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THE ACTION OF ULTRA-VIOLET LIGHT ON COLLOIDAL PLATINUM.

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Considerable experimental work has been recorded in the literature on the curious and as yet unexplained coagulating action of ultra-violet, β -, and X-rays on substances in the colloidal state.¹ Extraordinary as this effect appears, the case is still more complicated by the fact that these same rays have been employed by many investigators to produce certain hydrosols from the corresponding metals.² Moreover in some respects the evidence of one author often contradicts the results obtained by others, so that the entire subject is in a decidedly unsatisfactory state.

¹ Carey-Lea, "Kolloidales Silber und die Photohaloide." Doelter, "Das Radium und die Farben," Henri and Mayer, *Compt. rend.*, **138**, 521 (1903); Jorissen and Woudstra, *Z. Chem. Ind. Kolloide*, **8**, 8-11 (1911); Farmer and Parker, *THIS JOURNAL*, **35**, 1524 (1913); Long, *Kolloid-Z.*, **14**, 136-8 (1914); Stintzing, *Kolloidchem. Beihefte*, **6**, 231 (1914); Schaum, *Kolloid-Z.*, **15**, 103 (1914); Nordenson, *Z. physik. Chem.*, **90**, 603-37 (1915); Pihlbad, *ibid.*, **92**, 471-95 (1917).

² Leonard and Wolf, *Ann. Phys.*, [3] **37**, 443 (1889); Svedberg, *Ber.*, **42**, 4375 (1909); Zwaardemaker and Hagewind, *Proc. Acad. Sci. Amsterdam*, **21**, 131-7 (1918).

It seemed desirable, therefore, to make a study of this interesting field and to correlate and harmonize, if possible, the conflicting evidence.

With this end in view it was decided to begin the investigation with

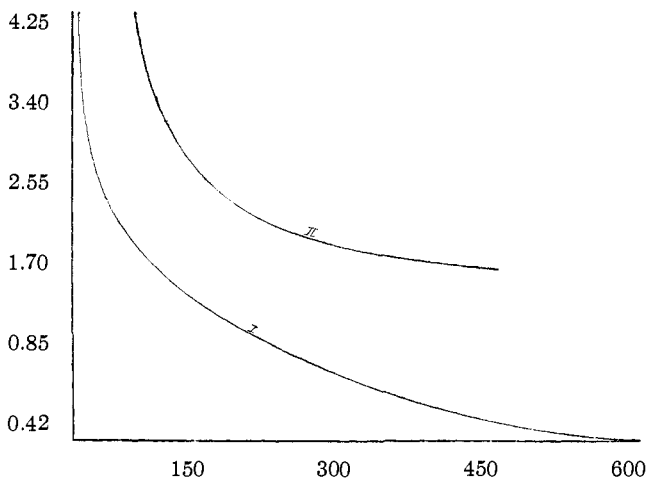


Fig. 1.—The ordinates represent the concentration of NaCl in millimols per liter in the reaction mixture. The abscissas represent the time in minutes necessary for the coagulation of one-half of the platinum in Solution B. Temperature of experiments = 20 to 22°. Curve I shows the results with the rays, Curve II without the rays.

as simple a case as possible, namely, the effect of ultra-violet rays on colloidal platinum, because the metals of the platinum group may be readily obtained in the colloidal state with a degree of purity greater than that of any other class of substances.

Experimental Method.

In order to determine the effect of the rays a carefully prepared reaction mixture was divided into two parts. One of these was placed in a crystallizing dish upon the submerged stage of a cooling system described later, covered with a quartz plate, the stirring device started and the ultra-violet light turned on. The other half of the sample, contained in a second crystallizing dish, was either placed in a thermostat, or it was set beside the first one on the submerged stage and covered with a glass plate to cut off the ultra-violet rays. Thus the two samples were treated exactly alike except that one was subjected to the action of light plus ultra-violet rays, while the other was exposed only to the light that would penetrate glass.

All reaction mixtures were invariably made up to a definite volume, usually 25 cc., at the beginning of each experiment. This was accomplished

by diluting 20 cc. of the stock solution with conductivity water, or with a solution of electrolyte in case the latter was employed.³

The Conductivity Water.—The water employed in this work was redistilled from 0.02 *N* alkaline permanganate solution through block tin condensers. One sample of water, after standing for 3 months in a well-stoppered, hard-glass bottle, had a conductivity of 4.10^{-6} mhos while another, immediately after it had been collected, had a conductivity of 5.10^{-7} mhos.

Platinum Solutions.—Platinum hydrasols were prepared by the well-known electrical colloidation method according to Bredig.⁴ The solutions were colored a rich brown and one of them at least was so stable that all the platinum had not settled out in two years' time. The concentration of the platinum in solution, determined by a method previously described by one of us,⁵ is given in connection with the various curves.

The conductivity of the platinum solutions was, of course, greater than that of the water from which they were made. Platinum solution B, after standing for 3 months in a well-stoppered, hard-glass bottle, had a conductivity of 1.2×10^{-5} mhos. Platinum solution C, after standing for 2 months, had a conductivity of 2.2×10^{-5} .

The Electrolytes.—Colloidal platinum solutions are so sensitive to bivalent and trivalent ions, such as Ba^{++} and Al^{+++} that it was found more convenient to employ sodium chloride as the electrolyte during accurate measurements. Nevertheless, some runs were made with barium chloride solutions and results of the same general nature were obtained. The sodium chloride solutions were made from conductivity water and sodium chloride that had been specially prepared for analytical standardizations.

Ultra-violet Light and Cooling System.—The source of the ultra-violet light was a Cooper-Hewett 220-volt quartz lamp. This was enclosed in a wooden case which had the dimensions $60 \times 90 \times 120$ cm. The front of the case was provided with swinging doors, and each door was fitted with a red glass window. By this means the operations could be watched without endangering the eyes, as red glass is particularly efficacious for cutting off the ultra-violet rays.

The lamp emits very considerable heat, so that a cooling system was necessary in order to maintain a constant temperature. This was secured by partially submerging the crystallizing dish containing the reaction mixture in a pneumatic trough placed inside the box. The trough was filled with water running at constant level.

³ In some of our first experiments no quartz plate was used, so that the light was allowed to strike directly upon the surface of the liquid. During protracted runs of this nature, 3 to 10 hours, small amounts of conductivity water were added from time to time in order to offset the slight loss of water due to evaporation.

⁴ Bredig, *Z. angew. Chem.*, **1898**, p. 195.

⁵ Spear, *THIS JOURNAL*, **30**, 195 (1908).

Another important factor to be considered is the distance of the surface of the reaction mixture from the source of light. This distance was maintained throughout our experiments at 15 cm. in order that the different runs might be comparable. Moreover, ultra-violet rays are absorbed almost entirely in the surface layers of the platinum solutions, so that it was necessary to stir the liquid in order to subject all portions to the action of the rays. This was effected by means of a small piece of platinum foil rotated by an electric motor.

The End-point.—If sufficient sodium chloride, which we will call the critical value, is added to cause the coagulation of platinum solutions within a few minutes, a change of color from brown to turbid gray takes place instantly on mixing the two solutions. The same change of color may be brought about by any amount of sodium chloride below this critical value, but a much longer time is necessary for the more dilute solutions of the salt. When these gray solutions are allowed to run through filter paper the filtrate is clear and colorless. During most of our work the experiment was allowed to proceed until such a clear colorless filtrate was obtained.

When very pure platinum solutions without added electrolyte were treated by the rays the time required for complete coagulation was sometimes as long as 20 to 30 hours. In such cases it was found more convenient to choose as the end-point the time necessary to reduce the color to that of a standard solution containing one-half the concentration of platinum possessed by the original reaction mixture. The standard solution was made by diluting a portion of the stock solution until the concentration of platinum was one-half that of the reaction mixture. The comparison of colors was made, of course, according to the usual colorimetric methods.

Cleansing the Apparatus.—All vessels that came in contact with the conductivity water or the platinum solutions were carefully cleaned with chromic acid, thoroughly rinsed with conductivity water and finally treated mouth downward for 30 minutes with steam from conductivity water.

Discussion of Results.

For the sake of economizing space, only a few of our results are given in Tables I and II. The data for a single series of experiments, Solution B, Table I, have also been reproduced in the form of curves in Fig. 1. Information concerning the concentrations of colloidal and electrolytic solutions, also the temperature and the time of coagulation, are given in connection with the tables and the curves. The time recorded is the average of 2 to 5 separate determinations.

TABLE I.

Temperature of runs = 20 to 22°.

Millimols. NaCl per liter in mixture.	Solution A. Conc. Pt.=0.024 g. per liter in mixtures.			Solution B. Conc. Pt.=0.038 g. per liter in mixture.			Solution C. Conc. Pt.=0.046 g. per liter in mixture.		
	<i>t</i> = Time in minutes for the coagulation of one-half the platinum.								
	<i>t</i> ₁ .	<i>t</i> ₂ .	Ratio. $\frac{t_2}{t_1}$.	<i>t</i> ₃ .	<i>t</i> ₄ .	Ratio. $\frac{t_4}{t_3}$.	<i>t</i> ₅ .	<i>t</i> ₆ .	Ratio. $\frac{t_6}{t_5}$.
	With rays.	Without.		With rays.	Without.		With rays.	Without.	
4.25	15	135	..	7	64
3.40	24	269	11	15	90	6.0	45	75	1.6
2.55	48	480	..	30	145
1.70	59	804	13	90	450	5.0	60	171	2.8
0.85	90	1270	..	240	105	240	...
0.42	120	349	201
0.21	157
0.00	600	<i>a</i>

^a The platinum was not completely coagulated in 2 years' time when Solution B was kept in the laboratory desk. Solutions A and C were kept for several months without any very appreciable coagulation of the platinum.

TABLE II.

Solution D.

Temperaturé = 16.8 to 17°.

With electrolyte present the acceleration due to the ultra-violet light is greater in dilute than in more concentrated colloidal solutions. Solution D showed very slight coagulation of the platinum in 2 months when no electrolyte was added and the rays were not employed.

Conc. NaCl in Millimols per liter.	Conc. Pt. in grams. per liter.	<i>t</i> = Time in minutes for complete coagulation of Pt.		Ratio $\frac{t_2}{t_1}$.
		With rays. <i>t</i> ₁ .	Without. <i>t</i> ₂ .	
17.1	0.081	18	35	1.9
17.1	0.073	35	93	2.6
17.1	0.064	64	180	2.8

In any consideration of the results of our experiments it should be constantly borne in mind that the effect of the rays as shown by our data is relative and not absolute. The magnitude of the influence depends upon several factors which we have endeavored to hold constant, namely, the intensity of the rays, the distance that separated the reaction mixture from the source of the ultra-violet light, the rate and manner of stirring and the temperature. However, in spite of these reservations with regard to magnitude, three general conclusions of a qualitative nature may be drawn from the experimental evidence. These three conclusions will be discussed in order.

I. Ultra-violet light greatly hastened the coagulation of colloidal platinum without the addition of any electrolyte, except possibly the carbon dioxide of the air, or that due to the dissolution of the hard glass from the

container. This conclusion is justified by the fact that in Solution B the platinum was one-half coagulated by the rays in 10 hours, while without the rays the platinum was not completely coagulated in 2 years. In the case of another solution, not previously referred to in this article, which had a slightly different concentration, even a shorter time was required to coagulate one-half the platinum.⁶

II. The second conclusion is that when electrolytes are present their influence on the coagulation is very greatly accelerated by the action of the ultra-violet light. This is clearly brought out by a comparison of Cols. 2, 5 and 8 of Table I, with Cols. 3, 6 and 9, respectively. The acceleration is even more apparent in Fig. 1, where Curve I represents the concentration of the electrolyte in millimols per liter plotted against the time in minutes required for the coagulation of one-half of the platinum in Solution B, and Curve II represents the same thing for Solution B where the ultra-violet light was not employed.

III. A third conclusion to be drawn from our results is covered by the statement that the accelerating action of the rays is greater in dilute solutions of the colloid than it is in the more concentrated. This is clearly indicated by the ratios in Cols. 4, 7 and 10, Table I, at two different concentrations of sodium chloride 3.40 and 1.70 millimols per liter, and further substantiated in Table II for three different concentrations of the same colloidal solution where the electrolyte was kept constant.⁷

This result might be anticipated in part when it is remembered that the ultra-violet light can penetrate into the dilute solutions of the colloid farther than it can into the more concentrated. It is unsafe to conclude, however, that this is the sole reason for the observed facts. As suggested by Nordenson¹ it may very well be that the rays react upon the medium rather than on the platinum particles, in which case the accelerating action should be greater when there are fewer colloidal aggregates to absorb the ultra-violet light.⁸

⁶ In order to determine whether or not the rays could coagulate colloidal platinum without the aid of some electrolyte other than water itself, it would be necessary to exclude the air during the distillation of the water, the formation of the colloidal platinum, and finally the treatment with the rays. The experiment would be difficult but not impossible.

⁷ It is unfortunate that our work was permanently interrupted before the concentrations could be varied over a greater range.

⁸ During the progress of work as yet unpublished it was found that the conductivity of sodium chloride solutions was slightly increased by the action of ultra-violet light. Minute quantities of hydrogen peroxide were also found to be present. Because these effects were so inappreciable it does not seem possible that the extraordinary acceleration of the rays can be attributed to these causes.

Summary.

In this article we have presented experimental evidence to show that ultra-violet light will precipitate colloidal platinum out of solutions that are free from electrolyte except the carbon dioxide of the air, or that due to the dissolution of hard glass.

We have also shown that when electrolytes are present their precipitating effect is very greatly accelerated by the action of ultra-violet rays.

The action of the ultra-violet light was shown to be greater in dilute solutions of the colloid than in the more concentrated.

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THE APPLICATION OF IDEAL SOLUTION EQUATIONS TO DILUTE AQUEOUS SOLUTIONS.

BY JAMES KENDALL.

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The relative lowering of the vapor pressure of water by addition of a normal, non-volatile solute is such a fundamental point in the study of solutions that one would expect physical chemists, at this late date, to have agreed upon some definite theoretical treatment of the topic. An examination of the literature will show, however, that this is far from being the case. In the following pages a brief analysis of the present situation is made, and an explanation of existent discrepancies indicated. The erroneous interpretation now given to certain equations derived from the law governing vapor-pressure depression for ideal solutions, when applied to aqueous solutions, is also discussed.

The Dilute-Solution Equation.—Most introductory text-books¹ follow Arrhenius² in deriving the equation for the vapor pressure of highly dilute solutions from van't Hoff's gas law for osmotic pressure, obtaining the relation³

$$(p_0 - p) / p_0 = n / N \quad (1)$$

where p_0 is the vapor pressure of pure solvent, p the vapor pressure of solution, and n/N is the ratio of the number of solute molecules to the number of molecules which the solvent would produce *if converted into*

¹ For example, Walker, "Introduction to Physical Chemistry," 1913, p. 193; Lehfeldt, "Physical Chemistry," p. 29.

² Arrhenius, *Z. physik. Chem.*, 3, 115 (1889).

³ This relation is strictly valid only for solutions of infinite dilution, constituting the limiting case of the more exact equation: $\ln(p_0/p) = n/N$. The difference between the calculated values for the two forms of the equation is, however, inappreciable even for a fairly concentrated solution. For an example see Lehfeldt, *op. cit.*, p. 31.