with felt except for a space of about 10 cm square at each end. One of these openings could be illuminated by an electric light which was extinguished except during an observation, while the other served as a window, to enable the tube to be observed through the telescope of a cathetometer. The contents of the tube were stirred by a bent wire which projected through a hole in the cork, and alcohol was gradually added from the third pyknometer (by lifting the cork and dropping in a little at a time) until a homogeneous solution was obtained. This needed 0.326 gram alcohol. The total weight of liquid in

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[1] Phys. Rev., 3, 27 (1895).

[2] Jour. Phys. Chem., 12, 709 (1908).

[3] Such as are used to introduce liquids into a boiling point apparatus. See Ostwald-Luther, Physico-Chemische Messungen, 2nd edition, p. 305.

the tube was thus 1.181 grams; the cathetometer gave the height of the liquid in the tube, hence from a previous calibration, its volume; from these data its specific gravity was obtained.

The three numbers: ether 0.354, water 0.501, alcohol 0.326, fix a point on the binodal curve; but as in the graphic representation which I have adopted, the sum of the weights of ether and water is represented always by 1.00, the three numbers must each be multiplied by 1.000/0.855, giving ether 0.414, water 0.586, alcohol 0.381, as the coordinates of the point in question. In the diagram, Fig. 1, the abscissa gives the amount of ether and the ordinate the amount of alcohol; the amount of water may be obtained by subtracting the value of the abscissa from unity.[1] The other points on the binodal curve (Fig. 1) were similarly obtained.

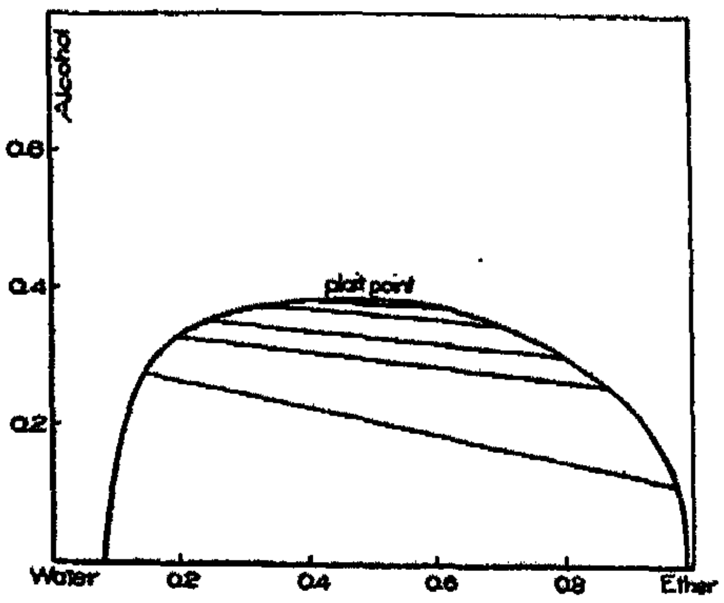

Fig. 1

The actual amount of ether used in determining the eleven points of the figure was 4.098 grams, and of alcohol 2.680 grams. About four hours work was required.

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[1] This representation, while not so symmetrical as the triangular diagram, has the advantage that the ordinates are directly proportional to the weights of alcohol used in the experiments. The vertical displacement of the points of the graph due to an error of one drop of alcohol per gram of ether and water, is thus the same in every region of the diagram.

Effect of Temperature

After measuring the volume, the tube was removed from the ice bath and placed for a few minutes in a beaker of water at about 20° C. In the experiments with ether-water-alcohol, the homogeneous solutions clouded on warming and separated into two layers. In all other cases they remained clear.[1]

Determination of Plait Point and Tie Lines

As the alcohol was added in the experiment just described, the lower (aqueous) layer increased in volume, while the upper (ethereal) decreased and finally disappeared. In a subsequent experiment in which the proportions of ether and water were 0.601 and 0.399, respectively, the reverse was observed, the lower layer diminishing and ultimately disappearing. The abscissa of the plait point consequently lies between 0.414 and 0.601. To determine it more closely, 0.556 gram of ether and 0.541 gram of water were weighed out, alcohol added in successive portions and the volumes of the two layers determined by the cathetometer after each addition. The results were as follows:

TABLE I

Alcohol gram	Ether 0.556 g lower layer cc	Water 0.541 g upper layer cc	Volume ratio
0.226	0.783	0.739	0.94
0.331	0.800	0.809	1.01
0.358	0.807	0.815	1.01
0.394	0.814	0.842	1.03
0.412	0.822	0.859	1.05
0.432	Homogenous	—	—

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[1] Except in the case ether-water-alcohol, mixtures to which almost enough alcohol (or other consolute liquid) has been added to make them homogenous, become so on removing from the ice bath and cloud again when replaced. Experiments numbered 35, 39, 50 were carried out at 15° C. because of the high melting point of one of the constituents; in these cases the homogenous solutions clouded on cooling, and cleared again on warming. In Meerburg's study of the binodal curves of systems containing trimethylamine, cases analogous to that of ether-water-alcohol were met with.

If it be assumed, as a ***first approximation***, that the specific gravities of the two layers are the same, the volume ratio will be the ratio of their weights. If then a straight line be drawn through the point which represents the composition ether 0.556, water 0.541, alcohol 0.226 (or ether 0.507, water 0.493, alcohol 0.206) to meet the binodal curve at each side so that the length of the portion of the line to the left of the point is 0.94 times the length of the portion of the line to the right, the points at which this line meets the binodal curve will give the compositions of the lower and upper layers, respectively, and the line will be a "tie line." The abscissa of the two ends of this line are 0.100 and 0.935, respectively. To make a *second approximation*, the volume of the lower and upper layers (0.783 cc and 0.739 cc) may be multiplied by the specific gravities of the solutions (abscissa 0.100 and 0.935), *viz.:* 0.98 and 0.79 respectively, giving 0.768 gram and 0.584 gram as the weights of the two layers, and 0.760 as the weight ratio. Shifting the line to correspond, gives 0.130 and 0.990 as the abscissa of the end points. A further approximation is in general unnecessary. Each line of Table I thus serves to place a tie line; their positions were checked by three further sets[1] of experiments with different relative quantities of ether and water. As near the plait point the tie lines are roughly parallel, the position of the plait point may be obtained graphically with fair accuracy. In the present instance its coordinates are ether 0.51, alcohol 0.39, indicated by a dot on the binodal curve (Fig. 1).

Source of Error and Precautions Taken

Nearly all the chemicals used were Kahlbaum's best, mostly from bottles opened for the occasion. In a few cases, however, where the guarantee of purity was not so good, the liquid was dried and fractionated until a satisfactory preparation was obtained.

The pyknometers were weighed to four places of deci-

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[1] In general only two sets of tie line determinations were made.

mals, but only three are recorded. They were always weighed immediately before and immediately after using, even where a series of measurements with the same liquids was in progress. In some cases the liquid was blown from the pyknometer, a tube 15 cm long of calcium chloride and soda-lime being used to prevent contamination by the breath; generally, however, it was found easier to add small definite amounts by squeezing a short piece of rubber tubing attached to the upper tube of the pyknometer and plugged with a bit of glass rod.

The attempt to substitute small burettes for the pyknometers was abandoned, as it was found impossible to keep the liquids in them at constant temperature.

To guard against evaporation, the tube in which the liquids were mixed was kept stoppered. In a number of cases it was weighed after the experiment and the loss thus determined directly; with volatile liquids on long standing (as in tie line determinations) this might reach as high as one percent. Table II gives the total weights and the losses in the experiments to determine the binodal curves for toluene-water-alcohol and for chloroform-water-carbinol respectively:

TABLE II

Toluene-water-alcohol		Chloroform-water-carbinol	
Added	Loss	Added	Loss
1.3594	0.0024	1.3122	0.0118
1.6416	0.0116	1.5174	0.0120
1.7512	0.0056	1.8742	0.0088
1.5764	0.0050	2.1664	0.0140
2.4756	0.0112	2.4426	0.0153
2.5806	0.0076	2.1092	0.0110
1.8362	0.0062	1.3517	0.0067
1.6854	0.0046	—	—
0.9570	0.0070	—	—

As in all the experiments the tube was at least one-third full of liquid, the composition of the liquid was not appreciably affected by the formation of vapor (at zero centigrade) within the tube.

In general there was no difficulty in deciding whether one phase was present, or two; the contents of the tube forming a more or less translucent, milky emulsion until the last drop of the consolute liquid suddenly cleared it. In a few cases,[1] ether-water-alcohol, for example, no such emulsion was formed and the end point was harder to determine. If a little lampblack[2] were added, however, it collected at the boundary between the two liquids, which thus became easily visible even when the amount of one phase was very small.

In order to get an idea of the probable accuracy with which the end point could be determined in such cases, saturated solutions of ether in water and of water in ether were made by shaking together equal volumes of water and ether. Some of the lower layer was pipetted off into a tared tube, weighed, and then the least amount of the upper layer of whose presence I could be positive was determined by adding it in very small drops until plainly visible, and then weighing. The same procedure was followed in the case of the upper layer, adding a small amount of the lower, and in both cases experiments were made with and without addition of lampblack. Using about one gram of the lower layer, and adding the upper in very small drops, I found as the mean of several trials that six or eight milligrams was the least amount of which I could be quite certain. The presence of the black does not greatly lessen the amount of the upper layer needed, but it facilitates its detection very decidedly. Before adding the upper layer the black is scattered in loose flakes over the surface or climbing up the sides of the tube; but the addition of a very small drop of the upper layer causes it to form a pronounced film on the surface, and to come down from the sides. This film forms again at once if dis-

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[1] Other experiments in which this occurred were Nos. 5, 11, 21, 31, 32, 33 and 34 (see Table V).

[2] Lycopodium will not go into the boundary. Indigo, carmine, and ultramarine dissolve, or seem to, in some of the liquids used.

turbed by stirring, but on the addition of a drop or two of alcohol, enough to render the system homogeneous, it is immediately dissipated, the black for the most part settling into the liquid and slowly to the bottom of the tube.

Using about the same amount (one gram) of the upper phase and adding small drops of the lower, I found that about twenty milligrams was the least amount of which I could be positive.

Another method of detecting the end point that proved useful with some substances[1] was to warm the liquid slightly until it became homogeneous and then to cool it again in the ice bath, when the second phase would separate as an emulsion, whose disappearance on addition of the consolute liquid could easily be noted.

In determining the tie lines it was usually necessary to let the mixture stand from a half hour to several hours before it separated into two layers whose volumes could be measured. In a number of cases complete separation did not occur in six or eight hours and recourse was had to a centrifuge.[2]

On addition of alcohol to mixtures of water and o-xylene, the densities of the upper and lower layers approach, finally become equal, and then when more alcohol is added the "upper" layer becomes the heavier, and the two change places.[3] In this case I could not obtain good separation on standing, even for twenty-four hours, or on centrifuging. Water, mesitylene and alcohol behave in an analogous manner, but separation is not so difficult.

The tubes used were calibrated by adding weighed amounts of water (of chloroform in a duplicate calibration) and determining with a cathetometer the distance from the bottom of the glass tube to the lowest and the highest points of the meniscus.

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[1] This plan was used in experiments Nos. 24, 25, 26, 27, 28, 29 and 37 (Table V).

[2] Experiments Nos. 3, 4, 26, 27, 28, 35, 37, 39, 42, 45 and 48.

[3] This occurred in experiments Nos. 4, 8, 28, 35, 39, 41, 43 and 49.

The volume of the meniscus cannot be neglected; it was calculated from the height of the meniscus by assuming[1] that the perpendicular section of the boundary liquid-air is an ellipse. From this assumption it follows that the volume of the meniscus is directly proportional to its height. With one of the tubes, for example, the volume was 0.025 cc per mm, and the height varied from about 1.8 mm to 2.5 mm, depending on the liquids used. On a total volume of one cc the "meniscus correction" thus amounts to five or six percent.

The cathetometer was a good instrument with glass scale, each division of the scale corresponding to one mm, the tenths being easily read with a vernier. With the tubes used, 0.1 mm corresponded to about 0.01 cc, or one percent on a volume of one cc. An error of one or two percent in the density might thus easily be made. Any greater accuracy, however, would be superfluous, as the densities were only used in placing the tie lines (see page 742).

As the object of the investigation was to study a large number of substances, extreme accuracy had to be sacrificed to the necessity for working with small quantities. The abscissa of points on the binodal curve are, of course, fairly accurate, probably well within one-half percent. But since a drop of alcohol, or of the other consolute liquids used in the experiments, weighs about 0.01 gram, the ordinates may be one or two percent out. From the agreement between duplicate experiments, and from the smoothness of most of the curves, I do not believe that the error in general exceeds this amount.

In placing the tie lines, much depends on the form of the curve. The nearer the "volume ratio" approaches unity, the less the error, and I have borne this in mind when planning the experiments.

The results furnish a view of a very extensive field. If it should prove necessary to examine any portion of it more

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[1] Ostwald: Lehrbuch, 1, 484.

minutely, the necessary experiments can be repeated on a larger scale. The experimental data are collected in Table V, and additional experimental details are given under "Notes on Table V," p. 757.

Discussion of the Results

Examination of Table III in which the coordinates of the plait points are collected, shows obvious stoichiometric regularities: With alcohol as consolute liquid, the three esters, ethyl acetate, propionate and isobutyrate, come together, in the order given; similarly with the three alcohols, benzyl, isobutyl and isoamyl. The hydrocarbons pinene, mesitylene, *o*- and *p*-xylene, and toluene come in the order given, but *m*-xylene stands out of its place at the head of the series. Amyl, isobutyl, propyl, and ethyl. bromides follow in the order named. Speaking roughly, the latter half of the table includes the liquids noticeably soluble in water, and with the exception of chloroform, only such; while the first half is taken up with hydrocarbons, brom and nitro derivatives. Except in the case of chloroform-propyl alcohol, the plait point is shifted to the right (less water) when carbinol is replaced by ethyl alcohol and the latter by propyl alcohol.

Table V. Inspection of Figs. 2, 3 and 4 shows, however, that there is no such regularity to be observed in the relative positions of the three binodal curves: in the case of brom-benzene, the highest curve is that for methyl alcohol, then ethyl alcohol, and propyl alcohol lowest; with chloroform the order is propyl, methyl, ethyl; and with carbon tetrachloride, methyl, proply, ethyl; at the extreme left of the figures, however, the order is methyl, ethyl, propyl, in every case. In the systems hexane-water-carbinol and heptane-water-carbinol the plait point is situated practically at the origin of coordinates; in other words, no matter what the proportions of carbinol, water and hexane (heptane) may be, if two layers are formed the upper layer

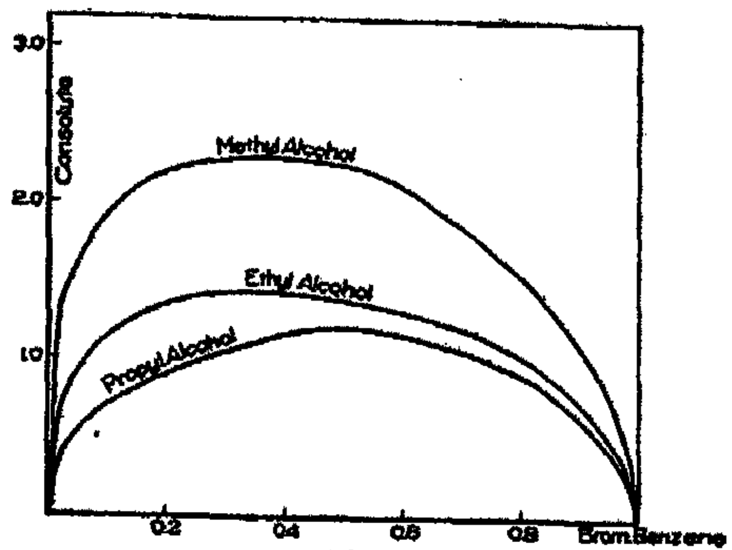

Fig. 2

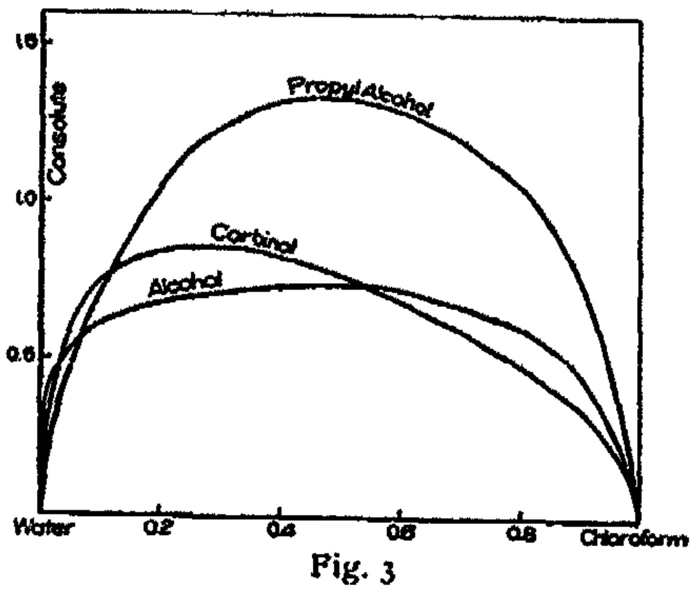

Fig. 3

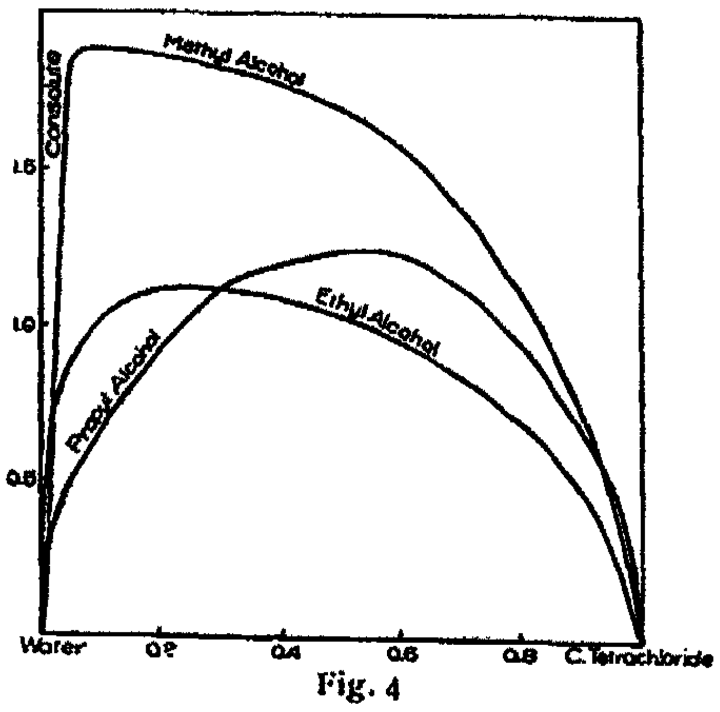

Fig. 4

will be practically pure hexane (heptane). The behavior of hexane and heptane is thus analogous to that of a solid (*e. g.* common salt) with carbinol and water: the amount dissolved varies with the proportion of water to carbinol, but neither of the latter substances is dissolved in the hydrocarbon or in the salt.

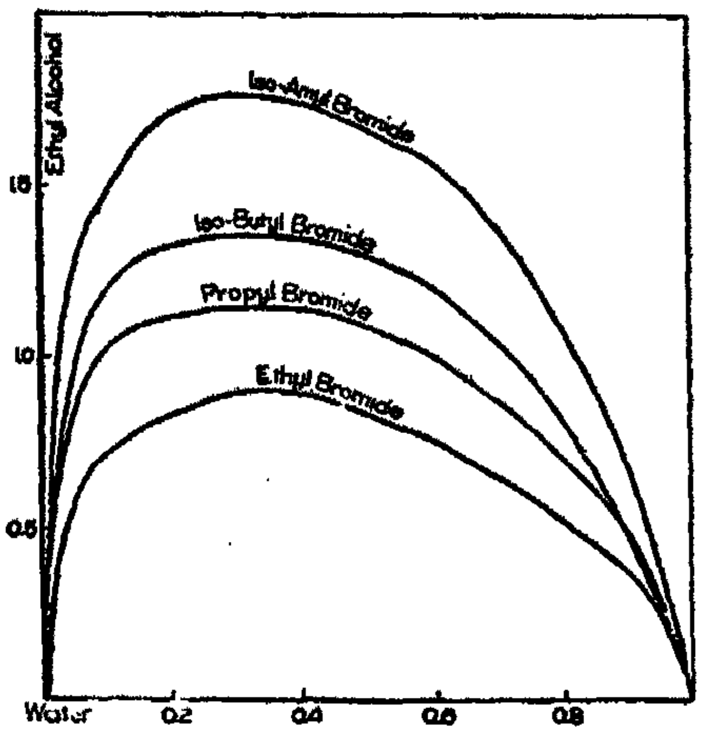

Fig. 5

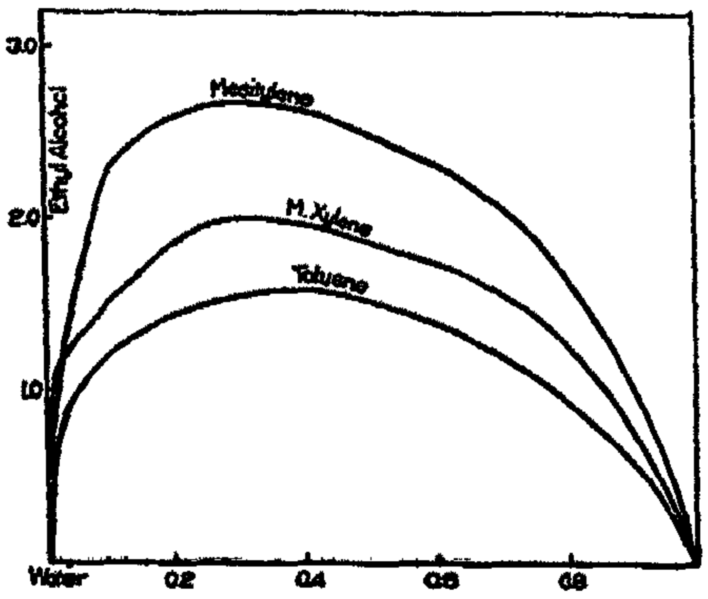

Fig. 6

TABLE III—COORDINATES OF PLAIT POINTS

Carbinol

System number		Water	Carbinol
33	Heptane	0	0
32	Hexane	0	0
6	Carbon tetrachloride	0.015	0.215
17	Brombenzene	0.02	0.40
11	Ethyl bromide	0.05	0.33
3	Chloroform	0.27	0.57

Propyl alcohol

System number		Water	Prop. alc.
4	Chloroform	0.49–0.56	1.3
8	Carbon tetrachloride	0.75	1.06
23	Bromtoluene	0.75	0.97
19	Brombenzene	0.75–0.85	0.90
13	Ethyl bromide	0.96	0.20

Alcohol

System number		Water	Alcohol
38	*m*-Xylene	0.01	0.10
41	Pinene	0.015	0.47
22	Bromtoluene	0.02	0.33
34	Heptane	0.02	0.38
40	Mesitylene	0.03	0.58
32	Hexane	0.03	0.59
18	Brombenzene	0.04	0.32
16	Isoamyl bromide	0.04	0.36
37	*o*-Xylene	0.04	0.53
44	*p*-Nitrotoluene	0.05	0.50
15	Isobutyl bromide	0.07	0.42
7	Carbon tetrachloride	0.08	0.39
14	Propyl bromide	0.08	0.42
39	*p*-Xylene	0.08	0.57
50	Nitrobenzene	0.09	0.49
49	Phenetol	0.10	0.55
9	Ethylene chloride	0.12	0.46
12	Ethyl bromide	0.17	0.45

TABLE III—(*Continued*)

Acetone				Alcohol			
System number		Water	Acetone	System number		Water	Alcohol
20	Brombenzene	0.51	1.6	25	Benzyl acetate	0.32	0.60
5	Chloroform	0.58	1.65	28	Benz. ethyl ether	0.33	0.71
				10	Ethylidene chlor.	0.33	0.72
				43	Methyl aniline	0.34	0.72
				36	Toluene	0.35–0.50	1.4
				42	Benzaldehyde	0.43	0.61
				1	Ether	0.49	0.38
				30	Diethyl ketone	0.50	0.41
				24	Ethyl acetate	0.52	0.30
				26	Ethyl propionate	0.54	0.53
				27	Ethyl butyrate	0.54	0.67
				45	*o*-Toluidene	0.50–0.60	0.49
				2	Chloroform	0.58	0.73
				48	Benzyl alcohol	0.62	0.42
				46	Isobutyl alcohol	0.65	0.21
				47	Isoamyl alcohol	0.73	0.43

	Carbinol		Alcohol		Propyl alcohol		Acetone	
Heptane	0	0	0.02	0.38				
Hexane	0	0	0.03	0.59				
Carbon tetrachloride	0.015	0.215	0.08	0.39	0.75	1.06		
Bromtoluene	—	—	0.02	0.33	0.75	0.97		
Brombenzene	0.02	0.40	0.04	0.32	0.75–0.85	0.90	0.51	1.6
Ethyl bromide	0.05	0.33	0.17	0.45	0.96	0.20	—	—
Chloroform	0.27	0.57	0.58	0.73	0.49–0.56	1.3	0.58	1.65

Equations for the Binodal Curve

The first attempt to set up an algebraical equation for a binodal curve was made by Tuchschmidt and Follenius,[1] who found that values of x calculated from the expression

$$xy = s - \frac{c}{x + b}$$

(where y gives the number of cc of carbon bisulphide which will dissolve in 10 cc of a spirit containing x percent alcohol by weight) agreed "beinahe vollständig" with the results of their experiments.

Pfeiffer[2] "expected to be able to express the equilibrium by the formula

$$(\alpha - x)(a - y)z = (w - z)xy$$

but the calculations were far from agreeing with the experiments."

Beginning in 1894[3] Bancroft published a series of papers on "Ternary Mixtures." He found that in a number of cases, including those investigated by himself and the alloys of Wright,[4] the curves were represented by the formula

$$xy^n = \text{const.},$$

where x and y are the amounts of the two immiscible liquids to a definite amount of consolute. In most cases, however, two equations with different constants were necessary to express the whole curve. It was thought that the corresponding logarithmic lines might cross at the plait point, but this is shown not to be the case by Waddell's experiments[5] on the system benzene-water-acetic acid and by my own measurements. Lincoln,[6] in repeating Waddell's ex-

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[1] Ueber die Löslichkeit des CS$_2$ in Alcohol. Ber. chem. Ges. Berlin, 4, 583 (1871).

[2] Ueber Lösungen von begrenzter Mischbarkeit. Zeit. phys. chem., 9, 444 (1892); see page 470 of his paper.

[3] Phys. Review, 3, 21 (1895), etc.

[4] See Bancroft's fourth paper, Jour. Phys. Chem., 3, 217 (1899).

[5] Jour. Phys. Chem., 2, 233 (1898).

[6] Ibid., 8, 248 (1904).

periments, found, contrary to that author, two straight lines; but the point of intersection does not correspond with the plait point given in Waddell's paper. Furthermore, in a number of the systems investigated by Bell[1] the lines plotted in logarithmic coordinates are distinctly curved, a fact that is true also in a number of my own results.

I have calculated the logarithmic coordinates for the present measurements, taking $\log \frac{w}{a}$ as ordinates and $\log \frac{1-w}{a}$ as abscissa, where w represents the weight of water and a the weight of consolute, to a total of one gram of water *plus* third liquid. The results are given under the various systems in Table V. The following list indicates the form of the corresponding graphs, the numbers referring to the System No. given in Table V.

Straight lines (between the limits of w given in the last col. of Table IV) Nos. 1, 3, 9, 11, 12, 14, 22, 25, 29, 32, 35, 36, 38, 39, 40, 41, 43, 44.

Concave upwards. Nos. 4, 8, 13, 19, 23, 28, 33, 39, 50.

Convex upwards. Nos. 2, 5, 6, 7, 10, 15, 16, 17, 18, 20, 26, 27, 28, 31, 37, 42.

Irregular. Nos. 24, 34, 45, 46, 47, 48.

In all cases where the logarithmic curve, or part of it, is straight, I have calculated, from the graphs, the two constants for the equation to the line, which for convenience has been written

$$\log \frac{w}{a} = -p \log \frac{1-w}{a} + \log \gamma \text{ ....} \quad \text{(A).}$$

The values of p and $\log \gamma$, calculated in this way, are given in the fifth and sixth columns in Table IV, the last column in the table showing the range of the values of w over which the line is straight.

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[1] Jour. Phys. Chem., 9, 531 (1905).

TABLE IV—EQUATION CONSTANTS

System number in Table V	System: Water and	p calc'd. from $\frac{1-w}{w}$	Log. γ calc'd. from log. $\left(\frac{0.5}{a}\right)^{p+1}$	p Calc'd. from log. graphs.	Log. γ Calc'd. from log. graphs.	Range of w over which log. line is straight
1	Ether—alcohol	0.92	0.21	0.965	0.227	0.1–0.9
2	Chloroform—alcohol	0.89	$\bar{1}.68$	—	—	—
3	Chloroform—carbinol	0.37	$\bar{1}.74$	0.40	$\bar{1}.72$	0.2–0.9
4	Chloroform—propyl alcohol	0.89	$\bar{1}.19$	—	—	—
5	Chloroform—acetone	1.67	$\bar{2}.57$	—	—	—
6	Carbon tetrachloride—carbinol	0.11	$\bar{1}.41$	—	—	—
7	Carbon tetrachloride—alcohol	0.33	$\bar{1}.58$	—	—	—
8	Carbon tetrachloride—prop. alcohol	1.08	$\bar{1}.18$	—	—	—
9	Ethylene chloride—alcohol	0.72	$\bar{1}.49$	0.598	$\bar{1}.522$	0.1–0.9
10	Ethylidene chloride—alcohol	0.49	$\bar{1}.68$	—	—	—
11	Ethyl bromide—carbinol	0.61	$\bar{1}.35$	0.603	$\bar{1}.354$	0.1–0.9
12	Ethyl bromide—alcohol	0.51	$\bar{1}.67$	0.479	$\bar{1}.679$	0.2–0.9
13	Ethyl bromide—prop. alcohol	0.89	$\bar{1}.34$	—	—	—
14	Propyl bromide—alcohol	0.57	$\bar{1}.46$	0.553	$\bar{1}.467$	0.1–0.8
15	Isobutyl bromide—alcohol	0.49	$\bar{1}.37$	—	—	—
16	Isoamyl bromide—alcohol	0.45	$\bar{1}.24$	—	—	—
17	Brombenzene—carbinol	0.64	$\bar{2}.93$	—	—	—
18	Brombenzene—alcohol	0.47	$\bar{1}.35$	—	—	—
19	Brombenzene—prop. alcohol	0.85	$\bar{1}.29$	—	—	—
20	Brombenzene—acetone	0.82	$\bar{1}.08$	—	—	—
21						
22	Bromtoluene—alcohol	0.54	$\bar{1}.14$	0.645	$\bar{1}.056$	0.1–0.8
23	Bromtoluene—prop. alcohol	0.82	$\bar{1}.36$	—	—	—
24	Ethyl acetate—alcohol	0.64	0.28	—	—	—
25	Benzyl acetate—alcohol	0.37	$\bar{1}.73$	0.351	$\bar{1}.734$	0.2–0.9

TABLE IV—(*Continued*)

System number in Table V	System: Water and	p calc'd. from $\frac{1-w}{w}$	Log. γ calc'd. from log. $\left(\frac{0.5}{a}\right)^{p+1}$	p	Log. γ	Range of w over which log. line is straight
				Calc'd. from log. graphs.		
26	Ethyl propionate—alcohol	0.51	$\bar{1}.97$	—	—	—
27	Ethyl butyrate—alcohol	0.47	$\bar{1}.82$	—	—	—
28	Benzyl ethyl ether—alcohol	0.39	$\bar{1}.67$	—	—	—
29	Isoamyl ether—alcohol	0.43	$\bar{1}.12$	0.407	$\bar{1}.141$	0.2–0.9
30	Diethyl ketone—alcohol	—	—	—	—	—
31	Hexane—carbinol	0.92	$\bar{3}.88$	—	—	—
32	Hexane—alcohol	0.72	$\bar{2}.67$	0.666	$\bar{2}.728$	0.2–0.9
33	Heptane—carbinol	0.85	$\bar{3}.70$	—	—	—
34	Heptane—alcohol	0.79	$\bar{2}.57$	—	—	—
35	Benzene—alcohol	0.59	$\bar{1}.40$	0.540	$\bar{1}.439$	0.1–0.9
36	Toluene—alcohol	0.61	$\bar{1}.22$	0.566	$\bar{1}.258$	0.2–0.9
37	*o*-Xylene—alcohol	0.59	$\bar{1}.09$	—	—	—
38	*m*-Xylene—alcohol	0.47	$\bar{1}.15$	0.60	$\bar{1}.060$	0.1–0.9
39	*p*-Xylene—alcohol	0.57	$\bar{1}.17$	0.552	$\bar{1}.118$	0.3–0.9
40	Mesitylene—alcohol	0.43	$\bar{2}.99$	0.549	$\bar{2}.911$	0.1–0.9
41	Pinene—alcohol	0.69	$\bar{2}.66$	0.69	$\bar{2}.650$	0.1–0.9
42	Benzaldehyde—alcohol	0.43	$\bar{1}.85$	—	—	—
43	Methyl aniline—alcohol	0.45	$\bar{1}.67$	0.503	$\bar{1}.647$	0.1–0.9
44	*p*-Nitrotoluene—alcohol	0.67	$\bar{1}.06$	0.749	$\bar{1}.031$	0.2–0.9
45	*o*-Toluidin—alcohol	0.54	0.03	—	—	—
46	Isobutyl alcohol—alcohol	0.54	0.61	—	—	—
47	Isoamyl alcohol—alcohol	0.67	0.08	—	—	—
48	Benzyl alcohol—alcohol	0.64	0.16	—	—	—
49	Phenetol—alcohol	0.61	$\bar{1}.23$	—	—	—
50	Nitrobenzene—alcohol	0.72	$\bar{1}.28$	—	—	—

The following considerations will give a clearer idea of the signification of these constants in the corresponding binodal curves.

From equation (A)

$$a^{p+1} = \frac{w}{r}(1-w)^p \text{..............(B).}$$

For the condition $da/dw = 0$, *i. e.*, for maximum a,

$$p = \frac{1-w}{w}$$

p, therefore, gives the ratio of the weight of immiscible liquid to water at the maximum point in the binodal curve.

For $w = 0.5$, *i. e.*, for the mixture of 0.5 gram water to 0.5 gram immiscible liquid, equation (B) becomes

$$a^{p+1} = \frac{(0.5)^{p+1}}{r}.$$

or

$$r = \left(\frac{0.5}{a}\right)^{p+1} \text{..................(C)}$$

where a is the amount of consolute necessary to make a half and half mixture of water and second immiscible liquid homogeneous.

The constants have been calculated in this way for all the experiments (including those for which the logarithmic curve is not straight) and are given in the third and fourth columns of Table IV. The logarithmic lines plotted by the use of these constants will correspond only approximately with the experiments, but will necessarily pass through the right point for $w = 0.5$. Even in the cases where the logarithmic graphs are straight the slope given by the interpolation formula may be slightly inaccurate owing to the difficulty of determining exactly the maximum point of the binodal curve.

Writing equation C in the form

$$\frac{\log r}{p+1} = \log(0.5) - \log a,$$

it will be noted that the left-hand term of the equation increases with decrease of a and *vice versa*. Since $\log \gamma$ varies in the different systems over a much wider range than $p + 1$, which with two exceptions lies between 1.3 and 2, $\log \gamma$ itself may be taken as a rough indication of the variation of a. Since, as was shown above, a is the amount of consolute required to make equal quantities of the two immiscibles homogeneous it might be expected that $\log \gamma$ would be small for the very insoluble pairs and *vice versa*. That this is approximately true is shown by the following list in which the systems are arranged in ascending order of $\log \gamma$ (the numbers refer to the System Nos. in Table IV):

Ascending order of $\log \gamma$: Nos. 33, 31, 34, 5, 41, 32, 17, 40, 44, 20, 37, 29, 22, 38, 39, 8, 4, 49, 36, 16, 50, 19, 13, 11, 18, 23, 15, 35, 6, 14, 9, 7, 28, 12, 43, 2, 10, 25, 3, 27, 42, 26, 45, 47, 48, 1, 24, 46.

It will be noted that the first part of the list contains heptane, hexane, pinene, brombenzene, mesitylene, etc., while in the latter part there are isobutyl alcohol, ethyl acetate, ether, etc.

Notes on Table V

Table V contains the data from the various measurements made. In all the experiments water was one of the non-miscible pair and so has been omitted in the headings, the names of the second non-miscible liquid and of the consolute liquid being used to designate the system. The columns headed "water" give the weight of water; the weight of the second non-miscible liquid in the system, and hence the abscissa in the graphs, may be found by subtracting the amount of water from unity. The second column (headed carbinol, alcohol, propyl alcohol or acetone) gives the weight of the consolute liquid necessary to make a homogeneous solution, *i. e.*, the ordinate in the graphs. These two numbers fix a point on the binodal curve. The figures in the "density" column are the densities of the homogeneous systems as determined by the cathetometer. For the convenience of any who may desire to use these results, interpolations of the even decimals have been made and inserted in the table; these interpolations which have been made from the plotted curves are given to two decimal places only, and are marked by an asterisk. The plait points are inserted in the tables in their proper places, and are indicated by the letters P. P. The two small columns headed "water-water," which appear at the bottom of most of the tables give the abscissa of the two ends of the tie lines. The lower, denser, phase is always given in the first column. The tables of logarithmic coordinates are referred to under "Equations for binodal curve," p. 752.

The temperature of the experiments was zero centigrade except where otherwise stated.

(4) Near the plait point separation was very slow; no even dividing line between the phases could be obtained.

Plait point between water 0.49 and 0.56:

(5) These mixtures do not become cloudy to any great extent. Near the plait point the two phases are so nearly the same in appearance that without the lamp black it was very difficult to see the dividing line.

(7) Kahlbaum's preparation, freshly distilled, b. p. 78°.

(9) The ethylene chloride was dried and redistilled, b. p. 83°–84°.

(11) The ethyl bromide was prepared in the laboratory. It was dried and fractionated, b. p. 38°–39°.

(13) The plait point seems to lie between the points water 0.950 and water 0.969, but though repeated attempts were made no tie lines were obtained.

(14) The first three tie lines are a first approximation only, but the radiation from the origin indicates that the bottom layer during the first part of the experiment was practically pure propyl bromide.

(17) The brombenzene was prepared by students in the organic laboratory. A fraction of 100 cc boiling at 154° was used for these measurements.

(19) Separated very slowly near the plait point. Did

not separate on standing twenty-four hours. Centrifuging was of no help.

Plait point between water 0.75 and 0.85:

(21) It was impossible to determine the end point accurately because the bromtoluene phase settles to the bottom as oily drops in a perfectly clear liquid, and the end could be determined only by the disappearance of the oily drops. The bromtoluene was freshly distilled, b..p. 182°–183°.

(24) At 0°, 10 grams ethyl acetate dissolve 0.301 gram of water. Ten grams of water at 0° dissolve 1.086 grams of ethyl acetate.

(28) Benzyl ethyl ether forms at first the upper layer. After the addition of a little alcohol it forms the bottom layer.

(29) The first two tie lines given are first approximation only.

(30) It was not found possible to carry this curve beyond the point water 0.70. From this point on, after the addition of a small amount of alcohol the mixture no longer separates into two layers but remains turbid and a great excess of alcohol does not remove this turbidity.

Plait point only near water 0.50:

(31) The hexane and heptane used were Kahlbaum's, "aus Petroleum." When carbinol is used as the consolute liquid the plait points lie so near the paraffine end of the graphs that tie line measurements are impossible. This means that the tie lines radiate from the origin and that hence all the solutions obtained by adding carbinol to any mixture whatever of hexane or heptane and water, are in equilibrium with practically pure hexane. To check this conclusion the following measurements of the refractive index were made:

(1) Three cc of hexane, 3 cc of carbinol, and one drop water were shaken well together, let stand to separate and the top layer (about 2 cc) was then transferred to the cylinder of the refractometer and its index of refraction determined.

(2) Five cc of hexane, 7 cc of carbinol and 4 drops water, treated as before. The top layer was approximately 3 cc. The refractive index of both top and bottom layers was determined. Upper layer μ_{14} = 1.38343, lower layer μ_{14} = 1.33935.

(3) Three cc of hexane, 1 cc of water, well shaken and separated by centrifuging, upper layer μ_{14} = 1.38381.

(4) Three cc. of hexane and an excess (about 2 drops) of carbinol, allowed to settle. Used the clear solution. μ_{14} = 1.38334.

The refractometer used (Pulfrich's "Refractometer für Chemiker") gave as the value of μ_{14} for distilled water at 14° C. 1.33295 as against 1.33232 given in the Landolt-Bornstein tables; for benzene it gave 1.50139 as against 1.50137 in the tables; pure hexane gave 1.38382 and carbinol 1.33070, all at 14° C.

(34) Plait point is about water 0.02, alcohol 0.38.

(36) Through an oversight no tie line measurements were made:

Plait point between water 0.35 and 0.50:

(37) In this case (as also in the cases of experiments numbered 4, 8, 28, 35, 39, 41, 43 and 49) while the xylene is at first the upper layer, after the addition of a small amount of alcohol, the xylene layer sinks through the watery layer and becomes the lower. This gives another method of obtaining approximately the tie lines in these mixtures. Just before the point at which the "top" layer becomes the "bottom" there is a point at which the densities of the two are identical and the density of either is the density of the total mixture. Add alcohol until the "top" layer just begins to sink into the "bottom" and determine the density of the total mixture at this point. The tie line will be represented by a line passing through the point which gives the composition of the system and cutting the binodal curve at a point on either side which has the density of the given system. The last tie line in the table above was obtained in this way.

The composition of the system was water 0.295, alcohol 0.740, density 0.89.

(38) The plait point lies to the right of the point water 0.010.

(43) The first tie line is a first approximation only. Kahlbaum's best preparation, fractionated twice, b. p. 195°.

(44) The sample of *o*-nitrotoluene was prepared in the laboratory, b. p. 223°–224°.

(45) B. p. 199°.

It was impossible to get a satisfactory tie line measurement because the layers would not separate well enough to enable one to read the volumes, even up to the point where one drop of alcohol made the mixture homogeneous.

The plait point comes between 0.50 and 0.60.

(46) Kahlbaum's preparation, slightly discolored.

Boiled with calcium turnings under reflux and fractionated. B. p. 107°–109°. The solubility of water in isobutyl alcohol at zero is 2.17 g water in 10 g and that of isobutyl alcohol in water is 1.15 g in 10 g water. The solubility decreases with rise of temperature.

(47) Kahlbaum's preparation free from pyridine. Dried over calcium turnings and distilled. B. p. 130°. The solubility in water at zero is 0.42 g in 10 g water and the solubility of water in isoamyl alcohol at zero is 0.81 g in 10 g alcohol.

TABLE V

(1) ether alcohol

Water	Alcohol	Density
0.041	0.161	0.78
0.087	0.224	0.79
*0.10	0.28	0.80
0.186	0.299	0.82
*0.20	0.305	0.82
0.299	0.354	0.85
0.399	0.376	0.86
P. P. 0.49	0.38	0.88
*0.50	0.39	0.88
0.586	0.381	0.90
*0.60	0.38	0.91
*0.70	0.37	0.93
0.712	0.365	0.93
*0.80	0.34	0.95
0.826	0.331	0.96
0.875	0.238	0.97
*0.90	0.16	0.97

(2) chloroform alcohol

Water	Alcohol	Density
0.093	0.434	1.19
*0.10	0.45	1.18
0.185	0.587	1.13
*0.20	0.60	1.12
*0.30	0.68	1.07
0.317	0.692	1.06
0.407	0.726	1.04
0.499	0.729	1.03
P. P. 0.58	0.73	—
0.596	0.733	1.01
0.689	0.710	0.99
*0.70	0.70	0.99
0.803	0.672	0.98
*0.90	0.61	0.98
0.912	0.608	0.98
—	—	—
—	—	—

Tie-lines

Water	Water
0.86	0.02
0.81	0.12
0.77	0.18
0.68	0.30
0.61	0.38

Tie-lines

Water	Water
0.10	0.97
0.22	0.90
0.43	0.72

(1) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.638$	0.593
0.20	0.810	0.412
0.30	0.933	0.301
0.40	0.034	0.210
0.50	0.108	0.108
0.60	0.198	0.022
0.70	0.277	$\bar{1}.909$
0.80	0.372	$\bar{1}.770$
0.90	0.750	$\bar{1}.796$
P. P. —	0.565	$\bar{1}.720$

(2) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.347$	0.301
0.20	0.523	0.125
0.30	0.645	0.013
0.40	0.742	$\bar{1}.918$
0.50	0.836	$\bar{1}.836$
0.60	0.913	$\bar{1}.737$
0.70	0.000	$\bar{1}.632$
0.80	0.076	$\bar{1}.474$
0.90	0.169	$\bar{1}.215$
P. P. —	$\bar{1}.900$	$\bar{1}.760$

TABLE V—(*Continued*)

(3) chloroform carbinol			(4) chloroform propyl alcohol		
Water	Carbinol	Density	Water	Propyl alcohol	Density
0.021	0.161	—	0.023	0.304	1.28
*0.10	0.35	1.17	0.074	0.631	1.13
0.132	0.400	1.16	*0.10	0.76	1.11
*0.20	0.49	1.12	*0.20	1.06	1.04
P. P. 0.27	0.57	—	0.240	1.128	1.02
0.276	0.572	1.09	*0.30	1.20	1.01
*0.30	0.60	1.08	0.346	1.250	1.02
0.368	0.666	1.07	*0.40	1.30	0.98
*0.40	0.70	1.05	*0.50	1.34	0.97
*0.50	0.77	1.02	0.511	1.340	0.96
0.519	0.783	1.01	0.606	1.320	0.98
*0.60	0.83	1.00	0.707	1.235	0.96
0.628	0.843	0.99	0.806	0.996	0.95
*0.70	0.86	0.98	0.903	0.672	0.97
*0.80	0.84	0.97	0.970	0.390	0.97
0.822	0.834	0.97	—	—	—
*0.90	0.74	0.96	—	—	—
0.943	0.622	—	—	—	—
0.987	0.267	0.98	—	—	—

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.00	0.70	0.10	1.00
0.01	0.58	0.13	1.00
0.03	0.55	0.24	1.00
0.05	0.51	0.27	1.00
0.11	0.45	—	—

(3) Logarithmic coördinates			(4) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.456$	0.410	0.10	$\bar{1}.119$	0.073
0.20	$\bar{1}.611$	0.213	0.20	$\bar{1}.276$	$\bar{1}.878$
0.30	$\bar{1}.699$	0.067	0.30	$\bar{1}.398$	$\bar{1}.766$
0.40	$\bar{1}.757$	$\bar{1}.933$	0.40	$\bar{1}.488$	$\bar{1}.664$
0.50	$\bar{1}.813$	$\bar{1}.813$	0.50	$\bar{1}.572$	$\bar{1}.572$
0.60	$\bar{1}.859$	$\bar{1}.683$	0.60	$\bar{1}.656$	$\bar{1}.482$
0.70	$\bar{1}.911$	$\bar{1}.543$	0.70	$\bar{1}.755$	$\bar{1}.387$
0.80	$\bar{1}.979$	$\bar{1}.377$	0.80	$\bar{1}.908$	$\bar{1}.305$
0.90	$\bar{1}.085$	$\bar{1}.131$	0.90	0.128	$\bar{1}.174$
P. P. —	$\bar{1}.676$	0.107	—	—	—

TABLE V—(*Continued*)

(5) chloroform acetone			(6) carbontetrachlorid: carbinol		
Water	Acetone	Density	Water	Carbinol	Density
0.012	0.501	1.18	P. P. 0.015	0.215	—
0.087	1.221	1.02	0.026	0.328	1.30
*0.10	1.30	1.01	*0.10	0.74	1.13
0.208	1.633	0.98	0.156	0.974	1.06
0.304	1.750	0.96	*0.20	1.10	1.04
0.344	1.742	0.96	0.235	1.208	1.03
*0.40	1.77	0.95	*0.30	1.40	1.00
0.481	1.738	0.94	0.316	1.403	0.99
*0.50	1.72	0.94	*0.40	1.68	0.97
P. P. 0.58	1.65	—	0.490	1.700	0.95
0.592	1.630	0.93	*0.50	1.71	0.95
*0.60	1.63	0.93	*0.60	1.77	0.93
*0.70	1.53	0.94	0.702	1.825	0.93
0.737	1.483	0.95	*0.80	1.88	0.92
0.800	1.321	0.95	0.852	1.890	0.92
0.900	1.144	0.97	*0.90	1.90	0.92
0.982	0.464	0.98	0.951	1.870	0.91
—	—	—	0.974	1.045	0.93

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.15	0.99	0.000	0.110
0.17	0.98	0.005	0.035
0.18	0.97		
0.19	0.96		
0.20	0.96		
0.21	0.95		
0.22	0.93		
0.25	0.91		
0.30	0.85		
0.51	0.66		

(5) Logarithmic coördinates			(6) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.886$	$\bar{1}.840$	0.10	$\bar{1}.131$	0.085
0.20	$\bar{1}.089$	$\bar{1}.691$	0.20	$\bar{1}.260$	$\bar{1}.862$
0.30	$\bar{1}.234$	$\bar{1}.602$	0.30	$\bar{1}.331$	$\bar{1}.699$
0.40	$\bar{1}.354$	$\bar{1}.530$	0.40	$\bar{1}.403$	$\bar{1}.580$
0.50	$\bar{1}.464$	$\bar{1}.464$	0.50	$\bar{1}.466$	$\bar{1}.466$
0.60	$\bar{1}.566$	$\bar{1}.390$	0.60	$\bar{1}.530$	$\bar{1}.354$
0.70	$\bar{1}.660$	$\bar{1}.292$	0.70	$\bar{1}.583$	$\bar{1}.215$
0.80	$\bar{1}.783$	$\bar{1}.180$	0.80	$\bar{1}.630$	$\bar{1}.027$
0.90	$\bar{1}.897$	$\bar{2}.943$	0.90	$\bar{1}.675$	$\bar{2}.721$
P. P. —	$\bar{1}.550$	$\bar{1}.406$	P. P. —	$\bar{2}.844$	0.661

TABLE V—(*Continued*)

(7) carbontetrachloride alcohol **(8) carbontetrachloride propyl alcohol**

Water	Alcohol	Density	Water	Propyl alcohol	Density
0.039	0.224	1.36	0.025	0.317	1.31
0.072	0.347	1.23	0.069	0.536	1.17
P. P. 0.08	0.39	—	*0.10	0.65	1.14
*0.10	0.45	1.20	0.200	0.949	1.07
0.156	0.598	1.16	0.270	1.070	1.03
*0.20	0.67	1.15	*0.30	1.12	1.02
0.238	0.746	1.10	0.40	1.20	0.99
*0.30	0.82	1.07	0.414	1.208	0.99
0.361	0.891	1.05	0.501	1.234	0.98
*0.040	0.94	1.03	0.600	1.195	0.97
0.501	1.040	1.00	*0.70	1.13	0.96
0.518	1.046	0.97	0.710	1.119	0.96
*0.60	1.00	0.97	P. P. 0.75	1.06	—
*0.70	1.11	0.96	0.806	0.912	0.96
0.750	1.105	0.95	*0.90	0.68	0.96
*0.80	1.10	0.94	0.911	0.645	0.96
0.887	1 104	0.95	0.987	0.354	0.96
*0.90	1.00	0.92	—	—	—
0.945	0.850	0.91	—	—	—
0.955	0.838	0.92	—	—	—
0.968	0.745	0.93	—	—	—

Tie-lines Tie-lines

Water	Water	Water	Water
0.01	0.30	0.21	0.99
0.02	0.22	0.47	1.00
0.03	0.16	0.56	0.99
0.05	0.13	0.52	0.90

(7) Logarithmic coördinates (8) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.347$	0.301	0.10	$\bar{1}.187$	0.141
0.20	$\bar{1}.475$	0.077	0.20	$\bar{1}.330$	$\bar{1}.930$
0.30	$\bar{1}.567$	$\bar{1}.931$	0.30	$\bar{1}.428$	$\bar{1}.796$
0.40	$\bar{1}.629$	$\bar{1}.805$	0.40	$\bar{1}.523$	$\bar{1}.699$
0.50	$\bar{1}.683$	$\bar{1}.683$	0.50	$\bar{1}.609$	$\bar{1}.609$
0.60	$\bar{1}.741$	$\bar{1}.565$	0.60	$\bar{1}.699$	$\bar{1}.523$
0.70	$\bar{1}.800$	$\bar{1}.432$	0.70	$\bar{1}.792$	$\bar{1}.424$
0.80	$\bar{1}.863$	$\bar{1}.260$	0.80	$\bar{1}.944$	$\bar{1}.342$
0.90	$\bar{1}.954$	$\bar{1}.000$	0.90	0.121	$\bar{1}.168$
P. P. —	$\bar{1}.312$	0.373	P. P. —	$\bar{1}.850$	$\bar{1}.373$

TABLE V—(*Continued*)

(9) ethylene chloride alcohol			(10) ethylidene chloride alcohol		
Water	Alcohol	Density	Water	Alcohol	Density
0.029	0.191	1.15	0.015	0.226	1.10
0.050	0.266	1.12	*0.10	0.43	1.03
*0.10	0.42	1.08	0.109	0.436	1.02
P. P. 0.12	0.46	—	0.195	0.586	1.01
0.208	0.670	1.01	*0.30	0.69	0.98
0.290	0.789	0.98	0.316	0.705	1.00
*0.30	0.80	0.98	P. P. 0.33	0.72	—
*0.40	0.93	0.96	*0.40	0.77	0.96
0.486	0.983	0.95	0.423	0.770	0.96
*0.50	0.99	0.95	*0.50	0.82	0.95
0.580	1.000	0.95	0.563	0.857	0.94
*0.60	1.01	0.94	0.667	0.87	0.94
*0.70	0.99	0.94	*0.70	0.88	0.93
0.790	0.958	0.94	0.765	0.864	0.93
*0.80	0.95	0.94	*0.80	0.86	0.93
0.905	0.842	0.96	*0.90	0.79	0.94
0.980	0.514	0.97	0.910	0.774	0.94
—	—	—	0.970	0.576	0.95

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.00	0.48	0.00	0.79
0.01	0.36	0.01	0.77
0.03	0.22	0.03	0.70
		0.11	0.61
		0.20	0.47

(9) Logarithmic coördinates			(10) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}$.377	0.331	0.10	$\bar{1}$.367	0.321
0.20	$\bar{1}$.475	0.077	0.20	$\bar{1}$.533	0.135
0.30	$\bar{1}$.574	$\bar{1}$.942	0.30	$\bar{1}$.638	0.006
0.40	$\bar{1}$.634	$\bar{1}$.810	0.40	$\bar{1}$.716	$\bar{1}$.892
0.50	$\bar{1}$.703	$\bar{1}$.703	0.50	$\bar{1}$.785	$\bar{1}$.785
0.60	$\bar{1}$.774	$\bar{1}$.598	0.60	$\bar{1}$.839	$\bar{1}$.663
0.70	$\bar{1}$.850	$\bar{1}$.482	0.70	$\bar{1}$.901	$\bar{1}$.533
0.80	$\bar{1}$.925	$\bar{1}$.323	0.80	$\bar{1}$.969	$\bar{1}$.367
0.90	0.029	$\bar{1}$.076	0.90	0.057	$\bar{1}$.102
P. P. —	0.416	0.282	P. P. —	$\bar{1}$.661	$\bar{1}$.969

TABLE V—(*Continued*)

(11) ethyl bromide carbinol | (12) ethyl bromide alcohol

Water	Carbinol	Density	Water	Alcohol	Density
0.027	0.202	1.27	0.033	0.240	1.23
P. P. 0.05	0.33	—	*0.10	0.37	1.15
0.064	0.393	1.18	P. P. 0.17	0.45	—
*0.10	0.54	1.14	0.189	0.493	1.09
0.194	0.868	1.08	*0.20	0.51	1.09
*0.20	0.86	1.05	*0.30	0.64	1.06
0.291	1.023	1.01	0.365	0.720	1.04
*0.30	1.04	1.01	*0.40	0.754	1.03
0.398	1.180	1.00	0.476	0.807	1.01
*0.40	1.18	0.99	*0.50	0.83	1.00
0.498	1.250	0.97	*0.60	0.89	0.99
*0.50	1.26	0.97	0.657	0.900	0.98
0.600	1.310	0.96	*0.70	0.89	0.97
*0.70	1.29	0.95	*0.80	0.83	0.96
0.750	1.270	0.95	0.837	0.797	0.96
*0.80	1.21	0.94	*0.90	0.73	0.97
0.816	1.100	0.95	0.948	0.623	0.98
*0.90	0.94	0.94	0.983	0.182	0.99
0.919	0.870	0.94	—	—	—
0.978	0 194	0.98	—	—	—

Tie-lines | Tie-lines

Water	Water	Water	Water
0.00	0.21	0.00	0.63
0.01	0.14	0.01	0.46
0.02	0.11	0.06	0.27
0.02	0.08		

(11) Logarithmic coördinates | (12) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.268$	0.222	0.10	$\bar{1}.432$	0.386
0.20	$\bar{1}.367$	$\bar{1}.969$	0.20	$\bar{1}.593$	0.196
0.30	$\bar{1}.460$	$\bar{1}.828$	0.30	$\bar{1}.671$	0.039
0.40	$\bar{1}.530$	$\bar{1}.706$	0.40	$\bar{1}.727$	$\bar{1}.903$
0.50	$\bar{1}.599$	$\bar{1}.599$	0.50	$\bar{1}.780$	$\bar{1}.780$
0.60	$\bar{1}.661$	$\bar{1}.485$	0.60	$\bar{1}.829$	$\bar{1}.653$
0.70	$\bar{1}.735$	$\bar{1}.367$	0.70	$\bar{1}.896$	$\bar{1}.527$
0.80	$\bar{1}.820$	$\bar{1}.218$	0.80	$\bar{1}.984$	$\bar{1}.382$
0.90	$\bar{1}.981$	0.027	0.90	0.091	$\bar{1}.137$
P. P. —	$\bar{1}.181$	0.459	P. P. —	$\bar{1}.577$	0.266

TABLE V—(*Continued*)

(13) ethyl bromide propyl alcohol

Water	Propyl alcohol	Density
0.039	0.367	1.21
0.088	0.615	1.11
*0.10	0.64	1.10
*0.20	0.85	1.05
0.215	0.800	1.05
*0.30	1.00	1.02
0.334	1.061	1.03
*0.40	1.09	1.00
0.413	1.092	1.01
0.509	1.124	0.98
0.584	1.115	0.96
*0.60	1.10	0.97
0.694	0.998	0.97
*0.70	0.90	0.96
0.80	0.81	0.96
0.860	0.671	0.96
*0.90	0.56	0.97
0.977	0.227	0.99
—	—	—

(14) propyl bromide alcohol

Water	Alcohol	Density
0.025	0.190	1.26
P. P. 0.08	0.42	—
*0.10	0.50	1.12
0.107	0.508	1.12
*0.20	0.72	1.06
0.231	0.700	1.04
*0.30	0.88	1.02
0.328	0.920	1.01
*0.40	1.01	0.99
0.432	1.181	1.00
0.496	1.096	0.98
*0.50	1.10	0.98
0.563	1.134	0.96
*0.60	1.15	0.96
0.695	1.140	0.95
*0.70	1.14	0.95
0.796	1.120	0.94
0.904	1.020	0.94
0.973	0.687	0.95

Tie-lines

Water	Water
0.00	0.96
0.00	0.80
0.00	0.53
0.00	0.34
0.01	0.27
0.02	0.21
0.03	0.16
0.04	0.14

(13) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.194$	0.148
0.20	$\bar{1}.372$	$\bar{1}.974$
0.30	$\bar{1}.477$	$\bar{1}.845$
0.40	$\bar{1}.565$	$\bar{1}.741$
0.50	$\bar{1}.650$	$\bar{1}.650$
0.60	$\bar{1}.737$	$\bar{1}.561$
0.70	$\bar{1}.850$	$\bar{1}.482$
0.80	$\bar{1}.995$	$\bar{1}.393$
0.90	0.200	$\bar{1}.252$
—	—	—

(14) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.301$	0.255
0.20	$\bar{1}.444$	0.046
0.30	$\bar{1}.533$	$\bar{1}.901$
0.40	$\bar{1}.598$	$\bar{1}.774$
0.50	$\bar{1}.658$	$\bar{1}.658$
0.60	$\bar{1}.718$	$\bar{1}.541$
0.70	$\bar{1}.788$	$\bar{1}.420$
0.80	$\bar{1}.854$	$\bar{1}.252$
0.90	$\bar{1}.946$	$\bar{2}.991$
P. P.	$\bar{1}.280$	0.341

TABLE V—(*Continued*)

(15) isobutyl bromide alcohol			(16) isoamyl bromide alcohol		
Water	Alcohol	Density	Water	Alcohol	Density
0.024	0.200	1.18	0.025	0.251	1.10
P. P. 0.07	0.42	—	P. P. 0.04	0.36	—
*0.10	0.52	1.09	0.189	0.636	1.01
0.124	0.607	1.06	*0.10	0.68	1.01
*0.20	0.83	1.01	*0.20	1.09	0.96
0.218	0.887	1.00	0.223	1.178	0.97
0.293	1.039	0.98	*0.30	1.37	0.94
*0.30	1.05	0.98	0.324	1.432	0.93
0.386	1.194	0.96	*0.40	1.57	0.93
*0.40	1.21	0.96	0.414	1.594	0.93
0.499	1.300	0.94	0.502	1.676	0.91
0.598	1.359	0.93	0.583	1.744	0.91
*0.60	1.35	0.93	*0.60	1.75	0.91
0.696	1.356	0.93	0.692	1.747	—
*0.70	1.36	0.93	*0.70	1.75	0.91
*0.80	1.32	0.92	*0.80	1.71	0.91
0.804	1.316	0.92	0.809	1.713	0.91
0.896	1.215	0.93	0.895	1.463	0.92
*0.90	1.20	0.93	*0.90	1.46	0.92
0.953	0.937	0.94	0.978	1.027	0.93

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.00	0.51	0.00	0.43
0.00	0.24	0.01	0.11
0.03	0.13	0.02	0.06

(15) Logarithmic coördinates			(16) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.284$	0.238	0.10	$\bar{1}.168$	0.122
0.20	$\bar{1}.382$	$\bar{1}.984$	0.20	$\bar{1}.264$	$\bar{1}.866$
0.30	$\bar{1}.456$	$\bar{1}.824$	0.30	$\bar{1}.340$	$\bar{1}.708$
0.40	$\bar{1}.519$	$\bar{1}.695$	0.40	$\bar{1}.406$	$\bar{1}.582$
0.50	$\bar{1}.586$	$\bar{1}.586$	0.50	$\bar{1}.476$	$\bar{1}.476$
0.60	$\bar{1}.648$	$\bar{1}.472$	0.60	$\bar{1}.535$	$\bar{1}.359$
0.70	$\bar{1}.712$	$\bar{1}.344$	0.70	$\bar{1}.602$	$\bar{1}.234$
0.80	$\bar{1}.783$	$\bar{1}.180$	0.80	$\bar{1}.670$	$\bar{1}.068$
0.90	$\bar{2}.875$	$\bar{2}.920$	0.90	$\bar{1}.790$	$\bar{2}.836$
P. P. —	$\bar{1}.222$	0.545	P. P. —	$\bar{1}.049$	0.426

TABLE V—(*Continued*)

(17) brombenzene carbinol

Water	Carbinol	Density
0.009	0.230	—
0.015	0.314	1.24
P. P. 0.02	0.40	—
0.031	0.453	1.16
*0.10	1.01	1.04
0.127	1.170	1.01
0.198	1.491	0.98
*0.20	1.50	0.98
0.237	1.751	0.96
*0.30	1.84	0.95
0.357	1.932	0.93
0.400	2.065	0.94
*0.50	2.24	0.91
0.551	2.290	0.90
*0.60	2.30	0.90
0.633	2.295	0.90
*0.70	2.28	0.89
*0.80	2.20	0.89
0.812	2.185	0.91
0.905	1.927	0.90
0.984	1.332	0.91

Tie-lines

Water	Water
0.00	0.07

(18) brombenzene alcohol

Water	Alcohol	Density
0.010	0.115	1.34
P. P. 0.04	0.32	—
*0.10	0.65	1.07
0.109	0.641	1.09
0.195	0.988	0.96
*0.20	1.00	0.96
*0.30	1.19	0.96
0.354	1.240	0.97
*0.40	1.30	0.98
0.414	1.326	0.98
0.498	1.385	—
*0.50	1.39	0.95
0.593	1.420	0.91
*0.60	1.43	0.91
0.695	1.434	0.90
*0.70	1.43	0.92
*0.80	1.36	0.93
0.840	1.305	0.92
*0.90	1.16	0.93
0.903	1.150	0.94
0.976	0.803	0.92

Tie-lines

Water	Water
0.00	0.22
0.00	0.16
0.01	0.09
0.02	0.06

(17) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.996$	$\bar{1}.950$
0.20	$\bar{1}.125$	$\bar{1}.727$
0.30	$\bar{1}.212$	$\bar{1}.580$
0.40	$\bar{1}.287$	$\bar{1}.463$
0.50	$\bar{1}.349$	$\bar{1}.349$
0.60	$\bar{1}.416$	$\bar{1}.240$
0.70	$\bar{1}.487$	$\bar{1}.119$
0.80	$\bar{1}.560$	$\bar{2}.958$
0.90	$\bar{1}.669$	$\bar{2}.714$
P. P. —	$\bar{2}.699$	0.389

(18) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.187$	0.141
0.20	$\bar{1}.301$	$\bar{1}.903$
0.30	$\bar{1}.402$	$\bar{1}.770$
0.40	$\bar{1}.488$	$\bar{1}.664$
0.50	$\bar{1}.556$	$\bar{1}.556$
0.60	$\bar{1}.623$	$\bar{1}.447$
0.70	$\bar{1}.690$	$\bar{1}.322$
0.80	$\bar{1}.770$	$\bar{1}.168$
0.90	$\bar{1}.890$	$\bar{2}.935$
P. P. —	$\bar{1}.097$	0.477

TABLE V—(*Continued*)

(19) brombenzene propyl alcohol			(20) brombenzene acetone		
Water	Alcohol	Density	Water	Acetone	Density
0.017	0.186	1.29	0.023	0.685	1.12
0.091	0.560	1.11	*0.10	1.13	1.01
*0.10	0.58	1.11	0.107	1.175	1.01
*0.20	0.87	1.05	*0.20	1.41	0.98
0.230	0.936	1.04	0.236	1.470	1.00
*0.30	1.05	1.02	*0.30	1.52	0.97
0.358	1.110	1.01	0.319	1.535	0.96
*0.40	1.15	1.00	*0.40	1.57	0.96
*0.50	1.19	0.97	0.402	1.570	0.96
0.512	1.195	0.97	*0.50	1.60	0.95
0.573	1.208	0.97	P. P. 0.51	1.60	—
*0.60	1.19	0.96	0.547	1.600	0.95
*0.70	1.09	0.95	*0.60	1.59	0.94
0.708	1.071	0.95	*0.70	1.55	0.93
*0.80	0.93	0.95	0.715	1.540	0.94
0.815	0.899	—	0.792	1.454	0.93
*0.90	0.71	0.96	*0.80	1.46	0.93
0.906	0.687	0.96	0.874	1.365	0.93
0.979	0.457	0.98	*0.90	1.30	0.93
—	—	—	0.980	0.849	0.95

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.35	1.00	0.11	0.94
0.54	1.00	0.15	0.86
0.51	0.99	0.29	0.73
0.33	0.77	0.38	0.64

(19) Logarithmic coördinates			(20) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.237$	0.191	0.10	$\bar{2}.947$	$\bar{1}.901$
0.20	$\bar{1}.362$	$\bar{1}.964$	0.20	$\bar{1}.152$	$\bar{1}.754$
0.30	$\bar{1}.456$	$\bar{1}.824$	0.30	$\bar{1}.295$	$\bar{1}.663$
0.40	$\bar{1}.541$	$\bar{1}.718$	0.40	$\bar{1}.406$	$\bar{1}.582$
0.50	$\bar{1}.624$	$\bar{1}.624$	0.50	$\bar{1}.495$	$\bar{1}.495$
0.60	$\bar{1}.703$	$\bar{1}.527$	0.60	$\bar{1}.577$	$\bar{1}.400$
0.70	$\bar{1}.808$	$\bar{1}.440$	0.70	$\bar{1}.655$	$\bar{1}.287$
0.80	$\bar{1}.935$	$\bar{1}.333$	0.80	$\bar{1}.739$	$\bar{1}.137$
0.90	0.103	$\bar{1}.149$	0.90	$\bar{1}.840$	$\bar{2}.886$
—	—	—	P. P. —	$\bar{1}.504$	$\bar{1}.486$

TABLE V—(*Continued*)

(21) bromtoluene carbinol	(22) bromtoluene alcohol

Water	Alcohol	Density
0.02	0.33	—
0.049	0.522	1.09
*0.10	0.87	1.06
0.146	1.086	1.01
*0.20	1.28	0.97
0.232	1.352	0.95
*0.30	1.54	0.94
0.386	1.700	—
*0.40	1.71	0.93
*0.50	1.81	0.92
0.534	1.850	0.92
*0.60	1.89	0.91
0.620	1.900	0.91
*0.70	1.89	0.90
0.785	1.800	0.91
*0.80	1.78	0.90
0.900	1.533	0.91
0.967	1.307	0.92

Tie-lines

Water	Water
0.00	0.13
0.00	0.10
0.00	0.07
0.01	0.06

(22) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.061$	0.015
0.20	$\bar{1}.194$	$\bar{1}.796$
0.30	$\bar{1}.290$	$\bar{1}.658$
0.40	$\bar{1}.369$	$\bar{1}.545$
0.50	$\bar{1}.441$	$\bar{1}.441$
0.60	$\bar{1}.502$	$\bar{1}.326$
0.70	$\bar{1}.569$	$\bar{1}.201$
0.80	$\bar{1}.653$	$\bar{1}.041$
0.90	$\bar{1}.770$	$\bar{2}.815$
P. P. —	$\bar{2}.783$	0.473

TABLE V—(*Continued*)

(23) bromtoluene propyl alcohol (24) ethyl acetate alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.032	0.252	1.23	0.080	0.100	0.91
*0.10	0.52	1.11	*0.10	0.13	0.91
0.104	0.529	1.10	0.201	0.228	0.93
0.188	0.755	1.04	0.203	0.222	0.93
*0.20	0.78	1.03	0.301	0.265	0.92
0.30	0.96	1.01	0.396	0.290	0.95
0.303	0.955	1.01	*0.40	0.29	0.95
*0.40	1.07	0.99	0.50	0.30	0.95
0.407	1.075	0.99	0.507	0.297	0.94
0.496	1.127	0.98	P. P. 0.52	0.30	—
*0.50	1.13	0.97	*0.60	0.31	0.96
0.560	1.124	0.96	0.611	0.310	0.96
0.598	1.139	0.96	0.689	0.304	0.96
*0.60	1.13	0.96	*0.70	0.31	0.96
0.677	1.075	0.95	0.803	0.282	0.97
*0.70	1.03	0.95	0.898	0.143	0.99
P. P. 0.75	0.97	—	—	—	—
0.797	0.909	0.94	—	—	—
*0.80	0.90	0.94	—	—	—
*0.90	0.72	0.95	—	—	—
0.925	0.660	0.95	—	—	—
0.987	0.424	0.96	—	—	—

Tie-lines Tie-lines

Water	Water	Water	Water
0.19	0.99	0.88	0.05
0.33	0.99	0.86	0.15
0.43	0.99	0.78	0.20
0.52	0.92	0.73	0.30

(23) Logarithmic coördinates (24) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.284$	0.238	0.10	$\bar{1}.886$	0.840
0.20	$\bar{1}.409$	0.011	0.20	$\bar{1}.943$	0.545
0.30	$\bar{1}.495$	$\bar{1}.863$	0.30	0.054	0.422
0.40	$\bar{1}.573$	$\bar{1}.749$	0.40	0.140	0.316
0.50	$\bar{1}.646$	$\bar{1}.646$	0.50	0.222	0.222
0.60	$\bar{1}.725$	$\bar{1}.549$	0.60	0.287	0.110
0.70	$\bar{1}.832$	$\bar{1}.464$	0.70	0.354	$\bar{1}.986$
0.80	$\bar{1}.949$	$\bar{1}.347$	0.80	0.456	$\bar{1}.854$
0.90	0.097	$\bar{1}.143$	0.90	0.799	$\bar{1}.845$
P. P. —	$\bar{1}.888$	$\bar{1}.411$	P. P. —	0.239	0.204

TABLE V—(*Continued*)

(25) benzyl acetate alcohol			(26) ethyl propionate alcohol		
Water	Alcohol	Density	Water	Alcohol	Density
0.023	0.120	1.05	0.023	0.138	0.90
0.099	0.317	1.03	0.085	0.257	0.91
0.197	0.459	0.97	*0.10	0.27	0.90
*0.20	0.46	0.99	0.102	0.373	0.90
*0.30	0.58	0.97	*0.20	0.38	0.90
0.38	0.601	0.96	0.305	0.453	0.92
P. P. 0.32	0.60	—	*0.40	0.49	0.91
*0.40	0.69	0.95	0.494	0.520	0.92
0.415	0.705	0.95	*0.50	0.52	0.92
0.489	0.770	0.95	P. P. 0.54	0.53	—
*0.50	0.78	0.94	0.602	0.532	0.93
0.593	0.841	0.94	0.698	0.547	0.94
*0.60	0.85	0.94	*0.70	0.55	0.94
0.700	0.880	0.93	0.799	0.517	0.95
0.781	0.883	—	*0.90	0.46	0.96
*0.80	0.88	0.93	0.914	0.443	0.97
0.888	0.818	0.94	—	—	—
*0.90	0.80	0.94	—	—	—
0.959	0.665	0.95	—	—	—

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.00	0.93	0.95	0.02
0.03	0.73	0.92	0.13
0.11	0.58	0.86	0.14
0.17	0.47	0.83	0.24
		0.76	0.34
		0.67	0.41

(25) Logarithmic coördinates			(26) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.499$	0.453	0.10	$\bar{1}.569$	0.523
0.20	$\bar{1}.638$	0.240	0.20	$\bar{1}.721$	0.323
0.30	$\bar{1}.714$	0.082	0.30	$\bar{1}.824$	0.192
0.40	$\bar{1}.763$	$\bar{1}.939$	0.40	$\bar{1}.912$	0.088
0.50	$\bar{1}.807$	$\bar{1}.807$	0.50	$\bar{1}.983$	$\bar{1}.983$
0.60	$\bar{1}.849$	$\bar{1}.673$	0.60	0.054	$\bar{1}.878$
0.70	$\bar{1}.901$	$\bar{1}.533$	0.70	0.105	$\bar{1}.737$
0.80	$\bar{1}.959$	$\bar{1}.356$	0.80	0.190	$\bar{1}.587$
0.90	0.051	$\bar{1}.097$	0.90	0.291	$\bar{1}.337$
P. P. —	$\bar{1}.727$	0.054	P. P. —	0.008	$\bar{1}.939$

TABLE V—(*Continued*)

(27) ethyl butyrate alcohol			(28) benzyl ethyl ether alcohol		
Water	**Alcohol**	**Density**	**Water**	**Alcohol**	**Density**
0.030	0.166	0.90	0.029	0.189	0.94
0.097	0.314	0.90	*0.10	0.37	0.92
*0.10	0.32	—	0.108	0.381	0.92
0.200	0.483	0.88	0.191	0.528	0.92
0.300	0.567	0.89	*0.20	0.54	0.92
0.401	0.628	0.90	0.274	0.648	0.92
0.506	0.659	0.91	*0.30	0.67	0.91
P. P. 0.54	0.67	—	P. P. 0.33	0.71	—
0.598	0.684	0.92	*0.40	0.78	0.91
*0.60	0.69	0.92	0.410	0.790	0.91
0.703	0.693	0.93	0.494	0.874	—
0.807	0.684	0.94	*0.50	0.87	0.91
*0.90	0.63	0.94	0.594	0.930	0.92
0.910	0.603	0.95	*0.60	0.93	0.92
—	—	—	*0.70	0.96	0.92
—	—	—	0.711	0.960	0.92
—	—	—	0.802	0.952	0.92
—	—	—	*0.90	0.86	0.93
—	—	—	0.920	0.793	0.94

Tie-lines		Tie-lines	
Water	**Water**	**Water**	**Water**
0.96	0.00	0.00	0.73
0.93	0.05	0.03	0.70
0.89	0.11	0.15	0.52
0.81	0.25		
0.72	0.36		
0.62	0.45		

(27) Logarithmic coördinates			(28) Logarithmic coördinates		
Water	**Log $\frac{w}{a}$**	**Log $\frac{1-w}{a}$**	**Water**	**Log $\frac{w}{a}$**	**Log $\frac{1-w}{a}$**
0.10	$\bar{1}.495$	0.449	0.10	$\bar{1}.432$	0.386
0.20	$\bar{1}.617$	0.219	0.20	$\bar{1}.569$	0.171
0.30	$\bar{1}.723$	0.091	0.30	$\bar{1}.651$	0.019
0.40	$\bar{1}.804$	$\bar{1}.980$	0.40	$\bar{1}.710$	$\bar{1}.886$
0.50	$\bar{1}.880$	$\bar{1}.880$	0.50	$\bar{1}.759$	$\bar{1}.759$
0.60	0.939	$\bar{1}.763$	0.60	$\bar{1}.810$	$\bar{1}.634$
0.70	0.004	$\bar{1}.636$	0.70	$\bar{1}.863$	$\bar{1}.495$
0.80	0.008	$\bar{1}.475$	0.80	$\bar{1}.924$	$\bar{1}.322$
0.90	0.155	$\bar{1}.201$	0.90	0.020	$\bar{1}.065$
P. P. —	$\bar{1}.906$	$\bar{1}.837$	P. P. —	$\bar{1}.667$	$\bar{1}.975$

TABLE V—(*Continued*)

(29) isoamyl ether alcohol			(30) diethyl ketone alcohol		
Water	Alcohol	Density	Water	Alcohol	Density
0.042	0.368	0.81	0.062	0.136	0.85
*0.10	0.70	0.82	*0.10	0.19	0.85
P. P. 0.11	0.74	—	0.105	0.201	0.86
0.121	0.793	0.82	*0.20	0.31	0.87
*0.20	1.20	0.83	0.219	0.317	0.87
0.233	1.324	0.83	0.298	0.356	0.88
0.298	1.573	0.83	0.400	0.392	0.89
0.406	1.876	0.84	0.453	0.410	0.90
*0.50	1.98	0.84	0.501	0.411	0.91
0.590	2.188	0.85	0.542	0.415	0.92
*0.60	2.19	0.85	0.593	0.404	0.91
0.698	2.240	0.86	—	—	—
*0.80	2.14	0.87	—	—	—
0.819	2.102	0.88	—	—	—
*0.90	1.87	0.89	—	—	—
0.914	1.792	0.89	—	—	—

Tie-lines

Water	Water
0.72	0.00
0.50	0.00
0.28	0.00
0.24	0.01
0.21	0.02
0.19	0.03

(30) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.721$	0.675
0.20	$\bar{1}.810$	0.412
0.30	$\bar{1}.921$	0.289
0.40	0.008	0.185
0.50	0.085	0.085
0.60	0.167	0.004

(29) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.174$	0.129
0.20	$\bar{1}.222$	$\bar{1}.824$
0.30	$\bar{1}.281$	$\bar{1}.649$
0.40	$\bar{1}.330$	$\bar{1}.506$
0.50	$\bar{1}.402$	$\bar{1}.402$
0.60	$\bar{1}.438$	$\bar{1}.262$
0.70	$\bar{1}.495$	$\bar{1}.127$
0.80	$\bar{1}.573$	$\bar{2}.971$
0.90	$\bar{1}.682$	$\bar{2}.728$
P. P. —	$\bar{1}.172$	0.080

TABLE V—(*Continued*)

(31) hexane carbinol

Water	Carbinol	Density
0.067	4.280	—
*0.10	4.69	0.80
0.160	5.090	0.80
*0.20	5.26	0.80
0.309	5.710	0.82
*0.40	6.17	0.81
0.414	6.240	0.82
0.509	6.365	0.83
*0.60	6.33	0.83
0.652	6.241	0.83
0.670	6.222	—
*0.70	6.13	0.84
0.80	5.49	0.85
0.830	5.012	0.85
*0.90	4.01	0.86
0.905	3.912	0.87
0.984	1.759	0.91

(31) Logarithmic coördinates

Water	$\text{Log}\ \frac{w}{a}$	$\text{Log}\ \frac{1-w}{a}$
0.10	$\bar{2}.329$	$\bar{1}.283$
0.20	$\bar{2}.580$	$\bar{1}.182$
0.30	$\bar{2}.720$	$\bar{1}.088$
0.40	$\bar{2}.812$	$\bar{2}.988$
0.50	$\bar{2}.896$	$\bar{2}.896$
0.60	$\bar{2}.977$	$\bar{2}.801$
0.70	$\bar{1}.058$	$\bar{2}.690$
0.80	$\bar{1}.164$	$\bar{2}.551$
0.90	$\bar{1}.351$	$\bar{2}.397$

(32) hexane alcohol

Water	Alcohol	Density
P. P. 0.03	0.59	—
0.035	0.64	0.75
*0.10	1.30	0.77
0.134	1.64	0.79
0.173	1.899	0.79
*0.20	2.04	0.79
0.272	2.415	0.81
*0.30	2.45	0.81
0.389	2.712	0.82
*0.40	2.73	0.82
*0.50	2.93	0.83
0.525	2.960	0.83
0.575	3.000	0.83
*0.60	3.00	0.83
0.702	2.918	0.83
*0.80	2.75	0.85
0.815	2.720	0.86
0.895	2.278	0.86
*0.90	2.23	0.86
0.986	1.056	—

Tie-lines

Water	Water
0.11	0.00
0.07	0.00
0.05	0.01

TABLE V—(*Continued*)

(32) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.886$	$\bar{1}.840$
0.20	$\bar{2}.991$	$\bar{1}.594$
0.30	$\bar{1}.088$	$\bar{1}.456$
0.40	$\bar{1}.166$	$\bar{1}.342$
0.50	$\bar{1}.232$	$\bar{1}.232$
0.60	$\bar{1}.301$	$\bar{1}.125$
0.70	$\bar{1}.383$	$\bar{1}.015$
0.80	$\bar{1}.464$	$\bar{2}.862$
0.90	$\bar{1}.606$	$\bar{2}.652$
P. P. —	$\bar{2}.706$	0.216

(33) heptane carbinol

Water	Carbinol	Density
0.034	4.78	—
*0.10	5.55	0.80
0.126	5.93	0.80
0.207	6.36	0.82
*0.30	7.30	0.82
0.321	7.46	0.82
0.400	8.22	0.82
*0.50	8.76	0.82
0.520	8.80	0.83
*0.60	8.65	0.83
0.672	8.05	0.83
*0.70	7.78	0.83
0.802	6.71	0.84
*0.90	4.40	0.87
0.962	2.96	0.91

(33) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.256$	$\bar{1}.210$
0.20	$\bar{2}.497$	$\bar{1}.100$
0.30	$\bar{2}.614$	$\bar{2}.982$
0.40	$\bar{2}.687$	$\bar{2}.863$
0.50	$\bar{2}.757$	$\bar{2}.757$
0.60	$\bar{2}.841$	$\bar{2}.665$
0.70	$\bar{2}.954$	$\bar{2}.586$
0.80	$\bar{1}.076$	$\bar{2}.474$
0.90	$\bar{1}.311$	$\bar{2}.357$

(34) heptane alcohol

Water	Alcohol	Density
0.038	0.704	0.79
*0.10	1.44	0.80
0.118	1.685	0.80
0.202	2.375	0.82
*0.30	2.82	0.81
0.341	2.940	0.82
0.388	3.015	0.82
*0.40	3.06	0.82
*0.50	3.16	0.83
0.545	3.168	0.83
*0.60	3.17	0.84
*0.70	3.10	0.85
0.725	3.080	0.85
0.804	2.960	0.87
0.907	2.305	0.88

(34) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.842$	$\bar{1}.796$
0.20	$\bar{2}.926$	$\bar{1}.528$
0.30	$\bar{1}.027$	$\bar{1}.395$
0.40	$\bar{1}.116$	$\bar{1}.293$
0.50	$\bar{1}.199$	$\bar{1}.199$
0.60	$\bar{1}.277$	$\bar{1}.101$
0.70	$\bar{1}.354$	$\bar{2}.986$
0.80	$\bar{1}.432$	$\bar{2}.830$
0.90	$\bar{1}.593$	$\bar{2}.638$

TABLE V—(*Continued*)

(35) benzene alcohol (temp. 15°)

Water	Alcohol	Density
0.013	0.170	0.86
0.063	0.356	0.87
P. P. 0.10	0.50	0.86
0.183	0.708	0.85
*0.20	0.86	0.86
0.298	0.917	0.88
*0.30	0.91	0.88
*0.40	1.07	0.87
0.409	1.080	0.87
*0.50	1.18	0.87
0.517	1.188	0.88
*0.60	1.22	0.88
0.614	1.200	0.88
0.681	1.210	0.89
*0.70	1.21	0.89
0.799	1.130	0.89
0.898	0.972	0.92
*0.90	0.97	0.92
0.980	0.590	0.94

(36) toluene alcohol

Water	Alcohol	Density
0.052	0.388	0.87
0.083	0.538	0.86
*0.10	0.61	0.86
0.121	0.705	0.86
*0.20	0.95	0.86
*0.30	1.21	0.86
0.351	1.323	0.86
*0.40	1.41	0.86
*0.50	1.53	0.87
0.530	1.551	0.87
*0.60	1.59	0.87
*0.70	1.56	0.88
0.759	1.494	0.89
*0.80	1.44	0.89
0.837	1.380	0.89
*0.90	1.23	0.91
0.930	1.148	0.92
0.972	0.817	0.94
—	—	—

Tie-lines

Water	Water
0.04	0.18

(35) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.301$	0.255
0.20	$\bar{1}.438$	0.040
0.30	$\bar{1}.518$	$\bar{1}.886$
0.40	$\bar{1}.573$	$\bar{1}.749$
0.50	$\bar{1}.627$	$\bar{1}.627$
0.60	$\bar{1}.692$	$\bar{1}.516$
0.70	$\bar{1}.762$	$\bar{1}.394$
0.80	$\bar{1}.850$	$\bar{1}.248$
0.90	$\bar{1}.967$	$\bar{1}.013$
P. P. —	$\bar{1}.301$	0.255

(36) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.215$	0.169
0.20	$\bar{1}.323$	1.925
0.30	$\bar{1}.394$	$\bar{1}.762$
0.40	$\bar{1}.453$	$\bar{1}.629$
0.50	$\bar{1}.514$	$\bar{1}.514$
0.60	$\bar{1}.577$	$\bar{1}.401$
0.70	$\bar{1}.652$	$\bar{1}.284$
0.80	$\bar{1}.745$	$\bar{1}.143$
0.90	$\bar{1}.864$	$\bar{2}.910$

TABLE V—(*Continued*)

(37) *o*-xylene alcohol

Water	Alcohol	Density
0.029	0.352	0.89
P. P. 0.04	0.53	—
*0.10	0.93	0.87
0.129	1.075	0.87
0.214	1.320	0.87
*0.30	1.53	0.87
0.312	1.560	0.86
*0.40	1.72	0.87
0.484	1.845	0.87
*0.50	1.87	0.87
*0.60	1.96	0.88
0.628	1.955	0.88
*0.70	1.94	0.88
0.792	1.813	0.89
*0.80	1.81	0.89
0.900	1.640	0.90
0.969	1.190	0.93

Tie-lines

Water	Water
0.00	0.64
0.00	0.21
0.00	0.16
0.00	0.13
0.00	0.11
0.02	0.88

(37) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.032$	$\bar{1}.986$
0.20	$\bar{1}.180$	$\bar{1}.783$
0.30	$\bar{1}.292$	$\bar{1}.660$
0.40	$\bar{1}.367$	$\bar{1}.543$
0.50	$\bar{1}.427$	$\bar{1}.427$
0.60	$\bar{1}.486$	$\bar{1}.310$
0.70	$\bar{1}.557$	$\bar{1}.189$
0.80	$\bar{1}.645$	$\bar{1}.043$
0.90	$\bar{1}.739$	$\bar{2}.785$
P. P. —	$\bar{1}.878$	0.054

(38) *m*-xylene alcohol

Water	Alcohol	Density
0.033	0.388	0.88
0.098	0.800	0.87
*0.10	0.81	0.87
0.162	1.125	0.85
*0.20	1.30	0.85
0.289	1.590	0.85
*0.30	1.61	0.86
*0.40	1.77	0.86
0.408	1.775	0.86
*0.50	1.90	0.87
0.588	1.965	0.87
*0.60	1.98	0.87
*0.70	2.01	0.88
0.724	2.000	0.88
0.795	1.870	0.89
*0.80	1.87	0.89
0.898	1.530	0.90
*0.90	1.530	0.90
0.977	1.168	0.92

(38) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.092$	0.046
0.20	$\bar{1}.187$	$\bar{1}.789$
0.30	$\bar{1}.271$	$\bar{1}.639$
0.40	$\bar{1}.354$	$\bar{1}.530$
0.50	$\bar{1}.420$	$\bar{1}.420$
0.60	$\bar{1}.482$	$\bar{1}.305$
0.70	$\bar{1}.542$	$\bar{1}.174$
0.80	$\bar{1}.631$	$\bar{1}.029$
0.90	$\bar{1}.770$	$\bar{2}.815$

TABLE V—(*Continued*)

(39) *p*-xylene alcohol (temp. 15°)

Water	Alcohol	Density
0.034	0.306	0.84
0.074	0.531	0.85
P. P. 0.08	0.57	—
*0.10	0.65	0.85
0.121	0.760	0.86
*0.20	1.05	0.85
0.211	1.092	0.85
0.286	1.310	0.85
*0.30	1.35	0.85
*0.40	1.56	0.85
*0.50	1.68	0.86
0.524	1.730	0.86
*0.60	1.77	0.86
0.622	1.783	0.86
0.702	1.743	0.87
0.807	1.625	0.88
*0.90	1.39	0.89
0.912	1.348	0.89
0.985	0.863	0.93

Tie-lines

Water	Water
0.00	0.26
0.01	0.19
0.02	0.16
0.04	0.14

(39) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.187$	0.141
0.20	$\bar{1}.280$	$\bar{1}.881$
0.30	$\bar{1}.347$	$\bar{1}.715$
0.40	$\bar{1}.409$	$\bar{1}.585$
0.50	$\bar{1}.474$	$\bar{1}.474$
0.60	$\bar{1}.530$	$\bar{1}.354$
0.70	$\bar{1}.605$	$\bar{1}.237$
0.80	$\bar{1}.694$	$\bar{1}.092$
0.90	$\bar{1}.811$	$\bar{2}.857$
P. P. —	$\bar{1}.147$	0.208

(40) mesitylene alcohol

Water	Alcohol	Density
P. P. 0.03	0.48	—
0.037	0.516	0.86
0.090	0.981	0.86
*0.10	1.09	0.85
0.164	1.473	0.85
*0.20	1.66	0.84
0.298	2.030	0.85
*0.30	2.04	0.85
*0.40	2.32	0.85
0.429	2.365	0.85
*0.50	2.52	0.85
*0.60	2.64	0.86
*0.70	2.68	0.87
0.714	2.670	0.87
0.801	2.490	0.87
0.890	2.325	0.89
*0.90	2.28	0.89
0.949	1.615	0.90

Tie-lines

Water	Water
0.00	0.15
0.00	0.10
0.00	0.08

(40) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.963$	$\bar{1}.917$
0.20	$\bar{1}.081$	$\bar{1}.683$
0.30	$\bar{1}.168$	$\bar{1}.536$
0.40	$\bar{1}.237$	$\bar{1}.413$
0.50	$\bar{1}.298$	$\bar{1}.298$
0.60	$\bar{1}.357$	$\bar{1}.181$
0.70	$\bar{1}.417$	$\bar{1}.049$
0.80	$\bar{1}.507$	$\bar{2}.905$
0.90	$\bar{1}.596$	$\bar{2}.642$
P. P. —	$\bar{2}.796$	0.306

TABLE V—(*Continued*)

(41) pinene alcohol			(42) benzaldehyde alcohol		
Water	Alcohol	Density	Water	Alcohol	Density
0.010	0.268	0.87	0.043	0.159	1.02
P. P. 0.015	0.47	—	0.102	0.283	1.01
0.055	1.001	0.85	*0.20	0.42	0.99
0.103	1.595	0.85	0.211	0.441	0.99
0.205	2.268	0.84	0.295	0.520	0.98
*0.30	2.67	0.84	*0.30	0.55	0.98
0.317	2.704	0.85	0.402	0.601	0.97
0.395	2.924	0.84	P. P. 0.43	0.61	—
*0.40	2.94	0.85	0.504	0.643	0.96
0.507	3.135	0.85	0.606	0.681	0.95
0.607	3.126	0.86	0.702	0.701	0.95
0.707	3.038	0.86	*0.80	0.67	0.95
0.806	2.799	0.87	0.817	0.675	0.95
0.906	2.331	0.89	0.898	0.615	0.96
0.965	1.639	0.91	*0.90	0.61	0.96
—	—	—	0.969	0.461	0.97

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.00	0.06	0.04	0.98
0.00	0.05	0.09	0.96
0.00	0.04	0.10	0.82
0.00	0.03	0.15	0.76
0.01	0.02	0.26	0.63
		0.31	0.57

(41) Logarithmic coördinates			(42) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{2}.799$	$\bar{1}.752$	0.10	$\bar{1}.548$	0.502
0.20	$\bar{2}.945$	$\bar{1}.547$	0.20	$\bar{1}.648$	0.250
0.30	$\bar{1}.051$	$\bar{1}.419$	0.30	$\bar{1}.737$	0.105
0.40	$\bar{1}.134$	$\bar{1}.310$	0.40	$\bar{1}.823$	$\bar{1}.999$
0.50	$\bar{1}.203$	$\bar{1}.203$	0.50	$\bar{1}.893$	$\bar{1}.893$
0.60	$\bar{1}.283$	$\bar{1}.107$	0.60	$\bar{1}.946$	$\bar{1}.770$
0.70	$\bar{1}.362$	$\bar{2}.994$	0.70	$\bar{1}.999$	$\bar{1}.631$
0.80	$\bar{1}.456$	$\bar{2}.854$	0.80	0.077	$\bar{1}.475$
0.90	$\bar{1}.587$	$\bar{2}.633$	0.90	0.169	$\bar{1}.215$
P. P. —	$\bar{2}.504$	0.321	P. P. —	$\bar{1}.848$	$\bar{1}.971$

TABLE V—(*Continued*)

(43) methyl aniline alcohol | (44) *p*-nitrotoluene alcohol

Water	Alcohol	Density	Water	Alcohol	Density
0.041	0.218	0.96	0.022	0.253	1.08
*0.10	0.37	0.95	P. P. 0.05	0.50	—
0.111	0.405	0.95	0.090	0.781	0.98
0.205	0.555	0.93	*0.10	0.84	0.97
*0.30	0.68	0.93	*0.20	1.29	0.96
0.331	0.721	0.93	0.235	1.40	0.93
P. P. 0.34	0.72	—	*0.30	1.57	0.92
0.392	0.756	0.93	0.337	1.649	0.92
*0.40	0.76	0.93	*0.40	1.73	0.91
0.498	0.835	0.93	0.411	1.767	0.91
*0.50	0.84	0.93	0.494	1.782	0.91
0.599	0.892	0.93	0.602	1.868	0.91
*0.60	0.89	0.93	0.706	1.816	0.91
0.697	0.901	0.93	*0.80	1.63	0.91
*0.70	0.91	0.93	0.809	1.607	0.91
*0.80	0.87	0.94	0.898	1.395	0.92
0.813	0.856	0.94	*0.90	1.30	0.92
0.902	0.734	0.95	—	—	—
0.959	0.581	0.96	0.944	1.105	0.93

Tie-lines | Tie-lines

Water	Water	Water	Water
0.67	0.00	0.00	0.14
0.59	0.05	0.02	0.10
0.55	0.12	0.03	0.08
0.51	0.16		
0.42	0.23		

(43) Logarithmic coördinates | (44) Logarithmic coördinates

Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.432$	0.386	0.10	$\bar{1}.076$	0.030
0.20	$\bar{1}.561$	0.163	0.20	$\bar{1}.190$	$\bar{1}.793$
0.30	$\bar{1}.645$	0.013	0.30	$\bar{1}.281$	$\bar{1}.649$
0.40	$\bar{1}.721$	$\bar{1}.897$	0.40	$\bar{1}.364$	$\bar{1}.540$
0.50	$\bar{1}.775$	$\bar{1}.775$	0.50	$\bar{1}.449$	$\bar{1}.449$
0.60	$\bar{1}.829$	$\bar{1}.653$	0.60	$\bar{1}.509$	$\bar{1}.333$
0.70	$\bar{1}.886$	$\bar{1}.518$	0.70	$\bar{1}.585$	$\bar{1}.217$
0.80	$\bar{1}.964$	$\bar{1}.362$	0.80	$\bar{1}.691$	$\bar{1}.089$
0.90	0.091	$\bar{1}.137$	0.90	$\bar{1}.840$	$\bar{2}.886$
P. P. —	$\bar{1}.674$	$\bar{1}.962$	P. P. —	$\bar{1}.000$	0.279

TABLE V—(*Continued*)

(45) *o*-toluidine alcohol			(46) isobutyl alcohol alcohol		
Water	Alcohol	Density	Water	Alcohol	Density
0.046	0.025	1.01	*0.30	0.13	0.87
*0.10	0.21	0.93	0.313	0.141	0.87
0.105	0.219	0.93	0.411	0.177	0.89
*0.20	0.32	0.97	0.498	0.194	0.90
0.222	0.346	0.97	*0.50	0.20	0.90
0.298	0.404	0.96	*0.60	0.20	0.92
*0.30	0.41	0.96	0.613	0.204	0.92
0.402	0.455	0.96	P. P. 0.65	0.21	—
*0.50	0.48	0.96	0.696	0.205	0.94
0.546	0.492	0.95	*0.70	0.21	0.94
0.580	0.493	0.95	*0.80	0.20	0.95
*0.60	0.50	0.96	0.868	0.189	0.96
0.698	0.499	0.96	—	—	—
*0.70	0.50	0.96	—	—	—
*0.80	0.49	0.96	—	—	—
0.810	0.485	0.96	—	—	—
0.902	0.462	0.98	—	—	—
0.973	0.262	—	—	—	—

Tie-lines

Water	Water
0.87	0.28
0.83	0.41
0.81	0.46
0.80	0.50

(45) Logarithmic coördinates			(46) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.678$	0.632	0.30	0.363	0.731
0.20	$\bar{1}.796$	0.398	0.40	0.372	0.548
0.30	$\bar{1}.864$	0.232	0.50	0.398	0.398
0.40	$\bar{1}.944$	0.120	0.60	0.477	0.301
0.50	0.018	0.018	0.70	0.533	0.165
0.60	0.079	$\bar{1}.903$	0.80	0.602	0.000
0.70	0.146	$\bar{1}.778$	0.868	0.662	$\bar{1}.844$
0.80	0.213	$\bar{1}.611$	P. P. —	0.491	0.222
0.90	0.291	$\bar{1}.337$	—	—	—

TABLE V—(*Continued*)

(47) isoamyl alcohol alcohol			(48) benzyl alcohol alcohol		
Water	**Alcohol**	**Density**	**Water**	**Alcohol**	**Density**
0.097	0.116	0.84	*0.10	0.13	1.03
*0.10	0.12	0.84	0.130	0.153	1.02
0.203	0.258	0.85	*0.20	0.26	1.00
0.306	0.396	0.86	0.209	0.268	1.00
0.398	0.427	0.88	0.295	0.347	0.98
0.503	0.449	0.89	*0.30	0.35	0.98
0.601	0.453	0.90	*0.40	0.39	0.98
0.706	0.434	0.92	0.422	0.392	0.98
P. P. 0.73	0.43	—	*0.50	0.40	0.97
0.804	0.411	0.94	0.512	0.403	0.97
0.900	0.369	0.96	*0.60	0.41	0.97
—	—	—	P. P. 0.62	0.42	—
—	—	—	0.621	0.417	0.98
—	—	—	*0.70	0.41	0.97
—	—	—	0.712	0.404	0.97
—	—	—	0.806	0.388	0.97
—	—	—	0.898	0.352	0.97
—	—	—	*0.90	0.35	0.98
—	—	—	0.960	0.139	0.99

Tie-lines		Tie-lines	
Water	**Water**	**Water**	**Water**
0.95	0.10	0.33	0.92
0.94	0.31	0.41	0.83
0.92	0.40		
0.87	0.53		
0.83	0.63		

(47) Logarithmic coördinates			(48) Logarithmic coördinates		
Water	**Log $\frac{w}{a}$**	**Log $\frac{1-w}{a}$**	**Water**	**Log $\frac{w}{a}$**	**Log $\frac{1-w}{a}$**
0.10	$\bar{1}.921$	0.875	0.10	$\bar{1}.886$	0.840
0.20	$\bar{1}.891$	0.493	0.20	$\bar{1}.880$	0.488
0.30	$\bar{1}.921$	0.288	0.30	$\bar{1}.933$	0.301
0.40	$\bar{1}.972$	0.148	0.40	0.011	0.187
0.50	0.047	0.047	0.50	0.097	0.097
0.60	0.122	$\bar{1}.946$	0.60	0.165	$\bar{1}.989$
0.70	0.209	$\bar{1}.841$	0.70	0.232	$\bar{1}.864$
0.80	0.290	$\bar{1}.688$	0.80	0.312	$\bar{1}.710$
0.90	0.387	$\bar{1}.433$	0.90	0.410	$\bar{1}.456$
P. P. —	0.230	$\bar{1}.798$	P. P. —	0.169	$\bar{1}.957$

TABLE V—(*Continued*)

(49) phenetol alcohol			(50) nitrobenzene alcohol (temp. 15°)		
Water	Alcohol	Density	Water	Alcohol	Density
0.018	0.157	0.96	0.035	0.248	1.08
P. P. 0.10	0.55	—	P. P. 0.09	0.49	—
0.103	0.554	0.93	*0.10	0.53	1.02
0.202	0.916	0.90	0.109	0.558	1.02
0.293	1.170	0.90	*0.20	0.86	0.97
*0.30	1.18	0.90	0.214	0.901	0.97
0.394	1.380	0.89	*0.30	1.09	0.94
*0.40	1.39	0.89	0.316	1.112	0.94
0.505	1.518	0.89	0.406	1.238	0.93
0.601	1.560	0.89	0.494	1.300	0.92
0.694	1.545	0.90	*0.50	1.31	0.92
*0.70	1.54	0.90	*0.60	1.34	0.92
0.802	1.449	0.91	0.636	1.333	0.92
*0.90	1.21	0.92	0.694	1.305	0.91
0.918	1.156	0.93	*0.70	1.30	0.91
—	—	—	0.806	1.212	0.92
—	—	—	*0.90	0.98	0.93
—	—	—	0.909	0.940	0.93
—	—	—	0.980	0.601	0.95

Tie-lines		Tie-lines	
Water	Water	Water	Water
0.00	0.38	0.00	0.42
0.01	0.26	0.00	0.33
0.04	0.18	0.01	0.24
0.05	0.17	0.03	0.16
0.06	0.15	0.05	0.14

(49) Logarithmic coördinates			(50) Logarithmic coördinates		
Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$	Water	Log $\frac{w}{a}$	Log $\frac{1-w}{a}$
0.10	$\bar{1}.260$	0.214	0.10	$\bar{1}.276$	0.230
0.20	$\bar{1}.337$	$\bar{1}.939$	0.20	$\bar{1}.367$	$\bar{1}.969$
0.30	$\bar{1}.405$	$\bar{1}.773$	0.30	$\bar{1}.440$	$\bar{1}.807$
0.40	$\bar{1}.459$	$\bar{1}.636$	0.40	$\bar{1}.512$	$\bar{1}.688$
0.50	$\bar{1}.517$	$\bar{1}.517$	0.50	$\bar{1}.582$	$\bar{1}.582$
0.60	$\bar{1}.585$	$\bar{1}.409$	0.60	$\bar{1}.651$	$\bar{1}.475$
0.70	$\bar{1}.658$	$\bar{1}.290$	0.70	$\bar{1}.731$	$\bar{1}.363$
0.80	$\bar{1}.742$	$\bar{1}.140$	0.80	$\bar{1}.820$	$\bar{1}.218$
0.90	$\bar{1}.871$	$\bar{2}.917$	0.90	$\bar{1}.963$	$\bar{1}.009$
P. P. —	$\bar{1}.260$	$\bar{2}.214$	P. P. —	$\bar{1}.264$	0.269

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Tuchschmidt and Follenius: Ber. chim. Ges. Berlin, 4, 583 (1871).	Water, alcohol, carb. bisulphide.
Berthelot and Jungfleisch: Ann. Chim. Phys., (4) 26, 396 (1872).	Acetic acid, water, ether; bromine, water, carb. bisulphide.
Duclaux: Ann. Chim. Phys., (5) 7, 264 (1876).	Benzene, water, acetic acid; amyl alcohol, water, alcohol; amyl alcohol, water, acetic acid; ether, water, acetic acid.
Draper: Chem. News, 35, 87 (——).	Water, ether, hydroch. acid.
Traube and Neuberg: Zeit. Phys. Chem., 1, 509 (1887).	Water, alcohol, ammon. sulph., etc.
Wright and Collaborators: Proc. Roy. Soc., 45, 461 (1889); 48, 25 (1890); 49, 156 and 174 (1891); 50, 37. (1891); 52, 11 (1892); 55, 130 (1894).	Alloys.
Proc. Roy. Soc., 49, 183 (1891).	Water, chloroform, acetic acid.
Bodländer: Zeit. phys. Chem., 7, 318 (1891).	Water, alcohol, amm. sulph.
Pfeiffer: Zeit. phys. Chem., 9, 469 (1892).	Water and alcohol with the following: mono-, di- and trichloracetic ester; amyl alcohol; methyl, ethyl, propyl, butyl and amyl formate; methyl, ethyl, propyl, butyl and amyl acetate; methyl, ethyl and propyl propionate; methyl, ethyl and propyl butyrate; methyl and ethyl valerate.
Schunke: Zeit. phys. Chem., 14, 331 (1894)	Water, ether, hydrochl. acid.
Linebarger: Am. Chem. Jour., 14, 380 (1892).	Water and alcohol with pot. carbonate, sod. carbonate, amm. sulphate, manganous sulphate; water and acetone with the same salts.
Krug and McElroy: Jour. Anal. Chem., 6, 153 (1892).	Water and acetone with sugar, dextrose, maltose, sucrose.
Bancroft: Phys. Review, 3, 21, 114 and 193 (1895); Jour. Phys. Chem., 1, 34, and 760 (1896); 3, 217 (1899).	Chloroform and water with alcohol, carbinol and acetone; benzene and water with alcohol, carbinol and ace-

Author and reference.	Ternary system.
	tone; ether and water with alcohol and carbinol; ethyl acetate and water with alcohol, carbinol and acetone; alcohol and water with the following: carbon bisulphid, methyl valerate, ethyl valerate, methyl butyrate, ethyl butyrate, amyl alcohol, mono-, di- and trichloracetic ester, ethyl isovalerate, isoamyl acetate, propyl butyrate, ethyl propionate, propyl propionate, propyl acetate, butyl acetate, amyl acetate, propyl formate, butyl formate, amyl formate.
Taylor: Jour. Phys. Chem., 1, 301 (1896); Ibid., 1, 461.	Water, benzene, alcohol (Binodal curve); water, benzene, alcohol (Tie-lines.
Schreinemakers: Zeit. phys. Chem., 22, 93 and 515 (1897).	Theory.
23, 417 (1897).	Water, sod. chloride, succinonitrile (Tie-lines and binodal curve).
23, 649 (1897).	Water, ether, hydrochl. acid (exp. data of Draper and Schunke); water, alcohol, amm. sulphate (exp. data of Bodländer and Traube and Neuberg).
25, 543 (1898).	Water, ether, succinonitrile.
26, 237 (1898).	Water, benzoic acid, succinonitrile.
27, 95 (1898).	Water, alcohol, succinontrile.
29, 577 (1899).	Water, phenol, aniline.
30, 460 (1899).	Water, phenol, salt.
33, 74 (1900).	Water and phenol with tartaric and racemic acids.
33, 78 (1900).	Water, phenol, acetone.
39, 485 (1902).	Water, phenol, acetone (Tie-lines).
43, 305 (1903) (exps. by Middelberg).	Water, silver nitrate, succinonitrile.
Waddell: Jour. Phys. Chem., 2, 233 (1898).	Benzene, water, acetic acid.
Snell: Jour. Phys. Chem., 2, 457 (1898).	Pot. chloride, acetone, water; water, alcohol, mang. sulphate (exp. data of Schiff and Linebarger); water, alcohol, amm. sulphate (exp. data of Traube and Neuberg).
Lincoln: Jour. Phys. Chem., 4, 161 (1900); Ibid., 8, 248 (1904).	Water, benzene, alcohol; water, benzene, acetic acid.

Author and reference.	Ternary system.
Meerburg: Zeit. phys. Chem., 40, 64 (1902).	Triethylamine and water with alcohol, ether, phenol.
Bell: Jour. Phys. Chem., 9, 531 (1905).	Water, alcohol, pot. carb., etc. (exp. data of Linebarger); water, acetone, sugar, etc. (exp. data of Krug and McElroy); water, acetone, pot. carbonate; water, alcohol, pot. carbonate; water, acetic acid, sod. carbonate; water, acetic acid, sugar; water, acetic acid, naph.; water, acetic acid, anethol; water, alcohol, benzophenone; water, acetic acid, benzophenone.
Miller and McPherson: Jour. Phys. Chem., 12, 709 (1908).	Water, chloroform, alcohol.

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University of Toronto,
May, 1910

NEW BOOKS

The Corrosion and Preservation of Iron and Steel. *By Allerton S. Cushman and Henry A. Gardner. 16 × 24 cm; pp. xx + 373. New York: McGraw-Hill Book Company, 1910. Price: $4.00 net.*—The following quotation, p. xix, shows the aim of the book.

"The tendency to rust is a characteristic inherent in the element known as iron, and will in all probability never be entirely overcome. Nevertheless, it is perfectly well known that there is the greatest variability both in the manner and rapidity with which different specimens and types of this metal and its alloys suffer from corrosion. Before substantial advance in the manufacture of resistant types and in the protection of all types can be made, a thorough understanding of the mechanism of corrosion and the function of protective coatings must be obtained.

"The demand of the engineer and architect for the most advanced knowledge regarding protective coatings for iron comes as a result of the failure of many types of paint now in use. Technical literature is replete with information regarding the protection of iron, but probably the most remarkable advance in knowledge of this subject has taken place during the last few years, and almost wholly as a result of a well-planned series of investigations recently undertaken by a number of independent workers. The aim of the authors is to present the latest developments on this phase of the subject in a general way so that the underlying principles which govern corrosion can be applied by each investigator to his own particular problem.

"So diverse a subject as the corrosion and preservation of iron would become encyclopedic, if the attempt were made to take up every phase in detail, or to abstract the literature of the subject from the technical and scientific journals of the world. The protection of boiler tubes presents a very different problem from the protection of bridge structures, and yet the same main principles can be applied to the consideration of each case. It is this point that the authors have had in mind, and while a number of specific cases of corrosion are presented and discussed the main object has been to treat the subject in a general way. For this reason no separate chapters are included on special phases of the problem, such for instance as the corrosion of boilers, the corrosion of fence wire, or the corrosion of ships, bottoms. All these subjects, as well as many other special cases of corrosion, are, however, brought up and treated as special instances to which the general discussion applies. On this account those readers who propose to use this work as a reference book in special cases of inquiry will depend upon the index to the volume rather than upon chapter headings to guide them."

The chapters are entitled: the problem of corrosion; theory of solution; theory of corrosion; application of electrolytic theory; the inhibition and stimulation of corrosion; the technical protection of iron and steel; the relation of pigments to the corrosion of iron; recent field tests on protective coatings for iron and steel; paints for various purposes; the testing and design of protective paints; properties of pigments; properties of paint vehicles.

The recent work on the corrosion of iron and steel has placed the electrolytic theory of corrosion on so sound an experimental basis that the time has come when the subject should be presented in book form. This is the book and the authors have done their task well. The subject is presented clearly, though not very concisely; and the chapter on the inhibition and stimulation of corrosion will be especially helpful. An interesting point is the observation, p. 108, that *busy* iron does not rust, presumably owing to the fact that "frequent and recurrent vibration was sufficient to break up specific points of potential difference on the surface."

"The case of steel rails is an interesting one, showing as it does, the effect of vibration on rusting. A rail which has been in service, but has been laid to one side, will rust all over, but especially at the ends where the vibration of the fish-plates has removed the mill-scale, and on the smooth top of the head. On the other hand, a quite remarkable fact, which has been universally confirmed and can be easily observed by any one, is that a rail while *in service* will not rust nearly as rapidly as one which is lying out of service. The rusting takes place in proportion to the service, and lines over which fast trains pass frequently, causing much vibration, will practically not rust at all, whereas the rails of turnouts or sidings, which undergo less service, and that of a slow nature, will rust to a certain extent. One observer (J. M. Heppel) has reported the case of some rails at Madras, India, which lost three pounds to the yard lying in the yard exposed to the sea air, while the rails in service nearby were not perceptibly affected. The top of a rail is compressed and smoothed down in service by the grinding of wheel tires, for there is always a certain amount of slip, especially during acceleration and retardation. Galvanic action between the smooth head of the rail and the rest of it has been suggested to explain this immunity from rust, but it is not at all likely that the foot would owe its protection to the thin stratum of denser metal so far removed from it. If that dense skin on the top of the rail were not crushed beyond its elastic limit, it would, on the contrary, tend to accelerate the corrosion of the steel in contact with it. The real reason for this difference of behavior seems to lie in the observed fact that oxidation is apparently arrested, or at least greatly retarded, by vibration. Explanation seems to stop at this point, but a simple theory can be built on the assumption that the vibration causes a shedding of the rust as soon as it is formed on the spots that are not protected by mill-scale, and there is, therefore, no acceleration of the action due to the accumulation of spongy and electro-negative rust. The average speed of corrosion of a vibrating body would be that of the formation of a first film of rust. Most of the actual rust on rails is probably due to the rapid evaporation of rain on the surface. In the case of rails in service, the first film of rust would be confined to bare spots and cracks in the mill-scale, and the vibration would prevent its working its way under the mill-scale as would happen if the rail were at rest. The top of the rail being denser might be expected to resist corrosion better when the rail is out of use; such is not the case, however. The surface has not only been subjected to hammering and crushing, but also to abrasion and rolling, and it has become short and crackeled and sometimes exfoliated; once laid aside, the smooth top of an old rail rusts very rapidly."

The following quotation from Toch, p. 274, is interesting. "By the use of China wood oil, paints are made which dry in damp atmospheres. The advantage which the Chinese and Japanese have had over the Europeans on this subject has been recognized for a long time. It is now known to have been due to their knowledge of the proper manipulation of China wood oil. For the making of marine paints and waterproof paints, China wood oil is indispensable."

On p. 30 there is an unimportant error in that aluminum is placed after zinc in the electrochemical series rather than before it.

The reviewer would have liked to see somewhere a definite statement that electromotive force measurements on polished pieces of metal indicate only the initial tendency to corrode and do not necessarily show anything in regard to the actual chemical corrosion which will take place in any solution. Striking instances of this are aluminum and nickel. Nickel should corrode practically as readily as iron while aluminum should corrode much more readily. This is true so long as we are dealing with the first traces of corrosion; but it is not true for experiments running any length of time. The oxide film acts as a protective coating in the case of nickel and of aluminum while it does not do so in the case of iron. In the case of some of the brass alloys, certain phases do not corrode readily because a protecting film of stannic oxide is formed.

Wilder D. Bancroft

Metallography. *By Cecil H. Desch. Edited by William Ramsay. 12 × 19 cm; pp. viii + 429. New York: Longmans, Green and Co., 1910. Price: $3.00 net.*—The subject is treated under the general headings: the diagram of thermal equilibrium; practical pyrometry and thermal analysis; the preparation of micro-sections; the microscopical examination of prepared sections; the crystallization of metals and alloys; undercooling and the metastable state; diffusion in the solid state; the physical properties of alloys; electromotive force and corrosion; the construction of the equilibrium diagram; the molecular condition of metals in alloys and the nature of intermetallic compounds; the plastic deformation of metals and alloys; the metallography of iron and steel; the metallography of industrial alloys; list of systems.

In most respects this book is very good indeed. The general account of thermal equilibrium is clear; attention is called to the inaccuracy of Tammann's method of thermal analysis; the chapter on pyrometry is good, though one is sceptical as to the statement, p. *121*, that the Morse pyrometer "is readily calibrated by observing a series of melting points of pure metals." The chapter on the preparation of micro-sections will be found useful as will also the chapter on the microscopical examination of prepared sections. The discussion of the crystallization of metals is exceptionally good and one would have been glad to have had more space given to the theory of "etching-pits."

Because Roberts-Austen found that solid gold diffuses into solid lead, most people draw the conclusion that any solid metal will diffuse into any other in time. The author does not make this mistake and says, p. *222*, that "the formation of a solid solution must be a necessary condition of true diffusion in an alloy. The author has perhaps gone to the other extreme. Equilibrium will also be reached if a compound is formed, though of course one might claim that that was not true diffusion.

Under physical properties, the author takes up density, thermal expansibility, hardness, electrical conductivity, thermoelectric power, and magnetic properties; but not tensile strength. The section on magnetic properties is excellent as far as it goes, though the reviewer would have welcomed an attempt at greater definiteness.

Under corrosion the author cites the work of Curry, of Lincoln, and of Rowland. He seems to think that the addition of small amounts of tin to brass should lessen the chemical corrosion by sea water; but he gives no reason for this and the point does not seem to be well taken. In the section on "the chemical examination of residues," the reviewer would have liked more references to the literature.

The chapter on the plastic deformation of metals is an excellent one. In the chapter on iron and steel the author gives Upton's diagram, of which he apparently approves, p. 379, though he finds it "difficult to believe that the beautifully defined eutectic structure found in white cast-irons is not a true eutectic, but a solid solution in a state of imperfect equilibrium."

There are one or two points to which the reviewer takes exception. On p. 319 the author implies that the quenching experiments of Heycock and Neville gave results of great accuracy. This is a mistake in so far as the determination of the solidus is concerned. The freezing point measurements of Heycock and Neville were extremely accurate; but their quenching experiments were not. Heycock and Neville let their alloys cool at a moderate rate to a given temperature and then quenched. The moderate rate of cooling gave them fairly large crystals; but it did not necessarily give them equilibrium conditions. The only way in which equilibrium conditions can be obtained is by chill-casting the alloy, annealing to equilibrium at the desired temperature and then quenching from that temperature. The inadequacy of Heycock and Neville's method is shown by the fact that they were unable to straighten out the β and γ fields in the copper-tin alloys, and also by the fact that they called the δ crystals Cu_4Sn.

On p. 277 the author says that "the electric potential assumed by an alloy in contact with an electrolyte is a property of high diagnostic value in the study of constitution." As a matter of fact, the measurement of electromotive force is of no value whatsoever, except in the very simplest cases. It enables us to find Cu_3Sn, a compound which nobody could miss under any circumstances. It does not help us in the slightest with the β, γ and δ crystals however. When the number of possible solid phases does not exceed three, the measurement of electromotive force is a tedious and unsatisfactory way of confirming what has already been found without trouble by the microscopic examination. In all other cases the method breaks down completely.

The reviewer would have liked to have seen a more detailed statement of how one determined the composition of a given solid phase by microscopical examination. It is very doubtful whether anybody could find out how to do it from anything in the book itself.

The experimental evidence is entirely against the author's view, p. 316, that errors from overheating are of the same magnitude as those from supercooling. *Wilder D. Bancroft*

Leçons sur les Alliages métalliques. *By J. Cavalier. 16 × 25 cm; pp. xix + 466. Paris: Vuibert et Nony, 1909. Price: paper, 12 francs.*—The first part of the book is introductory and deals with the chemical, thermal and metallographical study of alloys in general, and also with the physical and mechanical properties. In the second portion the author applies the knowledge previously acquired to selected concrete cases.

In some respects the book is very good. The pages on the method of residues, pp. 42–46, are clear and to the point. The bearing of surface tension, electromotive forces, etc., upon the application of the phase rule, p. 68, is brought out more clearly than is usually the case. The section on magnetism, pp. 170–176, is distinctly good and the author recognizes explicitly, p. 371, that there must be a δ iron above 1280° though he does not know that this modification was apparently prepared by Howe without recognizing it.

The diagram on p. 265 can be recommended for study to anybody who believes in the great value of electromotive force measurements or density determinations as a means of working out a complete temperature-connection diagram. The remarks on Chinese gongs, p. 274, ought to be helpful to some one. Guillaume's hypothesis in regard to the Heusler alloys, p. 416, is an interesting one, though it is not clear why it should not be tested and either proved or disproved.

The author is not familiar with Curry's work on the aluminum-copper alloys nor with that of Upton on the carbon steels. The principle of equivalence in the ternary brasses, p. 312, is certainly not exact. It would have been better to have brought out more clearly the relation or lack of relation between the diagram and the tensile strength or ductility in the cases of the bronzes and brasses. It is only by getting down to definite statements that we can prove or disprove anything. The addition of nickel is not necessary in order to obtain a plastic bronze with a high lead content, p. 279. It is solely a question of suitable stirring and of chill-casting. *Wilder D. Bancroft*

Die physikalisch-chemischen Eigenschaften der Legierungen. *By Bernhard Dessau. (Die Wissenschaft. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 33). 13 × 21 cm; pp. vi + 208. Braunschweig: F. Vieweg und Sohn, 1910. Price: paper, 7 marks; linen, 8 marks.*—This book is not likely to be very helpful. The author is a firm believer in Tammann's method of thermal analysis and is not familiar with its limitations. There is nothing to show how the microscopical method is actually to be used. No stress is laid on the importance of annealing and quenching. When speaking of the copper-tin diagram, p. 163, he says that "the discrepancies between the results of different investigations are unquestionably due in part to the different conditions under which the alloys solidified and cooled." This is quite true but the matter should not have been left there. The conditions were given and the author should have pointed out which experiments were carried out in the right way and which were not. As it is he does not get beyond Heycock and Neville's diagram for bronze.

Upton's diagram for iron and carbon is not mentioned. The chapter on magnetism is very poor. The author seems to think, p. 206, that the results obtained by measuring the electromotive force of unannealed alloys are more likely to be right than those obtained by thermal analysis or by microscopical examination.

Under tensile strengths the author cites Thurston's data instead of the more recent work. Thurston did not work with pure materials and he made no attempt to determine maximum tensile strengths. He was studying the results that might be expected from ordinary foundry practice. *W. D. B.*

Zur Kenntnis des Gerbprozesses. *By Johann von Schroeder. Sonderausgabe aus den Kolloidchemischen Beiheften. Monographien zur reinen und angewandten Kolloidchemie. Herausgegeben von Wolfgang Ostwald. Band I. 15 × 24 cm; pp. 58. Dresden: Theodor Steinkopff, 1909. Price: paper, 1.50 marks.*—Pulverized hide adsorbs no tannin from an alcoholic solution and is consequently not changed to leather. Tannin is adsorbed from an aqueous solution, but can at first be washed out to some extent. In the course of time the hide changes under the influence of the tannin into a less soluble form from which the tannin cannot be extracted. This insoluble or coagulated hide is leather. If the hide is made insoluble by treatment with formaldehyde, it loses most of its power to adsorb tannin.

When the pulverized hide is not sterilized, a good deal of the tannin is oxidized to gallic acid, presumably by bacteria. This change must be kept in mind and allowed for if one is trying to construct an adsorption isotherm.

The author made some experiments on the effect of tannin upon gelatine. He found that there was a striking parallelism between the adsorption of tannin by hides and the precipitation of gelatine by tannin. Pulverized hide, which has been treated with ammonium carbonate, does not adsorb tannin readily and tannin does not precipitate a neutral gelatine. Alcoholic tannin solution does not precipitate gelatine and does not react with hides. Tannin makes gelatine less soluble after a while and it is then much more difficult to wash the tannin out of the gelatine.

The effect of acetic acid is the same for the adsorption of tannin by hides and by gelatine; but sulphuric acid acts differently in the two cases.

Wilder D. Bancroft

Kolloidchemische Beihefte. (*Ergänzungshefte zur Kolloid-Zeitschrift*). *Monographien zur reinen angewandten Kolloichemie. Herausgegeben von Wolfgang Ostwald. Band I: Heft 1 u. 2. 16 × 23 cm; pp. 92. Dresden: Theodor Steinkopff. Price: paper, 1.20 marks.*—In this series it is intended to publish longer papers which could not appear in a single issue of the *Kolloid-Zeitschrift*. To the reviewer it would seem wiser to enlarge the latter, but there are doubtless special reasons in favor of the course adopted. The first paper in the series is by Johann von Schroeder on the "Theory of Tanning." This has appeared as a separate pamphlet and has been noticed in the preceding review.

The second paper is by Hans Mayer and is entitled: "An Electrical Method for Measuring the Changes Produced in Chromated Gelatine Films by Light." The author uses tinfoil electrodes and measures the resistance of the film. He finds that exposure to light increases the resistance and that the temperature coefficients are different for the exposed and the unexposed film. The light-sensitiveness of the film, as measured in percentage change of the conductance for a given exposure, decreases with the age of the plate, at first rapidly and then much more slowly.

The method is sensitive; but the interpretation of the results is difficult because there is a change in the composition of the chromium salt and a change in the properties of the gelatine. The values also vary very much with the amount of moisture in the film.

The author assumes that oxygen is set free when the bichromate is reduced by light. This seems absurd because we know that bichromate is not reduced in the absence of gelatine. Consequently the gelatine is oxidized by the bichromate and we are not dealing solely with a coagulation of the gelatine. A mistake of this sort rather destroys one's confidence in the author's conclusions.

Wilder D. Bancroft

Les Diastases oxydantes et réductrices des Champignons. *By Pierre Sée. 25 × 17 cm; pp. 38. Paris: Félix Alcan, 1910. Price: paper, 2 francs.*—The author has made a study of the juices of the ordinary field mushroom, *Agaricus campestris.* He finds at least three oxidases differing in stability: a ferment like laccase but differing in that it does not oxidize pyrogallol readily; a ferment like the one obtained by Rohmann and Spitzer from animal tissues; a diastase analogous to the tyrosinase of G. Bertrand. A catalase was also found which had considerable deoxidizing power, but apparently no power to cause the addition of hydrogen. There seem to be coferments for the oxidases but *none* for the catalase. No proferments were found for the oxidases or the catalase.

Wilder D. Bancroft

Zeitschrift für anorganische Chemie. *Begründet von Gerhard Krüss. Unter Mitwirkung zahlreicher Mitarbeiter herausgegeben von G. Tammann und Richard Lorenz. Generalregister der Bände 1–50 (1892–1906) nebst einer Abhandlung: "Ein Verfahren zur Registrierung anorganischer Stoffe" von Arthur Rosenheim und Ivan Koppel. 16 × 24 cm; pp. xx + 652. Hamburg und Leipzig: Leopold Voss, 1908. Price: paper, 25 marks.*—This index covers the years from 1892–1906. There is an index of authors, one of subjects, and one of laboratories. In addition there is an article on the cataloging of inorganic compounds. A volume of this sort takes a lot of time to prepare but it saves the people who use it an immense amount of time. So far as the reviewer can judge, the work has been done very well. In the index of laboratories, it is a slip to classify one of Richards' articles under Seal Harbor, Maine, Mount Desert, even though the article in question was written at Seal Harbor. *W. D. B.*

Die Unterscheidung der natürlichen und künstlichen Seiden. *Eine Praktische Anleitung zur mikroskopisch-chemischen Prüfung der Seiden für Untersuchungsämter, Lehranstalten, Industriellen, Zollbeamte usw. By Alois Herzog. 16 × 24 cm; pp. 78. Dresden: Theodor Steinkopff, 1910. Price: paper, 3 marks.*—The author has subjected the various kinds of silk to chemical, microscopical, and ultra-microscopical tests. The results of his investigations are shown in a series of superb photo-micrographs He also gives a plan of analysis which will enable people to recognize and identify the more important brands of silk on the market. As all this is done in seventy-seven pages, the book will be very valuable to the workers in this field. *Wilder D. Bancroft*

THE SPECIFIC HEAT OF LIQUID BENZOL AND OF ITS SATURATED VAPOR

BY J. E. MILLS AND DUNCAN MACRAE

Many measurements of the specific heat of different liquids have been made by various observers. If these measurements are examined it will be found that they contribute but little to any real knowledge of the laws that govern the energy changes involved. Isolated measurements have in many cases been made upon substances whose remaining physical constants are almost totally unknown. Such measurements, even if accurate, aid little in understanding the changes involved. Confining the attention to the thirty-odd liquids whose physical constants, such as the vapor pressure, density of the liquid and density of the saturated vapor at definite temperatures, and the critical data, have been carefully measured, one finds that for most of these liquids no measurements of the specific heat have been made. Isolated measurements[1] of the specific heat have been made upon hexane, heptane, octane, chlor-benzol, and methyl and ethyl formates. Somewhat more extended measurements[1] have been made upon water, methyl, ethyl and propyl alcohols, acetic acid, ether, isopentane, carbon dioxide, carbon disulphide, chloroform and benzol. A careful examination of these measurements makes it clear that more accurate and more extended work upon the specific heat of liquids is necessary before the subject can be discussed authoritatively. It was finally decided to measure the specific heat of benzol accurately and to plan for a future extension of the measurements over a wider range of temperature and to other substances.

The measurements of the specific heat of solid and liquid benzol obtained by previous workers are plotted and shown

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[1] Landolt, Börnstein, and Meyerhoffer's Physikalisch-chemische Tabellen. A. Battelli: Phys. Zeit., 9, 671 (1908). Nuovo Cimento, (5) 13, 418 (1907). Rend. Accad. Lincei, (5) 16, I, 243 (1907). G. Teichner: Drude's Ann., 13, 611 (1904). C. Dieterici: Ibid., 12, 154 (1903).

in Fig. 1. The diversity of results shown makes clear the necessity for the experimental work described below.

Several years ago one of the authors experimented with a Dewar beaker as a calorimeter and found that under the conditions of use it much surpassed in efficiency calorimeters

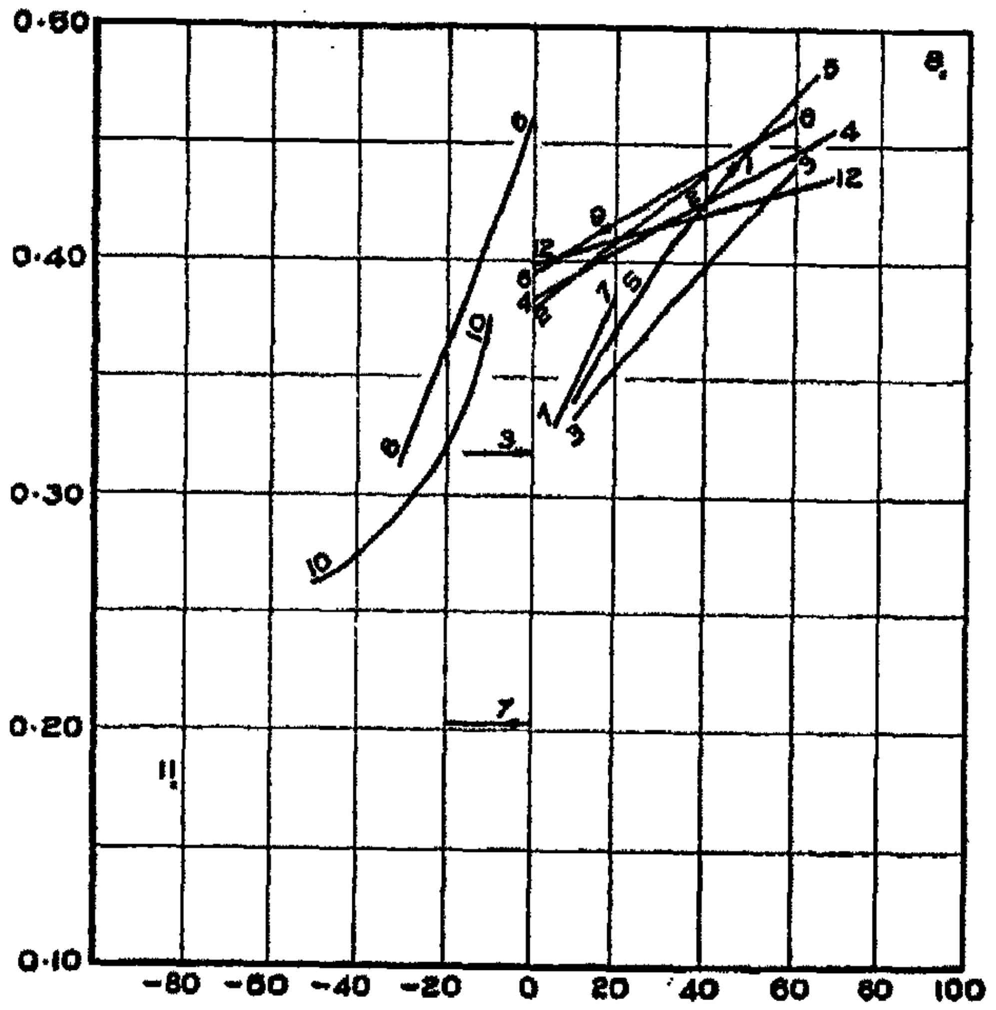

Fig. 1

1 Regnault: Mém. de l'Acad., 26, 262 (1862).
2 Schüller: Pogg. Ann., Ergänz., 5, 125 (1871).
3 W. Fischer: Wied. Ann., 28, 400 (1886).
4 R. Schiff: Liebig's Ann., 234, 300 (1886).
5 P. DeHeen and F. Deruyts: Bull. Acad. Belg., (3) 15, 168 (1888).
6 S. U. Pickering: Proc. Roy. Soc., 49, 11 (1890).
7 Jos. Ferche: Diss. Halle, 1890, Wied. Ann., 44, 365 (1891).
8 A. Schlamp: Ber. Oberhess. Ges. Naturw. u. Heilk., 31, 100 (1895).
9 C. Forch: Drude's Ann., 12, 202 (1903).
10 A. Bogojawlenski: Chemisches Centralblatt, 76, II, 945 (1905). Schriften d. Dorpater Naturfor. Ges., 13, 1 (1904).
11 P. Nordmeyer and A. L. Bernouilli: Verh. deutsch. phys. Ges., 9, 175 (1907).
12 Mills and MacRae.

in use up to that time. Dewar vessels have been rather frequently used for calorimetric work at low temperatures and since the investigation above cited was begun their use at ordinary temperatures purely as a calorimeter has been several times noted.[1] It was therefore decided to make use of a Dewar flask as a calorimeter, to fill the same nearly to the neck with a weighed quantity of benzol, and heat the benzol by means of a current of electricity passed through a platinum wire coil immersed in the benzol. The rise in temperature of the benzol and the heat added are determined. The calorimeter constant is separately determined by substituting water in the place of the benzol. The specific heat of the benzol can then be calculated. After much preliminary experimenting the details of the method were satisfactorily adjusted. The details of the apparatus and the various corrections necessary are described below.

The Dewar Flask.—The cooling curves of a series of double- and of triple-walled vacuum silvered Dewar flasks of 250 (double-walled only), 500 and 1000 cc capacity when filled with water up to the neck, were investigated, both when the flasks were stoppered and when they were open. The best of these flasks proved to be a 500 cc double-walled flask. That this flask should have proven better than the triple-walled flasks of the same, and of the larger size, was a matter of surprise, and indicated that there is considerable difference in the efficiency of flasks obtained from the same factory. The rate of cooling was greatly decreased when the flasks were stoppered and for this reason it was deemed best to use a very tightly stoppered flask, all evaporation from the flask being prevented.

The Platinum Wire Coil.—A small platinum wire was carefully coiled and the ends sealed into two glass tubes which were filled with mercury and passed through a suitable rubber stopper. The resistance of this coil was care-

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[1] L. J. Henderson and C. T. Ryder: Science, 27, 743 (1908). H. C. Dickinson, E. F. Mueller and E. B. George: Bull. Bureau Standards, 6, 379. J. Duclaux: Comptes rendus, 146, 120 (1908).

fully determined at a number of temperatures by means of the usual Wheatstone's bridge arrangement—the bridge having been previously calibrated. The resistance was found to vary linearly with the temperature between the values, 1.1975 ohms at 0° C and 1.5365 ohms at 100° C. Subsequently another coil of approximately the same resistance was used, but as it was found that the resistance of the wire when immersed in a liquid varied with the current passed through the wire, and also with the nature of the liquid in which the wire was immersed, its exact resistance was not determined. Under exactly comparable conditions this variation of the resistance is linear when plotted against the temperature.

The Ammeter.—A potentiometer, a resistance of 0.1 ohm capable of carrying 15 amperes without heating, and a Weston standard cell, all furnished by the Leeds & Northrup Co., and all checked by the Bureau of Standards, were used to measure the current. The units used were the International ohm and the value of the Clark cell at 15° C = 1.434 volts. A sensitive galvanometer furnished by Keiser and Schmidt was used in obtaining a balance and the combination worked perfectly. The current was obtained from storage batteries giving about 24 volts, and was regulated and held exactly constant during the experiment by means of slide wire resistances, usually of 11 ohms and of 90 ohms, placed in parallel. Approximate regulation before each experiment was made with the *11* ohm resistance, and exact regulation completed in a few seconds after the current was finally turned on for the experiment by use of the 90 ohm coil.

The Voltmeter.—The drop in voltage across the terminals of the platinum coil was obtained by means of a Weston Laboratory Standard Voltmeter. The voltmeter was frequently checked by use of the potentiometer, standard cell, etc., above mentioned. At no time did the voltmeter give absolute readings, the corrections, amounting usually to about 0.5 of one percent, being obtained from a curve constructed from the check readings above mentioned. The resistance coil of the instrument corresponding to the 15 volt scale had a resistance of 2606.3 ohms and required no correction for temperature. The 3 volt scale sometimes used had a resistance of 521.26 ohms and a temperature coefficient of $1 = 0.00035\ (t - 22.5°)$. A correction was made for the shunt current through the instrument.

The Time.—The time was measured by means of a small laboratory clock that struck each minute. Such a clock enables the current to be switched on and off, and the voltmeter and thermometer readings to be taken, at precisely the right moment, and is an indispensable part of the equipment for such work. It was compared with a clock giving standard time.

The Energy Added.—The calorie from 15° to 16° C is taken as equal to 41.88×10^6 ergs.[1] The total energy added is therefore equal to

1. 0.2388 × Time in seconds × Average corrected drop in voltage × Corrected amperes, calories.

In obtaining the average corrected drop in voltage, if the experiment lasts n minutes, and E_0, E_1, E_2, ... E_n, are the corrected voltmeter readings, then,

$$2. \qquad E_{\text{average}} = \frac{\frac{E_0 + E_n}{2} + E_1 + E_2 + + E_{n-1}}{n}.$$

The Thermometers.—Two thermometers, reading from —12° to 56° and from 32° to 70° in 1/10 of a degree, were used during the experiments. Corrections for the thermometers were certified by the Reichsanstalt. With the aid of a magnifying glass the thermometers could be read to 0.01°. Corrections for the exposed stem were made in the usual manner. Later the determinations were checked at low and at high temperatures by use of a Beckmann thermometer of the usual construction. The corrections necessary to

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[1] Ber. phys. Ges., 6, 578. Rowland, corrected by Day: Phys. Rev., 6, 194 (1898).

reduce to a hydrogen thermometer for the scale of this thermometer at different settings were furnished by the Bureau of Standards.

Heat Loss from the Calorimeter.—To obtain the necessary corrections for the loss or gain of heat from the calorimeter the thermometer was read for a sufficient time, usually 20 or 30 minutes, both before and after the experiment. The continued readings largely eliminated individual errors in the reading of the thermometer. The rates of cooling (or heating) obtained from the experiments with water and with benzol were plotted and it was found that the flask obeyed Newton's law of cooling with considerable accuracy even when a difference in temperature of 40° existed between the flask and the surrounding air. The fall in temperature per minute per degree difference of temperature between the flask and the surrounding air was found to be about 0.00043 for water and 0.00108 for benzol. Thus the flask was a remarkably efficient calorimeter.

The corrections for the loss or gain of heat by the flask can be accurately and simply made if the calorimeter rises evenly in temperature[1] from the beginning to the end of the experiment. Let θ_o and θ_n be the corrected temperatures at the beginning and at the end of the experiment respectively. Suppose that the experiment lasted n minutes and that v_o and v_n respresent the rate of cooling before and after the experiment. Then Newton's law being true, and the above condition as to the addition of heat being fulfilled, it is easily shown that the total rise of temperature of the calorimeter is,

$$3. \qquad \theta_n - \theta_o + \frac{n}{2}(v_o + v_n).$$

The "temperature before" ($= \theta_o \pm \frac{n}{2} v_o$) and "temperature after" ($= \theta_n \pm \frac{n}{2} v_n$), the experiment given in Tables 2 and 3, have been corrected for the heat lost by radiation.

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[1] See page 805.

The Lag of the Thermometer.—The lag of the thermometer itself behind the true temperature of the immediately surrounding liquid is entirely negligible. The method of determining this lag, and its effect, has been recently discussed several times.[1] The lag of any thermometer is usally equal to the rate of cooling of the calorimeter divided by the cooling constant b of the thermometer. This cooling constant is obtained on heating the thermometer and plunging it into a bath of constant temperature and noting the cooling curve of the thermometer. The equation of this cooling curve is, from Newton's law of cooling,

$$4. \qquad \frac{d\theta}{dt} = b\theta.$$

Now the experiments of Richards, Henderson and Forbes, and of Jäger and v. Steinwehr show that for a Beckmann thermometer b is quite variable but may be estimated as between 4 and 11. If therefore we suppose a rise in temperature of 10° during an experiment, the difference in the lag of the thermometer before and after the experiment, taking b equal to 4, would be 0.0027° with benzol and 0.0011° with water. Even with benzol the error is only 1/4000 of the total rise in temperature. In reality the error is less than this, for the bulb of the thermometer used was small, and while b was not determined, it could hardly have been so small as 4.

It must be noted that the above discussion of the thermometric lag supposes that no heat is lost along the stem of the thermometer. Now it is quite possible to imagine with the very efficient Dewar flask above described that the heat of the water in the calorimeter will escape faster along the thermometer stem than it does through the vacuum

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[1] M. Thiesen: Metron Beitr. (Normal Eichungskommission), 3, 13 (1881). J. Hartmann: Zeit. Instrumentkunde, 17, 14 (1897) F. M. Jäger and H. von Steinwehr: Verhandl. deutsch. phys. Ges., 5, 50, 353 (1903). Zeit. phys. Chem., 53, 153 (1905); 54, 428 (1906). T. W. Richards and A. B. Lamb: Proc. Am. Acad., 40, 659 (1904–05). T. W. Richards, L. J. Henderson and G. S. Forbes: Ibid., 41, 1 (1905–'06). W. P. White: Phys. Rev., 27, 526 (1908); 28, 462 (1909).

silvered walls of the vessel. In this case the thermometer would not only not lag behind the temperature of the calorimeter when it is cooling but would actually indicate a temperature lower than that of the liquid in the calorimeter. Yet even under such circumstances the above-described method would of course show a positive thermometric lag, the true lag in this case being negative.

In conclusion it may safely be said that unless the work requires an accuracy greater than 1 part in 4000 the lag of the thermometer itself may be neglected.

Difference of Temperature within the Calorimeter. Stirring.—The temperature of the platinum wire itself when immersed in a liquid and carrying a current rises above that of the surrounding liquid. If the thermometer is placed in the immediate neighborhood of the wire coil the temperature as indicated by the thermometer will be found to rise regularly at a very nearly constant rate during the experiment. This was determined from observations upon many experiments. The thermometer does not, however, indicate the average temperature of the liquid because this temperature is greatest at the platinum coil and decreases with the distance from the coil. If the bulb of the thermometer is in the immediate neighborhood of the coil, the thermometer indicates always a temperature above the average temperature of the entire liquid. The outside layers of the liquid, which really determine the radiation loss, are at a lower temperature than the average temperature of the liquid. Efficient stirring would tend greatly to diminish these inequalities in temperature. *Yet such stirring, under the conditions of the experiments detailed, contrary to the usual idea, is not a matter of necessity even for accurate work.* For within a minute after the electric current is turned on currents are set up in the liquid which cause it to circulate. When these currents have been once established the circulation is fairly rapid, the rapidity depending on the liquid and on the size of the current used. These currents were observed in a similar single-walled flask by means of suspended material placed in the flask. With water as the liquid, and a current of 5 amperes giving a rise in temperature of about one degree per minute, the circulation when established caused the water to rise from the bottom to the top of the flask in less than 15 seconds. Suppose, however, that the outside layer of water lags behind the true average temperature of the water by so much as 1°, equivalent to one minute. Then for an experiment lasting 10 minutes, with a rise of 10° in temperature, the error caused by the lag would be 0.0043, or an error of approximately 1/2500. When one considers that this difficulty (inequalities of temperature within the liquid) could not be wholly eliminated by stirring, that an allowance, usually uncertain, must be made for the heat added by stirring, and that the stirring apparatus must be so constructed as to prevent evaporation from the flask (otherwise more serious errors are introduced), the proposal that we have made to eliminate the stirring should certainly meet with favor. Immediately after the end of the experiment the electric wires are disconnected and the flask thoroughly shaken. This shaking is repeated at intervals before each reading of the thermometer. Similarly of course the flask should be shaken before the experiment.

We have hitherto regarded the heat as being evenly added to the calorimeter. Since the current is kept constant, the heat added varies as the resistance, which increases by about 1/400 of its value per degree. Could the entire contents of the calorimeter be kept precisely at its proper average temperature it would be practicable to allow for this increase of the resistance. The correction would amount usually to not more than 0.0001° and is of opposite sign to the more serious error caused by the lag of the liquid above mentioned. Hence it may safely be neglected.

The Calorimeter Constant.—The details of the experiments to determine the calorimeter constant given in the table below will be readily understood. The "Correction for vaporization" is a correction for the vaporization of the water into the neck of the flask, an empty space of about 60 cc existing there. The values used for the specific heat of water are based on the values given by Barnes and Cooke[1] based on the hydrogen thermometer, the International ohm, and the Clark cell at 15° C as equal to 1.4342 International volts. The water used was distilled and freshly boiled to free from dissolved air. The weight of the water was corrected for the buoyancy of the air, and allowance was made for the inequality in the length of the balance arms.

Experiments 15 to 19 inclusive were made with a Beckmann thermometer. In experiment 15, 16 and 17, the Beckmann was set at 5.95° and no bath was used. In experiments 18 and 19 the Beckmann was set at 60.02° and the calorimeter was surrounded by a bath kept at 56°.

Experiment 9 was a failure, due to an error in the thermometer reading and the details are omitted. On plotting the results of the experiments 1 to 14, it will be seen that they lie with great exactness on a line curved at its upper end, with the exception of experiments 5, 6, 11 and 14. Experiment 6 followed experiment 5 and it is pretty clear that an error must have been made in determining the intervening temperature change. In experiment 11 the voltmeter readings were irregular. We could not locate the error in experiment 14, nor in experiment 15 with the Beckmann thermometer.

A line through the results given will, we think, establish the calorimeter constant to within 0.3 of a calorie. This involves an accuracy of about one part in 1500 in the measurements directly concerned. Wherever in later experiments the Beckmann thermometer was used, the calorimeter constant, determined with its aid under the same conditions, was also used.

The Purity of the Benzol Used.—Kahlbaum's best thiophene free benzol was fractionated over a little phosphorus pentoxide through a Young's fractionating column of eight divisions until a constant boiling point was obtained. The

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[1] Phys. Rev., 15, 71 (1902).

TABLE 1—Calorimeter constant

	Number of experiment								
	1	2	3	4	5	6	7	8	10
Volts	6.9492	7.1182	6.3582	6.4945	6.6500	6.8102	6.9905	7.1385	6.4915
Amperes	4.9974	4.9973	4.9976	4.9975	4.9975	4.9974	4.9974	4.9973	4.9975
Time in minutes	10	10	10	10	10	10	10	8	10
Total calories added	4975.8	5096.7	4552.8	4650.3	4761.7	4876.3	5005.4	4089.0	4648.2
Correction for vaporization	1.5	2.1	0.3	0.3	0.7	0.9	1.7	2.3	0.3
Temperature before	46.974	57.261	8.386	18.482	28.534	38.598	49.224	59.425	18.520
Temperature after	57.613	68.103	18.166	28.481	38.731	49.085	59.930	68.137	28.517
Δt	10.639	10.842	9.780	9.999	10.197	10.487	10.706	8.712	9.997
Average temperature	52.29	62.68	13.28	23.48	33.63	43.84	54.58	63.78	23.52
Calories added per degree	467.56	469.90	465.50	464.95	466.90	464.90	467.38	469.09	464.93
Weight of water	452.65	452.65	452.08	452.08	452.08	452.08	452.08	452.08	452.06
Specific heat of water	0.9982	0.9994	1.0009	0.9983	0.9974	0.9975	0.9984	0.9995	0.9983
Total heat of water	451.84	452.38	452.49	451.32	450.91	450.95	451.28	451.86	451.29
Calorimeter constant	15.72	17.52	13.01	13.63	15.99	13.95	16.10	17.23	13.64

TABLE 1—Calorimeter constant (*Continued*)

	Number of experiment								
	11	12	13	14	15	16	17	18	19
Volts	6.6380	6.7975	6.9622	7.1257	5.0520	5.0385	5.0416	5.6546	5.6522
Amperes	4.9975	4.9974	4.9974	4.9973	3.9980	3.9980	3.9980	3.9978	3.9978
Time in minutes	10	10	10	10	8	9	7	7	9
Total calories added	4753.1	4867.2	4985.1	5102.1	2315.2	2597.6	2021.6	2267.2	2913.8
Correction for vaporization	0.7	0.9	1.6	2.3	0.1	0.1	0.1	1.1	1.4
Temperature before	27.693	37.715	47.475	57.762	1.096	0.293	1.683	1.138	0.227
Temperature after	37.895	48.155	58.139	68.600	6.046	5.888	6.021	5.991	6.456
Δt	10.202	10.440	10.664	10.838	4.950	5.595	4.338	4.853	6.229
Average temperature	32.80	42.93	52.81	63.18	9.52	9.04	9.80	63.58	63.36
Calories added per degree	465.83	466:10	467.32	470.55	467.65	464.26	466.02	466.95	467.55
Weight of water	452.06	452.06	452.06	452.06	449.85	448.53	450.09	449.51	450.93
Specific heat of water	0.9974	0.9975	0.9983	0.9995	1.0026	1.0028	1.0025	0.9995	0.9995
Total heat of water	450.89	450.94	451.29	451.84	451.01	449.78	451.21	449.29	450.71
Calorimeter constant	14.94	15.16	16.03	18.71	16.64	14.48	14.81	17.66	16.84

sample finally used showed a boiling point of 79.49° to 79.55°, the barometer varying meanwhile from 747.7 to 748.3. This was equivalent to a boiling point of 80.02° to 80.05° at 760 millimeters pressure.

The Specific Heat of Benzol.—The details of the determination of the specific heat of benzol are given in Table 2 below. The weight of the benzol given is corrected for the buoyancy of the air and for the inequality of the balance arms. Experiments 1 to 5 were consecutive experiments, and the results lie on a straight line nearly parallel to and somewhat below the results of the similar experiments 5 to 11. Therefore the specific heat of the benzol was determined both at high and at low temperatures with the Beckmann thermometer as detailed in experiments 12 to 15. The setting of the Beckmann in experiments 12 and 13 was at 5.95° and no bath was used. In experiments 14 and 15 the Beckmann was set at 60.02° and the calorimeter was kept in a bath at about 59.5°. The calorimeter constant determined with the Beckmann under similar conditions was used. The results of the check experiments show that the series of experiments 6 to 11 are correct, though we could never locate the exact trouble with the series 1 to 5.

The specific heat of benzol may therefore be taken as lying on a straight line passing through the points 0.3971 at 0° and 0.4369 at 70°. This line is shown in Figure 1, line 12, and the values at intervals of 10° taken from this line are given in Table 3. The values given do not agree with any previous measurement. We believe, however, that the results given are correct to within 1 part in 200.

The Specific Heat of the Saturated Vapor.—The heats of vaporization of benzol at intervals of 10° obtained by three different methods are given in Table 3 below.

The values in the column headed "Griffiths and Marshall" are from the formula, latent heat = $107.05 - 0.1581t$, obtained from the very accurate experiments[1] made by these workers at 20°, 30°, 40° and 50°.

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[1] Phil. Mag., 41 (1896).

TABLE 2—Specific heat of benzol

	Number of experiment								
	1	2	3	4	5	6	7	8	9
Volts	3.8314	3.9490	4.0577	4.1542	4.2435	3.7950	3.9000	4.0053	4.0975
Amperes	2.9985	2.9985	2.9984	2.9984	2.9984	2.9986	2.9985	2.9985	2.9984
Time in minutes	10	12	10	10	10	10	11	10	10
Total calories added	1646.1	2035.9	1743.2	1784.7	1823.0	1630.5	1843.1	1720.8	1760.3
Correction for vaporization	0.9	1.1	1.4	2.0	2.2	0.8	1.0	1.6	2.0
Temperature before	9.280	19.261	30.858	40.261	49.043	9.184	18.946	29.441	38.699
Temperature after	18.880	30.899	40.680	50.134	59.007	18.586	29.404	39.017	48.398
Δt	9.600	11.638	9.822	9.873	9.964	9.402	10.458	9.576	9.699
Average temperature	14.08	25.08	35.77	45.20	54.02	13.88	24.17	34.23	43.55
Calories added per degree	171.38	174.84	177.34	180.56	182.74	173.33	176.14	179.53	181.28
Calorimeter constant	12.93	13.79	14.60	15.30	16.07	12.92	13.70	14.48	15.20
Weight of benzol	393.12	393.12	393.12	393.12	393.12	395.19	395.19	395.19	395.19
Specific heat of benzol	0.4031	0.4096	0.4139	0.4204	0.4240	0.4059	0.4110	0.4176	0.4203

TABLE 2—Specific heat of benzol (*Continued*)

	Number of experiment					
	10	11	12	13	14	15
Volts	4.1839	4.2835	2.4789	2.4805	4.2945	2.8117
Amperes	2.9984	2.9984	1.9952	1.9952	2.9984	1.9946
Time in minutes	11	10	12	11	5	13
Total calories added	1977.2	1840.2	850.38	780.00	922.49	1044.61
Correction for vaporization	2.5	3.3	0.35	0.32	1.92	2.21
Temperature before	46.958	56.550	1.376	1.449	—0.013	—0.098
Temperature after	57.605	66.332	6.279	5.941	4.880	5.477
Δt	10.647	9.782	4.903	4.492	4.893	5.575
Average temperature	52.28	61.44	9.77	9.64	62.45	62.71
Calories added per degree	185.47	187.78	173.41	173.57	188.14	186.98
Calorimeter constant	15.85	17.05	14.67	14.64	17.20	17.22
Weight of benzol	395.19	395.19	394.38	395.20	393.87	393.08
Specific heat of benzol	0.4292	0.4320	0.4025	0.4022	0.4340	0.4319

The values in the column headed "Ther" are calculated from the data given by use of the well-known Clausius-Clapeyron thermodynamical equation

$$5. \qquad L = 0.0_43183\,T\frac{dP}{dT}(V - v) \text{ calories,}$$

where L is the heat of vaporization, T is absolute temperature, P is pressure in millimeters of mercury, and v and V are the volumes of a gram of the liquid and of its saturated vapor. The vapor pressure, density and volume of the liquid, and density and volume of the vapor at 70° are from observations by Young.[1] The density and volume of the vapor at 0° C are the theoretical values calculated on the supposition that the vapor behaves as a perfect gas at this temperature, a supposition that must be very nearly correct. The equation used for calculating the density is

$$6. \qquad D = 0.0_416014\,\frac{Pm}{T},$$

where m is the molecular weight and is equal to 78.05. The densities of the saturated vapor at 10° to 60° inclusive are obtained by extrapolating the equation given by Young.[2] This extrapolation gives results that cannot be far wrong since the theoretical densities serve as a guide to which the actual densities must approach as a limit.

The values of the heat of vaporization in the column headed "Mills" are obtained by using the equation

$$7. \qquad L = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) + E_e.$$

Here μ' is a constant for any particular substance and for benzol has the value 109.26. E_e is the energy expended in overcoming the external pressure as the liquid expands to the volume of the saturated vapor and is given by the equation

$$8. \qquad E_e = 0.0_43183\,P(V - v) \text{ calories.}$$

The values of E_e given in Table 3 have been slightly smoothed.

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[1] Sci. Proc. Roy. Dublin Soc., **12**, 374 (1910).

[2] Jour. Phys., Jan. (1909).

Equation 7 has been carefully and extensively studied[1] and seems to hold accurately for non-associated liquids at all temperatures.

Making use of these values of the heats of vaporization and the values of the specific heat of the liquid, it becomes possible to calculate the specific heat of the saturated vapor, for the energy necessary to change the liquid at 0° into the saturated vapor at 10° is the same whatever may be the method pursued to effect the change. Letting the subscripts denote temperature, and letting σ_L denote the total heat added to the liquid and σ_v that added to the vapor between the temperaure limits given, we have,

$$9. \qquad L_0 + \sigma_v = L_{10} + \sigma_L, \text{ or } \sigma_v = L_{10} + \sigma_L - L_0.$$

It should be understood that the method here used for obtaining the specific heat of the saturated vapor involves no assumption beyond the law of the conservation of energy, the values of the specific heat of the liquid and of the heat of vaporization being known.

The specific heat of the saturated vapor so calculated from the values of the heat of vaporization given by Griffiths and Marshall will lie, as can readily be seen, on a straight line, parallel to and 0.1581 below, the line giving the specific heat of the liquid. The values are given in Table 3. It is probable that the heat of vaporization, even at this low temperature (0° to 70°), does not vary exactly linearly with the temperature, and we think too much faith should not be placed in the values so derived.

Unfortunately the specific heats of the saturated vapor derived from the thermodynamically calculated heats of vaporization are even worse. The average values are given every 10° from 5° in Table 3. They defy smoothing. The thermodynamically calculated heats of vaporization are fairly accurate as can be seen from the extended data given

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[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905), 10, 1 (1906); 11, 132, 594 (1907); 13, 512 (1909). Jour. Am. Chem. Soc., 31, 1099 (1909).

TABLE 3—The specific heat of the saturated vapor of benzol

Temperature	Vapor pressure P	Density of liquid *d*	Volume of liquid *v*	Density of vapor D	Volume of vapor V	External energy E_e	ϵ_d	ϵ_D	$\epsilon_d - \epsilon_D$	Specific heat of liquid σ
0[1]	26.54	0.9001	1.1110	0.0_31215	8230	6.94	0.9655	0.04953	0.91597	0.3970
10	45.43	0.8894	1.1243	0.0_32024	4939	7.17	0.9617	0.05872	0.90298	0.4027
20	74.66	0.8789	1.1378	0.0_33208	3117	7.41	0.9579	0.06845	0.88945	0.4084
30	118.24	0.8685	1.1514	0.0_34911	2036	7.65	0.9541	0.07890	0.8752	0.4141
40	181.08	0.8575	1.1661	0.0_37290	1372	7.89	0.9500	0.09000	0.8600	0.4298
50	268.97	0.8466	1.1812	0.001052	950.6	8.13	0.9460	0.10170	0.8443	0.4255
60	388.58	0.8357	1.1966	0.001479	676.1	8.36	0.9419	0.11395	0.82795	0.4312
70	547.40	0.8248	1.2124	0.002040	490.3	8.52	0.9378	0.12682	0.81098	0.4369

Temperature	Heat of vaporization			Specific heat of saturated vapor				
	Griffiths and Marshall	Ther.	Mills	Griffiths and Marshall	Mills smoothed	Average for 10° at	Ther.	Mills
0[1]	107.05	106.11	107.02	0.2389	0.284	5	0.2258	0.2808
10	105.47	104.37	105.83	0.2446	0.282	15	0.3315	0.2815
20	103.89	103.63	104.59	0.2503	0.279	25	0.3122	0.2792
30	102.31	102.64	103.27	0.2560	0.277	35	0.3075	0.2749
40	100.73	101.55	101.85	0.2717	0.275	45	0.2806	0.2756
50	99.14	100.13	100.38	0.2674	0.273	55	0.2823	0.2723
60	97.56	98.67	98.82	0.2731	0.270	65	0.2370	0.2650
70	95.98	96.70	97.13	0.2788	0.268	—	—	—

[1] Benzol is a solid at 5.43°. The lines for the liquid are extrapolated to 0° for convenience.

in the papers cited, probably seldom diverging from the true value by so much as one calorie. But this comparatively small error is proportionately enormously magnified when the differential of the latent heat is the important factor. Measurements over a wider range of temperature are necessary before one could undertake to smooth out the effect of the individual errors of observation.

The specific heat of the saturated vapor calculated from the heats of vaporization under the heading "Mills," given by equation 7, are given at intervals of 5° in Table 3 and the smoothed values are also there given. We are inclined to believe that these smoothed values for the specific heat of the saturated vapor of benzol are fairly accurate. Observations over a wider range of temperature are, however, necessary before the values can be finally accepted.

The object of this research was to throw light upon the nature and cause of the energy changes involved during the rise in temperature of a liquid. Theoretical discussion of the results is postponed to a later paper.

Summary

1. A method for determining accurately the specific heat of a liquid at temperatures below its boiling point is described in detail. The method uses a 500 cc Dewar flask as a calorimeter and electrical heating of the liquid.

2. The specific heat of liquid benzol is found to vary linearly with the temperature between its freezing point and 70° C. The line passes through the values 0.3970 at 0° and 0.4369 at 70° C.

3. The specific heat of the saturated vapor of benzol has been determined, though further work is necessary to confirm the results obtained. The values tentatively given lie on a straight line passing through the values 0.284 at 0° and 0.268 at 70° C.

The above work was done in the Chemical Laboratory of the University of North Carolina.

July 23, 1910

MATHEMATICAL THEORY OF THE CHANGES OF CONCENTRATION AT THE ELECTRODE, BROUGHT ABOUT BY DIFFUSION AND BY CHEMICAL REACTION

BY T. R. ROSEBRUGH AND W. LASH MILLER

Owing to the chemical changes which accompany electrolysis, the composition of the electrolyte at the electrodes is different from that in the body of the solution. Diffusion currents are consequently set up which tend to remove these differences; and if convection be avoided, the concentration of any constituent at any point in the solution will depend only on the initial composition of the solution, and on the amounts which have been carried to or from the electrodes by diffusion and by electrolytic migration.

In the simpler cases, at all events, these changes of concentration are susceptible of mathematical treatment; Weber[1] and Sand[2] have considered the case of electrolysis with constant currents, and Warburg[3] has deduced an equation for the stationary state on electrolysis with a sinusoidal current through a diffusion layer of "infinite" length. The present paper deals with the whole problem in a systematic manner, and includes the discussion of electrolysis with intermittent, successive and sinusoidal currents, without restriction as to the duration of the electrolysis or the length of the column of liquid through which the diffusion takes place. The increasing application of the oscillograph to the study of instantaneous conditions at the electrode led us to pay particular attention to the changes which occur within the first fraction of a second after throwing on the current, while Richards'[4] work on electrolysis with alternating currents,

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[1] Wied Ann., 7, 536 (1879).

[2] Phil. Mag., [6] 1, 45 (1901); Zeit. phys. Chem., 35, 641 (1900).

[3] Wied. Ann., 67, 493 (1899).

[4] Trans. Am. Electrochem. Soc., 1, 221 (1902).

followed by the interesting experiments of LeBlanc[1] and of Reichinstein[2] with copper electrodes in cyanide solutions, induced us to include the case of non-instantaneous chemical reactions between the primary products of electrolysis and the other constituents of the solution.

The results of the investigation, however, are not perfectly general; for in leading up to Eqs. (*iii*) and (*xiv*) it has been assumed that both the diffusion constant and the flow due to electrolytic migration are independent of the concentration, and that the rate of the secondary reaction if any occur is proportional to the concentration of the constituent whose amount at the electrode is directly affected by the electrolysis—assumptions, which, in many cases, are not even approximately true. To treat the diffusion constant as a function of the concentration, or to consider reactions whose rates are proportional to any other than the first power of the concentration under consideration, would alter the whole nature of the differential equation involved; the restrictions thus imposed have been disregarded only in the comparatively simple, though important, case of prolonged electrolysis with a constant current.

To fix the ideas, electrolysis may be supposed to take place in a vessel of uniform cross section ($\mathcal{S}$ cm^2), bounded at the ends by the electrodes. The surface of each electrode is then identical in area and form with the cross section of the electrolyte, the current density will be uniform throughout, and the concentrations will be constant over each section of the solution taken parallel to the electrodes. The results of the argument are, however, equally applicable to the case of electrolysis with a rotating cylindrical electrode in a uniform field; in such cases, as shown by the experiments of Noyes and Whitney on rates of solution,[3] the electrode may be regarded as surrounded by an adherent layer of solution of uniform thickness through which diffusion takes place;[4]

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[1] Zeit. phys. Chem., 46, 213 (1903); Zeit. Elektrochemie, 11, 705 (1905).

[2] Zeit. Elektrochemie, 15, 734 (1909).

[3] Zeit. phys. Chem., 23, 689 (1897).

[4] Ibid., 47, 52 (1904).

with electrodes of ordinary dimensions this film has been found to be so thin[1] that the difference between the areas of its outer and inner surfaces may be neglected.

The direction normal to the surface of the electrodes is taken as the axis of x; it is assumed that at some fixed point on this axis the composition of the electrolyte (or at least the concentration z of the constituent under discussion) remains unaltered throughout the experiment, and this point is taken as the origin, $x = 0$, from which the values of x are reckoned. The "*solution condition*," then, adopted throughout this paper is that at $x = 0$, $z = z_0$ for all values of t, or

$$[\textit{For } x = 0] \qquad \partial z/\partial t = 0 \qquad (i).$$

In Weber's experiments, where solutions of zinc sulphate were electrolyzed for long periods of time between stationary zinc electrodes, such a point of constant concentration evidently lies midway between the two electrodes; in experiments with a rotating electrode it will lie on the outer surface of the adherent liquid film, no matter how long the electrolysis proceeds if constituents removed at the cathode are replaced at the anode and vice versa, for some time at all events if the amount of electrolyte in the cell is large compared with that destroyed per minute by the electrolysis.

The position of one of the electrodes is defined by $x = l$; the other electrode is left out of consideration altogether, for as long as there is a section of the electrolyte where the concentration of one of the constituents remains unaltered, changes in the concentration of that constituent at one of the electrodes cannnot affect conditions at the other. It is true that some new substance, for instance acid formed at the anode, might on reaching the cathode affect the diffusion constants or the electrolytic migration of the others there; such cases, however, are excluded from consideration for other reasons (see pg. 820).

The distance in centimeters between the electrode under consideration and the section of fixed concentration is thus

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[1] Zeit. phys. Chem., 47, 56 (1904).

denoted by l. Weber took the surface of one of his electrodes as origin and denoted the distance to the other by L; his L is thus twice l; with rotating electrodes, however, or stirred electrolytes, l is evidently quite independent of the distance between the electrodes.

At the moment of throwing on the current, the solution is supposed to be uniform throughout the vessel; thus the "*initial condition*" adopted in all the deductions of this paper is, that at $t = 0$, $z = z_0$ for all values of x or

$$[\textit{For } t = 0] \qquad \partial z/\partial x = 0 \qquad (ii).$$

When the current is thrown on, diffusion and migration begin.

Diffusion and Migration.—The rate of diffusion of any constituent away from one of the electrodes (*i. e.*, the number of equivalents of that substance per second which is carried by diffusion across each square centimeter of the cross section of the vessel) may be different at different points of the diffusion layer. At any point x, however, it is proportional to the concentration gradient at that point in the line connecting the electrodes; that is, to the difference of concentration per centimeter in the direction of the x axis, or

$$\textit{Rate of diffusion from electrode} = k\,\partial z/\partial x \quad - \quad - \quad - \quad (\textit{Fick}),$$

where z is the concentration of the constituent in question, expressed in equivalents per cubic centimeter; if $\partial z/\partial x$ be negative, diffusion will occur *towards* the electrode.

The rate of electrolytic migration of the same constituent, or the number of equivalents per second carried across each square centimeter of the cross section of the vessel by the current $\mathcal{J}$ amperes, is given by the expression

$$\textit{Rate of migration from electrode} = \frac{\mathcal{J}}{96540\,\mathcal{A}} \cdot \frac{zu}{\Sigma zu} \quad (\textit{Kohlrausch}),$$

where u is the mobility of the constituent in question and z its concentration; Σzu indicates the sum of the products of the mobilities of the various ions each into its own concentration. The sign of this expression (the direction in which the migration takes place) evidently depends on the direction of the electric current, and on whether the constituent to which z refers acts as anion or cation; it is *negative* if the motion is *toward* the electrode.

Excluding for the present the possibility of secondary reactions in which the products of electrolysis take part, these two factors determine the total rate of flow, which accordingly is given by

$$\textit{Rate of flow from electrode} = k\frac{\partial z}{\partial x} + \frac{\mathcal{J}}{96540\,\mathcal{A}}\cdot\frac{zu}{\Sigma zu},$$

and the rate of accumulation, $\partial z/\partial t$, at any point x is determined by the difference between the rates of flow to and from that point:

$$\frac{\partial z}{\partial t} = k\frac{\partial^2 z}{\partial x^2} + \frac{\partial}{\partial x}\left(\frac{\mathcal{J}}{96540\,\mathcal{A}}\cdot\frac{zu}{\Sigma zu}\right).$$

In some cases the second term on the right vanishes or may be neglected, leaving

$$\partial z/\partial t = k\partial^2 z/\partial x^2. \qquad (iii)$$

This occurs, for instance, (*a*) if $u = 0$, *i. e.*, if the constituent in question is a non-electrolyte; (*b*) if $zu/\Sigma zu$ is small, as when z refers to the concentration of copper in a solution of copper sulphate containing excess of sulphuric acid; (*c*) if the solution contains only one salt (in which case $zu/\Sigma zu$ becomes Hittorf's "transport number") whose transport number is not affected by change in concentration; (*d*) if the solution contains several salts with a common ion (the "constituent" under consideration) and if the ions of the opposite sign all have the same mobility; when the case is analogous to (*c*). Throughout Parts I and II of the present paper, (*iii*) is assumed to hold.

Electrode condition.—Let G represent the number of equivalents per second of the constituent under consideration caused to appear in the solution at each square centimeter of the surface of the electrode by the action of the current $\mathcal{J}$.

G will usually be related to $\mathcal{J}$ by an expression of the form

$$G = \frac{\mathcal{J}}{96540\,\mathcal{A}}\left(1 + \frac{zu}{\Sigma zu}\right)$$

in which the first term on the right measures the amount formed by chemical changes (oxidation, reduction, solution of the electrode, etc.), and the second term the amount brought up to (but, naturally, not past) the electrode surface by migration. At the anode in a solution of copper sulphate with excess of sulphuric acid, for instance, the first term would be positive and the second term zero if the "constituent under consideration"—to which z refers—were copper; if it were sulphuric acid, the first term would be zero and the second positive; in either case, if the electrode were a cathode, G would be negative.

The effect of the electrolysis on the concentration of this constituent in the solution is the same as though it were being carried into the solution through the surface of the electrode by the concentration gradient

$$[\mathit{For}\ x = l] \qquad \partial z/\partial x = G/k \qquad (iv)$$

which would produce the same gain that is actually brought about by the electrolysis. Eq. (*iv*) is therefore introduced as the "electrode condition" corresponding to the current $\mathcal{J}$ amperes. In the first Section of this paper, "Constant Current," G will be treated as independent of t; under "Successive Currents" it will be supposed to change abruptly at definite moments; while under "Sinusoidal Currents" it will be treated as a continuous function of the time. In the first Part of the paper it will be assumed that for a given value $\mathcal{J}$, of the current, G is not affected by the composition of the solution at the electrode; in the second Part, account will be taken of the fact that the nature of the chemical action at the electrode may change abruptly when the concentration reaches a certain value; Part III admits the possibility of secondary reactions at the electrode.

The mathematical problem then is, to find a solution for the differential equation (*iii*) which will satisfy the "boundary conditions" (*i*), (*ii*) and (*iv*). In the case of linear and homogeneous equations, like (*iii*), where the only coefficient k is a constant, there is no difficulty in finding particular solutions; from these, general solutions can be built up by multiplying each particular solution by an arbitrary constant and taking the sum. With such general solutions, however, in which the constants have arbitrary values, "ist so gut wie nichts gewonnen."[1] The main point is to find values for these multipliers such that the boundary conditions may be satisfied; and no general rules have as yet been laid down for finding them. Eq. (*iii*), however, has been made the subject of detailed study by Fourier and others in connection with the theory of the flow of heat,[2] and Weber[3] has shown how the boundary conditions of the present problem may be introduced; an equation corresponding to (15) of the present paper has already been obtained by him.

PART I

REACTIONS AT THE ELECTRODE INDEPENDENT OF THE CONCENTRATION z. SECONDARY REACTIONS EXCLUDED

Sec. 1.—Constant Current

One particular solution of (*iii*) is

$$z = Cx + D$$

and another is

$$z = (A \sin Ex + B \cos Ex)e^{-E^2kt} .$$

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[1] Riemann, Die Partiellen Differential-Gleichungen der math. Physik, 4th Ed., Vol. i, pg. 153 (1900).

[2] In his "Introduction to the Theory of Fourier's Series and Integrals, and the Mathematical Theory of the Conduction of Heat" (Macmillan, 1906). H. S. Carslaw has collected a large number of cases in which problems analogous to the present have been solved, but as condition (iv) does not correspond to any easily realizable experimental condition except in the case of electrolysis, no problems satisfying that condition have been included; in the case of a heat problem, condition (iv) would correspond to a fixed rate of loss of heat from one end of a cylinder, independent of its temperature.

[3] Wied. Ann., 7, 536 (1879).

The expression built up from these, *viz.*,

$$z = (A_1 \sin E_1x + B_1 \cos E_1x)e^{-E_1^2kt} + (A_2 \sin E_2x + B_2 \cos E_2x)e^{-E_2^2kt} + etc. + Cx + D,$$

or briefly

$$z = \sum_{n=1}^{\infty} \{(A_n \sin E_nx + B_n \cos E_nx)e^{-E_n^2kt}\} + Cx + D, \quad (1)$$

proves sufficiently general to allow the introduction of (*i*), (*ii*) and (*iv*).

To introduce (*i*).—From (1)

$$[For\ x = 0] \qquad z = D + \Sigma B_n e^{-E_n^2kt}. \qquad (2)$$

The expression on the right may be made constant and equal to z_0 for all values of t, as required by condition (*i*), by setting

$$B_1 = 0, \qquad B_2 = 0, \qquad B_3 = 0, etc. \qquad (3)$$

so that, from (2), (3) and (*i*)

$$D = z_0. \qquad (4)$$

To introduce (*iv*).—From (1), (3) and (4),

$$[For\ x = l] \qquad \frac{\partial z}{\partial x} = C + \sum_{n=1}^{\infty} A_n e^{-E_n^2kt}.\cos E_n l \qquad (5)$$

whence by (*iv*),

$$C + \sum_{n=1}^{\infty} A_n e^{-E_n^2kt}.\cos E_n l = \frac{G}{k}. \qquad (6)$$

This is possible, for all values of t, only if each term involving t is separately made zero; this may be accomplished by setting

$$\cos E_n l = 0, \quad i.e., \ E_n = \frac{(2n-1)\pi}{2l}, \qquad (7)$$

n being any integer.

From (6) and (7) there follows

$$C = G/k. \qquad (8)$$

To introduce (*ii*).—Setting $t = 0$ in (1), and substituting the values of B, D and E_n given by (3), (4) and (7), there follows

$$[\textit{For } t = 0] \quad z = z_0 + Cx + \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l}, \tag{9}$$

whence by (*i*)

$$0 = Cx + \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l}. \tag{10}$$

Fourier has shown that for values of f between 0 and $\pi/2$ (see Appendix)

$$f = \frac{4}{\pi}\left(\sin f - \frac{1}{9}\sin 3f + \frac{1}{25}\sin 5f - \textit{etc.}\right), \tag{11}$$

whence (writing $\frac{\pi x}{2l}$ for f)

$$Cx = \frac{8lC}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{(2n-1)^2}\sin\frac{(2n-1)\pi x}{2l}. \tag{12}$$

Substituting this expression for Cx in (10)

$$\sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2l} = \frac{-8lC}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{(2n-1)^2}\sin\frac{(2n-1)\pi x}{2l} \tag{13}$$

whence

$$A_n = \frac{(-1)^n}{(2n-1)^2}\cdot\frac{8lC}{\pi^2}. \tag{14}$$

Thus, by substituting in (1) the values for B, D, E_n and A_n from (3), (4), (7) and (14), an expression is obtained,

$$z - z_0 = \frac{Gx}{k} + \frac{8lG}{\pi^2 k}\sum_{n=1}^{\infty}\frac{(-1)^n}{(2n-1)^2}\cdot e^{-\frac{(2n-1)^2\pi^2 kt}{4l^2}}\cdot\sin\frac{(2n-1)\pi x}{2l}, \tag{15a}$$

which satisfies the differential equation (*iii*) and the conditions (*i*), (*ii*) and (*iv*), if the current[1] remains constant from $t = 0$, the moment of throwing on the current, up to the moment t.

Inspection of (15*a*) shows that the right-hand member

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[1] The equations deal only with G, which however is proportional to the current, see page 821.

is divisible by G. From this it appears that in experiments with the same electrolyte, carried out at the same temperature (hence with fixed value of k) and with the same rate of stirring (fixed value of l), the amount of change in concentration $(z-z_0)$ in a given time will be proportional to G and therefore to the current. It may also be concluded that if in a series of experiments (with fixed values of k and l) the currents (and therefore the values of G) be proportional to the initial concentrations (z_0), the values of z after any given duration of electrolysis (t) will likewise be proportional to the initial concentrations.

For the sake of brevity, (15*a*) may be written

$$z-z_0 = Cx + \frac{8lC}{\pi^2}\sum\frac{(-1)^n}{m^2}e^{-m^2at}\sin mgx, \qquad (15b)$$

where $m = 2n-1$, $C = G/k$, $a = \pi^2k/4l^2$, $g = \pi/2l$, and Σ is written for $\sum\limits_{n=1}^{\infty}$. Since $(-1)^n \sin mgx = -\cos mg(l-x)$, (15*b*) may be put in the more convenient form,

$$\frac{z-z_0}{Cl} = \frac{x}{l} - \frac{8}{\pi^2}\sum\frac{1}{m^2}e^{-m^2at}\cos mg\xi, \qquad (15c)$$

where all the terms after the sign of summation are positive; ξ is here written as an abbreviation for $l-x$, the distance of the point x from the electrode. In this equation, the term on the left expresses the change in concentration as a fraction of the maximum change that could be brought about at the electrode by the same current;[1] the first term on the right gives the distance from the origin $(x = 0)$ as a fraction of the total length of the diffusion layer; and $at = \pi^2kt/4l^2$ in the exponent gives the time in units which depend on k and l only.[2]

The concentrations at the electrode, which are the most important from an experimental point of view, may be ob-

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[1] *i. e.*, if left to act for "infinite" time, see p. 828, footnote. This "physical" interpretation of Cl is allowable within certain limits only (see Part II); the geometrical interpretation (fig. 1) holds in all cases.

[2] $a = \pi^2k/4l^2$ is spoken of later as the "time constant."

tained by substituting l for x in (15); $\cos mg\xi$ then becomes unity, and (15c) reduces to

$$[\textit{For } x = l] \qquad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} \sum \frac{1}{m^2} e^{-m^2 at}. \qquad (16)$$

Methods of Computation

First term approximation.—The first five terms of the series in (16) are:

$$e^{-at},\ \frac{1}{9} e^{-9at},\ \frac{1}{25} e^{-25at},\ \frac{1}{49} e^{-49at},\ \frac{1}{81} e^{-81at}.$$

The second term will be one percent or less of the first term if $\frac{1}{9} e^{-9at} = \frac{1}{100} e^{-at}$ or less, *i. e.*, if at be 0.301 or more; and it will be one per thousand of the first term if at be 0.589 or more; in both cases the remainder of the series is negligible. Thus in computing values of $(z - z_0)/Cl$ for values of at above 0.6, the first term of the series, neglecting all the others, will give results accurate to one-tenth percent; under these conditions (17) may therefore be used in place of (16).

$$[\textit{For } at \textit{ large, and } x = l] \quad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2} e^{-at} \quad \textit{approx.} \quad (17)$$

But as at becomes smaller, the number of terms that have to be taken into account rises rapidly. In computing $(z-z_0)/Cl$ for $x = l$ and $at = 0.03$, for instance, the values of the first five terms (each multiplied by $8/\pi^2$) are 0.78664, 0.06875, 0.01532, 0.00378, 0.00088, respectively, and all five have to be evaluated in order to find $(z - z_0)/Cl$ to three places of decimals.

Parabolic approximation.—Thomson and Cayley[1] have shewn that

$$\sum_{n=1}^{\infty} e^{-\frac{(2n-1)^2\pi^2}{4f^2}} \cos \frac{(2n-1)\pi y}{f} =$$

$$\frac{f}{2\sqrt{\pi}} \left(e^{-y^2} - e^{-(y-f)^2} - e^{-(y+f)^2} + e^{-(y-2f)^2} + e^{-(y+2f)^2} - \textit{etc.}\right). \quad (18)$$

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[1] Quarterly Journal of Mathematics, 1, 316 (1857).

Substituting 0 for y, and at for $\pi^2/4f^2$, this gives

$$\sum_{n=1}^{\infty} e^{-(2n-1)^2 at} = \frac{1}{4}\sqrt{\frac{\pi}{at}}\left\{1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-\frac{n^2\pi^2}{4at}}\right\}. \quad (19)$$

For small values of at the sum on the right may be neglected, giving

$$[\textit{For } \underline{at} \textit{ small}] \quad \sum_{n=1}^{\infty} e^{-(2n-1)^2 at} = \frac{1}{4}\sqrt{\frac{\pi}{at}} \quad \textit{approximately.} \quad (20)$$

Multiplying both sides by dt and integrating between the limits 0 and t there follows

$$[\textit{For } \underline{at} \textit{ small}] \quad \sum_{n=1}^{\infty} \frac{1}{m^2}\left(1 - e^{-(2n-1)^2 at}\right) = \frac{1}{2}\sqrt{\pi at} \textit{ approx.}, \quad (21)$$

whence

$$[\textit{For } x = l, \underline{at} \textit{ small}] \quad \frac{z - z_0}{Cl} =$$

$$1 - \frac{8}{\pi^2}\sum \frac{1}{m^2} e^{-m^2 at} = \frac{4}{\pi^{3/2}}\sqrt{at} \textit{ approx.}, \quad (22a)$$

or, substituting for at its value $\pi^2 kt/4l^2$,

$$[\textit{For } x = l \ \underline{at} \textit{ small}] \quad (z - z_0)/C = 1.129\sqrt{kt} \textit{ approximately.} \quad (22b)$$

TABLE I

Values of $(z - z_0)/Cl$ at the electrode

at	Parabolic approx.		True value (Eq. 16)	First term approx.	
	Calc. (Eq. 22a)	Error		Error	Calc. (Eq. 17)
0.4	0.45432	0.00012	0.45420	0.00246	0.45666
0.5	0.50795	0.00059	0.50736	0.00100	0.50836
0.6	0.55643	0.00169	0.55474	0.00041	0.55515

The figures of Table I show that for all practical purposes the accurate expression (16) may be replaced by the "first term approximation" (17) for values of at above 0.5, and by the "parabolic approximation" (22) for values of at below 0.5. It may not be out of place to emphasize the fact that the applicability of either of these approximations depends not on the value of either l, k, or t alone, but on that of $at = \pi^2kt/4l^2$; the parabolic approximation, for instance, holds not only for the case "$l = \infty$",[1] as shown by Sand but it also holds for any other value of l provided kt be small enough.

TABLE II

Values of $(z - z_0)/Cl$ at the electrode

at	$(z - z_0)/Cl$	at	$(z - z_0)/Cl$	at	$(z - z_0)/Cl$
0	0	0.5	0.507	1.4	0.800
0.05	0.164	0.6	0.555	1.5	0.819
0.1	0.227	0.7	0.597	2.0	0.890
0.2	0.321	0.8	0.636	2.786	0.950
0.3	0.393	0.9	0.670	4.395	0.990
0.4	0.454	1.0	0.702	∞	1.000

As shown by the figures of Table II, ninety-nine percent of the total change of concentration at the electrode that a given current can accomplish is completed when at reaches 4.40. The actual number of seconds corresponding to a given value of at depends, obviously, on the "time constant" $a = \pi^2k/4l^2$, *i. e.*, on the values of k and l; if, for example, $k = 4 \times 10^{-6}$ cm^2/sec., and $l = 3.14 \times 10^{-4}$ cm (numbers within the range of those experimentally met with) at gives the duration of electrolysis in hundredths of a second; if the stirring were slower, however, and l rose to 3.14×10^{-3} cm, at would give the time in seconds.

The Stationary State

When the current has flowed long enough, the "stationary state" is reached, the equation for which may be obtained direct from (*iii*) by putting $\partial z/\partial t = 0$, or from (15) by setting $t = \infty$; the exponential term then becomes zero, and (15*c*) reduces to

$$[\textit{For } t = \infty\,^{2}] \quad z - z_0 = Cx \tag{23}$$

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[1] Sand, Phil. Mag., [6] 1, 45 (1901).

[2] Practically speaking, for such values of at as make the sum term in (15) negligible. If one percent of $z - z_0$ be "negligible" from the point of view of the experimenter, $at = 4.40$ is high enough, so that for $k = 4 \times 10^{-6}$ and $l = 3.14 \times 10^{-4}$ cm, 0.044 second would be an "infinite" value of t.

i. e., there is a linear gradient of concentration throughout the diffusion layer.

The summation on the right of (15) thus shows the difference between the concentrations at any moment of the electrolysis and those at the stationary state; as with increasing t this term decreases, and ultimately vanishes, it will be spoken of as the "evanescent term" of (15) to distinguish it from the "stationary term" Cx.

The Stationary Term when k is a Function of z

Throughout this paper, the diffusion constant is supposed to be independent of the concentration; in the present paragraph, however, the important—but mathematically simple—case of the stationary state with constant current is dealt with on the assumption that k is a function of z. The equations deduced in this paragraph are not made use of in what follows.

Setting $k = f(z)$, the differential equation has the form:

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(f(z)\frac{\partial z}{\partial x}\right). \tag{A}$$

As however at the stationary state, z depends on x alone, (A) may be replaced by the "ordinary" differential relation

$$\frac{d}{dx}\left(f(z)\frac{dz}{dx}\right) = 0. \tag{B}$$

Hence $f(z)\frac{dz}{dx}$ has a constant value for all values of x; at the electrode this is known to be equal to G; therefore,

$$f(z)\frac{dz}{dx} = G, \tag{C}$$

and

$$\int_{z_0}^{z} f(z)dz = \int_{0}^{x} G dx = Gx; \tag{D}$$

therefore,

$$x = \frac{1}{G}\int_{z_0}^{z} f(z)dz, \tag{E}$$

which whenever $f(z)$ is known gives x explicitly in terms of z.

For example, if $f(z) = k_0 + k_1 z$ (F)

$$Gx = (k_0 z + \frac{1}{2} k_1 z^2) - (k_0 z_0 + \frac{1}{2} k_1 z_0^2). \tag{G}$$

From this, if desired, z may be expressed in terms of x, thus

$$z = \frac{-k_0 + \sqrt{k_0^2 + 2k_1(Gx + k_0 z_0 + \frac{1}{2} k_1 z_0^2)}}{k_1}. \tag{H}$$

Similarly in many other cases it is possible to pass from Eq. (E) to one expressing z in terms of x; when this is not possible, a graph may be drawn.

The "Limiting Current"

The "limiting current" for the change $z' - z_0$ is defined to be that current which at $t = \infty$ is just sufficient to bring the concentration at the electrode from z_0 to z'; it may be denoted by $\mathscr{I}'$ and the corresponding value of C by C'. Substituting z' for z, and l for x in (23),

$[\textit{For } t = \infty \textit{ and } x = l]\ z' - z_0 = C'l,$

$$\text{whence } C' = \frac{z - z_0}{l}, \text{ and } \mathscr{I}' = \frac{96540\,\mathscr{A}k(z' - z_0)}{l(1 + zu/\Sigma zu)}. \tag{24}$$

Thus any experiment in which z', z_0, and $\mathscr{I}'$ are measured may serve to determine the ratio k/l. In the special case where $z' = 0$, $\mathscr{I}'/z_0 = \dfrac{96540\,k\mathscr{A}}{(1 + zu/\Sigma zu)l}$. This relation has been used by Nernst and Merriam[1] and others for the determination of k/l.

As indicated by the heading of the table, the numbers entered in Table II give the values of $(z - z_0)/Cl$ at the electrode for different values of at. Since, however, from (24), $(z' - z_0)/Cl = C'/C = \mathscr{I}'/\mathscr{I}$, these same numbers give the limiting current $\mathscr{I}'$ corresponding to any arbitrary change of concentration at the electrode if the time (at) is known at which some known current $\mathscr{I}$ just brings about the same change. For example, the limiting current corresponding to

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[1] Zeit. phys. Chem., 53, 235 (1905).

any change of concentration at the electrode is 0.164 times the current that will bring about the same change in the time $at = 0.05$. Conversely, the reciprocals of the numbers under $(z - z_0)/Cl$ give the current necessary to bring about any given change of concentration in a given time at, if the limiting current corresponding to the same change be known; to accomplish a given change in the time $at = 0.10$ requires 4.41 times the limiting current corresponding to that change. The "change of concentration" easiest recognized in the laboratory is often that from z_0 to 0.

Determination of k and of l

As both k and l are involved in (16), two experiments are in general required to determine both or either of them; one of these experiments may be a determination of the ratio k/l by means of the limiting current as indicated above, and the other a measurement in which the time needed to bring about some known change of concentration at the electrode is determined. If this second measurement be so planned that $at \geq 0.5$, the "single term" approximation (17) may be employed; writing η for the ratio k/l supposed known, this gives

$$l = \frac{0.4343\,\pi^2\eta t}{4\,log_{10}\left[\frac{\pi^2}{8}\left(1 - \frac{\eta(z' - z_0)}{G}\right)\right]} = \frac{1.072\,\eta t}{0.09121 + log_{10}\left(1 - \frac{\eta(z' - z_0)}{G}\right)}. \qquad (25)$$

If at be less than 0.5, however, so that the "parabolic approximation" (22*b*) is applicable, k may be determined by means of it directly from one experiment, the change of concentration at the electrode under those circumstances being independent of l. This method of finding k has been employed by Sand; in his experiments, however, l was taken to be "infinite," and was not determined.

Graphical Representation

The curves of Fig. 1 give the values of $(z - z_0)/Cl$ through the diffusion layer (for any fixed values of C, k, and l), for $t = 0$, for $t = \infty$ and for ten values of at ranging from 0.1 to 1.0; the curves have been drawn with fair accuracy, values of $(z - z_0)/Cl$ may be estimated from them to within one percent of the value of Cl. As is clear from (15), values of z itself are not fixed by C, k, and l; the point $z = 0$ is therefore not marked on the diagram.

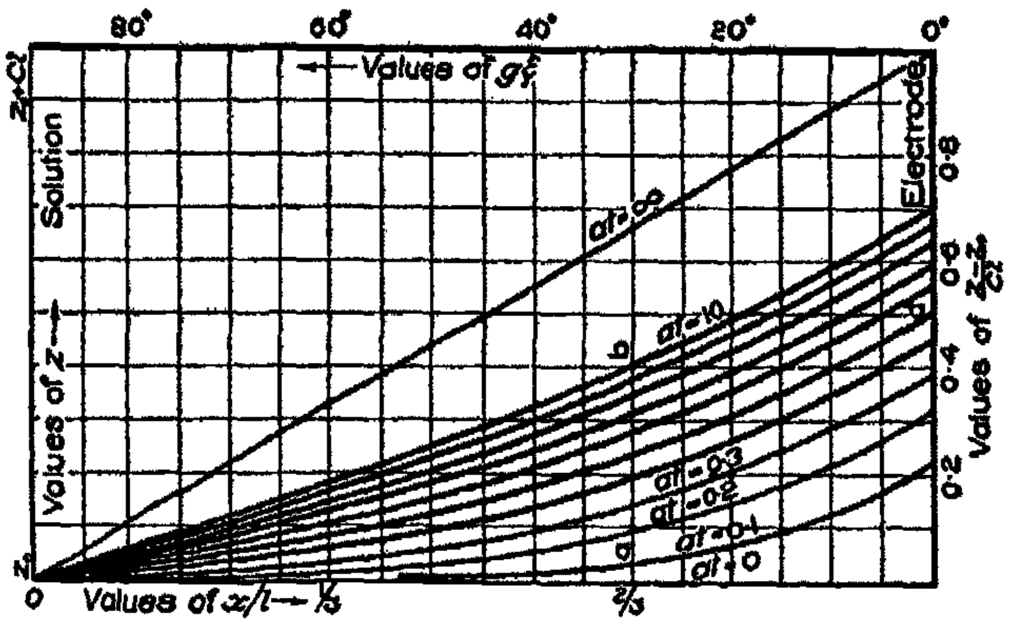


Fig. 1

In Fig. 2, the same data are plotted on a time base; the curves give the progress of the concentration change with the time (from $at = 0$, to $at = 1.0$) at ten equidistant cross-

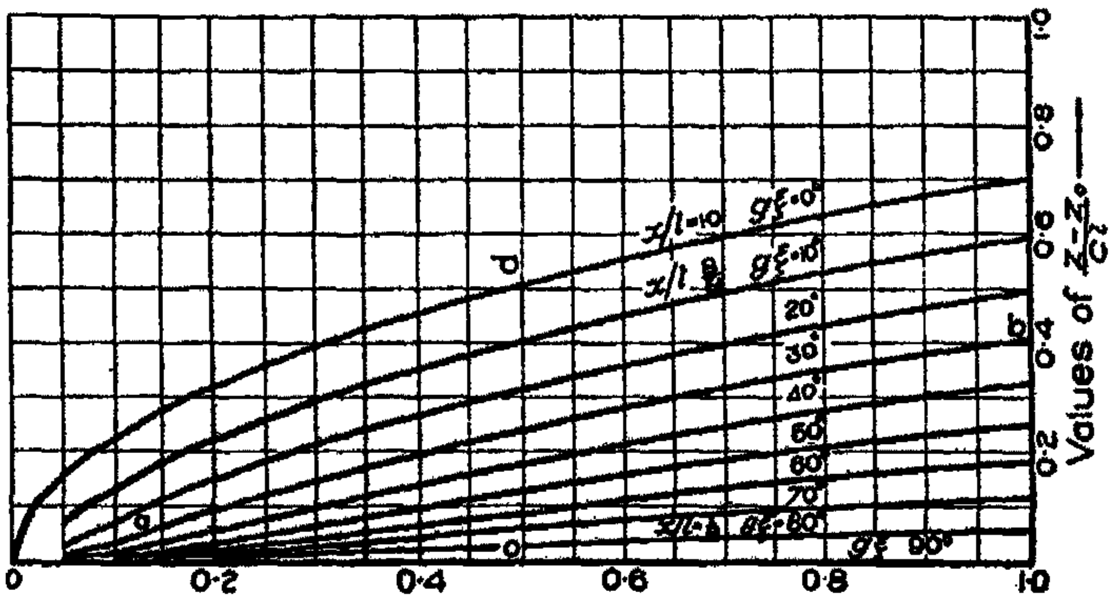


Fig. 2

sections of the diffusion layer. The line *ab* in Fig. 1 corresponds to the curve *ab* in Fig. 2, and the line *od* in Fig. 2 to the curve *od* in Fig. 1.

In Fig. 3, the relative change of concentration at the electrode, $(z - z_0)/Cl$ is plotted for the interval $at = 0$ to $at = 5.0$; in Fig. 4 the same data are plotted with logarithmic coordinates

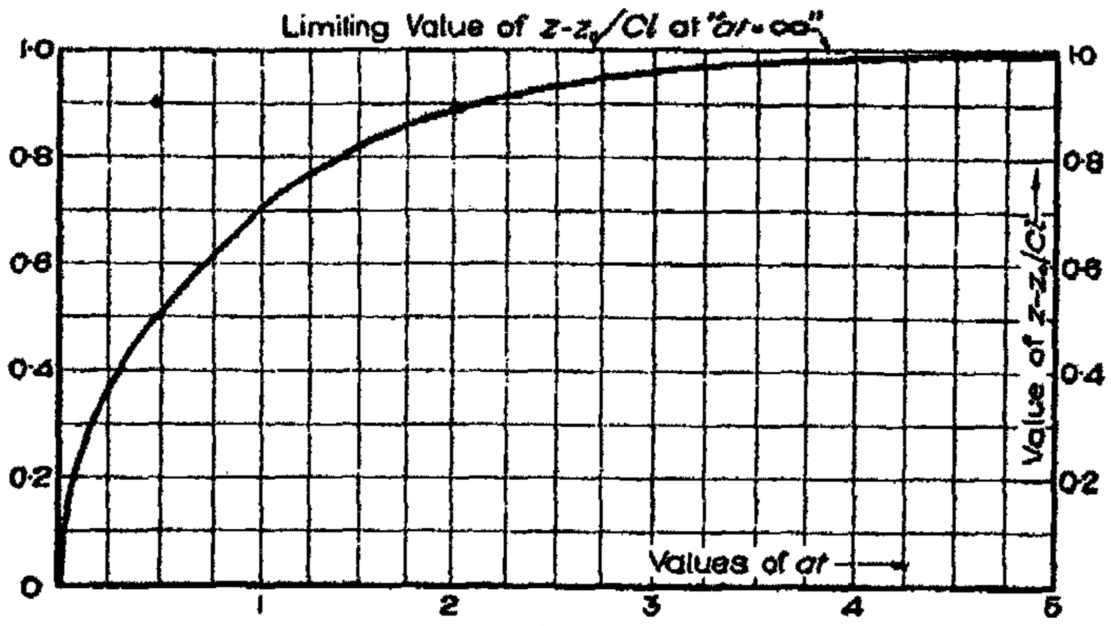


Fig. 3

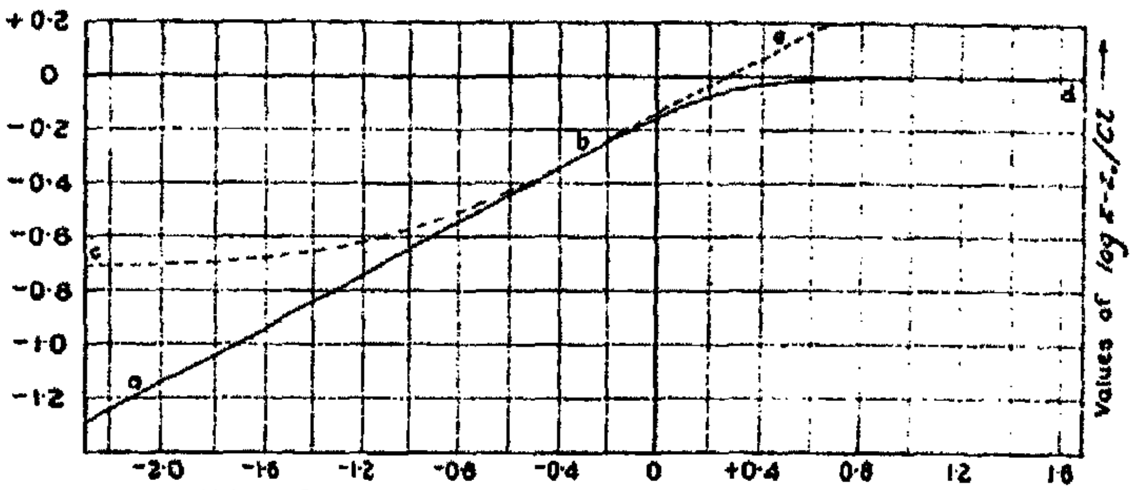


Fig. 4

(from $\log_{10} at = -2.30$ to 1.7, *i. e.*, from $at = 0.005$ to $at = 50$). The curve *dbc* represents the "first term approximation," the straight line *ca* the parabolic approximation, and the full line *abd* the true values of $\log_{10}(z - z_0)/Cl$.

Curve I of Fig. 5 gives the concentrations throughout the diffusion layer at $at = 0.5$ for fixed values of C and k

and for $l = l_1$; curve II gives the concentrations at $at = 0.1$ for the same values of C and k but for $l_2 = l_1\sqrt{5}$. Since a varies inversely as l^2, t as well as C and k is the same for both curves, and the figure serves to illustrate the conclusion of (22*b*) that for small values of at, $(z - z_0)/C$ at the electrode is independent of l. As shown by the figure, the change of concentration initiated at the electrode has hardly yet had time at $at = 0.1$ to spread more than half way to the "point of constant concentration," $x = 0$; shifting this point still further to the left could therefore have no effect on the concentration at the electrode.

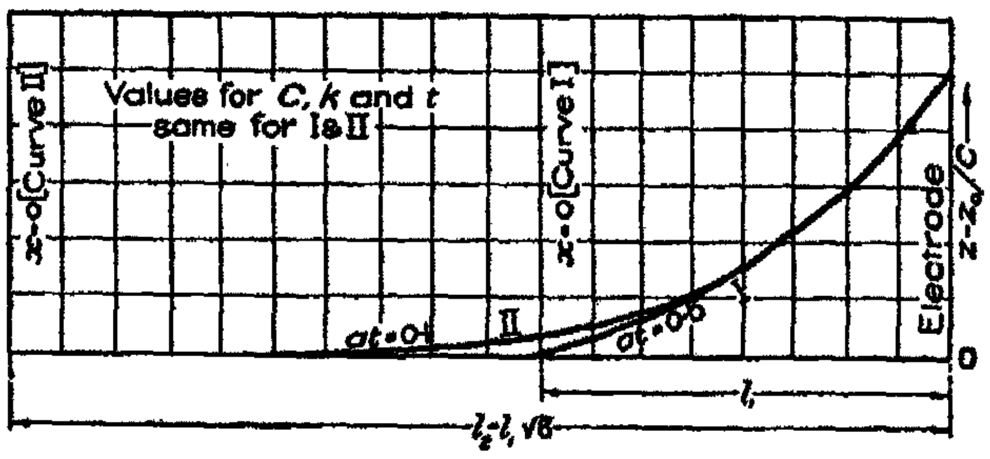


Fig. 5

Sec. 2.—Successive Currents in General

Eq. (15) and those deduced from it in the preceding paragraphs are applicable only when the current (and consequently C) remains constant during the electrolysis. It is now proposed to deal with the more general case where the currents $\mathcal{J}_1$, $\mathcal{J}_2$, $\mathcal{J}_3$, corresponding to C_1, C_2, C_3, etc., act successively, C_1 from $t = 0$ to $t = t_1$, C_2 from t_1 to t_2, C_3 from t_2 to t_3, etc; as before, at $t = 0$, $z = z_0$ for all values of x.

Up to the moment t_1, the values of z are given by (15); in particular,

$$[For\ t = t_1]\ z - z_0 = C_1x - \frac{8lC_1}{\pi^2}\sum\frac{1}{m^2}e^{-m^2at_1}\cos mg\xi \qquad (26a)$$

$$= C_2x + (C_1 - C_2)x - \frac{8lC_1}{\pi^2}\sum\frac{1}{m^2}e^{-m^2at_1}\cos mg\xi \qquad (26b)$$

$$= C_2x - \frac{8l}{\pi^2}\sum\frac{1}{m^2}(C_1e^{-m^2at_1} + C_2 - C_1)\cos mg\xi, \qquad (26c)$$

the last transformation being effected by means of (12), which, since $(-1)^{n+1} \sin mgx = \cos mg\xi$, may be brought into the form

$$Cx = \frac{8lC}{\pi^2}\sum\frac{1}{m^2}\cos mg\xi. \tag{27}$$

Between $t = t_1$ and $t = t_2$ values of z are given by the expression

$[For\ t_1<t<t_2]\quad z-z_0 =$

$$C_2x-\frac{8l}{\pi^2}\sum\frac{1}{m^2}\{C_1e^{-m^2at_1}+\overline{C_2-C_1}\}\,e^{-m^2a(t-t_1)}\cos mg\xi \tag{28}$$

which satisfies *ii*, *iii*, *iv*,[1] and the condition that at $t = t_1$ the values of z along the x axis are those consequent on the action, from $t = 0$ to $t = t_1$, of the current $\mathcal{J}$.

In general

$[For\ t_{p-1}<t<t_p]\quad z-z_0 =$

$$C_px-\frac{8l}{\pi^2}\sum\frac{1}{m^2}\Big\{C_1e^{-m^2at}+\overline{C_2-C_1}\,e^{-m^2a(t-t_1)}+\ldots\ldots$$

$$+\overline{C_r-C_{r-1}}\,e^{-m^2a(t-t_{r-1})}+\ldots+\overline{C_p-C_{p-1}}\,e^{-m^2a(t-t_{p-1})}\Big\}\cos mg\xi \tag{29a}$$

$$=C_px-\frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{m^2}\Big\{C_1e^{-m^2at}+\sum_{r=2}^{p}\overline{C_r-C_{r-1}}\,e^{-m^2a(t-t_{r-1})}\Big\}\cos mg\xi. \tag{29b}$$

The expression inside the brackets $\{\}$ can be rearranged thus:

$$\{C_1(e^{-m^2at}-e^{-m^2a(t-t_1)})+C_2(e^{-m^2a(t-t_1)}-e^{-m^2a(t-t_2)})+\ldots$$
$$+C_r(e^{-m^2a(t-t_{r-1})}-e^{-m^2a(t-t_r)})+\ldots+C_pe^{-m^2a(t-t_{p-1})}\}$$

so that (29) may also be written

$$[For\ t_{p-1}\leqq t\leqq t_p]\ z-z_0=C_px-\frac{8l}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{m^2}\Big\{C_pe^{-m^2a(t-t_{p-1})}+$$

$$\sum_{r=1}^{p-1}C_r(e^{-m^2a(t-t_{r-1})}-e^{-m^2a(t-t_r)})\Big\}\cos mg\xi. \tag{29c}$$

---

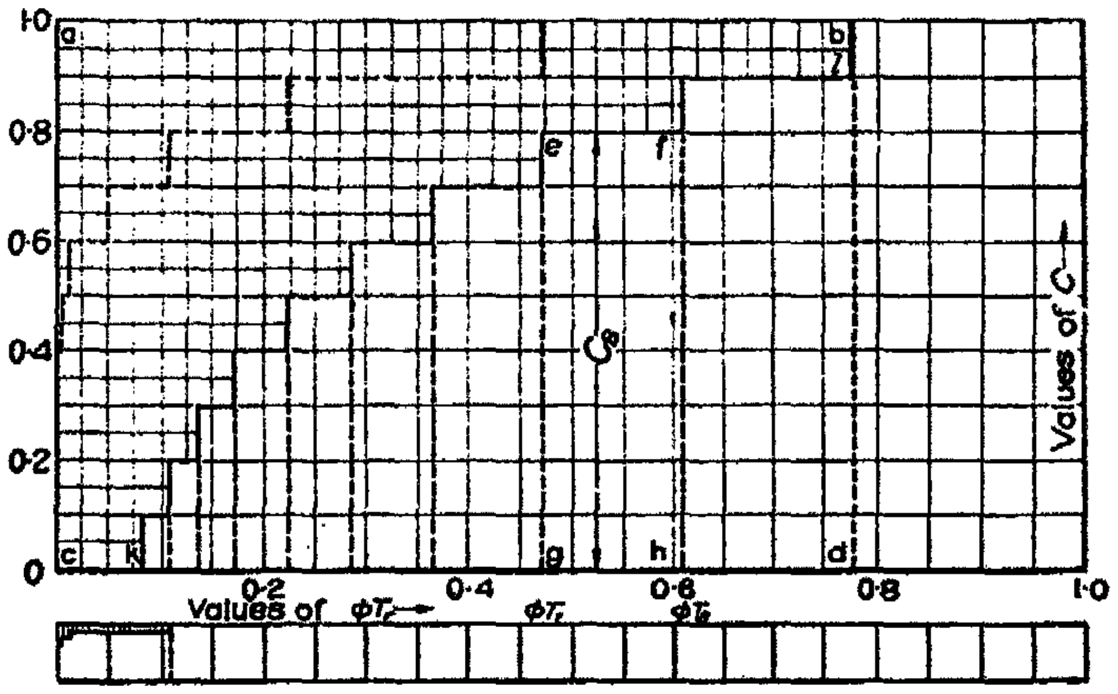
[1] This is obvious if it be noted that the expression within the brackets $\{\}$ is a function of m only, not of x or t.

Finally, if T_r be written for $t-t_r$, the time elapsed since the current corresponding to C_r ceased to act, and ϕT_r for $e^{-m^2a(t-t_r)}$,

$$[For\ t_{p-1} < t < t_p] \quad z - z_0 = C_p x - \frac{8l}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{m^2} \Big\} C_p \phi T_{p-1} - \sum_{r=1}^{p-1} C_r(\phi T_r - \phi T_{r-1}) \Big\} \cos mg\xi \qquad (29d)$$

which lends itself to graphical representation.

Figs. 6 and 7 illustrate the case of electrolysis by a succession of currents beginning at $t = 0$ with one ampere, followed by 2, 3, 4, . . . 10 amperes, each passing through the solution for the equal interval $at = 0.25$. The abscissae of the two figures give the values of ϕT_r for $n = 1$ and $n = 2$ respectively, and the ordinates the values of C and of $C/9$ respectively for the ten currents; thus Fig. 6 corresponds to the first term of the n-sum in (29*d*) and Fig. 7 to the second term. The area *abdc* equals $C_{10}\phi T_9$ (corresponding to $C_p\phi T_{p-1}$); *efhg* equals $(\phi T_8 - \phi T_7)C_8$, *kefld* equals $\sum_{r=1}^{p-1} C_r(\phi T_r - \phi T_{r-1})$, and *ackeflb* equals the whole expression within the $\{\;\}$



Figs. 6 and 7

brackets of (29*d*), for $n = 1$. The broken line in the upper left-hand corner of Fig. 6 represents the first term of the n-sum for the same ten currents each persisting for $at = 0.75$ instead of $at = 0.25$; the great reduction of the { } term of (29*d*) is obvious. It is quite clear from the figure, that the effect of previous history is much less on the second than on the first term, so that in deciding how far back it is necessary to go in taking account of the previous currents, the first term only need be considered.

Equation (29) in its various forms is the most general expression for $z - z_0$, all others given in Part I of this paper are deducible from it: Eq. (15) for instance results when $C_1 = C_2 = \ldots\ldots = C_p$; equations for the periodic recurrence of a finite number of currents are deduced from (29) in Secs. 3 and 4; and Sec. 5 shows how the periodic recurrence of an infinite number of currents each but slightly different from the preceding may be dealt with. As usual, by substituting l for x, whereupon $\cos mg\xi$ becomes unity, expressions for the experimentally important concentrations at the electrode may be obtained.

Sec. 3.—Periodic Currents. I. Cycles with Two Beats

In the first "beat" the current $\mathcal{J}_1$ acts for θ_1 seconds, in the second beat the current $\mathcal{J}_2$ for θ_2 seconds; these two "beats" make up a "cycle" of duration $\theta = \theta_1 + \theta_2$ seconds, which may be repeated again and again. It is convenient to introduce the symbol τ to represent the time elapsed since the beginning of the beat which is in progress at the moment t, t being counted as always from the moment $t = 0$ when the first current is thrown on; at $t = 0$, $z = z_0$ for all values of x.

In applying (29) to this case,

$$\begin{aligned} C_1 = C_3 = C_5, \textit{ etc.} \quad & \theta_1 = t_1 = (t_3 - t_2) = (t_5 - t_4) = (t_7 - t_6), \textit{ etc.} \\ C_2 = C_4 = C_6, \textit{ etc.} \quad & \theta_2 = (t_2 - t_1) = (t_4 - t_3) = (t_6 - t_5), \textit{ etc.} \\ & \theta \;= t_2 = (t_4 - t_2) = (t_6 - t_4), \textit{ etc.} = \theta_1 + \theta_2. \end{aligned}$$

Thus, during the pth beat, if p be odd ($p = 2q + 1$), $C_p = C_1$, and $t = q\theta + \tau$; if p be even $(p = 2q)$, $C_p = C_2$, and $t = (q - 1)\theta + \theta_1 + \tau$.

In the first case (p odd) on making these substitutions (29) becomes

$$[p\ odd]\quad z - z_0 = \tag{30a}$$

$$C_1 x - \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}\Big\{C_1 + (C_2 - C_1)[e^{m^2a\theta_1}(1 + e^{m^2a\theta} + e^{2m^2a\theta} + \ldots.$$

$$+ e^{(q-1)m^2a\theta}) - e^{m^2a\theta}(1 + e^{m^2a\theta} + e^{2m^2a\theta} + \ldots. + e^{(q-1)m^2a\theta})]\Big\}\cos mg\xi,$$

whence, summing the geometrical series, eliminating q, and rearranging,

$$[p\ odd]\ z - z_0 = C_1 x + \frac{8l(C_2 - C_1)}{\pi^2}\sum\frac{e^{-m^2a\tau}}{m^2}\cdot\frac{e^{m^2a\theta} - e^{m^2a\theta_1}}{e^{m^2a\theta} - 1}\cos mg\xi$$

$$- \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}\{C_1 + (C_2 - C_1)\frac{e^{m^2a\theta} - e^{m^2a\theta_1}}{e^{m^2a\theta} - 1}\}\cos mg\xi. \tag{30b}$$

Similarly, it may be shown that where p is even

$$[p\ even]\ z - z_0 = C_2 x + \frac{8l(C_1 - C_2)}{\pi^2}\sum\frac{e^{-m^2a\tau}}{m^2}\cdot\frac{e^{m^2a\theta} - e^{m^2a\theta_2}}{e^{m^2a\theta} - 1}\cos mg\xi$$

$$- \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}\{C_1 + (C_2 - C_1)\frac{e^{m^2a\theta} - e^{m^2a\theta_1}}{e^{m^2a\theta} - 1}\}\cos mg\xi. \tag{31}$$

In (30*b*) and (31), the term involving e^{-m^2at}, which decreases with increasing t and ultimately vanishes, may be spoken of as the "evanescent term"; it is the same in both equations, so that on plotting with z and t as axes the evanescent term would be represented by a continuous curve with no abrupt changes of direction at the beginning of a new beat. A plot of the "stationary terms" from the two equations (what is left of the right-hand members of (30*b*) and (31) when the evanescent term has been withdrawn) would give a zigzag line.

If x be replaced by l in these equations (and consequently $\cos mg\xi$ by unity) expressions for the concentrations at the electrodes are obtained. If t be set $= \infty$ thus reducing the evanescent term to zero, expressions for the concentrations at the stationary state are obtained. If τ be set $= 0$ (and consequently $e^{-m^2a\tau}$ = unity) expressions for the concentrations at the beginnings of odd or even beats (*i. e.*, at the ends of even or odd beats) respectively are obtained. If $C_2 = C_1$ the expression for constant current, (15), is obtained; if $C_2 = -C_1$ the equations apply to the simplest form of alternating current, and if $C_2 = 0$ to "intermittent" currents. Special cases of the latter will be examined in detail (see pages 840 and 843).

If the first, third, etc., beats last long enough to bring about a linear distribution of concentration throughout the diffusion layer, *i. e.*, if in (31), $a\theta_1 = \infty$ (see foot-note, page 828) the concentrations throughout the even beats will be represented by

$$[\textit{For } \theta_1 = \infty]\; z - z_0 = C_2x + \frac{8l(C_1 - C_2)}{\pi^2}\sum\frac{e^{-m^2a\tau}}{m^2}\cos mg\xi. \quad (32)$$

Centre and Amplitude of Swing

When the stationary state is reached, *i. e.*, when the evanescent term has become zero or approximately so, the concentration at any point in the diffusion layer oscillates between two extreme values, one at the end of each beat. Half the sum of the extreme values of the concentration change gives the "centre of swing" or mean value of the concentration change at that point; half their difference gives the "amplitude" or greatest deviation of the concentration above and below its mean value. An expression for the amplitude, and one for $z - z_0$ at the centre of swing, may accordingly be obtained by taking half the difference and half the sum respectively of the values of $z - z_0$ given by (30*b*) and (31) after setting $t = \infty$ and $\tau = 0$.

$$[\textit{Amplitude}]\;\; \frac{1}{2}(C_1 - C_2)x + \frac{4l(C_1 - C_2)}{\pi^2}\sum\frac{1}{m^2}\,\frac{e^{m^2a\theta_1} + e^{m^2a\theta_2} - 2e^{m^2a\theta}}{e^{m^2a\theta} - 1}\cos mg\xi. \quad (33)$$

$$[\textit{At centre}]\;\; z - z_0 = \frac{1}{2}(C_1 + C_2)x + \frac{4l(C_1 - C_2)}{\pi^2}\sum\frac{1}{m^2}\,\frac{e^{m^2a\theta_1} - e^{m^2a\theta_2}}{e^{m^2a\theta} - 1}\cos mg\xi. \quad (34)$$

Very Large and Very Small Values of θ

If both θ_1 and θ_2 are large, the concentration at any point oscillates between $z_0 + C_1x$ and $z_0 + C_2x$; on evaluating the θ fractions in (33) and (34), $\frac{1}{2}(C_1 + C_2)x$ is accordingly found as the expression for $z - z_0$ at the centre, and $\frac{1}{2}(C_1 - C_2)x$ for the amplitude.

When $a\theta$ is very small, the centre is $\left(C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta}\right)x$ and the amplitude is very small; *i. e.*, the "zigzag" becomes almost a straight line. Thus the stationary state reached by electrolysis with a rapidly interrupted, alternated, or varied two-beat current is practically the same as would be reached by electrolysis with a constant current of the same number of coulombs per second (reckoned algebraically). Progress towards the stationary state is likewise the same in the two cases, as may be seen by evaluating the evanescent term of (30*b*) or (31) for very small values of θ_1 and θ_2. Stationary and evanescent terms together give:

[*For θ very small*] $z - z_0 =$

$$\left(C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta}\right)x - \frac{8l}{\pi^2}\left(C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta}\right)\sum\frac{e^{-m^2at}}{m^2}\cos mg\xi. \quad (35)$$

It may be noticed that this equation becomes equivalent to (15*c*) on writing $C_1\frac{\theta_1}{\theta} + C_2\frac{\theta_2}{\theta} = C$.

A Special Case of Intermittent Currents

To obtain an expression for the concentration changes at the electrode during electrolysis with an intermittent current, where the periods of electrolysis with the current C, and the intermissions, each last $0.5/a$ seconds, equations (30*b*) and (31) may be used setting $x = l$, $C_2 = 0$, $C_1 = C$, $a\theta_1 = a\theta_2 = 0.5$; so that $at = 0.5(p - 1) + a\tau$, where $a\tau$ changes from 0 to 0.5 during each beat.

The evanescent term (which of course is the same for both equations) and the two stationary terms are as follows:

$$\left.\begin{array}{ll}
[\textit{Evanesc. term}] & -\dfrac{8lC}{\pi^2}\displaystyle\sum\frac{1}{m^2}\frac{e^{-m^2at}}{e^{0.5m^2}+1} \\
[\textit{Stat. term, } p \textit{ odd}] & Cl-\dfrac{8lC}{\pi^2}\displaystyle\sum\frac{1}{m^2}\frac{e^{m^2(0.5-a\tau)}}{e^{0.5m^2}+1} \\
[\textit{Stat. term, } p \textit{ even}] & \dfrac{8lC}{\pi^2}\displaystyle\sum\frac{1}{m^2}\frac{e^{m^2(0.5-a\tau)}}{e^{0.5m^2}+1}.
\end{array}\right\} \quad (36)$$

Fig. 8 gives a graph of the evanescent term, and the stationary terms of (36) and their sum, *i. e.*, the values[1] of $(z - z_0)/Cl$ at the electrode.

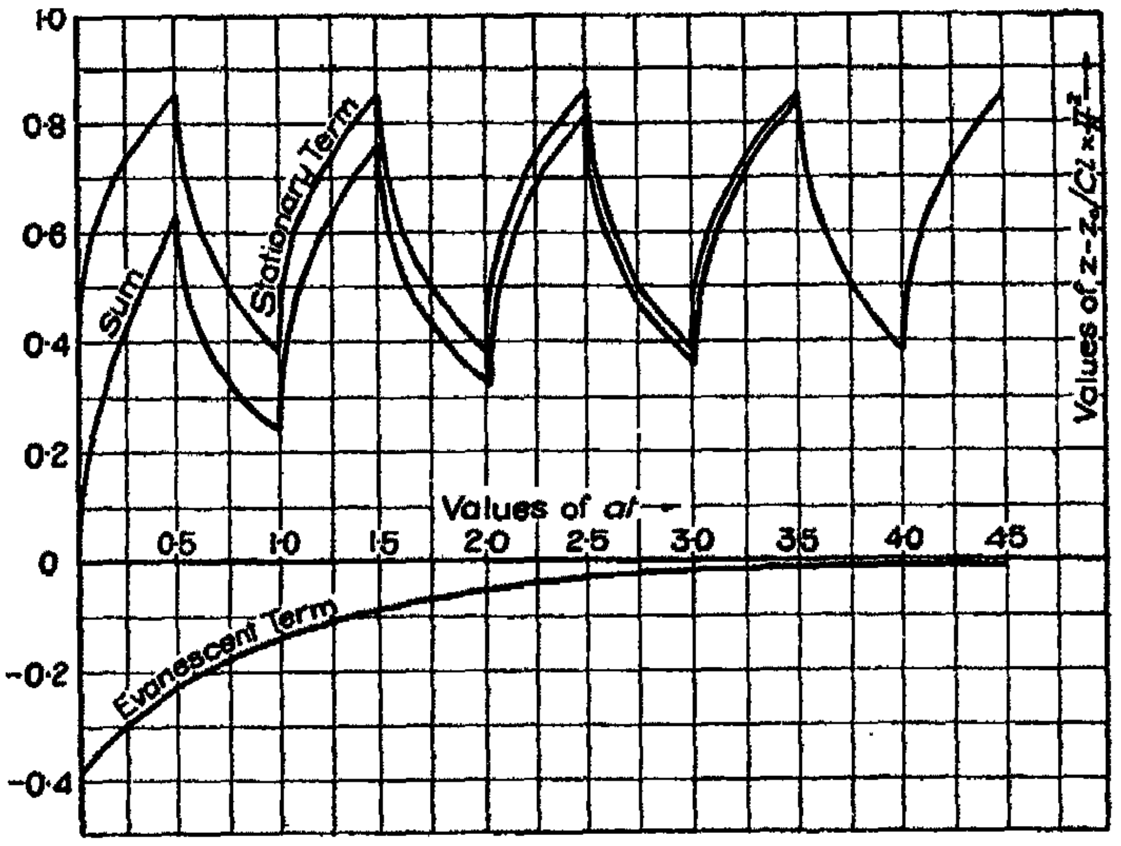


Fig. 8

Table III gives, for a number of values of $a\theta_1$ the values of $(z - z_0)/Cl$ at the electrode at the end of the 1st, 2d, 3d, 4th, and ∞th beats of current (*i. e.*, for $p = 1, 3, 5, 7$, and ∞). The numbers under $p = 1$ are the same as those of Table II, those under $p = \infty$ are calculated from the stationary term of (31) after setting $x = l$, $\tau = 0$, $C_2 = 0$,

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[1] The values actually plotted, however, are those here described multiplied by $\pi^2/8 = 1.2337$.

$C_1 = C$; for purposes of computation this term is best put in the form:

$$[For\ p = \infty]\quad \frac{z - z_0}{Cl} = 1 - \frac{8}{\pi^2}\sum \frac{1}{m^2}\cdot\frac{1}{e^{m^2 a\theta_1} + 1}. \qquad (37)$$

The figures in a horizontal line of Table III thus give the ordinates of the peaks of $(z - z_0)$ - t - curves, such as "Sum" in Fig. 8 which corresponds to the line opposite $a\theta_1 = 0.5$. As the sum of the extreme values of $z - z_0$ at the electrode when $\theta_1 = \theta_2$ is $C_1 l$ (twice the "centre," Eq. 34), the difference between unity and the figure under $p = \infty$ gives the ordinates of the lowest points reached by the curve when the stationary state is attained.

Just as with Table II, however, the figures of Table III are susceptible of a second interpretation. Writing $\mathcal{J}''$ for the intermittent current (when $\theta_1 = \theta_2$) which just brings the concentration at the electrode from z_0 to the arbitrary value z' at the end of a beat of current, the figures of Table III obviously give $(z' - z_0)/C''l$ for various values of $a\theta_1$ and p. But by (24), $(z - z_0)/l = C'$, where C' corresponds the limiting current $\mathcal{J}'$, *i. e.*, to the constant current which at $t = \infty$ can just reduce the initial concentration by the same amount. Therefore,

$$(z_0 - z')\,Cl = C'/C'' = \mathcal{J}'/\mathcal{J}''. \qquad (38)$$

and the reciprocals of the figures in Table III *give the intermittent currents* needed with different values of $\theta_1 = \theta_2$ to bring the concentration at the electrode to any arbitrary value at the end of the first, second, etc., beats of current, *as multiples of the limiting current* corresponding to the same change of concentration.

Thus, for example, if one ampere acting continuously is just sufficient to bring the concentration at the electrode from z_0 to any selected value z', the table shows that 1/0.507 amp. will be needed to bring about the same change in the time $a\theta_1 = 0.5$; while 1/0.625 amp. will do, if the current is allowed to pass for $a\theta_1 = 0.5$ and then again for the same period, after a pause of equal duration.

TABLE III

Values of $(z - z_0)/Cl$ at the electrode

Values of $a\theta_1 = a\theta_2$	$p = 1$	$p = 3$	$p = 5$	$p = 7$	$p = \infty$
2.00	0.890	0.903	0.903	0.903	0.903
1.50	0.819	0.851	0.852	0.852	0.852
1.00	0.703	0.771	0.781	0.782	0.782
0.50	0.507	0.625	0.668	0.684	0.693
0.10	0.227	0.299	0.353	0.395	0.586
0.05	0.160	0.212	0.250	0.281	0.561
0.01	0.072	0.095	0.112	0.126	0.527
0.005	0.049	0.067	0.079	0.089	0.519
0	0	0	0	0	0.500

The Simplest Alternating Currents

If C_1 and C_2 as defined by (*iv*) and (8) are of opposite signs, (30*b*) and (31) give the concentrations during electrolysis with the simplest form of alternating currents.

In the very simplest case, the two currents will be equal in strength, *i. e.*, $C_2 = -C_1$, and the beats will be of equal duration, *i. e.*, $\theta_1 = \theta_2$; on making these substitutions it will be found that (for both odd and even beats)

$$[\textit{For } t = \infty \textit{ and } x = l] \quad \frac{z - z_0}{C_1 l} = 2\left[\frac{z - z_0}{Cl}\right] - 1 \qquad (39)$$

where the expression in square brackets denotes the corresponding values of $(z - z_0)/C_1 l$ (at $t = \infty$ and $x = l$) calculated for electrolysis with the simplest intermittent current, $C_2 = 0$, $\theta_1 = \theta_2$.

Thus by doubling the ordinates of the "stationary" curve in Fig. 8 and subtracting unity, points may be obtained for a graph of the concentrations at the stationary state when electrolyzing with the simplest alternating current, where $a\theta_1 = a\theta_2 = 0.5$. Similarly, ordinates for the peaks of the stationary curves for different values of $a\theta$ may be obtained by doubling the numbers under $p = \infty$ in Table III and subtracting unity.

In some cases it may be interesting to know the relation between C_1/C_2, θ_1, and θ_2 that will just bring $z - z_0$ to some previously determined value at the end of a given beat of current. At the surface of a silver electrode in a solution of copper salt, it may be assumed, for the purpose of illustration, that when C is positive silver will go into solution, and that when C is negative silver (and not copper) will be redeposited so long as there is any left in the solution at the electrode. If there were no silver in the solution originally, part of that dissolved by the current (during the "anode beat." $C = C_1$) would diffuse away from the electrode; so in order to prevent the deposition of copper during the succeeding "cathode" beat ($C = C_2$, where C_2 as defined by (8) and (*iv*) is negative) either C_2 must be arithmetically less than C_1 or θ_2 must be less than θ_1.

Assuming that the two beats are of equal duration ($\theta_1 = \theta_2$), and that the stationary state has been reached, the concentration at the electrode at the end of a cathode beat will be represented by

$$\frac{z - z_0}{C_1 l} = 1 + \frac{8}{\pi^2}\left(\frac{C_2}{C_1} - 1\right)\sum \frac{1}{m^2}\,\frac{e^{m^2 a\theta_1}}{e^{m^2 a\theta_1} + 1}. \tag{40}$$

Supposing $z_0 = 0$, *i. e.*, that there is (practically) no silver in the main body of the solution, the smallest value of C_1 that will prevent the deposition of copper during the cathode beats (where the current corresponds to C_2) may be calculated by setting $z = 0$ and solving for C_1/C_2.

The result is:

$$\frac{1}{1 - C_2/C_1} = \frac{8}{\pi^2}\sum \frac{1}{m^2}\,\frac{e^{m^2 a\theta_1}}{e^{m^2 a\theta_1} + 1}. \tag{41a}$$

Values of the expression on the right have been tabulated (for another purpose) under $p = \infty$ in Table III; indicating them for the moment by N,

$$C_1/C_2 = -N/(1 - N). \tag{41b}$$

The values in the following Table (IV) have been calculated by (41*b*). As an instance of their application, if $a\theta_1 = a\theta_2 = 0.5$, a current of 2.26 amperes while the silver was anode would be needed to prevent the deposition of copper by a current of one ampere in the opposite direction;

and a quantity of silver equal to that dissolved by the action of $\frac{1}{2}(2.26 - 1.00) = 0.63$ amperes acting for $\theta_1 + \theta_2 = 1.0/a$ seconds would pass through the diffusion layer into the outside solution during each cycle of $1.0/a$ seconds duration.

TABLE IV

$a\theta_1 = a\theta_2 =$	0	0.005	0.01	0.05	0.10	0.50	1.00	1.50	2.00
$-C_1/C_2 =$	1.00	1.08	1.11	1.28	1.42	2.26	3.59	5.76	9.31

Conversely, the concentration of the electrode solution at which black copper begins to be deposited during the electrolysis of copper sulphate solutions, and the effect of acid, etc., on that concentration, might be determined by measuring θ_1, θ_2, C_1, and C_2 in suitably planned experiments.

Sec. 4.—Periodic Currents. II. Cycles with Four Beats.

One case only need be considered in detail. If the two currents referred to in the discussion of cycles with two beats be obtained from a commutator made of copper bars separated by some insulating material, (30*b*) and (31) are not strictly applicable; for in reality the cycle will consist of four beats, the first lasting θ_1 seconds with a current corresponding to C_1, the second for the short period d seconds during which the brush is passing the insulation and no current flows, the third for θ_2 seconds with current corresponding to C_2, and finally the fourth with no current for d seconds again. The duration of the cycle may be represented by $\theta = \theta_1 + \theta_2 + 2d$.

By inserting the proper values in (29*c*) the following expressions may be obtained:

$$[For\ p = 4q + 1]\quad z - z_0 = C_1x - \frac{8l}{\pi^2}\sum\frac{e^{-m^2ar}}{m^2}(C_1 + B_m)\cos mg\xi + \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}B_m\cos mg\xi \qquad (42)$$

$$[For\ p = 4q + 3]\quad z - z_0 = C_2x - \frac{8l}{\pi^2}\sum\frac{e^{-m^2ar}}{m^2}\left[C_2 + C_1\left\{e^{-m^2a(\theta_1+d)} - e^{-m^2ad}\right\} + B_me^{-m^2a(\theta_1+d)}\right]\cos mg\xi + \frac{8l}{\pi^2}\sum\frac{e^{-m^2at}}{m^2}B_m\cos mg\xi. \qquad (42)$$

where

$$B_m(e^{m^2a\theta} - 1) = C_1(1 - e^{m^2a\theta_1}) + C_2\left\{e^{m^2a(\theta_1 + d)} - e^{m^2a(\theta_1 + \theta_2 + d)}\right\}.$$

If $d = 0$, the two equations (42) reduce to (30*b*) and (31) respectively. It may be noticed that their evanescent terms are identical.

Sec. 5.—Periodic Currents. III. Sinusoidal Currents, Fourier Form.

If the difference between any two successive currents be infinitely small, and the number of currents be infinite, the difference $C_r - C_{r-1}$ in (29*b*) becomes a differential, and the summation with respect to r becomes an integration. Values for the concentration-changes during electrolysis with a sinusoidal current, where

$$[\textit{At and after } t = 0] \quad C = M \sin(\omega t + \alpha)$$

may thus be obtained.

Writing u in place of t_r to save printing, (29*b*) becomes:

$$z - z_0 = Mx \sin(\omega t + \alpha) - \frac{8l}{\pi^2}\sum\frac{1}{m^2}\left\{Me^{-m^2at}\sin\alpha\right.$$
$$\left.+ \int_0^t M\omega e^{-m^2a(t-u)}\cos(\omega u + \alpha)du\right\}\cos mg\xi, \quad (43a)$$

$$= Mx \sin(\omega t + \alpha) - \frac{8l}{\pi^2}\sum\frac{1}{m^2}\left\{Me^{-m^2at}\sin\alpha\right.$$
$$+ \frac{M\omega e^{-m^2at}}{m^4a^2 + \omega^2}\left[e^{m^2at}(\omega \sin\overline{\omega t + \alpha} + m^2a\cos\overline{\omega t + \alpha})\right.$$
$$\left.\left. - (\omega\sin\alpha + m^2a\cos\alpha)\right]\right\}\cos mg\xi. \quad (43b)$$

$$= Mx\sin(\omega t + \alpha)$$
$$- \frac{8lM\omega}{\pi^2}\sum\frac{1}{m^2}\frac{\omega\sin\overline{\omega t + \alpha} + m^2a\cos\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi$$
$$- \frac{8lMa}{\pi^2}\sum\frac{m^2a\sin\alpha - \omega\cos\alpha}{m^4a^2 + \omega^2}e^{-m^2at}\cos mg\xi. \quad (43c)$$

$$= \frac{2Mk}{l}\sum\frac{m^2a\sin\overline{\omega t + \alpha} - \omega\cos\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi$$
$$- \frac{2Mk}{l}\sum\frac{m^2a\sin\alpha - \omega\cos\alpha}{m^4a^2 + \omega^2}e^{-m^2at}\cos mg\xi. \quad (43d)$$

(43*d*) being derived from (43*c*) by using (27) and writing $\pi^2 k/4l^2$ for a in the coefficient of the summation.

The last term on the right of (43*c*) and (43*d*) constitutes the "evanescent term", while the first term and the first sum together in (43*c*) or the first sum in (43*d*) form the "stationary term" which alone remains when the stationary state is reached. If $\omega = 0$, (43) reduces to (15) with $M \sin\alpha$ in place of C.

The same method may obviously be employed for expressing the concentration changes produced by currents which vary with the time according to any other law. Writing $C = f(t)$, (29) becomes

$$z - z_0 = xf(t) - \frac{2k}{l}\sum\left\{\frac{f(t)}{m^2a} - e^{-m^2at}\int_0^t e^{m^2au}f(u)du\right\}\cos mg\xi. \quad (44a)$$

$$= \frac{2k}{l}\sum\left\{e^{-m^2at}\int_0^t e^{m^2au}f(u)du\right\}\cos mg\xi. \quad (44b)$$

The Stationary State When $l\sqrt{\frac{\omega}{k}}$ *is Large*

The exponential multiplier, e^{-m^2at}, causes the series in the evanescent term to converge more rapidly than that in the stationary term; with large values of l particularly, the convergence of the latter is very slow. In the next section another form of the stationary term will be obtained which is more suitable for computation; here it is proposed to find the special value assumed by the stationary term of (43*d*) when $l\sqrt{\frac{\omega}{k}} = \infty$.

The stationary term may be written

$$\sum_{n=1}^{\infty}\frac{2m^2akM\sin\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi$$
$$-\sum_{n=1}^{\infty}\frac{2kM\omega\cos\overline{\omega t + \alpha}}{m^4a^2 + \omega^2}\cos mg\xi. \quad (45a)$$

Defining[1] $H = x\sqrt{\frac{\omega}{k}}$, $\mu = \sqrt{\frac{\omega}{2k}}$, and $\psi = m\sqrt{\frac{k}{\omega}} = \frac{(2n-1)\pi}{2l}\sqrt{\frac{k}{\omega}}$; while n increases by unity, ψ increases by $\Delta\psi = \frac{\pi}{l}\sqrt{\frac{k}{\omega}}$.

Introducing these symbols (45*a*) becomes

$$\frac{\sqrt{2}.M\sin\overline{\omega t+\alpha}}{\pi\mu}\sum_{n=1}^{\infty}\frac{\psi^2\cos H\psi}{\psi^4+1}\Delta\psi$$

$$-\frac{\sqrt{2}.M\cos\overline{\omega t+\alpha}}{\pi\mu}\sum_{n=1}^{\infty}\frac{\cos H\psi}{\psi^4+1}\Delta\psi. \qquad (45b)$$

As $l\sqrt{\frac{\omega}{k}}$ increases, ψ decreases; until when $l\sqrt{\frac{\omega}{k}} = \infty$, $\Delta\psi = d\psi$ and the summation from $n = 1$ $\left(\text{or } \psi = \frac{\pi}{2l}\sqrt{\frac{k}{\omega}}\right)$ to $n = \infty$ becomes an integration between the limits 0 and ∞.

$$\left[\textit{For } l\sqrt{\frac{\omega}{k}} = \infty\right] \textit{Stat. term} = \frac{\sqrt{2}M\sin\overline{\omega t+\alpha}}{\pi\mu}\int_0^{\infty}\frac{\psi^2\cos H\psi}{\psi^4+1}d\psi$$

$$-\frac{\sqrt{2}M\cos\overline{\omega t+\alpha}}{\pi\mu}\int_0^{\infty}\frac{\cos H\psi}{\psi^4+1}d\psi. \qquad (46a)$$

By using the partial fractions $\frac{2\psi^2}{1+\psi^4} = \frac{i}{1+\psi^2 i} - \frac{i}{1-\psi^2 i}$, and $\frac{2}{1+\psi^4} = \frac{1}{1+\psi^2 i} + \frac{1}{1-\psi^2 i}$, where $i = \sqrt{-1}$, and setting ϕ^2 alternately equal to $\psi^2 i$ and to $-\psi^2 i$ these integrals may be made to depend upon the known form

$$\int_0^{\infty}\frac{\cos n\phi}{\phi^2+1}d\phi = \frac{\pi}{2}e^{-n}.$$

Their values are:

$$\left.\begin{aligned}\int_0^{\infty}\frac{\psi^2\cos H\psi}{\psi^4+1}d\psi &= -\frac{\pi}{2}e^{-\frac{H}{\sqrt{2}}}\sin\left(\frac{H}{\sqrt{2}}-\frac{\pi}{4}\right)\\ \int_0^{\infty}\frac{\cos H\psi}{\psi^4+1}d\psi &= \frac{\pi}{2}e^{-\frac{H}{\sqrt{2}}}\sin\left(\frac{H}{\sqrt{2}}+\frac{\pi}{4}\right).\end{aligned}\right\} \qquad (47)$$

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[1] This use of the letters H, ϕ and ψ, is restricted to equations (45) and (46).

Introducing these values in (46*a*) and rearranging

$$\left[\textit{For } l\sqrt{\frac{\omega}{k}} = \infty\right] \textit{ Stat. term} = \frac{-M}{\mu\sqrt{2}}\, e^{-\mu\xi} \cos\left(\omega t + \alpha - \mu\xi + \frac{\pi}{4}\right) \quad (46b)$$

$$= \frac{M}{\mu\sqrt{2}}\, e^{-\mu\xi} \sin\left(\omega t + \alpha - \mu\xi - \frac{\pi}{4}\right). \quad (46c)$$

This expression has already been obtained by Warburg,[1] for "$l = \infty$,"[2] direct from the differential equation, by means of a Fourier's integral.

Sec. 6.—Sinusoidal Currents Continued (Hyperbolic Form)

The expression (43) for the concentrations throughout the diffusion layer during electrolysis with a sinusoidal current, which has been deduced in the preceding section, is in many cases very inconvenient for purposes of computation. In the present section another form will be obtained; for this purpose, however, it is necessary to go back to the original differential equation.

In (1), *viz.*:

$$z - D = Cx + \Sigma(A_n \sin E_n x + B_n \cos E_n x)e^{-E_n^2 kt} \qquad (1)$$

the "stationary term" (S) is Cx, it fulfils the conditions

[*Solution condition*] *At* $x = 0$, $\partial S/\partial t = 0$ *for all values of* t (*v*)
[*Electrode condition*] *At* $x = l$, $\partial S/\partial x = C$ *for all values of* t (*vi*)

while the "evanescent term" (V), *viz.* the summation, is made to fulfil the conditions

[*Solution condition*] *At* $x = 0$, $\partial V/\partial t = 0$ *for all values of* t (*vii*)
[*Electrode condition*] *At* $x = l$, $\partial V/\partial x = 0$ *for all values of* t (*viii*)
[*Initial condition*] *At* $t = 0$, $V + S = 0$ *for all values of* x (*ix*)

by assigning suitable values to A_n B_n and E_n. Each term separately is a particular solution of the differential equation (*iii*).

By the use of Fourier's series, as illustrated on pg. 824, it is obviously possible to make the evanescent term comply

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[1] Wied. Ann., 67, 493 (1899).

[2] See page 854.

with the three conditions *vii*, *viii*, and *ix*, no matter what S may be; so that if it were possible to construct a stationary term which was a solution of (*iii*) and for which in addition

[*Solution condition*] *At* $x = 0$, $\partial S/\partial t = 0$ *for all values of* t (*v*)
[*Electrode condition*] *At* $x = l$, $\partial S/\partial x =$
$M \sin(\omega t + \alpha)$ *for all values of* t, (*x*)

an expression could be obtained directly for the values assumed by z during electrolysis with the current $\mathscr{I} = \dfrac{96540\,\mathscr{A}\,Mk \sin(\omega t + \alpha)}{1 + zu/\Sigma zu}$ amperes (see pg. 821).

This course is followed in the succeeding paragraphs, and the resulting equation (59), while identical in meaning with (43), is much more convenient in form for certain computations.

(*a*) *The Stationary Term, S*

A hint as to the general form with which to begin, is furnished by the exponential form of the evanescent term in (1).

Let $$S = (A_1 e^{\gamma x} + A_2 e^{-\gamma x})e^{\gamma^2 kt} + (B_1 e^{\lambda x} + B_2 e^{-\lambda x})e^{\lambda^2 kt}. \quad (48)$$

By differentiating it will be seen at once that to satisfy (*v*) it is necessary to set

$$A_2 = -A_1, \text{ and } B_2 = -B_1. \quad (49)$$

Because of (*x*) — writing A for A_1, and B for B_1, and putting $M \sin(\omega t + \alpha)$ in the exponential form[1] —

$$\gamma A(e^{\gamma l} + e^{-\gamma l})e^{\gamma^2 kt} + \lambda B(e^{\lambda l} + e^{-\lambda l})e^{\lambda^2 kt} = \frac{M}{2i}(e^{i(\omega t + \alpha)} - e^{-i(\omega t + \alpha)}) \quad (50)$$

---

[1] The relations used in making the transformations of these paragraphs are:

$i = \sqrt{-1}$
$2 \cos y = e^{iy} + e^{-iy}$ $2i \sin y = e^{iy} - e^{-iy}$
$2 \cosh y = e^{y} + e^{-y}$ $2 \sinh y = e^{y} - e^{-y}$
$\sinh 2y = 2 \sinh y \,.\, \cosh y$
$\cosh 2y = \cosh^2 y + \sinh^2 y$
$\cosh^2 y - \sinh^2 y = 1$
$\sqrt{i} = (1 + i)/\sqrt{2}$ $\log \text{nat}\, i = (-1)^{n+1}(2n - 1)i\pi/2$
$\sqrt{-i} = (1 - i)/\sqrt{2}$

which can be satisfied by setting

$$\gamma^2 k = i\omega, \quad whence\ \gamma = (1 + i)\sqrt{\frac{\omega}{2k}} \tag{51}$$

$$\lambda^2 k = -i\omega,\ whence\ \lambda = (1 - i)\sqrt{\frac{\omega}{2k}}, \tag{52}$$

$$A = \frac{Me^{i\alpha}}{2i\gamma(e^{\gamma l} + e^{-\gamma l})}, \quad B = \frac{-Me^{-i\alpha}}{2i\lambda(e^{\lambda l} + e^{-\lambda l})}. \tag{53}$$

Introducing these values of A, B, γ, l into (48), (*iii*) (*v*) and (*x*) are satisfied, and the result may be written

$$S = \frac{M}{2\mu}\{(J - H)(F\,cos - G\,sin) + (J + H)(F\,sin + G\,cos)\} \tag{54a}$$

$$= \frac{-M}{2\mu}\{(JG - HF)(sin - cos) - (HG + JF)(sin + cos)\}, \tag{54b}$$

$$= \frac{-M}{\mu\sqrt{2}}\{(JG - HF)cos\,\overline{\omega t + \alpha - \tfrac{3}{4}\pi} + (HG + JF)sin\,\overline{\omega t + \alpha - \tfrac{3}{4}\pi}\} \tag{54c}$$

$$= \frac{M}{\mu\sqrt{2}}\sqrt{(F^2 + G^2)(H^2 + J^2)}\,.\,sin\,(\omega t + \alpha + \gamma - \tfrac{1}{4}\pi), \tag{54d}$$

where

$$\mu = \sqrt{\frac{\omega}{2k}},$$

$F = cosh\,l\mu\ cos\,l\mu/(cos^2 l\mu + sinh^2 l\mu),$

$G = -\ sinh\,l\mu\,.\,sin\,l\mu/(cos^2 l\mu + sinh^2 l\mu),$

$H = sinh\,\mu x\,.\,cos\,\mu x,$

$J = cosh\,\mu x\,.\,sin\,\mu x,$

$\gamma = tan^{-1}(JF + HG)/(HF - JG),$

"*sin*" and "*cos*" are written, in (54*a*) and (54*b*) only, for *sin* $(\omega t + \alpha)$ and *cos* $(\omega t + \alpha)$ respectively.

Conversion of the Hyperbolic Form of S into the Fourier Form

To check this result, (54) may be converted into the stationary term of (43); the form (54*a*) is the most convenient for the transformation. It is first necessary to develop J and H as series of sines of odd multiples of $\pi x/2l$

Writing $m = 2n - 1$, $P = 2l\mu/\pi$, $\Theta = \pi x/2l$, the series are:

$$J = \cosh \mu x \,.\, \sin \mu x = \cosh P\Theta \,.\, \sin P\Theta \quad =$$

$$4P(-1)^{\frac{m-1}{2}} \sum \frac{(m^2 + 2P^2)\cosh l\mu \,.\, \cos l\mu - (m^2 - 2P^2)\sinh l\mu \,.\, \sin l\mu}{m^4 + 4P^4} \sin m\Theta.$$

$$H = \sinh \mu x \,.\, \cos \mu x = \sinh P\Theta \,.\, \cos P\Theta \quad =$$

$$4P(-1)^{\frac{m-1}{2}} \sum \frac{(m^2 + 2P^2)\cosh l\mu \,.\, \cos l\mu - (m^2 - 2P^2)\sinh l\mu \,.\, \sin l\mu}{m^4 + 4P^4} \sin m\Theta.$$

On carrying out the multiplications and additions indicated in (54a), writing g for $\pi/2l$, and replacing $(-1)^{\frac{m-1}{2}}$ $\sin m\Theta$ by $\cos mg\xi$, the expression for S becomes

$$S = \frac{2Mk}{l} \sum \frac{m^2g^2k \sin(\omega t + \alpha) - \omega \cos(\omega t + \alpha)}{m^4g^4k^2 + \omega^2} \cos mg\xi, \quad (54c)$$

which is identical with the stationary term of (43)

(*b*). *The Evanescent Term, V.*

Let[1] $V = (Ae^{\beta x} + Be^{-\beta x})e^{\beta^2 t}$. (55)

As in the case of the stationary term, condition (*vii*) requires that

$$B = -A.$$

Condition (*viii*) requires that

$$A\beta(e^{\beta l} + e^{-\beta l})e^{\beta^2 kt} = 0 \textit{ for all values of } t$$

which may be satisfied by setting

$$e^{\beta l} + e^{-\beta l} = 0, \textit{ i. e. } e^{2\beta l} = -1, \text{ or } \beta l = \log nat\ i,$$

whence

$$\beta = \frac{(-1)^{n+1}(2n - 1)i\pi}{2l}$$

where n is any positive integer. On substituting these values

---

[1] This use of the letter β is restricted to (55).

of B and β, (writing one term for each value of β) and converting into the trigonometrical form, (55) becomes

$$V = \sum 2A_n i(-1)^{n+1} e^{\frac{-(2n-1)^2\pi^2 kt}{4l^2}} \sin \frac{(2n-1)\pi x}{2l}, \qquad (56a)$$

$$= \sum 2i(-1)^{\frac{m-1}{2}} A_n e^{-m^2g^2kt} \sin mgx, \qquad (56b)$$

$$= \sum 2iA_n e^{-m^2g^2kt} \cos mg\xi, \qquad (56c)$$

m being written for $2n - 1$, g for $\pi/2l$, and ξ for $l - x$.

But, by (ix)

$$\sum 2iA_n \cos mg\xi = \frac{-2Mk}{l} \sum \frac{m^2g^2k \sin\alpha - \omega\cos\alpha}{m^4g^4k^2 + \omega^2} \cos mg\xi. \qquad (57)$$

Therefore,

$$V = \frac{-2Mk}{l} \sum \frac{m^2g^2k \sin\alpha - \omega\cos\alpha}{m^4g^4k^2 + \omega^2} e^{-m^2g^2kt} \cos mg\xi, \qquad (58)$$

which is identical with the evanescent term of $(43d)$ since $g^2k = a$.

(c) *The Complete Expression*, $S + V$

Thus from (54) and (58)

$$[\textit{For sinusoidal current}] \quad z - z_0 = S + V$$

$$= \frac{M}{\mu\sqrt{2}} \sqrt{(F^2 + G^2)(H^2 + J^2)} \,.\, \sin(\omega t + \alpha + \gamma - \tfrac{1}{4}\pi)$$

$$- \frac{2Mk}{l} \sum \frac{m^2a \sin\alpha - \omega\cos\alpha}{m^4a^2 + \omega^2} e^{-m^2at} \cos mg\xi. \qquad (59)$$

Equation (59) is the "hyperbolic form" of (43).

Values of $z - z_0$ *at the electrode* may be obtained by replacing x by l (and consequently $\cos mg\xi$ by unity). Thus, when the *stationary state* is reached

$$[\textit{Stat. at elec.}] \quad z - z_0 =$$

$$\frac{M}{2}\sqrt{\frac{k}{\omega}} \frac{\sqrt{\sinh^2 2\mu l + \sin^2 2\mu l}}{\sinh^2 \mu l + \cos^2 \mu l} \sin(\omega t + \alpha + \gamma - \tfrac{1}{4}\pi), \qquad (60)$$

where

$$\mu = \sqrt{\frac{\omega}{2k}}$$

and

$$[\textit{at electrode}]\ \gamma = \tan^{-1}\frac{\sin 2\mu l}{\sinh 2\mu l}. \qquad (61)$$

With increasing values of $l\mu$, cos $l\mu$ and sin $l\mu$ vanish in comparison with sinh $l\mu$, while sinh $2l\mu$ approaches equality with 2 sinh² $l\mu$. The value of the fraction $\frac{\sqrt{\sinh^2 2l\mu + \sin^2 2l\mu}}{\sinh^2 l\mu + \cos^2 l\mu}$ thus approaches 2, and the value of "γ at the electrode" (61) approaches zero. Thus from (60)

$$[\textit{For } t = \infty, \textit{ at electrode}]\ z - z_0 = M\sqrt{\frac{k}{\omega}}\sin(\omega t + \alpha - \tfrac{1}{4}\pi). \qquad (62)$$

The same results may be obtained by setting $\xi = 0$ in (46c); by means of (60), however, the limits within which the convenient equation (62) may be used can be ascertained. By looking up tables[1] of the hyperbolic functions it will be found that the substitution of (62) for (60) cannot introduce an error of more than one-half percent if $l\mu = l\sqrt{\frac{\omega}{2k}} \geq 3$. Assuming $\omega = 377$ (*i. e.*, 60 cycles per second), and $k = 4 \times 10^{-6}$ (an average value) it follows that l is practically "infinite" for the purposes of this equation when it reaches 5×10^{-4} centimeters.

Amplitude

When the stationary state is reached, the values of z swing equally above and below z_0; the maximum values of $z - z_0$ being reached when $\sin(\omega t + \alpha + \gamma - \frac{1}{4}\pi) = 1$. An expression for the "amplitude" may accordingly be found by substituting this value in the stationary term of (59), or in (60) if the amplitude at the electrode be sought. From (46c) it follows that when $l = \infty$ the amplitude at any point in the diffusion layer is $\frac{M}{2}\sqrt{\frac{k}{\omega}}e^{-\mu\xi}$.

Lag

The electric current is at its maximum when $\omega t + \alpha = \frac{1}{2}\pi$;

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[1] Smithsonian Mathematical Tables; Hyperbolic Functions, Washington, published by the Smithsonian Institution 1909.

when the stationary state is reached, the concentration reaches its maximum whenever $\omega t + \alpha + \gamma - \frac{1}{4}\pi = \frac{1}{2}\pi$ (see Eq. 59). The difference, $\frac{1}{4}\pi - \gamma$, gives the phase difference or "lag" of the concentration wave behind the wave of current at the stationary state. The lag at the electrode may be found by computing γ from (61) and subtracting from $\pi/4$.

The angle γ is a function of $l\mu$ whose value rapidly falls off with increase in $l\mu$, while alternating in sign.

Illustration

As an illustration, a number of values of $(z - z_0)/M$ at the electrode have been computed for the case that $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$, $\omega = 377$ (60 cycles per second), and $\alpha = \frac{1}{2}\pi$ (*i. e.*, at the moment of throwing on the current, the latter is at its maximum). Fig. 9 gives a graph of the evanescent term, of the stationary term, and of their sum, *i. e.*, the values of $(z - z_0)/M$ at the electrode. The "current" wave is drawn on an arbitrary scale to illustrate the

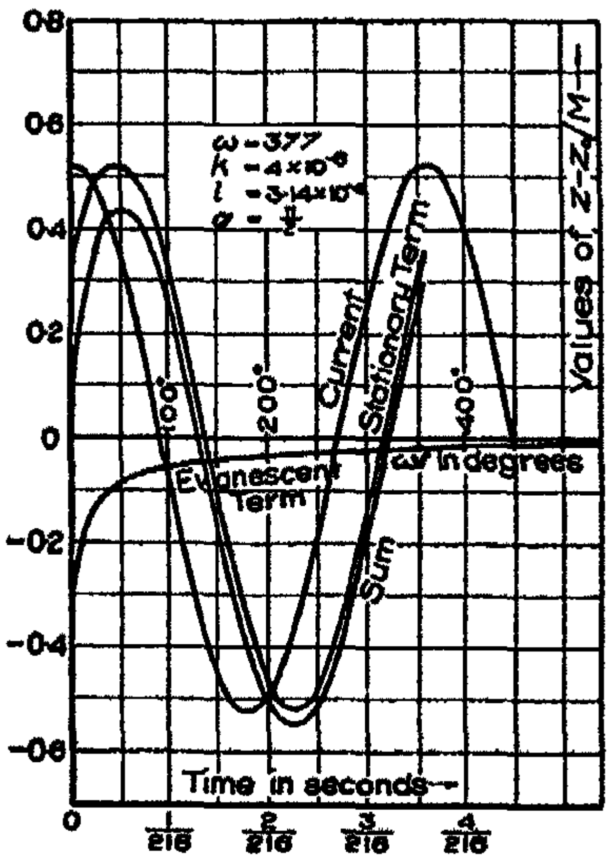
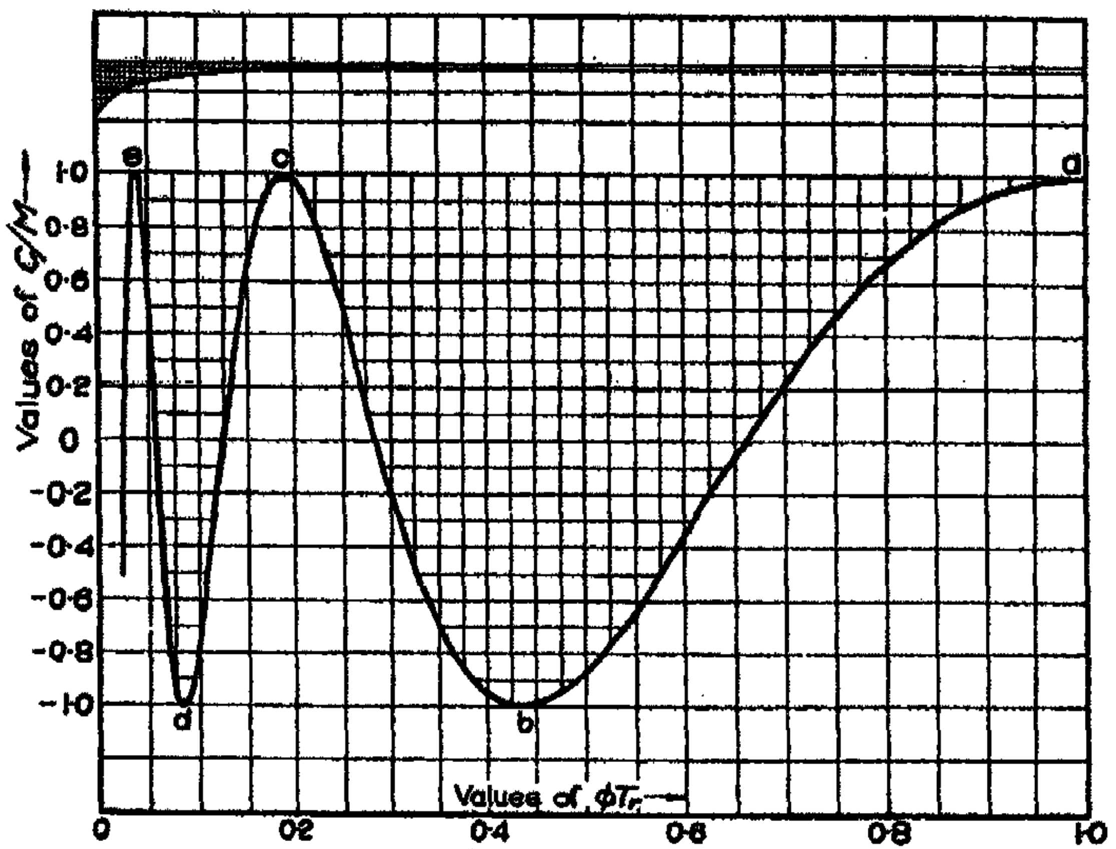


Fig. 9

difference in phase, (lag). Figs. 10 and 11 apply to the same case; the areas *abc*, *cde*, etc., above the curve correspond to the expression within the { } brackets of (29*d*).



Figs. 10 and 11

Sec. 7.—Superposed Currents

Since all the equations of this Part satisfy the same "initial" condition and the same "solution" condition, and since the sum of a number of solutions of the linear differential equation (*iii*) is likewise a solution, the concentration changes produced by any number of currents acting simultaneously may be obtained by adding together the right hand members of the equations which give the concentration changes that would be produced by each current taken separately. Thus the effects produced by approximately sinusoidal currents could be computed if the current were analyzed in the ordinary way, and expressed as the sum of a pure sinusoidal current and its higher harmonics.

Other problems may be handled in the same way. Suppose, for instance, that the sinusoidal current for which $C = M \sin (\omega t + \alpha)$, and the direct current for which $C = C_1$

both enter the solution by the same electrode; when the stationary state is reached, the amplitude of the concentration variation at the electrode caused by the sinusoidal current alone would be

$$\frac{M}{2}\sqrt{\frac{k}{\omega}\,\frac{\sqrt{\sinh^2 2\mu l + \sin^2 2\mu l}}{\sinh^2 \mu l + \cos^2 \mu l}} \tag{63}$$

while that caused by the direct current alone would be zero; (63) thus gives the maximum deviation of z above and below the centre of swing. If the sinusoidal current acted alone, the centre of swing would be at $z = z_0$; if the direct current acted alone, the centre would be at $z = z_0 + C_1 l$; thus

$$C_1 l - \frac{M}{2}\sqrt{\frac{k}{\omega}\,\frac{\sqrt{\sinh^2 2\mu l + \sin^2 2\mu l}}{\sinh^2 \mu l + \cos^2 \mu l}} \tag{64}$$

gives the lowest value of $z - z_0$ reached at the electrode during electrolysis.

If the electrode were of silver, for instance, in a solution of copper sulphate practically free from silver (*i. e.*, $z_0 = 0$), the ratio between the two currents that would just prevent the concentration of the silver salt at the electrode from falling to zero during the cycle might be found by setting the expression (64) equal to zero and solving for $\sqrt{2}\,C_1/M$ (since the reading[1] on the alternating current ammeter is proportional to $M/\sqrt{2}$, and that on the direct current ammeter to C_1). This ratio is a function of $l^2\omega/k$, *i. e.*, of the time constant and of the duration of the cycle. If $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$ cm., and $\omega = 377$, the reading on the direct current ammeter would be 0.469 times that on the alternating.

If $\mu l \geq = 3$, the *sinh* fraction in (64) is very closely equal to 2.00, and $C_1/M = \sqrt{k}/l\sqrt{\omega}$.

Measurements of this nature might prove an easy means

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[1] In order that this may be true exactly as stated in the case under consideration it is necessary that the composite current be obtained synthetically from two separate circuits having the cell in their only common part. The alternating current ammeter must then be in the alternating current circuit and not in series with the cell.

of finding the ratio k/l^2; if a "limiting current" were likewise determined (see pg. 830) the two measurements would give both k and l.

PART II

THE REACTION AT THE ELECTRODE CHANGES WHEN z AT THE ELECTRODE ATTAINS THE VALUE ζ

At the cathode in an acid solution of copper sulphate, the concentration of the copper, z, decreases when the current is thrown on; all values of $z - z_0$ will therefore be negative, they may be computed by (15*c*) remembering that G as defined in the Introduction, and therefore C as defined by (8), are negative. The curves *oad* for $at = 0.25$, *obe* for $at = 0.35$, *ofg* for $at = 0.50$, and *oh* for $t = \infty$, in Fig. 12 were so obtained; they differ from the corresponding curves in Fig. 1 only in scale, and in that $z - z_0$ is measured downward to indicate decrease in z as the electrode is approached.

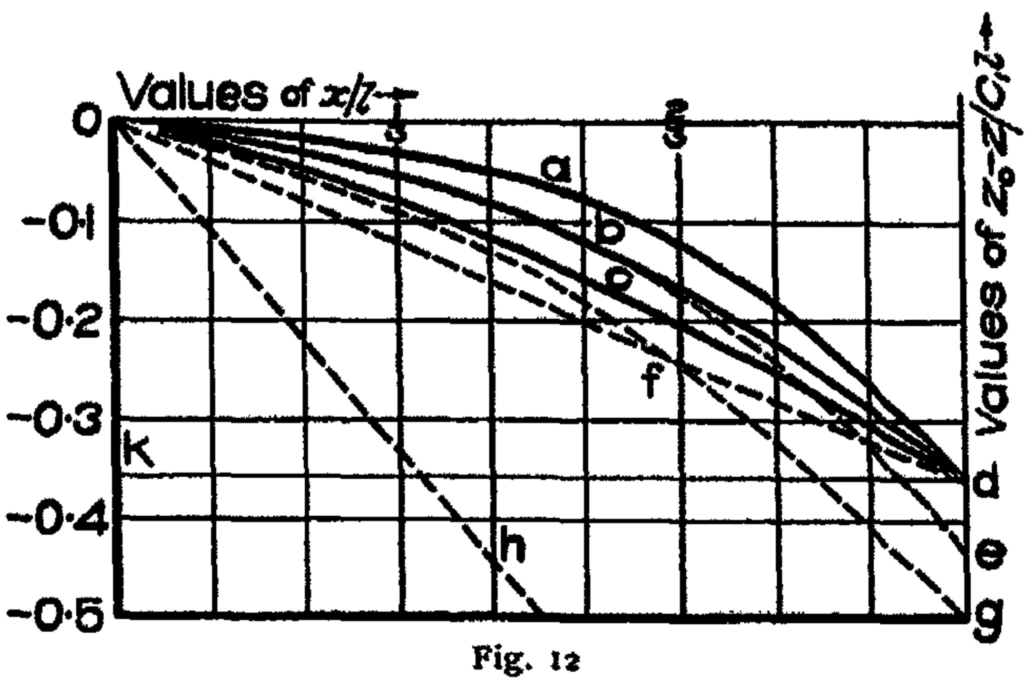

Fig. 12

As noted on pg. 832, (15*c*) merely fixes a relation between $(z - z_0)/Cl$, x/l, and at, irrespective of the absolute values of z, x, and t; the values of $(z - z_0)/Cl$ correspond to $z = 0$, and therefore the height in the figure of the horizontal line corresponding to $z = 0$, will vary from case to case. Assuming it to have the position given by *kd* in Fig.

12, z at the electrode will reach zero at $at = 0.25$; from that moment on, Eq. (15) which predicts still further fall in z (as indicated by the dotted lines obe, ofg, oh) ceases to be applicable, and must be replaced by another.

Sec. 8.—Constant Current

This new equation must be a solution of the differential equation (*iii*, Fick's law, pg. 820), it must also fulfil the "solution condition" (*i*, pg. 818), but the "electrode condition (*iv*, pg. 821) must be replaced by

$$[\textit{Electrode condition}]\ \textit{At } x = l, \textit{ and } t > \vartheta,\ \partial z/\partial t = 0 \qquad (xi)$$

which says that from a certain value of t (*viz:* ϑ) onwards, the concentration at the electrode remains unaltered at the value ζ; at the cathode in the copper solution $\zeta = 0$.

The "initial condition" (*ii*, pg. 819) also must be replaced, by

$$[\textit{Condition at } t = \vartheta]\ z - z_0 =$$

$$C_1 x - \frac{8C_1 l}{\pi^2}\sum \frac{1}{m^2}\cdot c^{-\frac{m^2\pi^2 k\vartheta}{4l^2}}\cdot \cos\frac{m\pi(l-x)}{2l} \qquad (xii)$$

signifying that at $t = \vartheta$, the values of z are those caused by the operation of the constant current C_1 for ϑ seconds.

From (1), introducing the special values of B_n and D from (3) and (4), and writing c instead of C_1, q instead of n and ρ instead of E_n to avoid confusion with the formulas of Part I, the equation

$$z - z_0 = cx + \sum_{q=1}^{\infty} A_q e^{-\rho^2 kt} \sin \rho x \qquad (65)$$

may be obtained, which satisfies (*iii*) and (*i*). To satisfy (*xi*) it is necessary that

$$\rho = \frac{q\pi}{l} \qquad (66)$$

as may be found by differentiating, etc., in the manner illustrated on pg. 823.

At the electrode, $z = \zeta$, and $x = l$, (hence $\sin \rho x = 0$) so that

$$c = \frac{\zeta - z_0}{l}. \qquad (67)$$

Introducing these values of ρ and c, (65) becomes

$$z - z_0 = \frac{\zeta - z_0}{l}\, x + \sum_{q=1}^{\infty} A_q\, c^{-\frac{q^2\pi^2 kt}{l^2}} \sin\frac{q\pi x}{l}. \tag{68}$$

and satisfies *i*, *iii*, and *xi*.

To introduce (*xii*), the two expressions for $z - z_0$ at the moment $t = \vartheta$ obtainable from (*xii*) and (68) may be equated; replacing $(\zeta - z_0)/l$ by its value from (*xii*), *viz.*:

$$\frac{\zeta - z_0}{l} = C_1 - \frac{8C_1}{\pi^2} \sum \frac{1}{(2n-1)^2} \cdot e^{-\frac{(2n-1)^2\pi^2 k\vartheta}{4l^2}} \cdot \cos\frac{(2n-1)\pi(l-x)}{2l} \tag{69}$$

and rearranging

$$\sum_{q=1}^{\infty} A_q\, e^{-\frac{q^2\pi^2 kt}{l^2}} \sin\frac{q\pi x}{l} =$$

$$-\frac{8lC_1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \cdot e^{-\frac{(2n-1)^2\pi^2 k\vartheta}{4l^2}} \left(\cos\frac{(2n-1)\pi(l-x)}{2l} - \frac{x}{l} \right) \tag{70a}$$

$$= \frac{-8lC_1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \cdot e^{-\frac{(2n-1)^2\pi^2 k\vartheta}{4l^2}} \sum_{q=1}^{\infty} \frac{2(2n-1)^2(-1)^q}{q\pi(\overline{2n-1}^2 - 4q^2)} \sin\frac{q\pi x}{l} \tag{70b}$$

(70*b*) being obtained by substituting an equivalent Fourier's series for the expression in brackets at the right of (70*a*) (see Appendix).

The value of A_q may now be found, for any fixed value of q, by removing the $\sum\limits_{q=1}^{\infty}$ sign from both sides of (70*b*) and simplifying. Inserting the value so found in (68), there results:

$$z - z_0 = \frac{\zeta - z_0}{l}\, x +$$

$$\frac{16lC_1(-1)^{q+1}}{\pi^3} \sum_{n=1}^{\infty} \sum_{q=1}^{\infty} \frac{e^{-\frac{\pi^2 k}{4l^2}(4q^2\overline{t-\vartheta} + \overline{2n-1}^2\vartheta)}}{q(\overline{2n-1}^2 - 4q^2)} \cdot \sin\frac{q\pi x}{l} \tag{71}$$

which satisfies all four relations *i*, *iii*, *xi* and *xii*.

The symbol $\sum\limits_{n=1}^{\infty}\sum\limits_{q=1}^{\infty}$ signifies that the value of the expression on the right of (71) is to be computed for each value of q (for instance $q = 1$) combined with every value of n ($n = 1, 2, 3, \ldots$) in turn; then for the next value of q, ($q = 2$) combined with every value of n, and so on; the sum of all these results is to be used in finding $z - z_0$.

Equation (71) is applicable whenever, for any reason, the concentration z at the electrode remains constant after reaching a certain value ζ. The case $\zeta = 0$ is no doubt the commonest, but cases where $\zeta - z_0 > 0$ may perhaps be met with where the product of electrolysis crystallizes at the electrode thus forming a saturated solution there; other cases where ζ differs from zero may be sought in the electrolysis of solutions containing excess of a second salt whose decomposition voltage is only slightly greater than that of the salt to whose concentration z refers.

Illustration

In the case taken as illustration, ($\zeta = 0$, $a\vartheta = 0.25$) the constant current C_1 brings the concentration at the electrode from z_0 to zero in $0.25/a$ seconds; therefore, from (22*a*),

$$C_1 l = -2.784 z_0.$$

Hence

[*for* $0 \leqq t \leqq 0.25$] $(z_0 - z)/z_0 =$

$$2.784\frac{x}{l} - 2.257\sum\frac{1}{m^3}e^{-m^2at}\cos mg\xi, \quad \text{(from 15}c\text{)}$$

and

[*for* $t > 0.25$] $(z_0 - z)/z_0 =$

$$x/l - 1.436(-1)^q\sum_{n=1}^{\infty}\sum_{q=1}^{\infty}\frac{e^{-4q^2(at-0.25)-0.25m^2}}{q(m^2-4q^2)}\cdot\sin\frac{q\pi x}{l}, \quad \text{(from 71)}$$

whence,

At the points $x/l =$	0	0.25	0.50	0.75	1.00
[1] when $at = 0.35$, $(z - z_0)/C_1 l =$	0	0.039	0.097	0.208	0.359
[1] when $at = 0.50$, $(z - z_0)/C_1 l =$	0	0.058	0.138	0.237	0.359

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[1] Corresponding values of $(z_0 - z)/z_0$ may be obtained by multiplying by 2.784.

These points determine the curves *obd* and *ocd* in Fig. 12; *ofd*, the straight line joining o and *d*, gives the concentrations at $t = \infty$.

Sec. 9.—Successive Currents

At some moment t ($t > \vartheta$), suppose that the current corresponding to C_1 is changed to a current corresponding to C_2. In the case chosen for illustration ($\zeta = 0$), if C_2 be numerically greater (algebraically less) than C_1, z at the electrode will remain equal to ζ; if C_2 lie between C_1 and the limiting current corresponding to ζ (*viz.*: $C' = (\zeta - z_0)/l$, Eq. 24) the concentration at the electrode will ultimately remain at ζ, although if $t - \vartheta$ be not too great it may momentarily rise above ζ and then fall again.

If, however, C_2 be (numerically) less than C', the concentration at the electrode will rise permanently above ζ. From the moment t_1 at which this change of current occurs, the following conditions will hold, *viz.*:

[*Fick's law*] $\partial z/\partial t = k\,\partial^2 z/\partial x^2$. (*iii*)
[*Solution condition*] For $x = 0$, $\partial z/\partial t = 0$. (*i*)
[*Electrode condition*] For $x = l$, $\partial z/\partial x = C_2$. (*iv*)
["*Initial*" *condition*] For $t = t_1$, $z - z_0$ = an expression obtainable by writing t_1 for t in (71). (*xiii*)

The first three may be complied with by setting $t = t_1$ in (*1*), and substituting the values of B_n, D and E_n given by (3), (4), and (7) respectively; v is written instead of n to avoid confusion with the first summation. To introduce the "condition at $t = t_1$" the expression on the right of (*xiii*) must be converted into a series proceeding by sines of odd multiples of $\pi x/2l$ (see Appendix); the A_v's may then be found in the usual way. On carrying out these operations there results:

$$[For\ t \gtrless t_1]\ z - z_0 = C_2 x + \frac{8l}{\pi^3}\left(\frac{\zeta - z_0}{l} - C_2\right)\sum_{n=1}^{\infty} \frac{e^{-m^2 a(t-t_1)}}{m^3} \cos mg\xi$$

$$- \frac{128\,C_1 l}{\pi^4}\sum_{n=1}^{\infty}\sum_{q=1}^{\infty}\sum_{v=1}^{\infty} \frac{e^{exp}.\cos(2v-1)\pi\xi}{(2n-1^2-4q^2)(2v-1^2-4q^2)}, \qquad (72)$$

where, as usual, $m = 2n - 1$, $g = \pi/2l$, $a = \pi^2 k/4l^2$, $\xi = l - x$ and the exponent of e (indicated by "exp" in (72)) is

$$\frac{-\pi^2 k}{4l^2}[(2n-1)^2\vartheta + 4q^2(t_1-\vartheta) + (2v-1)^2(t-t_1)]. \qquad (73)$$

If $t_1 - \vartheta$ be very large, the exponential factor of the triple sum becomes zero, and only the first two terms of (72) remain. Large values of $t_1 - \vartheta$, however, correspond to a linear fall of concentration throughout the diffusion layer at the moment $t = t_1$; the single sum term of (72) can accordingly be deduced from (1), (3), (4), and (7) by introducing the condition.

$$[\textit{For } t = t_1] \quad z_0 - z = (z_0 - \zeta)x/l. \qquad (xiv)$$

in place of (*xiii*), or it may be derived from (31), the general equation for a cycle of two beats, by making $\theta_1 = \infty$ see; (32).

Illustration

If for instance the constant current corresponding to C_1 which brings the concentration at the electrode to zero at $at = 0.25$ (see preceding section) persist till $at = 0.50$, the values of $(z - z_0)/C_1 l$ at the electrode from $at = 0$ to $at = 0.25$ will be given by points on the curve *oa* of Fig. 13, which except in scale and the direction in which $(z - z_0)/C_1 l$ is measured, is identical with the first part of the curve of Fig. 3. From $at = 0.25$ to $at = 0.5$ the concentration will remain stationary at $z = 0$ (Fig. 13, line *ad*).

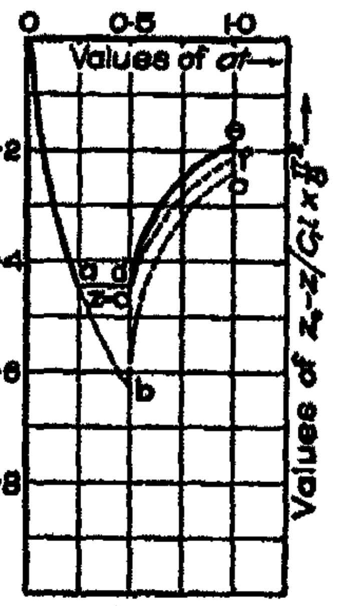

Fig. 13

Now let the current be shut off and be succeeded by a pause ($C_2 = 0$) lasting from $at = 0.50$ till $at = 1.0$, as in the "special case of interrupted currents" illustrated in Sec. 3. The concentrations at the electrode will rise, following the curve *de* of Fig. 13, points for which have been calculated by means of (72).

To show the effect of the new electrode condition (*xi*), the curve for $at = 0$ to $at = 1.0$ of Fig. 8 has been drawn again in Fig. 13; it is represented by the broken line *oabc*. The curve *df* (points for which were computed from the first two terms only of Eq. 72) gives the concentrations that would be found during the second beat, if the first current had persisted long enough to bring about a linear concentration gradient throughout the diffusion layer. The difference between *de* and *df* in Fig. 13 corresponds to that between *ocd* and *ofd* in Fig. 12.

An equation involving triple summation would suffice to trace the concentrations during the first part of the third beat, *i. e.*, until the concentration at the electrode again became zero; but each time the "electrode condition" changes from (*iv*) to (*xi*) or back again the order of the summation is increased by unity. Simplifications are introduced if one of the beats is of long duration; but in general it would probably be easier to plan experiments in which the conditions discussed in this Part are avoided, than to carry out the computations that would otherwise be necessary. Illustrations of how this may be accomplished are given in Part III.

PART III

SECONDARY REACTIONS

In Parts I and II of this paper all changes of concentration occurring in the solution during electrolysis have been ascribed to electrolytic migration and to the diffusion of the products of electrolysis from the electrode, or, as the case may be, to the diffusion toward the electrode of such of the constituents of the solution as were consumed at that point. It will now be assumed that, apart from the effect of diffusion, the concentrations of the products of electrolysis may be lowered by the occurence of "secondary" reactions, *i. e.*, reactions between the products of electrolysis and the other constituents of the solution; and the special assumption will be made that the rate at which such reactions proceed is proportional to the concentration of the substance whose concentration is represented by z.

The rate of change of concentration of such a constituent at any point in the diffusion layer will therefore be represented by

$$[\textit{Differential equation}]\ \partial z/\partial t = k\,\partial^2 z/\partial x^2 - Kz, \qquad (xiv)$$

where K is the "velocity constant" of the secondary reaction. As is well known, K in general depends on the temperature, and on the concentrations of the other constituents of the solution, and even if these factors be kept constant many reactions have been discovered for which the rate is not proportional to the concentration of the disappearing substance; there are enough cases in which the rule holds, however, to make it worth discussion, while to assume that the rate might be proportional to any other than the first power of z would wholly change the nature of the differential equation.

The suggestion that the rates of such almost "instantaneous" reactions as that between copper salts and cyanides might be determined by electrolytic experiments is due to LeBlanc, who has already carried out a number of experiments from which the order of magnitude of such rates may be inferred. The following paragraphs suggest methods for determining K directly; if carried out at different temperatures and with different concentrations of the other reagents, the effect of these factors on the rate of the reaction might also be determined.

To simplify the discussion, it will further be assumed that the secondary reaction is practically "complete," *i. e.*, leads in time to the total destruction of the primary product of the electrolysis; thus the z_0 of Parts I and II becomes zero, and conditions (*i*) and (*ii*) are replaced by

$$[\textit{Solution condition}]\ \textit{At } x = 0,\ z = 0 \textit{ for all values of } t \qquad (xv)$$

$$[\textit{Initial condition}]\ \textit{At } t = 0,\ z = 0 \textit{ for all values of } x \qquad (xvi)$$

while the electrode condition remains the same as before

$$[\textit{Electrode condition}]\ \textit{At } x = l,\ \partial z/\partial x = G/k = C. \qquad (iv)$$

Sec. 10.—Constant Current

The "stationary term" of the new equation may be found by setting $\partial z/\partial t = 0$ in (*xiv*), whence

$$[At\ t = \infty] \quad 0 = k.d^2z/dx^2 - Kz \qquad (74)$$

the solution of which is

$$z = A_1 \cosh bx + A_2 \sinh bx, \text{ where } b = \sqrt{K/k}. \qquad (75)$$

Condition (*xv*) leads to $A_1 = 0$, and (*iv*) to

$$A_2 = C/(b \cosh bl),$$

so that the stationary term becomes

$$[For\ t = \infty \quad z = C \sinh bx/(b \cosh bl.) \qquad (76)$$

The evanescent term, which must satisfy (*xiv*) and (*xv*), and for which at the electrode $\partial z/\partial x$ must equal zero (so as not to interfere with *iv*), may be derived from the form

$$\sum_{n=1}^{\infty} A_n e^{-(K+m^2a)t} \cos \frac{(2n-1)\pi(l-x)}{2l} \qquad (77)$$

by determining the coefficients A_n so that at $t = 0$ the sum of stationary and evanescent terms will vanish, *i. e.*, so that

$$\sum_{n=1}^{\infty} A_n \cos \frac{(2n-1)\pi(l-x)}{2l} = -\frac{C.\sinh bx}{b.\cosh bl}. \qquad (78)$$

This is accomplished (as illustrated in Secs. 1 and 8) by expanding the hyperbolic expression as a series of sines of $m\pi x/2l$, and introducing in (78).

Combining stationary and evanescent terms, the solution of (*xiv*) which satisfies (*xv*), (*xvi*), and (*iv*) is found to be

$$z = \frac{C \sinh bx}{b \cosh bl} - \frac{2kC}{l} \sum \frac{e^{-\psi t}}{\psi} \cos mg\xi \qquad (79)$$

where C, k, l, t, x, have the meanings implied in (*xiv*), (*xv*), (*xvi*) and (*iv*) and explained at length in the Introduction and Part I; $m = (2n-1)$, $g = \pi/2l$, $\xi = l - x$, $b = \sqrt{K/k}$, and ψ is written for $K + m^2a = K + (2n-1)^2\pi^2k/4l^2$.

$\sum$ is used for $\sum\limits_{n=1}^{\infty}$. An expression for the concentrations at the electrode may be obtained by setting $x = l$ in (79).

$$[For\ x = l] \quad z = \frac{C}{b}\ tanh\ bl - \frac{2kC}{l}\sum \frac{e^{-\psi t}}{\psi}. \tag{80}$$

On consulting tables of the hyperbolic functions, it will be found that when $bl \leq 0.15$, *tanh bl* may be replaced by bl with an error not exceeding eight-tenths of one percent; the stationary term then becomes Cl as in (15). Assuming $k = 4 \times 10^{-6}$ as in the former illustrations, $bl = l\sqrt{K/k} \leq 0.15$ implies $K \leq 0.09$ when $l = 10^{-3}$ cm, and $K \leq 9.0$ when $l = 10^{-4}$ cm. Perhaps the highest values of K that can be measured satisfactorily by the direct methods of chemical kinetics[1] do not exceed $K = 0.09$, corresponding to a fall of the concentration to one half its original value every eight seconds, thus if the secondary reaction takes place at any ordinarily measurable rate, the stationary term of (80) becomes Cl.

On the other hand, when $bl \geq 3.0$, *tanh bl* may be replaced by unity with an error not exceeding one-half percent; and the stationary term of (80) becomes $C\sqrt{k/K}$, $= G/\sqrt{Kk}$. Assuming $k = 4 \times 10^{-6}$ as before, this gives $K \geq 36$ if $l = 10^{-3}$ cm, and $K \geq 3600$ if $l = 10^{-4}$ cm as the values that must be reached by K if this approximation is to be employed.

Erf approximation. Evaluation of the evanescent part of (80) by simple addition of the terms is quite impossible when K is large, on account of the slow convergence; if at be small, however, an approximately equivalent expression, based on the equation of Thomson and Cayley (Eq. 18) may be employed.

Writing

$$\frac{2kC}{l}\sum_{n=1}^{\infty}\left(\frac{e^{-(K+m^2a)t}}{K+m^2a} - \frac{1}{K+m^2a}\right) =$$

$$-\frac{2kC}{l}\sum_{n=1}^{\infty}\int_0^t e^{-(K+m^2a)t}\,dt = -\frac{2kC}{l}\int_0^t\left(e^{-Kt}\sum_{n=1}^{\infty}e^{-m^2at}\right)dt \tag{81}$$

---

[1] Such a case was studied by Miss Benson, Jour. Phys. Chem., 7, 356 (1903).

the summation in the last expression may be replaced by its approximate value (*viz.:* $\frac{1}{2}\sqrt{\frac{\pi}{at}}$) from (20), and the term $\frac{2kC}{l}\sum\frac{1}{K+m^2a}$ by its equivalent *viz.:* $\frac{C}{b}$ *tanh bl*, so that $\frac{C}{b}\tanh bl - \frac{2kC}{l}\sum\frac{e^{-\psi t}}{\psi} =$ (*approximately*)

$$\frac{kC}{2l}\sqrt{\frac{\pi}{a}}\int_0^t e^{-Kt}t^{-\frac{1}{2}}\,dt = \frac{2C}{b\sqrt{\pi}}\int_0^{\sqrt{Kt}} e^{-y^2}\,dy, \quad (82)$$

and equation (80) reduces to

$$[\textit{For } \underline{at} \textit{ small}] \quad z = \frac{2C}{b\sqrt{\pi}}\int_0^{\sqrt{Kt}} e^{-y^2}\,dy = \frac{G}{\sqrt{kK}}\frac{2}{\sqrt{\pi}}\,Erf\sqrt{kt}. \quad \textit{approx.} \quad (83)$$

Values of the "probability integral," $\frac{2}{\sqrt{\pi}}\,Erf\,y = \frac{2}{\sqrt{\pi}}\int_0^y e^{-y^2}\,dy$ are tabulated in most books on Least Squares;[1] when the argument is zero, the probability integral is likewise zero, and the integral reaches 0.99 when the argument reaches 1.8; the maximum value of the integral is unity.

Sec. 11.—Successive Currents in General

To obtain an expression for the concentrations when a current corresponding to C_1, after passing for the interval $t = 0$ to $t = t_1$, is succeeded by a current corresponding to C_2 which persists from $t = t_1$ to $t = t_2$, and so on, as described in Sec. 2, (79) may be written

$$[\textit{For } t = t_1] \quad z = \frac{C_2 \sinh bx}{b\cosh bl} - (C_2 - C_1)\frac{\sinh bx}{b\cosh bl} - \frac{2k}{l}\sum\frac{C_1}{\psi}\cdot e^{-\psi t_1}\cos mg\xi, \quad (84a)$$

$$= \frac{C_2 \sinh bx}{b\cosh bl} - \frac{2k}{l}\sum\frac{1}{\psi}(C_1e^{-\psi t_1} + C_2 - C_1)\cos mg\xi. \quad (84b)$$

---

[1] For instance, Merriman and Johnson each give a four-place table, while Bertrand (*Calcul des Probabilités*) and De Morgan (*On Probabilities*) each give a seven-place table, the argument in each case advancing by 0.01. A far more elaborate table in which the argument advances generally by 0.001 is given by Burgess *Trans. Edin. Roy. Soc.*, 39, 257 (1899).

Proceeding as indicated in Sec. 2, the general expression for the concentrations during the pth beat may be obtained:

$$[\textit{For } t_{p-1} \overset{=}{<} t \overset{=}{<} t_p] \quad z = C_p \frac{\sinh bx}{b \cosh bl} - \frac{2k}{l} \sum_{n=1}^{\infty} \frac{1}{\psi} \Big\{ C_1 e^{-\psi t}$$

$$+ \sum_{r=2}^{p} (C_r - C_{r-1}) e^{-\psi(t - t_{r-1})} \Big\} \cos mg\xi, \quad (85a)$$

$$= C_p \frac{\sinh bx}{b \cosh bl} - \frac{2k}{l} \sum_{n=1}^{\infty} \frac{1}{\psi} \Big\{ C_p \Phi T_{p-1}$$

$$+ \sum_{r=1}^{p-1} C_r (\Phi T_{r-1} - \Phi T_r) \Big\} \cos mg\xi, \quad (85b)$$

where

$$T_r = t - t_r, \textit{ and } \Phi T_r = e^{-\psi(t - t_r)},$$

whence the expressions for the concentrations during the progress of odd and even beats in two-beat cycles:

$$[\textit{For } p \textit{ odd}]\; z = \frac{C_1 \sinh bx}{b \cosh bl} + \frac{2k}{l}(C_2 - C_1) \sum \frac{e^{-\psi r}}{\psi} \cdot \frac{e^{\psi\theta} - e^{\psi\theta_1}}{e^{\psi\theta} - 1} \cos mg\xi$$

$$- \frac{2k}{l} \sum \frac{e^{-\psi t}}{\psi} \{ C_1 + (C_2 - C_1) \frac{e^{\psi\theta} - e^{\psi\theta_1}}{e^{\psi\theta} - 1} \} \cos mg\xi. \quad (86)$$

$$[\textit{For } p \textit{ even}]\; z = \frac{C_2 \sinh bx}{b \cosh bl} + \frac{2k}{l}(C_1 - C_2) \sum \frac{e^{-\psi r}}{\psi} \cdot \frac{e^{\psi\theta} - e^{\psi\theta_2}}{e^{\psi\theta} - 1} \cos mg\xi$$

$$- \frac{2k}{l} \sum \frac{e^{-\psi t}}{\psi} \{ C_1 + (C_2 - C_1) \frac{e^{\psi\theta} - e^{\psi\theta_1}}{e^{\psi\theta} - 1} \} \cos mg\xi. \quad (87)$$

From (86) and (87) expressions for the amplitude and for the concentration at the centre of swing in the case of two-beat cycles may be obtained (see pg. 839); they are:

$$[\textit{Amplitude}] \quad \tfrac{1}{2}(C_1 - C_2) \frac{\sinh bx}{b \cosh bl}$$

$$+ \frac{k}{l}(C_1 - C_2) \sum \frac{1}{\psi} \cdot \frac{e^{\psi\theta_1} + e^{\psi\theta_2} - 2e^{\psi\theta}}{e^{\psi\theta} - 1} \cos mg\xi. \quad (88)$$

$$[\textit{At centre}] \quad z = \tfrac{1}{2}(C_1 + C_2) \frac{\sinh bx}{b \cosh bl}$$

$$+ \frac{k}{l}(C_1 - C_2) \sum \frac{1}{\psi} \cdot \frac{e^{\psi\theta_1} - e^{\psi\theta_2}}{e^{\psi\theta} - 1} \cos mg\xi. \quad (89)$$

When θ_1 and θ_2 are very large, the concentrations at any point in the diffusion layer oscillate between $(C_1 \sinh bx)/(b \cosh bl)$ and $(C_2 \sinh bx)/(b \cosh bl)$; when θ is very small, the amplitude is practically zero, and the concentration at the centre of swing is $\left(C_1 \frac{\theta_1}{\theta} + C_2 \frac{\theta_2}{\theta}\right) \sinh bx/(b \cosh bl.)$

Sec. 12.—Simple Alternating Current

If the current corresponding to C_1 pass for θ_1 seconds through a copper electrode into a solution of potassium cyanide, making the copper anode, and if then the current corresponding to C_2 make the copper cathode for the same interval θ_1 seconds, and be succeeded by C_1 for θ_1 seconds and so on; the ratio between the two currents that will just bring the concentration at the electrode to zero at the end of the cathode beats when the stationary state has been reached, may be found by setting $x = l$, $t = \infty$, $z = 0$, $\tau = 0$, and $\theta = 2\theta_1$ in (86).

Making these substitutions, and dividing the numerator of the θ fraction by its denominator, the result may be put in the form

$$\frac{C_1}{C_1 - C_2} = \frac{2kb}{l \tanh bl}\left\{\sum \frac{1}{\psi} - \sum \frac{e^{-\psi\theta_1}}{\psi} + \sum \frac{e^{-2\psi\theta_1}}{\psi} - \sum \frac{e^{-3\psi\theta_1}}{\psi} + etc.,\right\} \quad (90)$$

and if $a\theta_1$ be small enough to justify the use of the Erf approximation,

$$\frac{C_1}{C_1 - C_2} = 1 - \left[1 - (\coth bl)\frac{2}{\sqrt{\pi}} Erf \sqrt{K\theta_1}\right] + \left[1 - (\coth bl)\frac{2}{\sqrt{\pi}} Erf \sqrt{2K\theta_1}\right] - etc. \quad (91)$$

For high values of $l\sqrt{\frac{K}{k}}$, $\coth bl$ becomes unity, and the ratio between the two currents is independent of k and of l, becoming in fact a function of $K\theta_1$.

In making an actual computation, $\frac{2k}{l}\sum\frac{1}{\psi}$ would be replaced by its value $(\tanh bl)/b$ and the Erf approximation would be used for the first few summations of (90) where direct summation would be too laborious; for higher values of the negative exponent, however, where the Erf approximation becomes less reliable, direct summation is easy.[1]

As an example, if $k = 4 \times 10^{-6}$, $l = 3.1416 \times 10^{-4}$, $K = 400$, and the duration of each beat $\theta_1 = 0.0005$ seconds, the two currents would stand in the ratio of 68.97 to 31.03 or $G_2 = -0.4499\ G_1$.

If C_1/C_2 were determined in the laboratory, K could be found by (90) and (91); the easiest way, no doubt, would be to compute C_1/C_2 for a number of assumed values of K, plot the results, and find K from the observed C_1/C_2 by interpolation. If, however, in the experimental work, the currents in the two beats had been equal, and if it were attempted to calculate K from an experimental determination of the relative amounts of copper dissolved during the anode beat and redeposited during the cathode beat (*i. e.*, from the net loss of weight of the electrode)[2] or from an oscillographic determination of the moment during the cathode beat at which the concentration at the electrode fell to zero, the problem would become analogous to those of Part II; multiple summations would have to be employed, and the computations would become complicated and laborious.

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[1] When $\theta_1 = 0.0005$ and $a = 100$, the following are the true values and the Erf approximations respectively of the sums in (90), beginning with the first containing an exponential factor:

Number	1	2	3	4
True value	0.0020552	0.0014426	0.0010587	0.0007939
Erf approx.	0.0020552	0.0014426	0.0010587	0.0007939
Number	**5**	**6**	**7**	**8**
True value	0 0006031	0.0004619	0.0003557	0.0002749
Erf approx.	0.0006031	0.0004618	0 0003555	0 0002745

In the case of the last term mentioned in this table, which involves $e^{-8\psi\theta_1}$, the first two terms only of the summation suffice for the determination of five significant figures and the Erf approximation can thus in this case be dispensed with before it becomes inaccurate.

[2] As, for instance, in LeBlanc's experiments.

The quantity of cuprion[1] per square centimeter of electrode area left in the diffusion layer at the end of the cathode beat, *viz.:*

$$\int_0^l z dx = \frac{C_1 k(1 - \operatorname{sech} bl)}{K} + \frac{4k}{\pi}(C_2 - C_1)\left[\sum \frac{(-1)^{n+1}}{m\psi} - \sum \frac{(-1)^{n+1} e^{-\psi\theta_1}}{m\psi} + \sum \frac{(-1)^{n+1} e^{-2\psi\theta_1}}{m\psi} \text{ etc.}\right] \quad (92)$$

is by no means negligible; in the case taken as illustration it amounts to 4.5099×10^{-4} G_1, as against 5.000×10^{-4} G_1 equivalents brought into the solution during an anode beat (the sum of the series in square brackets in (92) is 0.0009931, and $C_2 = -0.4499$ C_1).

This is why an estimation of K from the experimentally determined ratio C_1/C_2, based on the rough and ready hypothesis that diffusion may be altogether neglected, and that at the end of the cathode beat (when $z = 0$ at both ends of the diffusion layer) the amount of cuprion in the diffusion layer may be neglected, leads to results very wide of the mark.[2]

The number of equivalents of cuprion that pass out from the diffusion layer into the body of the solution, per sq. cm of electrode surface, during an anode beat, may be found by multiplying the concentration gradient at the solution (at $x = 0$) by $k.d\tau$ and integrating:

$$k\int_0^{\theta_1}\left(\frac{\partial z}{\partial x}\right)_{x=0} d\tau = \frac{C_1\theta_1}{\cosh bl} - \frac{k\pi}{l^2}(C_2 - C_1)\sum \frac{m}{\psi^2}\frac{(-1)^{n+1}}{1+e^{-\psi\theta_1}}(e^{-\psi\theta_1} - 1). \quad (93)$$

A similar expression for the cathode beat may easily be obtained. In the case taken for illustration these quantities are not large. An approximate value for the loss during the cycle may be found, without summing the series of (93), by assuming that the loss would be the same as that caused by a constant current of average strength, $C = \frac{1}{2}(C_1 + C_2) = 0.275$ C_1, acting throughout the cycle.

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[1] Copper not combined with cyanide is meant.

[2] See under the next heading.

Using the formula for the stationary state (Eq. 76) this gives

$$k\int_0^{\theta_1}\left(\frac{\partial z}{\partial x}\right)_{x=0} d\tau = \frac{0.275C_1k\theta}{\cosh bl} \text{ approximately, } = 0.237 \times 10^{-4}G_1. \quad (94)$$

The loss from the diffusion layer during a complete cycle ($\theta = 2\theta_1 = 0.001$ seconds) is thus about five percent of that dissolved from the electrode during an anode beat.

Approximate Calculation of K from the Current Ratio

The quantity of cuprion in the diffusion layer opposite each sq. cm of electrode surface, (which in this paragraph only will be represented by y), is thus subject to change by the operation of three causes. It is being added to by electrolysis at the rate of G equivalents per second, it is being diminished by the chemical action of the cyanide at the rate of Ky equivalents per second, and there is a loss (which being small may be treated as constant throughout the cycle) of L equivalents per second into the main body of the solution.

Thus

$$[\textit{Anode beat}]\frac{dy}{d\tau} = G_1 - Ky - L;\ [\textit{Cathode beat}]\frac{dy}{d\tau} = G_2 - Ky - L. \quad (95)$$

Integrating between the limits 0 and θ_1, and θ_1 and $2\theta_1$, respectively, and writing w for the number of equivalents of cuprion remaining in the diffusion layer at the end of a cathode beat ($\tau = 0$, or $\tau = 2\theta_1$), there results

$$Kw = G_1 - L - (G_1 - G_2)\frac{e^{K\theta_1}}{e^{K\theta_1}+1}. \quad (96)$$

Inserting the values found in the previous paragraph, *viz.:* $G_2 = -0.4499G_1$, $w = 4.5099 \times 10^{-4}G_1$, and $L = 0.0237\,G_1$, Eq. (96) gives $K = 398$ in place of the true value $K = 400$.

Suppose, however, that the current ratio had been determined experimentally, and that it was proposed to calculate K without taking account of diffusion at all, *i. e.*, from

$$-G_2/G_1 = e^{-K\theta_1} \tag{97}$$

which may be obtained from (96) by setting $w = 0$ and $L = 0$, the wholly erroneous result $K = 1597$ would be obtained. The error is mainly due to neglecting w; if in (96) w be given its true value and L be set equal to zero, K comes out equal to 435.

Conditions Connoted by Large Values of $l\sqrt{\frac{K}{k}}$

During the discussion of (91) it was pointed out that when $l\sqrt{\frac{K}{k}}$ is large, C_1/C_2 is independent of k and l; according to (96), however, the current ratio can be independent of k and l only when the amount of cuprion left in the diffusion layer at the end of a cathode beat is likewise independent of the same two variables. The following considerations may help to make the reason for these relations clear.

If in any series of experiments z remains constantly zero at any fixed point in the solution, that point might be taken as $x = 0$, *i. e.*, its distance from the electrode might be taken as l; to keep $z = 0$ at any point *further* from the electrode could have no effect on the diffusion, and consequently to give l any *greater* value in any system of equations applicable to the case could have no effect on the results of the computations. By lessening k or increasing K the point at which z remains practically equal to zero is brought nearer to the electrode; and it follows from what has just been said, that when once it is nearer than the point selected as "$x = 0$" for the given system, the "solution condition" is without effect. Large values of t bring the evanescent terms to zero, and thus destroy the influence of the "initial condition;" if both circumstances occur together, the only equations influencing the result are the "differential equation" and the "electrode condition," which for any given value of k, *viz.*: k_1 may be written

$$\frac{\partial z}{\partial t} = k_1 \frac{\partial^2 z}{\partial \xi^2} - Kz \ (xiva); \qquad k_1 \frac{\partial z}{\partial \xi} = -G \qquad (iv\,a)$$

Suppose that in two cases the diffusion constants are k_1 and $k_2 = k_1/r^2$, respectively, where r is any constant multiplier. Replacing k_1 in (*xiv a*) and (*iv a*) by k_1/r^2 the equations for the second case will be

$$\frac{\partial z}{\partial t} = k_1 \frac{\partial^2 z}{\partial (r\xi)^2} - Kz; \quad k_1 \frac{\partial z}{\partial (r\xi)} = -rG \qquad (98)$$

and it is obvious that (if conditions are such that the "initial" and "electrode" conditions may be neglected) the same values of z will be met with in both cases if $r\xi$ and rG in the second case have the same values as ξ and G in the first case, respectively; that is, when the current, and the distance from the electrode, of the points compared, are both r times less in the second case than in the first. Consequently (since, other things being equal, z is proportional to G) if the currents be *equal* in the two cases, the values of z at comparable points will be *r times greater* in the second case than in the first.

Hence, if the diffusion layer be imagined to be divided into corresponding laminae in the two cases, these being r times as thin in the second case as in the first and having concentrations r times greater, each will contain the same quantity of the component to which z refers. Further as explained above since the values of z in both cases fall to zero with increasing ξ and remain at zero, the impaired laminae having zero values of z will not affect the total, and therefore the total quantity of the component in the two cases being the sum of the same items must be the same. That is to say, the number of equivalents contained in the diffusion layer will be under these conditions independent of K.

Conditions that keep $z = 0$ at $\xi < l$ obviously prevent all loss from the diffusion layer into the main body of the solution, by destroying the concentration gradient at $\xi = l$; for large values of $l\sqrt{\frac{K}{k}}$ therefore, the integral expanded in (93) must reduce to zero.

Sec. 13.—[1]Sinusoidal Currents, Fourier Form

The general expression where $C = f(t)$, from which the expression for the sinusoidal current may be derived as a special case is:

$$z = \frac{\sinh bx}{b \cosh bl} f(t) - \frac{2k}{l}\sum_{n=1}^{\infty}\left\{ \frac{f(t)}{\psi} e^{-\psi t}\int_0^t e^{\psi u}.f(u).du\right\}\cos mg\xi. \quad (99a)$$

$$= \frac{2k}{l}\sum_{n=1}^{\infty}\left\{ e^{-\psi t}\int_0^t e^{\psi u}.f(u).du\right\}\cos mg\xi. \quad (99b)$$

Setting $f(t) = M \sin (\omega t + \alpha)$, this becomes

$$z = M \sin(\omega t + \alpha)\frac{\sinh bx}{b \cosh bl}$$
$$- \frac{2kM\omega}{l}\sum\frac{1}{\psi}\,\frac{\omega \sin(\omega t + \alpha) + \psi \cos(\omega t + \alpha)}{\psi^2 + \omega^2}\cos mg\xi$$
$$- \frac{2kM}{l}\sum e^{-\psi t}\frac{\psi \sin \alpha - \omega \cos \alpha}{\psi^2 + \omega^2}\cos mg\xi. \quad (100a)$$

$$= \frac{2kM}{l}\sum\frac{\psi \sin(\omega t + \alpha) - \omega \cos(\omega t + \alpha)}{\psi^2 + \omega^2}\cos mg\xi$$
$$- \frac{2kM}{l}\sum e^{-\psi t}\frac{\psi \sin\alpha - \omega \cos\alpha}{\psi^2 + \omega^2}\cos mg\xi. \quad (100b)$$

Where the harmonic analysis of a current is known it can be seen that for each component of the current there will be in the value of z a term expressible either in this form or in that of the next section.

Sec. 14.—Sinusoidal Currents, Hyperbolic Form

As in Part I, the stationary term may be expressed in a form more suitable for computation by the use of hyperbolic functions.

Starting out from (48), and introducing the new conditions, it will be found that the values obtained for A and B are those given by (49), but that the exponents γ and λ must be defined as follows:

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[1] With regard to the applicability of these results see under Sec. 15.

$$\gamma^2 k = K + i\omega \text{ and } \lambda^2 k = K - i\omega, \tag{101a}$$

whence

$$\gamma = \beta + \delta i \text{ and } \lambda = \beta - \delta i, \tag{101b}$$

where

$$\beta^2 + \delta^2 = \frac{\sqrt{K^2 + \omega^2}}{k}, \beta^2 - \delta^2 = K/k, \text{ and } 2\beta\delta = \omega/k. \tag{101c}$$

Introducing these values in (48), the following expression for the stationary term is obtained

$$z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{4}}} \cdot \frac{\sqrt{\cosh^2 x\beta - \cos^2 x\delta}}{\sqrt{\cosh^2 l\beta - \sin^2 l\delta}} . \sin \chi \tag{102}$$

where

$$\chi = \omega t + \alpha + \tan^{-1}(\coth x\beta \,.\, \tan x\delta) - \tfrac{1}{2}\tan^{-1}(\omega/K), \\ - \tan^{-1}(\tanh l\beta \,.\, \tan l\delta). \tag{103}$$

On setting $K = 0$ in (102) it is reduced to (54); on setting $\omega = 0$ it is reduced to (76); and by means of suitable expansions of the hyperbolic functions it may be converted into the "Fourier" form, (stationary term of equation 100).

The evanescent term may be obtained from the general form

$$\sum_{=1}^{\infty} A_n \frac{1}{\psi} e^{-\psi t} \cos mg\xi, \tag{104}$$

(which satisfies (*xiv*), (*xv*), and the condition that when $x = l$, $\partial z/\partial t = 0$), by expanding (102) in a series of sines of $mg\xi$ and determining the values of A_n as in sec. (6*b*). The resulting evanescent term is identical with that of (100).

Combining both terms, the "hyperbolic form" of the expression for sinusoidal currents becomes:

$$z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{4}}} \cdot \frac{\sqrt{\cosh^2 x\beta - \cos^2 x\delta}}{\sqrt{\cosh^2 l\beta - \sin^2 l\delta}} \sin \chi \\ - \frac{2Mk}{l} \sum_{n=1}^{\infty} e^{-\psi t} \frac{\psi \sin \alpha - \omega \cos \alpha}{\psi^2 + \omega^2} \cos mg\xi \tag{105}$$

in which χ has the meaning given in (103), and β and δ those implied in (101*c*).

An expression for the *amplitude* at the stationary state may be found by setting $\sin \chi = 1$; the concentration at the centre of swing is zero. The "*lag*" is given by

$$[Lag]\ \tan^{-1}(\tanh l\beta.\ \tan l\delta) + \tan^{-1}(\omega/K) - \tan^{-1}(\coth x\beta.\ \tan x\delta). \quad (106)$$

Concentrations at the electrode may be found by substituting l for x in (105); in the evanescent term, this has the effect of making $\cos mg\xi$ unity, while the stationary term becomes

$$[For\ t = \infty,\ x = l]\ z = \frac{Mk^{\frac{1}{2}}}{2(K^2 + \omega^2)^{\frac{1}{2}}} \frac{\sqrt{\sinh^2 2\beta l + \sin^2 2\delta l}}{\sinh^2 \beta l + \cos^2 \delta l} \sin \chi_l \quad (107)$$

where

$$\chi = \omega t + \alpha + \tan^{-1} \frac{\sin 2l\delta}{\sinh 2l\beta} - \tfrac{1}{2} \tan^{-1}\left(\frac{\omega}{K}\right). \quad (108)$$

If $\beta l \geq 3$, $\sinh \beta l$ becomes ≥ 10, and the circular functions may be neglected in comparison with the hyperbolic. The fraction then becomes $\sinh 2\beta l/\sinh^2 \beta l$ which for values of $\beta l \geq 3$ is very nearly equal to 2.00; thus (with a maximum possible error of one-half percent), when the stationary state is reached

$$[For\ x = l,\ \beta l \geq 3] \quad z = \frac{Mk^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{2}}} \sin \chi. \quad (109)$$

Sec. 15.—Superposed Currents

As in Part I, the effect of a number of currents acting simultaneously may be found by adding the right hand members of the equations which express the effects of each of them alone. In fact, the assumption made throughout this Part, that $z_0 = 0$, deprives many of the equations of their validity unless when thought of as parts of such a sum; according to (107), for instance, the concentrations at the electrode would be *negative* during a large part of the cycle on electrolysis with a pure sinusoidal current.

When the stationary state has been reached during electrolysis with a sinusoidal current, the amplitude of the concentration variation at the electrode may be found by setting $\sin \chi_l = 1$ in (107). The centre of swing is zero with the sinusoidal current alone, but it may be raised to any desired height, $C_1 \frac{\tanh bl}{b}$, by superposing the direct current corresponding to C_1. If $C_1 \frac{\tanh bl}{b}$ be greater than the amplitude, z at the electrode will never fall to zero; and the condition that z just touches zero once in the cycle is expressed by

$$0 = \frac{C_1}{b} \tanh bl - \frac{Mk^{\frac{1}{2}}}{2(K^2 + \omega^2)^{\frac{1}{4}}} \frac{\sqrt{\sinh^2 2\beta l + \sin^2 2\delta l}}{\sinh^2 \beta l + \cos^2 \delta l} \qquad (110)$$

whence the ratio of the two ammeter readings $\frac{C_1\sqrt{2}}{M}$ may be found:

$$\frac{C_1}{M} = \frac{1}{2} \frac{b}{\tanh bl} \frac{k^{\frac{1}{2}}}{(K^2 + \omega^2)^{\frac{1}{4}}} \frac{\sqrt{\sinh^2 2l\beta + \sin^2 2l\delta}}{\sinh^2 l\beta + \cos^2 l\delta}; \qquad (111)$$

the limit of (111) for $K = 0$ is the expression obtainable by equating (64) to zero.

With the ordinary alternating current of 60 cycles per second, $\omega = 377$; assuming $k = 4 \times 10^{-6}$, $l = 3.14 \times 10^{-4}$, and $K = 500$, the ratio C_1/M will be 0.912, and the ratio of the ammeter readings, 1.290 provided the arrangement is as described in the footnote to Sec. 7.

The ratio is a function of $l\sqrt{\frac{\omega}{k}}$ and $\frac{\omega}{K}$ so that if it be determined experimentally, and if in addition ω and a be known, K may be calculated. As the value of C_1 for which z at the electrode just touches zero should be recognizable by voltmeter or oscillograph or by weighing the electrode, (111) should lead to a convenient experimental method of determining the velocity constants of rapid "secondary" reactions. The ratio C_1/M will vary from the value discussed in Sec. 7 when K is zero, to 1 when K increases without limit (the value 1 would imply, in the case of a copper electrode in cyanide solution, that the copper never became cathode). Other things being equal, increasing ω brings the ratio nearer zero.

For large values of K, *tanh bl* becomes unity, and the *sinh* fraction of (111) reduces to 2.0; in this case the relation between the current ratio and the value of K takes the simple form

$$\left(\frac{C_1}{M}\right)^4 = \frac{K^2}{K^2 + \omega^2}, \qquad (112)$$

and K may be determined without knowledge of k or l.

APPENDIX

Note on the Construction of Special Trigonometrical Series to Represent Arbitrary Functions

If it be required to express a given function of x, $f(x)$, between given values of x as the sum of a series of sines and cosines of multiples of a variable θ chosen so as to have its increment in a constant ratio to that of x and to vary from 0 to 2π between these given limits of x, the problem admits of but one solution; and Fourier has shown that the coefficients of the general terms of the series, *viz.*, $\sin m\theta$ and $\cos m\theta$ will be $\frac{1}{\pi}\int_0^{2\pi} f(x) \sin m\theta . d\theta$ and $\frac{1}{\pi}\int_0^{2\pi} f(x) \cos m\theta . d\theta$ respectively, for all integral values of m not zero, while the constant term or coefficient of $\cos 0\theta$ is $\frac{1}{2\pi}\int_0^{2\pi} f(x) . d\theta$.

If, however, it be agreed that the series shall represent the given function for a limited range only (less than 2π) of values of θ, an infinite number of solutions are possible; and the problem becomes determinate only when the value of the series for the remainder of the interval 2π of θ is specified. Advantage may be taken of this to impose additional conditions on the nature of the series by which the given function is to be represented.

If, for example, it be sufficient to find a series that will represent the function over the assigned range in values of x for values of θ between $\theta = 0$ and $\theta = \pi$, no conditions being imposed as to the value of the series when θ lies between π and 2π, the value of the series in the latter range may be so chosen as to make the coefficients of either the sine terms or the cosine terms of the series equal to zero.

The first may be accomplished by making the series represent the ordinates of a curve with values of θ as abscissae, whose ordinates between $\theta = 0$ and $\theta = \pi$ are the corresponding values of $f(x)$ over the given range in the values of x, and which is continued between $\theta = \pi$ and $\theta = 2\pi$ by its mirror image in the ordinate at $\theta = \pi$. Representing by $\psi(x)$ the values of the ordinates throughout the whole range from $\theta = 0$ to $\theta = 2\pi$, the integral $\frac{1}{\pi}\int_0^{\pi} \psi(x)\ sin\ m\theta.d\theta$ will then be equal in magnitude and opposite in sign to $\frac{1}{\pi}\int_{\pi}^{2\pi} \psi(x)\ sin\ m\theta.d\theta$ and therefore $\frac{1}{\pi}\int^{2\pi} \psi(x)\ sin\ m\theta.d\theta$ will be zero, while $\frac{1}{\pi}\int_0^{2\pi}\psi(x)\ cos\ m\theta.d\theta$ will be equal to $\frac{2}{\pi}\int_0^{\pi}\psi(x)\ cos\ m\theta.d\theta$, and the constant term $\frac{1}{2\pi}\int_0^{2\pi}\psi(x).d\theta$ to $\frac{1}{\pi}\int_0^{\pi}\psi(x).d\theta$; so that the series which represents $\psi(x)$ for all values of θ between $\theta = 0$ and $\theta = 2\pi$, and therefore *inter alia* represents $f(x)$ over the given range in x for values of θ between $\theta = 0$ and $\theta = \pi$, will consist of cosines only (besides the constant term). Thus the coefficient of the general term $cos\ m\theta$ will be $\frac{2}{\pi}\int_0^{\pi} f(x) cos\ m\theta.d\theta$ and the constant term is as just stated, or equivalently $\frac{1}{\pi}\int_0^{\pi} f(x).d\theta$.

If on the other hand the ordinates of the curve represented by the series be equal to $f(x)$ for values of θ between $\theta = 0$ and $\theta = \pi$, while the part of the curve between $\theta = \pi$ and $\theta = 2\pi$ is formed from the first part by revolution through 180° round the point $\theta = \pi$ on the axis of abscissae, the cosine terms disappear and the coefficient of the general term $sin\ m\theta$ is $\frac{2}{\pi}\int_0^{\pi} f(x) sin\ m\theta.d\theta$, there being here no constant term.

These "cosine series" and "sine series" are discussed in all works dealing with Fourier series; the textbooks with which we are familiar, however, do not point out that still further conditions may be imposed on the nature of the series if the range of values of θ through which it is to represent $f(x)$ be still further restricted. Such conditions are met with in practice; for instance, in order to obtain Eq. (54*e*) Eq. (72) and Eq. (79) of the present paper (see also Eq. 11) it was necessary to find a series of *sines of odd multiples* of $\theta = \pi x/2l$ which would represent a given function of x between the limits $\theta = 0$ and $\theta = \pi/2$. This condition is complied with if the series be constructed to represent the ordinates of a curve, whose ordinates between $\theta = 0$ and $\theta = \pi/2$ are equal to $f(x)$, and which is continued in the second quadrant by its mirror image in the vertical through the point $\theta = \pi/2$, while the second half is formed from the first by rotation through 180° around the centre $\theta = \pi$ on the axis of abscissae. For such a case $\int_0^{2\pi} \psi(x).\cos m\theta.d\theta = 0$ as stated above, while $\frac{1}{\pi}\int_0^{2\pi} \psi(x) \sin m\theta.d\theta$ is zero when $m = 2n$, and equals $\frac{4}{\pi}\int_0^{\frac{\pi}{2}} \psi(x).\sin m\theta.d\theta$ or $\frac{4}{\pi}\int_0^{\frac{\pi}{2}} f(x).\sin m\theta.d\theta$ when $m = 2n - 1$. So that the series which represents $f(x)$ for all values of θ between $\theta = 0$ and $\theta = \frac{\pi}{2}$, will consist of sines of odd multiples only of θ and the coefficient of the general term, *viz.*, $\sin(2n - 1)\theta$ will be $\frac{4}{\pi}\int_0^{\frac{\pi}{2}} f(x).\sin (2n - 1)\,\theta.d\theta$.

Similarly, the general term of the series which represents $f(x)$ for values of θ between $\theta = 0$ and $\theta = \frac{\pi}{2}$ and which consists of cosines of odd multiples only of θ, is

$$\frac{4}{\pi}\cos(2n-1)\theta.\int_{0}^{\frac{\pi}{2}} f(x).\cos(2n-1)\theta.d\theta.$$

The extension to the other three quadrants which this series is made to define is obtained as follows: revolve the curve in the first quadrant about the point $\theta = \frac{\pi}{2}$ on the axis of abscissae through 180° to define the second quadrant, and then for the second half take the mirror image of the first two quadrants in the ordinate at $\theta = \pi$.

It is to be noted, however, that these extensions are introduced merely for the purpose of explanation, and, as the results above show, do not need to be represented graphically or introduced into the formulae.

Although values different from zero may be obtained from the above formulae for the coefficients of terms which are not to appear in the series, no use is to be made of such values, as the formula is not valid for any such purpose. Similarly in the last case for which the formula is given (cosines of odd multiples) there is no constant term, whatever be the mean value of $f(x)$ over the given range in x.

University of Toronto,
July, 1910

CONTENTS.

The following contractions are employed throughout:

$$a = \pi^2 k/4l^2 \qquad \mu = \sqrt{\frac{\omega}{2k}}$$

$$b = \sqrt{\frac{K}{k}} \qquad \sum = \sum_{n=1}^{\infty}$$

$$C = G/k \qquad \xi = l - x$$

$$g = \pi/2l \qquad \psi = K + m^2 a$$

$$m = 2n - 1$$

Equations presenting different algebraical forms of the same relations are given the same number, but distinguished by the use of the letters *a*, *b*, *c*, etc.

THE BEHAVIOR OF COPPER ANODES IN CHLORIDE SOLUTIONS

BY SAUL DUSHMAN

INTRODUCTION

In connection with some experiments on the electrolytic etching of copper alloys, my attention was drawn to the behavior of pure copper anodes in solutions of chlorides. I found that it was possible to make the copper dissolve wholly as cupric or wholly as cuprous salt or as a mixture of these in any desired proportions, by varying the current density or the concentration of chloride in solution. The observation that increasing the concentration of chloride increases the proportion of cuprous salt formed,[1] suggested that there may be equilibrium at the surface of the electrode between metallic copper and the cuprous and cupric salts in solution. The effect on the proportion of cuprous salt consequent on lowering the current density,[2] stirring the solution,[3] or increasing the rate of circulation,[4] may also be explained in the same manner; for all these processes tend to lessen the difference in composition between the solution at the electrode and that in the body of the electrolyte, *i. e.*, they raise the concentration of the chloride and diminish that of the dissolved copper salts at the surface of the anode,[5] and thus increase the proportion of cuprous salt formed.[6]

The assumption of equilibrium at the electrode is not new,[7] it has been put forward to explain the behavior of gold anodes

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[1] See experiments 1–6 Table I.

[2] See experiments 10–12 Table II.

[3] Compare experiments 7 and 8 5 and 9 Table I.

[4] See experiments 13–16 Table II.

[5] See abstract of preliminary work, Trans. Roy. Soc. Can. Sec. III, p. 26 (1907).

[6] A brief account of these experiments was given at the meeting of the American Chemical Society at *Toronto, June 1907*.

[7] Foerster: Elektrochemie wässr. Lösungen, p. 212, etc.

TABLE I

Beaker experiments. Stationary electrodes. Hydrochloric acid solutions. Area of electrodes = 2.5 × 2.5 cms

No.	Concentration	Current density (Amps/cm^2) gram	Total copper dissolved gram	Percent cupric	Percent cuprous	Stirring
1	N/1	0.02286	0.760	0	100	Yes
2	N/10	0.02286	0.429	87	13	Yes
3	N/40	0.02286	0.341	100	0	Yes
4	N/1	0.00514	0.602	0	100	Yes
5	N/2	0.00514	0.508	30	70	Yes
6	N/4	0.00514	0.372	77	23	Yes
7	N/1	0.00416	0.609	0	100	Yes
8	N/1	0.00416	0.422	53	47	No
9	N/2	0.00514	0.360	80	20	No

TABLE II

Beaker experiments. Circulating electrolyte. Rotating anode. Solution N/10 HCl. Duration of each experiment, 30 minutes

	Volume circulated liters	Current density (Amp./cm^2)	Total copper dissolved	Percent cupric	Percent cuprous
10	10.6	0.016	0.2392	16.0	84.0
11	11.0	0.107	0.9403	94.0	6.0
12	10.0	0.300	2.7000	100.0	0.0
13	15.7	0.109	1.0107	88.2	11.8
14	33.5	0.109	1.0523	83.7	16.3
15	39.0	0.109	1.0910	79.3	20.7
16	48.4	0.109	1.1354	74.4	25.6

in chloride solutions[1] of copper anodes in sulphate solutions[2] and of anodes of tin, antimony and bismuth in a number of different electrolytes.[3] *In no case however have quantitative measurements been made by which the hypothesis of equilib-*

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[1] Wohlwill: Zeit. Elektrochemie, 4, 405 (1898).

[2] Foerster and Seidel: Zeit. anorg. Chem., 14, 106 (1897).

[3] K. Elbs and H. Thummel: Zeit. Elektrochemie, 10, 364 (1904); K. Elbs and J. Forssell: Ibid., 8, 760 (1902); K. Elbs: Ibid., 8, 512 (1902); K. Elbs and F. Fischer: Ibid., 7, 343 (1900).

rium could be controlled, and the object of the experiments described in this paper is to supply this deficiency.[1]

My electrolyses were consequently carried out under conditions that allowed the concentrations of the various constituents of the solution at the anode to be ascertained; and the concentrations so determined were compared with the requirements of the Mass Law.

APPARATUS

In designing the apparatus it was necessary first to provide a uniform field, so that the current density might be the same at every part of the anode, second, to exclude air as far as possible, so that there might be no "chemical" solution of the anode, and third, to keep the copper salts from reaching the cathode, so that the composition of the electrolyte might depend only on the anode reactions. Arrangements had also to be made for varying the composition and rate of circulation of the electrolyte, as well as the rate of rotation of the anode. The current was determined by an ammeter and a copper (or silver) voltameter in the circuit.

Fig. 1. shows the apparatus finally used.[2] It consisted of two porous cylinders P_1 and P_2 cemented to the cylinder E and the bottom piece F which were of hard rubber, and a rotating copper anode A making contact by means of a wire W with a shaft S and holder H. A plug of hard rubber T was provided with a threaded perforation so that it could be tightened against the copper tube as shown in the diagram. The tube could therefore be taken off the shaft and weighed. Rubber rings *r* and pieces of tubing *b* prevented any electrolyte entering the tube. The access of air to the solution passing over the anode was prevented by means of hydro-

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[1] NOTE.—After these experiments were well under way, an abstract of a paper originally published in Russian appeared in Chem. Cent. 2, 1243 (1907) in which the hypothesis is advanced that equilibrium exists at the surface of copper anodes in chloride solutions and of mercury anodes in nitrate solution. No quantitative measurements however are given except in the case of mercury in solution of potassium nitrate.

[2] A description of an earlier form of apparatus will be found in Trans. Am. Electrochem. Soc., 13, 314 (1908).

chloric acid (of the same strength as that circulating through the cell) which was contained in the circular groove R in which rotated the hard rubber cover C. The electrolyte entering B passed over the anode, through the glass tube K

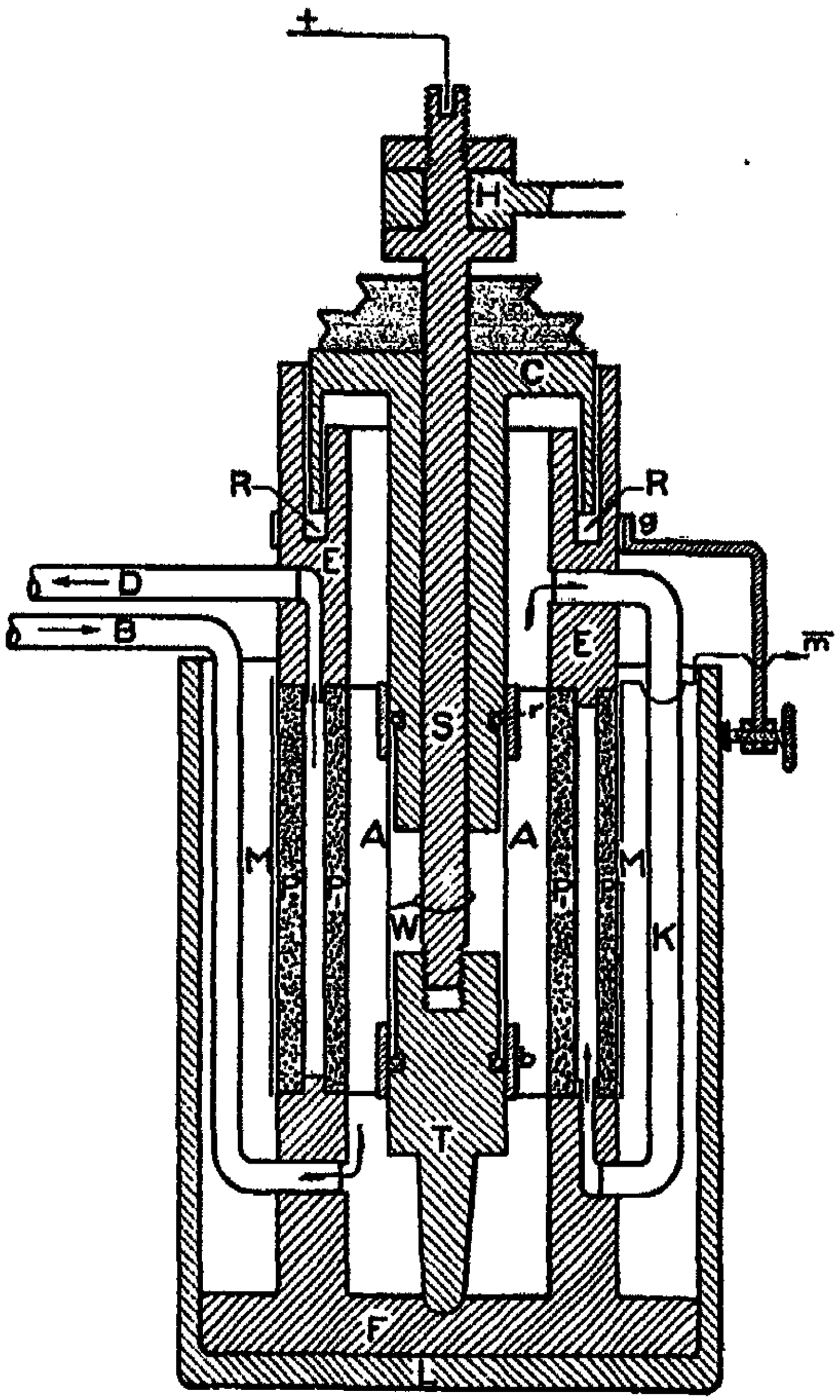

Fig. 1

into the compartment between the two porous cylinders and left it by means of the exit tube D. The cathode consisted of a platinum gauze M wrapped around the outside of P. The different parts of the apparatus were cemented together with a cement consisting of one part rubber and three parts resin. Three rubber-tipped screw clamps *k* attached to a brass ring *g* and clamped to the glass jar L (which contained the cathode solution) prevented any lateral motion of the cell when the anode was set rotating.

The stock solution, contained in a tubular 12-liter bottle, was freed from air by exhaustion (a mercury manometer was used to indicate the degree of exhaustion), and was then saturated with purified carbon dioxide gas. During the electrolysis, this solution was kept under an atmosphere of the gas and furthermore on its way from the tubulus into the inlet tube B of the cell it was joined by a stream of carbon dioxide gas; in this manner the cell could be filled with the gas before electrolysis, and oxidation of cuprous salt formed during the experiment was reduced to a minimum. After circulating through the cell once, the electrolyte passed into a measuring cylinder and was then discarded.

With these precautions to exclude air, the loss of weight of the anode when rotated (without current) was extremely small as is evident from the following data:

Hydrochloric acid (1.84×10^{-3} N) was circulated through the cell for one hour. In the first two experiments air-saturated solution was used, in the third, solution which had been completely freed from air by exhaustion and saturated with carbon dioxide gas, and in the fourth, a mixture of equal volumes of air-saturated and carbonated solutions.

No.	V	L	$10^3L/V$
1	3.2	0.0148	4.6
2	2.4	0.0085	3.5
3	2.7	0.0008	0.3
4	2.2	0.0050	2.3

Under V is given the number of liters of solution circulated, and under L, the loss in weight of the copper tube. It appears from these results that the rate of solution of the copper in hydrochloric acid solutions containing air is approximately proportional to the concentration of oxygen.

In another experiment with 5×10^{-3} N acid, 6.0 liters solution (air-free) were circulated in an interval of 7 hours and only 0.0028 gram was dissolved,[1] corresponding to 0.45×10^{-3} gram per liter.

THE CONCENTRATIONS IN THE BODY OF THE SOLUTION

To find the quantity of cupric and cuprous salts, respectively, formed during an experiment, the total copper dissolved in an experiment (P grams) was compared with the copper (Q) or silver, deposited in a voltameter in the circuit. Then 2(P-Q) gms is the weight of copper dissolved as cuprous salt, and 2Q-P is the weight of copper as cupric.

The concentrations of the cupric and cuprous salts in the electrolyte, expressed in *mols per litre*,[2] may therefore be represented by

$$[\text{Cupric}] = \frac{2Q - P}{63.6\,V}$$

$$[\text{Cuprous}] = \frac{2(P - Q)}{63.6\,V},$$

where V is the total volume of the electrolyte passed through the cell (in liters).[3] In the calculations which follow, it is assumed that the cupric salt is totally dissociated in solution into the ions $\overset{++}{\mathrm{Cu}}$ and $\overset{-}{\mathrm{Cl}}$, so that

$$[\overset{++}{\mathrm{Cu}}] = \frac{2Q - P}{63.6\,V}. \qquad \text{(I)}$$

The cuprous salt on the other hand is assumed to exist in two forms,[4] $\overset{+}{\mathrm{Cu}}$ and $\overset{-}{\mathrm{CuCl_2}}$, so that

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[1] As the anode itself weighed about 75 g. these small losses could not be determined with accuracy.

[2] By one mol cuprous or cupric salt is understood the quantity containing 63.6 g. copper. The concentrations in the body of the solution are distinguished by square brackets.

[3] This assumes that the solution passing through the cell arrives at a stationary composition in an interval of time which is very small compared to the total duration of the experiment.

[4] Bodländer and Storbeck: Zeit. anorg. Chem., 31, 1 (1902). In a paper which will be published shortly, these equilibrium experiments will be discussed more fully.

$$[\overset{+}{\mathrm{Cu}}] + [\overset{-}{\mathrm{CuCl_2}}] = \frac{2(\mathrm{P}-\mathrm{Q})}{63.6\,\mathrm{V}}. \qquad \text{(II)}$$

It was thought by Bodländer and Storbeck that the ratio $\overset{+}{\mathrm{Cu}}/\overset{-}{\mathrm{CuCl_2}}$ would be given by

$$(\overset{+}{\mathrm{Cu}}) \times (\overset{-}{\mathrm{Cl}})^2 = \mathrm{K}'(\overset{-}{\mathrm{CuCl_2}}) \qquad \text{(III)}$$

corresponding to the chemical equation

$$\overset{+}{\mathrm{Cu}} + 2\overset{-}{\mathrm{Cl}} \rightleftarrows \overset{-}{\mathrm{CuCl_2}}.$$

Careful examination of their results, and some work of my own, however, shows that the "constant," K′, varies from 1.22×10^4 to 6.13×10^4 in different experiments. I have consequently thought it best to plot

$$y = \frac{(\overset{+}{\mathrm{Cu}})}{(\overset{+}{\mathrm{Cu}}) + (\overset{-}{\mathrm{CuCl_2}})}$$

from their experiments (Table III) with different values of $(\overset{-}{\mathrm{Cl}})$ and to use the graph (Fig. 2) instead of equation (III).

TABLE III

Solubility determinations of cuprous chloride in potassium chloride solutions (Bodländer and Storbeck)

$\overset{-}{\mathrm{Cl}}$	$(\overset{+}{\mathrm{Cu}})$	$(\overset{+}{\mathrm{Cu}}) + (\overset{-}{\mathrm{CuCl_2}})$	y
4.55	0.398	0.646	0.616
4.38	0.246	0.484	(0.508)[1]
4.65	0.336	0.589	0.570
5.03	0.263	0.534	0.492
5.28	0.178	0.460	0.387
6.37	0.175	0.514	0.340
9.97	0.233	0.761	0.306
13.76	0.282	1.022	0.276
17.80	0.205	1.122	0.183

(N. B. All the concentrations in this table are expressed in millimols per liter.)

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[1] This determination was not used in plotting the curve. In the graph (see p. 906) the "chlorion" is in the same units as those used in the above table.

THE CONCENTRATIONS AT THE ELECTRODE

Immediately at the surface of the anode, the concentrations of the copper salts are greater than those in the body of the solution, the difference depending on the rate at which the copper is being dissolved. If it be assumed that the copper salt formed must diffuse through an adherent liquid film of constant thickness, l cms., and that the "diffusion-constant," k (in cm²/sec.) is independent of the concentration, then the difference in concentration due to the diffusion is given by

$$\frac{10^3 l}{k} \times \frac{(\text{Mols salt formed per second})}{(\text{Area of electrode in cms}^2)}.^1$$

These assumptions may be made in the case of the copper salts and hydrochloric acid, so that if the concentrations at the anode be distinguished from those in the body of the solution by the use of curved brackets, $\{\}$,

$$\{\overset{+}{\text{Cu}}\} + \{\text{Cu}\overset{-}{\text{Cl}}_2\} = \frac{2(\text{P} - \text{Q})}{63.6}\left(\frac{1}{\text{V}} + \frac{10^3 l}{k_1 \text{A} t}\right) \qquad \text{(IV)}$$

$$\{\overset{++}{\text{Cu}}\} = \frac{(2\text{Q} - \text{P})}{63.6}\left(\frac{1}{\text{V}} + \frac{10^3 l}{k_2 \text{A} t}\right) \qquad \text{(V)}$$

where k_1 is the diffusion-constant of cuprous salt, k_2 that of cupric, A, the area of the electrode-surface (in cms²) and t, the duration of the electrolysis in seconds.

Values of $\{\overset{-}{\text{Cl}}\}$, the concentration of chlor ion at the electrode, may be calculated from the equation,

$$\frac{4(\text{P} - \text{Q})(1 - y)}{63.6\, t} = \frac{k_3 \text{A}}{10^3 l}\left([\overset{-}{\text{Cl}}] - \{\overset{-}{\text{Cl}}\}\right) + \frac{\text{HQ}}{31.8\, t}, \qquad \text{(VI)}^2$$

where the term on the left denotes twice the number of mols $\text{Cu}\overset{-}{\text{Cl}}_2$ formed per second at the electrode; the first term on the right, the number of mols $\overset{-}{\text{Cl}}$ reaching the anode per second by diffusion; and the last term, the number of mols

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[1] Since k, l, and the area of the electrode are measured in cm-units, the factor 10^3 is necessary to convert the concentration difference into *mols per liter*.

[2] k_3 is the diffusion constant of hydrochloric acid and H, the transport number of chlorine in the solution.

$\overline{\text{Cl}}$ transported electrolytically to the anode per second. Thus,

$$\{\overline{\text{Cl}}\} = [\overline{\text{Cl}}] - \frac{10^3 l[2(\text{P}-\text{Q})(1-y)-\text{HQ}]}{31.8\,k_2\text{A}t}. \qquad \text{(VII)}$$

As in my experiments $\{\overline{\text{Cl}}\}$ and $[\overline{\text{Cl}}]$ do not differ greatly, an approximate value of

$$y = \frac{[\overset{+}{\text{Cu}}]}{[\overset{+}{\text{Cu}}] + [\overline{\text{CuCl}_2}]}$$

calculated on the assumption that $\{\overline{\text{Cl}}\}$ and $[\overline{\text{Cl}}]$ are equal, is sufficiently accurate for the purpose of equation (VII).

Using the value of $\{\overline{\text{Cl}}\}$ calculated according to this equation, the ratio,

$$Y = \frac{\{\overset{+}{\text{Cu}}\}}{\{\overset{+}{\text{Cu}}\} + \{\overline{\text{CuCl}_2}\}} \qquad \text{(VIII)}$$

was determined from the graph.

APPLICATION OF THE MASS LAW

Eliminating $\{\overset{+}{\text{Cu}}\} + \{\overline{\text{CuCl}_2}\}$ from (IV) and (VIII), and comparing the result with (V), there follows,

$$\frac{\{\overset{++}{\text{Cu}}\}}{\{\overset{+}{\text{Cu}}\}^2} = \frac{\frac{(2\text{Q}-\text{P})}{63.6}\left(\frac{1}{\text{V}} + \frac{10^3 l}{k_2\text{A}t}\right)}{\left(\frac{2Y(\text{P}-\text{Q})}{63.6}\left(\frac{1}{\text{V}} + \frac{10^3 l}{k_2\text{A}t}\right)\right)^2}. \qquad \text{(IX)}$$

According to the Mass Law applied to the reaction,

$$\overset{\circ}{\text{Cu}} + \overset{++}{\text{Cu}} \rightleftarrows 2\overset{+}{\text{Cu}}$$

the expression (IX), in which nothing but experimentally determinable quantities appear, ought to be a constant. In the tables which follow I have denoted it by K.

Of the quantities involved in (IX), Q, P, V, A, t, and Y

have already been discussed; there remain only the two ratios l/k_1 and l/k_2. These were determined directly as described in the following sections; in order to check the results, l itself was determined (page 899) and the resulting values of k_1 and k_2, were compared with those deducible from theoretical considerations.

In calculating Y, two other constants were employed, *viz.*, H and k_3. Of these H = 0.167 is taken from the recent measurements of Noyes and Kato,[1] which are in accord with those of Jahn.[2] The diffusion constant of hydrochloric acid, $k_3 = 2.67 \times 10^{-6}$ is obtained from the work of Öholm[3] by averaging his results from 0.01 and 0.02 normal acid and converting into the units (cm^2/sec.) of the present paper.

Determination of l/k_2

The following method for the determination of this constant suggested itself during the course of the investigation.

Solutions containing hydrochloric acid and copper chloride in known quantities were passed through the cell of the apparatus shown in Fig. 1, while the copper cylinder A was revolving without current. The loss in weight (W grams) of the copper was determined while V liters of the solution passed through the cell in the interval t seconds.

Under these circumstances the cupric chloride at the immediate surface of the copper is reduced almost quantitatively to cuprous salt.[4] Assuming that the rate of reduction of the cupric chloride is very much greater than the rate at which it is renewed by diffusion,[5] it follows that the concentration of cupric chloride at the immediate surface of the copper must be practically zero, and consequently that the

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[1] A. A. Noyes and Y. Kato: Zeit. phys. Chem., 62, 420 (1908).

[2] H. Jahn: Zeit. phys. Chem., 58, 641 (1907).

[3] L. W. Öholm: Zeit. phys. Chem., 50, 309 (1904).

[4] Bodländer and Storbeck: Zeit. anorg. Chem., 31, 1 (1902).

[5] Bodländer and Storbeck's experiments; loc. cit. show that the reduction is very rapid.

rate of flow of cupric chloride through the diffusion-film is equal to its rate of reduction. That is,

$$\frac{\mathrm{W}}{63.6\,t} = \frac{k_2\mathrm{A}}{10^3 l}\,[\overset{++}{\mathrm{Cu}}] \qquad \text{(X)}$$

where $[\overset{++}{\mathrm{Cu}}]$ denotes the concentration of cupric chloride in the body of the solution (in mols per liter). The following table gives the experimental data, together with the values of l/k_2 calculated by means of (X).

Table IV[1]

Temp. = 18°, A = 47, rate of rotation = 1600 per minute

No.	[HCl]	$[\overset{++}{\mathrm{Cu}}]$	W	t	V	l/k_2
1	0.0930	0.0497	0.2220	3600	2.2	2350
2	0.0920	0.0484	0.3496	5400	3.5	2220
3	0.0964	0.0072	0.1497	3600	3.1	500
4	0.0966	0.0059	0.1697	4800	3.4	495
5	0.0933	0.0035	0.1565	5400	3.25	360

These measurements show that while l/k_2 increases very rapidly with the dilution in concentrated solution, it tends to attain a constant value for extremely dilute solutions. As the concentrations of cupric chloride obtained in the electrolytic experiments were all less that used in experiment 5 of the above table, the assumption may be made that l/k_2 is constant for these concentrations, and for reasons which will be discussed subsequently (in the section on diffusion constants) the value $l/k_2 = 333$ has heen used in the calculations which follow.

Determination of l/k_1

The solubility experiments described in the previous section were also used for the determination of l/k_1. Assuming that at the immediate surface of the copper the solution is saturated with cuprous chloride, values of {*Total Cuprous*}

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[1] In experiments 3, 4, and 5, the quantity of cupric salt reduced to cuprous has been allowed for when calculating $[\overset{++}{\mathrm{Cu}}]$.

may be calculated from the solubility measurements of Bodländer and Storbeck[1] and inserted in the equation,

$$\frac{\mathrm{W}}{63.6\,t} = \frac{1}{2} \times \frac{k_1\mathrm{A}}{10^3 l}(\{\text{Total Cuprous}\} - [\text{Total Cuprous}]), \quad \text{(XI)}$$

whence values of l/k_1 may be calculated. In this equation the expressions in curved brackets { } and square brackets [ ] denote concentrations (in mols per liter) at the electrode and in the solution respectively, and W, t, and A have the same values as in Table IV. The values of [*Total Cuprous*] have been calculated by the relation,

$$[\text{Total Cuprous}] = \frac{2\,\mathrm{W}}{63.6\,\mathrm{V}}. \quad \text{(XII)}$$

TABLE V

No.	{Total Chlorine}	{Total Cuprous}	[Total Cuprous]	l/k_1
1	0.1890	0.00850	0.00318	(125.0)
2	0.1890	0.00850	0.00313	122.6
3	0.1107	0.00500	0.00152	125.0
4	0.1099	0.00495	0.00157	142.9
5	0.1028	0.00463	0.00152	160.4
			Average =	138.0

In the subsequent calculations of this paper, the value, $l/k_1 = 138$ has consequently been used.

While the values of l/k_1 and of l/k_2 determined in the above manner give sufficient information for the purpose of equation (IX), it nevertheless seemed desirable to obtain independent values of l, k_1 and k_2, so that the latter might be compared with the values deducible from the mobilities by means of Nernst's formula. These determinations, which

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[1] Loc. cit. For the concentrations of chlorine used in these solubility experiments,

$$\{\text{Total Cuprous}\} = \frac{\{\text{Total Chlorine}\}}{22.2}$$

are detailed in the following paragraphs resulted in the adoption of a valve of l/k_3 slightly lower than the lowest found in Table IV.

Determination of *l* the Thickness of the Film

A. From Experiments with Oxalic Acid

Ackerberg,[1] using a platinized platinum anode, found that the rate of oxidation of oxalic acid dissolved in large excess of sulphuric acid (20 percent conc. H_2SO_4 by volume), may be represented by the equation.

$$\frac{dx}{dt} = \frac{k(B-x)}{V}, \qquad \text{(XIII)}$$

when high current densities are used and the electrolyte is stirred. In this equation, dx/dt gives the number of equivalents oxalic acid oxidized per second and B is the number of equivalents oxalic acid in V liters of the solution at $t = 0$.

Nernst and Brunner[2] and Lorenz[3] have shown that this result is in accord with the hypothesis of diffusion towards the electrode, according to which the number of equivalents oxidized per second is equal to that diffusing to the electrode in the same time. That is, for current densities greater than the limiting value, k (in equation XIII) $= k_4\ A/10^8l$, where k_4 is the diffusion constant of oxalic acid (in cm^2/sec.), A, the area of the electrode (in cms^2) and l the thickness of the film (in cms).

Making this substitution in (XIII) and integrating, we find.

$$\frac{k_4A}{10^8lV} = \frac{2.3}{t_2-t_1}\left(\log_{10}\frac{B-x_1}{V} - \log_{10}\frac{B-x_2}{V}\right), \qquad \text{(XIII}a\text{)}$$

where x_1 and x_2 are the number of equivalents oxalic acid oxidized at the end of intervals t_1 and t_2 respectively.

From a knowledge of k_4, A, and the rate of oxidation of a solution of oxalic acid in maximum conductivity sulphuric acid, it is therefore possible to determine l. The value of

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[1] Ackerberg: Zeit. anorg. Chem., 31, 161 (1902).

[2] Zeit. phys. Chem., 47, 52, 56 (1904).

[3] Electrochemie, 1905, pp. 239-44.

k_4 was calculated from the mobility of $\overline{C_2O_4}$ by applying Nernst's equation[1] as modified by Abegg and Bose,[2]

$$k_4 = \frac{u}{2} \times \frac{0.04485}{86400}. \qquad \text{(XIV)}$$

Since $u = 39$ for decinormal oxalic acid, therefore $k_4 = 1.01 \times 10^{-5}$.

In order to obtain a value for l under conditions as nearly similar as possible to those obtaining in the electrolytic experiments with hydrochloric acid solution, the same shaft and stirring arrangement were used as that described on page 888. The copper tube, however, was covered with platinum foil and platinized according to the directions of Kohlrausch and Holborn,[3] and the cell of Fig. 1 was replaced by a porous pot of about 750 cc capacity surrounded by a cylindrical cathode of lead. The electrolyte for the anode compartment contained about 3.5 g crystallized oxalic acid and 200 cc concentrated sulphuric acid per liter, that for the cathode compartment contained the same amount of sulphuric but no oxalic acid.

During the electrolysis, 10 cc samples of the anode solution were pipetted out at definite intervals and titrated against standard permanganate.

TABLE VI

Rate of oxidation of oxalic acid

No.	Current	t	$t_2 - t_1$	$\frac{B-x}{V}$	V	l
—	—	0	—	0.0592	—	—
1	0.45	3600	3600	0.0454	0.63	10.1×10^{-3}
2	0.95	5400	1800	0.0392	0.62	9.3×10^{-3}
3	1.35	6300	900	0.0362	0.61	9.1×10^{-3}
					Average	9.5×10^{-3}

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[1] Nernst: Theoret. Chem., III Auflage, p. 361.

[2] Zeit. phys. Chem., 30, 545 (1899).

[3] The electrode was platinized while rotating, thus securing a smooth deposit.

B. From Experiments with Copper Sulphate

In the electrolysis of a solution containing both copper sulphate and sulphuric acid, the concentration of the copper at the immediate surface of the cathode is lowered as the current density is increased until a value of the latter is attained at which the concentration is practically zero. Increasing the current density still more causes hydrogen to be liberated along with the copper, which is indicated by an abrupt rise in voltage over the cell.

Just before this point is reached the amount of copper removed from the electrolyte is equal to that carried to the electrode by diffusion, since in the presence of sulphuric acid migration of the copper may be neglected. Thus,

$$\frac{\mathrm{I}' \times 31.8}{96540} = \frac{k_6 \mathrm{A}}{10^3 l} [\mathrm{CuSO_4}], \qquad \text{(XV)}$$

where I′/A is the current density at which hydrogen first appears, k_6 is the diffusion constant (in cm²/sec.) of copper sulphate and the expression in square brackets denotes concentration in grams per liter.

Working with the apparatus described on p. 888 (where A = 47) I found I′ = 0.069 at 18° C and 1600 revolutions per minute (see Tables VII and VIII). The diffusion constant of copper sulphate is given by Wiedeburg[1] as $0.4479 \times 10^{-5} \times (1 - 3.467c)$ where c denotes the concentration in grams of copper per cm³. Sand[2] found the same value for solutions of copper sulphate in sulphuric acid (0.0881 to 0.1804 normal). For the concentration of copper used in the experiments recorded in Tables VII and VIII $k_6 = 0.44 \times 10^{-5}$. Hence using $\mathrm{I}' = 0.069$, $l = 4 \times 10^{-3}$.

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[1] Wied. Ann., 41, 675 (1890).

[2] Phil. Mag. [6], 1, 45 (1901).

TABLE VII

Determination of limiting current

Experiment I		Experiment II	
Voltage	Current	Voltage	Current
0.125	0.021	0.125	0.020
0.160	0.025	0.160	0.026
0.200	0.035	0.190	0.030
0.280	0.057	0.240	0.040
0.300	0.067	0.320	0.067
0.340	0.110	0.380	0.120
—	I′ = 0.067	—	I′ = 0.068

TABLE VIII

Determination of limiting current

While these readings were taken, the electrolyte was allowed to flow over the cathode as in the experiments of Tables X and XI.

Experiment III		Experiment IV	
Voltage	Current	Voltage	Current
0.17	0.022	0.18	0.020
0.20	0.030	0.20	0.025
0.25	0.040	0.26	0.033
0.34	0.065	0.32	0.050
0.38	0.110	0.37	0.067
0.40	0.115	0.42	0.110
0.40	0.122	0.48	0.140
—	I′ = 0.070	—	I′ = 0.070

The value of l obtained by the oxalic method is higher than that obtained by the second. This is probably due to the value selected for the diffusion-constant of oxalic acid. The diffusion constant for copper calculated from the mobility (at the concentration used in the above experiments) is 0.7×10^{-5} while the direct experiments quoted above gave 0.44×10^{-5}. If the calculated value of the diffusion constant of oxalic acid be reduced in the same proportion, l as calculated by the first method becomes 6×10^{-3}.

Diffusion Constants of Cupric and Cuprous Chlorides

Although the diffusion constant for copper sulphate has been determined for concentrated aqueous solutions and for solutions containing sulphuric acid (see above p. 899) there are no data for the diffusion constant of copper in very dilute solutions of cupric chloride containing hydrochloric acid. From the values of l/k_2 in Table IV and the result $l = 4 \times 10^{-3}$, the following numbers are calculated for k_2.

TABLE IX

No.	$\{\overset{++}{\mathrm{Cu}}\}$	k_2
1	0.0479	0.17×10^{-5}
2	0.0485	0.18×10^{-5}
3	0.0072	0.80×10^{-5}
4	0.0059	0.81×10^{-5}
5	0.0035	1.11×10^{-5}

These numbers show that k_2 increases with the dilution. Using the value 50.5 for the mobility of $\overset{++}{\mathrm{Cu}}$ at infinite dilution,[1] k_2 may be calculated from the equation

$$k_2 = \frac{u}{2} \times \frac{0.04485}{86400} \qquad \text{(XIV)}$$

which gives $k_2 = 1.30 \times 10^{-5}$. As mentioned previously the concentrations of cupric chloride obtained in the electrolytic experiments were all less than that of the most dilute solution of Table IX. Accordingly the average of 1.30×10^{-5} and 1.11×10^{-5}, that is 1.2×10^{-5}, has been taken as the value of k_2 in the electrolytic experiments. Hence $l/k_2 = 333$.

The diffusion constant of cuprous chloride dissolved in hydrochloric acid may be calculated similarly from the value

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[1] The mobility of $\overset{++}{\mathrm{Cu}}$ for binary electrolytes at infinite dilution is given by Kohlrausch and Holborn as 50. By analogy with $\overset{++}{\mathrm{Zn}}$ the value of the mobility of $\overset{++}{\mathrm{Cu}}$ in $CuCl_2$ may be taken as about 50.5.

of $l/k_1 = 138$, and is found to be 2.9×10^{-6}. Although this value is noticeably higher than any that might be deduced from the mobility of $\bar{\text{Cl}}$ or from the analogy of $\text{Cu}\bar{\text{Cl}}_2$ with other complex ions, yet it seems unlikely that the value of k_1 can be less than 2.9×10^{-5} (that is, assuming $l = 4 \times 10^{-8}$) for in that case it would be necessary to assume that the solution at the immediate surface of the copper is supersaturated with respect to cuprous chloride.[1]

DISCUSSION OF RESULTS

Table X gives, together with the experimental data, the values of K calculated according to equation IX. The numbers so found vary between 0.5×10^4 and 3.5×10^4. Bodländer and Storbeck's work in which copper powder and cuprous chloride were shaken with solutions of potassium chloride gives $K = 1.5 \times 10^4$. Considering the wholly different nature of the two series of experiments this agreement must be regarded as a remarkable confirmation of the theory of the electrolysis set forth in the introduction.

As, however, the values of K calculated according to equation IX, are largely and unequally affected by the unavoidable error of experiment, I have thought that a recalculation of the anode losses, assuming the constant $K = 1.5 \times 10^4$ would furnish a more satisfactory test of the validity of the theory.

In making this recalculation, $K = 1.5 \times 10^4$; $l/k_1 = 1.38$ and $l/k_2 = 3.33$ were substituted in equation IX, which then becomes,

$$\frac{\dfrac{(2Q-P)}{63.6}\left(\dfrac{1}{V} + \dfrac{3.33}{At}10^5\right)}{\left[\dfrac{2y(P-Q)}{63.6}\left(\dfrac{1}{V} + \dfrac{1.38}{At}10^5\right)\right]^2} = 1.5 \times 10^{-4}. \qquad \text{(XVI)}$$

For each experiment the proper values of Q, t, A and V, were then introduced and a value of y taken from the graph

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[1] In some of the experiments of Table IV, the copper cylinder became covered with a white coating of cuprous chloride.

on the assumption that $\{\overline{\mathrm{Cl}}\} = [\overline{\mathrm{Cl}}]$. The resulting quadratic equation in $(P - Q)$ was solved, giving the value of P entered under "*P calc.*" next to the observed values.

In most of the experiments the observed and calculated anode losses agree to within 3 to 4 milligrams, although the conditions were varied to quite a large extent. Thus, the concentration of hydrochloric acid was varied from 4.65×10^{-3} to 16.15×10^{-3} normal, the current from 0.013 to 0.051 ampere, the anode area from 18 to 47 cm^2, and the rate of circulation of the electrolyte from 0.242 to 2.361 cm^3 per second.

The greatest discrepancies between "*P calc.*" and "*P obs.*" are to be found in those experiments whose duration was rather long, *e. g.*, Nos. 28, 35, 38, 43 and 57. This was undoubtedly due to oxidation of cuprous salt by air, which in spite of all precautions, must have entered the cell. A similar reason is to be assigned for the high anode losses observed with small currents. From the table it is seen that the differences in concentration of the cupric and cuprous salts at the electrode and in solution were very considerable, so that the corrections for diffusion were in many cases the main items in the calculation of K. Consequently any errors in measuring A or V/t, or any slight variation in the rate of stirring during the experiment affected the calculated value of K considerably. The fact that for low values of $\overline{\mathrm{Cl}}$, the anode losses calculated are uniformly greater than those observed (see experiments 7, 8, 12–16) must be ascribed to an error in the determination of y, which is quite probable in view of the form which the graph for it assumes for values of $\overline{\mathrm{Cl}}$ less than 5.5×10^{-3} (see Fig. 2).

As a further test of the validity of the theory I have also performed four experiments (see Table XI) in which a solution, approximately 9.0×10^{-3} normal in hydrochloric acid and 0.171×10^{-3} molar in cupric chloride was used as elec-

TABLE X

Room temperature; 1600 revs. per minute

No.	$10^4 \times [Cl]$	I (Amp.)	P obs.	P calc.	Q	V	t	$10^4 \times V/t$
1	11.60	0.0505	0.0752	0.0802	0.0599	2.99	3600	8.31
2	8.22	0.0498	0.1422	0.1460	0.1110	3.28	7200	4.56
3	13.50	0.0470	0.1438	0.1528	0.1113	5.80	7200	8.06
4	8.22	0.0436	0.1173	0.1174	0.0900	2.58	6000	4.30
5	9.18	0.0385	0.0613	0.0631	0.0456	6.43	3600	17.86
6	8.75	0.0250	0.0778	0.0850	0.0576	9.84	7200	13.68
7	5.29	0.0231	0.0402	0.0430	0.0297	2.53	3600	7.03
8	5.55	0.0253	0.0406	0.0439	0.0299	2.54	3600	7.05
9	12.60	0.0454	0.1469	0.1464	0.1080	3.45	7200	4.79
10	6.61	0.0246	0.0391	0.0404	0.0489	6.20	3600	17.22
11	4.65	0.0249	0.0691	0.0645	0.0502	2.32	6120	3.78
12	5.30	0.0250	0.1223	0.1278	0.0888	7.22	10800	6.68
13	5.27	0.0246	0.0407	0.0426	0.0293	2.47	3600	6.86
14	5.27	0.0246	0.0608	0.0635	0.0438	3.65	5400	6.75
15	5.24	0.0190	0.0800	0.0853	0.0570	6.20	9000	6.89
16	5.54	0.0246	0.0619	0.0630	0.0437	3.78	5400	7.00
17	9.14	0.0243	0.0410	0.0420	0.0288	6.70	3600	18.61
18	8.38	0.0252	0.0644	0.0641	0.0445	3.36	5400	6.22
19	8.05	0.0249	0.1106	0.1025	0.0738	2.18	9000	2.42
20	10.50	0.0450	0.0742	0.0761	0.0513	8.50	3600	23.61
21	8.65	0.0250	0.0863	0.0861	0.0593	4.87	7200	6.76
22	9.47	0.0300	0.1332	0.1340	0.0922	4.60	9000	5.11
23	5.22	0.0134	0.0694	0.0735	0.0476	7.15	10800	6.62
24	8.24	0.0247	0.0888	0.0865	0.0606	3.25	7440	4.36
25	9.34	0.0246	0.0644	0.0644	0.0437	9.57	5400	17.72
26	10.00	0.0225	0.1940	0.1900	0.1320	4.43	18000	2.46
27	5.48	0.0250	0.0656	0.0651	0.0442	3.63	5400	6.72
28	10.00	0.0430	0.4370	0.3980	0.2934	5.20	22600	2.41
29	16.15	0.0452	0.0810	0.0775	0.0536	2.80	3900	7.18
30	9.20	0.0229	0.0411	0.0400	0.0272	6.86	3600	19.05
31	9.21	0.0250	0.0742	0.0752	0.0491	4.10	6000	6.84
32	7.97	0.0248	0.0669	0.0620	0.0440	1.87	5400	3.46
33	6.05	0.0253	0.0683	0.0672	0.0450	3.48	5400	6.45
34	11.93	0.0240	0.0727	0.0710	0.0477	10.53	6000	17.55
35	8.20	0.0243	0.1530	0.1420	0.1006	4.30	12600	3.41
36	9.15	0.0251	0.0950	0.0973	0.0620	5.15	7500	6.87
37	9.26	0.0136	0.0310	0.0321	0.0202	7.84	4500	17.50
38	8.96	0.0350	0.1964	0.1830	0.1288	4.71	11700	4.02
39	9.00	0.0253	0.0924	0.0924	0.0601	5.80	7200	8.05
40	9.45	0.0400	0.1942	0.1800	0.1260	5.45	9000	6.06
41	7.90	0.0241	0.0880	0.0805	0.0575	2.30	7200	3.19
42	8.80	0.0194	0.0710	0.0703	0.0460	5.14	7200	7.14
43	8.96	0.0290	0.1840	0.1740	0.1200	5.45	12600	4.33
44	9.85	0.0420	0.1860	0.1740	0.1210	7.90	9000	8.79
45	10.00	0.0450	0.0782	0.0740	0.0505	3.60	3600	10.00
46	11.80	0.0236	0.0879	0.0828	0.0560	6.29	7260	8.66
47	9.37	0.0301	0.0837	0.0804	0.0535	3.89	5400	7.19
48	9.26	0.0133	0.0434	0.0430	0.0275	10.30	6300	16.35
49	8.45	0.0247	0.0924	0.0863	0.0585	2.95	7200	4.10
50	6.04	0.0252	0.0483	0.0440	0.0299	2.40	3600	6.66
51	8.95	0.0144	0.0548	0.0555	0.0341	5.30	7200	7.36
52	8.99	0.0194	0.0746	0.0720	0.0464	4.50	7200	6.25
53	12.00	0.0234	0.0904	0.0802	0.0558	3.05	7200	4.24
54	9.75	0.0200	0.0789	0.0749	0.0474	4.95	7200	6.12
55	9.31	0.0247	0.0967	0.0921	0.0585	4.80	7230	6.64
56	11.98	0.0140	0.0498	0.0477	0.0291	10.97	6300	17.42
57	8.46	0.0180	0.1397	0.1266	0.0824	7.60	14400	5.28
58	11.77	0.0137	0.0706	0.0636	0.0405	7.85	9000	8.73

TABLE X—(*Continued*)

No.	A	Percent Cuprous	$10^3 \times$ [Cupric]	$10^3 \times$ {Cupric}	$10^3 \times$ {Cuprous}	$10^3 \times$ Cu-{prous}	$10^3 \times \{\overline{\mathrm{Cl}}\}$	$\bar{\gamma}$	$10^{-4} \times$ K
1	15.0	25.5	0.235	3.84	0.161	0.95	11.08	0.294	3.1
2	18.0	28.0	0.383	4.26	0.300	1.34	7.35	0.326	1.9
3	18.0	29.2	0.214	3.40	0.176	1.23	12.47	0.283	2.6
4	18.0	30.3	0.382	3.42	0.322	1.42	7.24	0.328	1.5
5	18.0	31.5	0.073	2.42	0.077	1.13	8.14	0.320	1.8
6	23.5	34.2	0.060	1.22	0.064	0.58	8.20	0.319	3.4
7	47.0	35.2	0.119	0.71	0.130	0.40	5.07	0.485	1.9
8	47.0	35.4	0.119	0.71	0.132	0.40	5.31	0.376	3.0
9	18.0	36.5	0.315	3.11	0.355	1.66	11.05	0.295	1.3
10	18.0	37.2	0.047	1.56	0.052	0.92	5.97	0.348	2.4
11	47.0	37.7	0.212	0.78	0.252	0.74	4.54	0.615	0.8
12	47.0	37.7	0.120	0.69	0.146	0.43	5.05	0.490	1.5
13	47.0	38.7	0.113	0.66	0.146	0.44	5.01	0.500	1.4
14	47.0	39.0	0.115	0.66	0.146	0.44	5.02	0.500	1.4
15	47.0	40.6	0.086	0.40	0.117	0.35	5.10	0.475	1.4
16	47.0	42.0	0.106	0.63	0.152	0.46	5.21	0.400	1.8
17	18.0	42.0	0.039	1.39	0.057	0.89	8.28	0.319	1.7
18	23.5	43.2	0.117	1.16	0.186	0.87	7.65	0.323	1.5
19	23.5	43.6	0.267	1.18	0.531	1.28	7.21	0.328	0.7
20	35.2	45.0	0.053	1.23	0.085	0.35	9.63	0.308	1.8
21	23.5	45.5	0.104	1.10	0.174	0.87	7.90	0.320	1.4
22	37.5	46.0	0.175	0.97	0.280	0.81	8.90	0.313	0.7
23	47.0	46.0	0.057	0.32	0.096	0.28	5.05	0.490	1.7
24	23.5	46.5	0.157	1.13	0.273	0.97	7.48	0.325	1.1
25	18.0	47.3	0.038	1.28	0.068	0.99	8.31	0.318	1.3
26	35.2	48.0	0.025	0.82	0.440	0.85	9.52	0.309	1.2
27	47.0	48.0	0.099	0.57	0.185	0.55	5.18	0.425	1.1
28	35.2	49.0	0.453	1.49	0.433	0.83	9.07	0.311	2.2
29	18.0	51.1	0.147	2.10	0.306	2.00	13.94	0.274	0.7
30	18.0	51.1	0.031	1.11	0.064	0.99	8.14	0.320	1.1
31	47.0	51.2	0.092	0.54	0.192	0.58	8.77	0.315	1.8
32	23.5	52.0	0.268	1.05	0.377	1.14	7.09	0.329	0.8
33	47.0	52.0	0.098	0.55	0.210	0.61	5.62	0.360	1.1
34	18.0	52.3	0.034	1.18	0.075	1.08	10.72	0.299	1.1
35	23.5	52.5	0.175	1.02	0.384	1.15	7.33	0.327	0.8
36	47.0	53.0	0.089	0.52	0.201	0.61	8.68	0.315	1.4
37	18.0	53.5	0.019	0.63	0.043	0.62	8.57	0.315	1.6
38	37.5	53.6	0.204	0.94	0.451	1.12	8.12	0.319	0.7
39	47.0	53.8	0.075	0.51	0.175	0.59	8.53	0.316	1.5
40	35.2	54.0	0.167	1.12	0.393	1.31	8.36	0.318	0.7
41	23.5	54.0	0.184	1.02	0.417	1.20	7.01	0.330	0.7
42	47.0	54.4	0.064	0.39	0.153	0.47	8.43	0.317	1.7
43	37.5	54.5	0.162	0.78	0.370	0.95	8.30	0.317	0.9
44	30.5	55.0	0.111	1.13	0.259	1.29	8.64	0.314	0.7
45	35.2	55.4	0.099	1.03	0.242	1.17	8.88	0.313	0.8
46	18.0	55.9	0.062	1.06	0.157	1.20	10.52	0.300	0.8
47	47.0	56.4	0.094	0.57	0.244	0.76	8.76	0.315	1.0
48	18.0	57.8	0.014	0.44	0.049	0.66	8.54	0.316	1.0
49	47.0	58.0	0.131	0.51	0.360	0.79	7.94	0.320	0.8
50	47.0	61.3	0.075	0.43	0.241	0.71	5.51	0.366	0.7
51	47.0	61.4	0.040	0.25	0.123	0.39	8.63	0.316	1.6
52	47.0	62.2	0.161	0.87	0.203	0.56	8.55	0.316	2.7
53	18.0	62.5	0.109	0.96	0.357	1.51	10.55	0.299	0.5
54	47.0	62.8	0.049	0.26	0.195	0.55	9.25	0.310	0.9
55	47.0	64.7	0.067	0.38	0.250	0.74	8.71	0.315	0.7
56	18.0	71.1	0.012	0.40	0.059	0.85	10.96	0.295	0.6
57	30.5	71.2	0.052	0.35	0.119	0.40	7.76	0.321	2.1
58	18.0	74.3	0.021	0.29	0.076	0.58	10.72	0.299	1.0

trolyte. In these experiments equation IX assumes the form:

$$\frac{\{\overset{++}{\mathrm{Cu}}\}}{\{\overset{+}{\mathrm{Cu}}\}^2} = \frac{\frac{(2Q-P)}{63.6}\left(\frac{1}{V}+\frac{10^3 l}{k_1 A t}\right) + 0.171 \times 10^{-3}}{\left[\frac{2Y(P-Q)}{63.6}\left(\frac{1}{V}+\frac{10^3 l}{k_1 A t}\right)\right]^2}. \quad (IXa)$$

In the Introduction the qualitative effect of changes in rate of stirring was discussed. Table XII gives the data for three electrolyses which were carried out with lower rates of stirring than that used in the other experiments. Under R is given the rate of stirring in revolutions per minute, and in the last column of the table, under C, is given the number of an experiment in Table X in which all the other variables were the same and which may thus be used for comparison. These experiments show that in accordance with the requirements of the theory the proportion of cuprous salt formed is less when the rate of stirring is decreased.

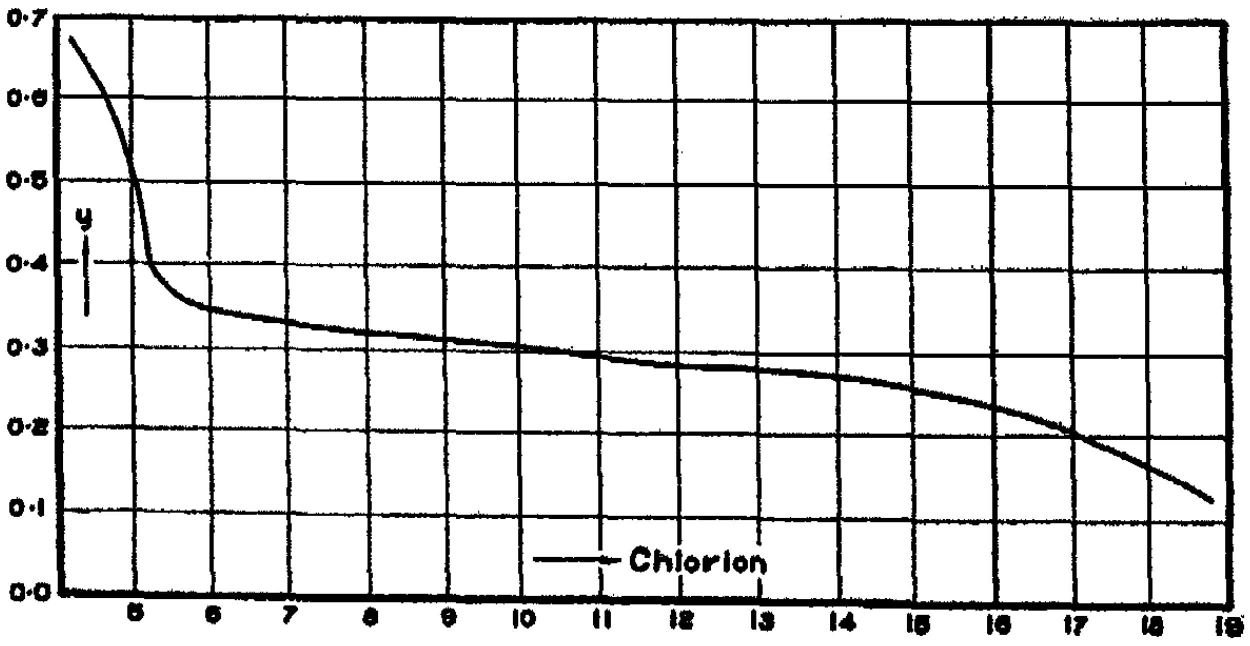

Fig. 2

TABLE XI

Concentration of $\overset{++}{\mathrm{Cu}}$ in stock solution, 0.171×10^{-3} mols per liter.
Area of electrode = 23.5 cm². R = 1600. Room temp.

No.	$10^3 \times$ [Cl]	I (Amp.)	P obs.	Q	V	t	$10^4 \times$ V/t	Percent Cuprous
1	9.31	0.025	0.0990	0.0590	5.55	7200	7.64	67.7
2	9.31	0.025	0.0448	0.0290	5.23	3600	14.50	54.5
3	9.16	0.018	0.0728	0.0443	5.20	7200	7.23	64.3
4	9.20	0.018	0.0739	0.0450	5.65	7200	7.89	64.3

No.	$10^3 \times$ [Cupric]	$10^3 \times$ {Cupric}	$10^3 \times$ [Cuprous]	$10^3 \times$ {Cuprous}	$10^3 \times$ $\{\overline{\mathrm{Cl}}\}$	Y	$10^{-4} \times$ K
1	0.396	2.83	0.229	1.253	8.05	0.320	0.6
2	0.382	4.73	0.095	0.288	8.34	0.318	1.2
3	0.219	0.71	0.172	1.138	8.27	0.319	0.6
4	0.216	0.71	0.169	0.904	8.30	0.319	0.9

TABLE XII

Area of electrode = 18 cms². Room temp.

R	$10^3 \times$ [Cl]	I (Amp.)	P	Q	V	t	$10^4 \times$ V/t	Percent Cuprous	C
800	16.3	0.047	0.0896	0.0858	3.7	5400	6.86	4.3	29
1100	15.8	0.053	0.0681	0.0638	2.7	3600	7.50	7.0	29
1100	12.0	0.024	0.0804	0.0560	2.83	7200	3.92	43.5	53

In conclusion, I desire to express my thanks to Professor W. Lash Miller under whose direction the above investigation was carried out, for many valuable suggestions and kind encouragement during its progress.

SUMMARY

Having found that it was possible to make copper dissolve anodically in hydrochloric acid wholly as cupric or wholly as cuprous or as a mixture of these in any desired proportions depending upon the concentration of acid, current density, rate of stirring and rate of circulation of the electrolyte, it suggested itself that there may be equilibrium

at the surface of the anode between metallic copper and the cupric and cuprous salts in solution according to the equation,

$$\overset{++}{\mathrm{Cu}} + \overset{\circ}{\mathrm{Cu}} \rightleftarrows 2\overset{+}{\mathrm{Cu}}.$$

A number of experiments were therefore undertaken to test this supposition quantitatively.

As the concentrations of the cupric and cuprous salts at the electrode were very different from those in the solution—sometimes they were twenty times as great—they had to be calculated from the latter by allowing for diffusion.

In these calculations there was required a knowledge of l/k_1 and l/k_2 (where l denotes the thickness of the diffusion-film and k_1 and k_2 are the diffusion constants of cuprous and cupric salts respectively). A method was therefore devised for obtaining these constants experimentally.

Electrolyses were carried out in which the concentration of hydrochloric acid was varied from 4.65×10^{-3} to 16.15×10^{-3} normal, the current from 0.013 to 0.051 ampere, the anode area from 18 to 47 cms², and the rate of circulation of the electrolyte through the cell varied from 0.242 to 2.361 cm³ per second. It was found that the fraction of copper dissolved as cuprous varied from 25 to 74 per cent.

From the values of the concentrations at the electrode as calculated for all these experiments, values of the "constant" $K = \{\overset{++}{\mathrm{Cu}}\}/\{\overset{+}{\mathrm{Cu}}\}^2$ were determined. These were found to be in good agreement with the number deduced from the equilibrium experiments of Bodländer and Storbeck in which copper powder and cuprous chloride were shaken with solutions of potassium chloride.

Finally, the fraction of copper dissolved as cuprous salt at a rotating anode in hydrochloric acid, with varying conditions of concentration of acid, current density, rate of rotation and rate of circulation of the electrolyte, was calculated from this theory and found to be in good accord with the experimental results.

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Toronto University.

NEW BOOKS

Principles of Chemical Geology. *A Review of the Application of the Equilibrium Theory to Geological Problems. By James Vincent Elsden. 14 × 22 cm: pp. viii + 222. New York: The Macmillan Company, 1910. Price: $1.60 net.* —The author has done a praiseworthy service in collecting the widely scattered facts and hypotheses wherein the principles of physical chemistry have been applied to geological problems. The first chapter deals with the definition of liquid and solid, and very wisely substitutes the terms amorphous and crystalline for the former. Singularly enough, on page 148 it is not clear that he has held fast to the above distinction. This chapter on the states of matter, is followed by one on viscosity and its effect on crystallization. Here we find the fact, much overlooked by geologists, that glasses are supercooled liquids. Later, on page 116 he refers to glasses as examples of solid solutions. In this he follows the earlier writers to whom the necessity of distinguishing between rigid liquids and relatively soft crystalline matter was not so important. It would have been wiser to eliminate the word "solid" altogether. The third chapter is devoted to the vexed problem of diffusion in magmas. Here he might have insisted more upon the fact that we can not be sure the various magmas were ever in a state of homogeneous fusion. This point, while difficult to demonstrate at present, is most important in any effort to deduce from its final condition the changes through which a rock has passed. The fourth chapter discusses surface tension, colloidal suspension and capillary phenomena. Vapor pressure, water of crystallization and constitution, zeolites, and hydration and dehydration in nature are briefly, though suggestively, treated in Chapter V. Polymorphous forms are considered in Chapter VI. On page 103 occurs the statement that wollastonite melts at 1250°. This is an error. Its real melting point *as such* has never been satisfactorily determined, so that the subsequent reasoning, while possibly correct, is wrong in fact. On page 104, the relation quartz $\rightleftarrows$ tridymite has since been shown by Wright to be quartz $\rightleftarrows$ cristoballite.

Under aluminum silicates, the author has necessarily followed Vernadsky. This investigator was in error as to the relative stability and reversibility of aluminum silicates, sillimanite alone being the stable form. Andalusite and cyanite change into sillimanite when heated, while the reverse change does not occur. This later work is, however, too recent to have been worked into the book.

Chapter VII, on salt solutions, gives a brief summary of Van't Hoff's work on the Stassfurt salts. It seems to the reviewer unwise to call *c* in Fig. 13 an eutectic. At 25° it acts like one but the term belongs to crystallization with changing temperature, and not to isothermal crystallization. The point is really on a boundary curve and confusion of ideas must result from calling it eutectic.

"Attempts to determine the mutual solubility of silicate minerals in one another have recently been made. . . .and definite results have not been realized." Here the author has followed Doelter. It seems improbable that the author means to distinguish between fusion and solubility curves; we must therefore conclude that his pen slipped, for he quotes completely worked out systems later. He does not emphasize as he might well have done, that the attempts to which he referred were invalidated by an unfortunate effort to determine by wholly inadequate methods the fusion curves of minerals which were oxidizing during the experiment.

Chapter VIII. Eutectic Theory. The author refers to four *eutectics* in the copper-zinc series, and six in the copper-tin. With one exception in each series, the points he mentions are inversion points and not eutectics. In effect on the structure as well as in the nature of the reactions involved, there is a great difference between the two terms.

It might well have been noted that Van't Hoff's law was not deduced for any such concentrations as have been used in applying it to minerals, and that there is no reason to suppose it will apply without modification. It certainly does not apply to concentrated aqueous solutions. Neither are the heats of fusion known for minerals. The errors in the older determinations were probably much greater than the values sought.

Ternary systems receive *two pages.* The ninth chapter discusses solid solutions, following Roozeboom in part.

Chemical equilibrium, Mass Law, Electrolytic Dissociation (the doctrine is swallowed whole including the statement that "it is to the ions, therefore, that all chemical reactions are believed to be due,") Reaction Velocity, Catalysis, Influence of Pressure and Strain, furnish the material for the closing chapter.

When one considers the mass of contradictory, half understood suggestions and faulty observations, which the author has had to coördinate, one has to congratulate him on the success with which he has maintained a safe course. The application of physical chemistry to geological problems is fraught with many difficulties and Roozeboom's comment—"*Dabei läuft noch viel Unklarheit unter und eine grosse Neigung zu verfrühter Generalisirung*"—should never be omitted from a book of this kind. Certainly in the last chapters of the book one could wish for more insistence upon the fact that the simple relations in two or three component systems must not be applied to polycomponent systems with the enthusiastic indifference to facts which some geologists have shown. Nevertheless, it is a book which every chemist could read with profit. Whether geologists can assimilate it without other preparation, the reviewer can not know. In any case, every geologist must sooner or later be able to comprehend the chemical hypotheses here set forth and the chemists must learn a little geology.

The book is readable, interesting and suggestive. It should find a wide circle of friends.

E. S. Shepherd

A Course in Inorganic Chemistry for Colleges. *By Lyman C. Newell. 12 × 18 cm: pp. iv + 594. Boston: D. C. Heath and Co., 1909. Price: bound, $2.00.*—This is a compact, well bound little book, printed in good sized type, free from misprints and illustrated with instructive figures. The five full page portraits of chemists appear to have been selected somewhat at random and should have been accompanied by biographical sketches or, better yet, omitted. The margins are too narrow for annotations, a fault which is growing prevalent in the effort to diminish the cost, if not the price, of texts.

It is substantially, the author's previous work, "Descriptive Chemistry" with additions. By vigorous compression all the topics one would expect to find in a much larger text have been included. Many of them are adequately treated and some of the numerous concise descriptions of technical processes are works of art. Desirable as brevity is, too great brevity makes dry reading and may become a fault. In some cases at least, the condensation has been carried so far that what is left is not worth while. The reviewer believes it is a sheer impossibility to give a student all the information he needs to understand and appreciate all those subjects in so small a compass. The author has made one of the best attempts extant to attain the impossible.

The book is well adapted to cram the maximum number of superficial descriptions into a student in the minimum time, but it is not well adapted to cultivate in him an ability to think for himself. It has so many admirable features it will doubtless be widely used in high schools, but it is not thorough enough for a college text. *S. Lawrence Bigelow*

A Manual of Volumetric Analysis. *By Virgil Coblentz. Second edition, revised, completely reconstructed and enlarged by Anton Vorisek. 16 × 24 cm; pp. viii + 234. Philadelphia: P. Blakiston's Son & Co., 1909. Price: $1.75 net.*—The book is rather a compendium of volumetric methods than a manual for laboratory classes. In chapter I apparatus and manipulations are fully dealt with. The selection of 20° C. as the standard temperature for volumetric solutions is highly commendable. It would be well to add a table under "calibrations" giving corrected weights of the volume unit of water for 20° C. through the range of average temperatures, accounting for air displacement and the expansion coefficients of representative glasses.

The remaining four chapters treat of determinations and cover a wide range of inorganic, organic and pharmaceutical problems. The methods include determinations by neutralization, oxidation and reduction, precipitation and comparison of colors, each group being conveniently subdivided.

The neutralization reaction is discussed from the standpoint of ionization. Indicators are exhaustively classified. Under each group of determinations the precipitation and standardization of volumetric solutions and the selection of indicators are fully treated. The descriptions of the different determinations are brief.

Unfortunately the book is marred by careless editing. The number of typographical errors vitiating formulae, calculations and the English construction is large. For example, the formulation of equation I on page 100 is incorrect: (V_oSO_4) should read $(VO)SO_4$ on page 149; signs are wrong in the second equation on page 27; 1500 cc. should read 150 cc. on page 43; 50 Cc. should read 500 cc. on page 44; 53.00 g. should read 5.3 g. on page 47; the expression "with 10 Cc. of ten per cent of pure sulphuric acid" on page 99 is wrong; etc., etc.

Further, chemical terms are misused. For example, hypoiodide, sulphocyanide; complex salts are referred to as double salts; "parts" by weight are mentioned where "grams" would be better usage; the symbol for cubic centimeters is unnecessarily capitalized; etc.

The book will not be stimulating to the student. It deserves a place in the reference library by reason of the large number and wide scope of the determinations presented. *William Gabb Smeaton*

A Manual of Qualitative Analysis. *By J. F. McGregory. Revised edition, 14 × 21 cm; pp. xiv + 135. Boston: Ginn and Company, 1909. Price: $1.00.* —The revised edition of the manual develops a disciplinary course, suitable for average conditions, by an excellent procedure avoiding analytical tables and "short cuts." More space is devoted to dry reactions than the scope of the book warrants, but this chapter is masterfully treated, as would be expected of the author.

The manual does not stimulate interest and will not develop the reasoning capacity of the student to the extent that is desirable in qualitative analysis. It lacks analytically fundamental explanations of reactions and operations based upon mass action, chemical equilibria and electrolytic dissociation. The student using it will not make consistent progress in chemistry, for he will lose touch with vitally important principles already familiar to him from general chemistry.

The editing has been inconsistent in that spelling reform is applied to chemical terms and not elsewhere. There are no typographical errors.

William Gabb Smeaton

An Elementary Treatise on Qualitative Chemical Analysis. *By J. F. Sellers. Revised edition. 12 × 19 cm; pp. vii + 176. Boston: Ginn and Company, 1909. Price: $1.00.*—The revised edition does not differ essentially from the original. Part I, including slightly less than half the book, deals with analytical operations from a general standpoint. The "theory of analytical operations" is a condensed adaptation of the theory of solutions and the theory of electrolytic dissociation. The chapter on "methods of analytical separation" includes dry tests and resembles corresponding sections of Ostwald's "Foundations of Analytical Chemistry." In view of the elementary nature of the book the excellent section on flame coloration and spectroscopy should be shortened. Descriptive experiments are interspersed through these chapters. To increase the number and broaden the scope of these experiments and to emphasize the bearing of mass action upon analytical operations would be a material improvement.

Part II deals with reactions and separations and develops a serviceable system of analysis. Some of the processes of separation have been revised for this edition. Discussions of general topics such as "chemistry of cyanogen compound, chemistry of sulpho-compounds, influence of ammonium salts, etc.," are inserted at suitable points. This feature is commendable.

The appended reference notes may escape casual observation since the method of referring to them is not explained in the text. It would be better to incorporate these excellent notes in the body of the text.

As a whole the book is stimulating. It should satisfy the requirements of most elementary courses in qualitative analysis. Typographical errors are practically eliminated.

William Gabb Smeaton

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