with the curve from Fig. 1 for runs at 25°. An increase in temperature evidently causes a slight increase in the proportion of H_2 which combines with Cl_2.

When the O_2/Cl_2 ratio is 20, a rough estimate gives a value 0.57 for the fraction (H_2 in H_2O)/(total H_2) in the 0° runs and a value 0.40 for the fraction in the 85° runs. Corresponding to these figures are values for the ratio $dH_2O/dHCl$, 0.65 at 0° and 0.33 at 85°. The activation energy calculated for such a change of rate with temperature would be about 1600 calories, which is therefore the difference in activation energies between the reactions leading to HCl formation and those leading to H_2O formation. Since the relative rates at which HCl and H_2O are formed depends on the distribution of H atoms between reactions 3 and 9

$$H + Cl_2 = HCl + Cl \quad (3)$$
$$H + O_2 = HO_2 \quad (9)$$

the value 1600 may be considered as the difference in activation energies for these two reactions. Both 3 and 9 are highly exothermic and presumably require very little activation, so 1600 calories is a reasonable figure for the difference in activation energies. Bodenstein and Schenk calculate a value 1900 calories for this quantity from some work of Hertel[8] on the temperature coefficient of the HCl reaction.

Summary

The rates of formation of HCl and H_2O in illuminated mixtures of H_2, Cl_2 and O_2 have been measured for high concentrations of O_2. As the ratio O_2/Cl_2 increases, the ratio (H_2O formed)/(HCl formed) approaches a limit between 1 and 2.

The rate at which the limit is approached increases slightly with increasing concentrations of H_2 and HCl. It is possible that the value of the limit also may be somewhat higher when high concentrations of H_2 or HCl are present.

The rate of approach to the limit shows a slight dependence on the temperature, indicating that the activation energy for the reactions leading to HCl formation is slightly greater than for those leading to H_2O formation.

The existence of this limit proves that the Nernst chains must be ended by a reaction $H + O_2 = H_2O$ rather than by $Cl + O_2 = ClO_2$. The occurrence of this latter reaction to a slight extent is not prohibited, but it must be of secondary importance compared to the former.

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[8] Hertel, *Z. physik. Chem.*, **B15**, 325 (1932).

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[CONTRIBUTION FROM THE RICE INSTITUTE]

A Procedure for the Preparation of Uniform Nephelometric Suspensions

BY ARTHUR F. SCOTT AND FRANK H. HURLEY

It is a well-known fact that the optical properties of silver chloride suspensions are influenced by the conditions attending their preparation. Although no systematic study of these conditions has been made, there is sufficient evidence[1] to indicate that the rate of addition of the precipitant is a factor of primary importance. It would appear, therefore, that the reproducibility of nephelometric suspensions would be increased considerably if the precipitant could be added in exactly the same manner in every preparation, a condition which cannot be fully satisfied by the usual procedure of adding the precipitant dropwise ("stirring" method) or of pouring the sample of solution into the precipitant ("pouring" method). The present paper describes a device whereby the desired condition of uniform addition of the precipitant may be achieved readily.

A convenient form of this precipitating device, designed to meet the special requirements of the analysis of a pure chloride compound by the Richards method, is shown in Fig. 1.[2] In analyses of this sort, suspensions of silver chloride are prepared by the addition of a 2-ml. portion of the precipitant, either silver nitrate ("excess Ag") or sodium chloride ("excess Cl") solutions, to a 20-ml. sample of the supernatant analytical solution, which is saturated with silver chloride. To fill the vessel, shown upright in Fig. 1, it is

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[1] Kleinmann, *Biochem. Z.*, **99**, 149 (1919); Scott and Moilliet, THIS JOURNAL, **54**, 208 (1932); Kober, *Ind. Eng. Chem.*, **10**, 558 (1918).

[2] The design of this vessel is adapted from one used by Jolibois [*Compt. rend.*, **169**, I, 1096 (1919)] to produce rapid and uniform mixing of two solutions. See also Sheppard and Lambert, "Colloid Symposium Monograph," **6**, 265 (1928).

first placed in a horizontal position and the measured samples of the analytical solution and precipitant are introduced through the openings a and b, respectively, and flow into the bent arms of A and B, which serve as reservoirs. The vessel is then brought quickly to the vertical position, whereupon the solutions flow together through the outlet stem directly into the nephelometer tube. The outlet stem is provided with small bulbs to ensure thorough mixing. By choosing tubes and capillaries of proper dimensions, the rate of flow of the two liquids can be so regulated that the two arms empty almost simultaneously. For a 20-ml. sample of analytical solution and a 2-ml. portion of precipitant, suitable diameters of the various tubes are as follows: tubes A and B, 25 mm. and 10 mm., capillary forks, approximately 1 mm. and 0.85 mm., outlet stem, 1 mm.

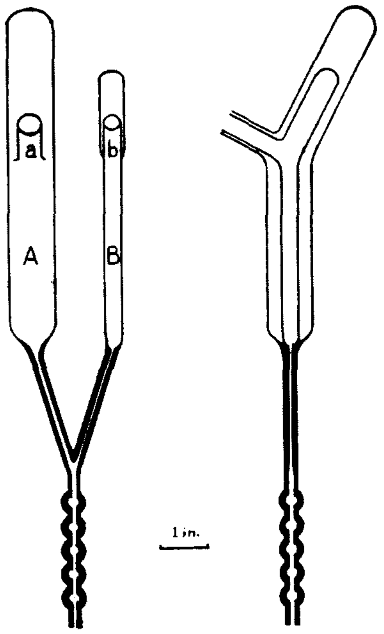

Fig. 1.

Two "uniform" precipitating vessels of the above design were constructed, both with a time of outflow of forty-three seconds. One was used solely for "excess Ag" suspensions and the other for "excess Cl." The manipulation of these vessels offered no trouble whatsoever. They were easily rinsed and, when not in use, they rested horizontally on simple supporting blocks, in which position the open ends were readily covered with glass caps to exclude dust.

Reproducibility of Suspensions.—In order to ascertain the degree of reproducibility attainable by the use of the "uniform" method of precipitation, the turbidities of duplicate suspensions prepared by the addition of "excess Cl" to samples of a saturated silver chloride solution, 0.1 molar in nitric acid, were compared in the nephelometer. The two suspensions were prepared within a few minutes of each other and the comparison of their turbidities was made within ninety minutes after their preparation. Of 19 pairs so tested, 14 showed no detectable difference in turbidity, 3 showed a difference of 2%, 1, a difference of 3%, and 1, a difference of 5%. On one occasion six "excess Ag" suspensions were prepared in rapid succession from a silver chloride solution, 0.2 molar in nitric acid. The intercomparison of the six suspensions showed that their opalescences were the same. The results of these experiments are evidence that the suspensions produced by the "uniform" method are probably reproducible within the limits of uncertainty involved in reading the nephelometer. No such degree of reproducibility as that shown above has been obtained in this Laboratory when either the "stirring" or "pouring" methods were employed. The aforementioned experiments as well as the following were all carried out at room temperature, about 27°.

Change of Turbidity with Time.—There has always been some question as to the correct period of time to be allowed before the examination of the turbidities of suspensions in the nephelometer. To investigate the effect of time on turbidity a number of experiments were carried out, the results of which will be briefly summarized. Suspensions formed by the addition of either "excess Ag" or "excess Cl" solution to a saturated silver chloride solution, 0.1 molar with respect to nitric acid, maintained a constant opalescence for the first ninety minutes after their preparation, whether prepared by the "stirring" or "uniform" method. Suspensions prepared by the first of these methods did not attain a constant turbidity until ten minutes had elapsed, whereas with the second method a maximum opalescence was reached almost immediately. At an acid concentration of 1.6 molar, the suspensions prepared by the "uniform" method of precipitation showed essentially the same development of turbidity as with the less concentrated acid. However, when the "stirring" method was used, both "excess Ag" and "excess Cl" suspensions showed a maximum turbidity after ten minutes which persisted for only about half an hour. In all experiments, the standard opalescence employed was that of the pairs of suspensions described in the preceding paragraph. Preliminary experiments had shown that these suspensions had, very shortly after their formation, the same turbidity as that of similar suspensions which had been standing as long as two hours.

Effect of the Silver Ion on Turbidity.—The possibility that the precipitation of silver chloride from its saturated solution differs perceptibly from the precipitation of silver chloride from other chlorides was first pointed out by Richards and Staehler.[3] To examine this point, four solutions of sodium chloride, 0.2 molar in nitric acid, were prepared. To each were added varying amounts of silver ion. The chloride content was then precipitated by the addition of excess silver nitrate, and the turbidities of the several suspensions were compared in the nephelometer against the suspension prepared from the solution containing equivalent amounts of silver and chloride ions. The results are summarized in the table.

Molar concn. of Cl $\times 10^{-6}$	7.0	7.0	7.0	7.0
Molar concn. of Ag $\times 10^{-6}$	0.0	2.1	4.2	7.0
Relative turbidity (uniform)	1.00	1.02	0.99	(1.00)
Relative turbidity (stirring)	0.97	1.04	1.04	(1.00)

It is clear from these figures that the amount of silver present in the chloride solutions before precipitation has no appreciable effect on the turbidities produced when the chloride content is precipitated, at the concentration of chloride used, roughly that of a saturated solution of silver chloride at 0°. The conditions of these experiments correspond in general to those involved in the "standard solution" method of analysis, recently proposed by Johnson.[4]

The Influence of Extra Ions.—In atomic weight determinations, the saturated solution of silver chloride always contains in addition to nitric acid an extra ion introduced by the hydrolysis of the halide sample being analyzed. The question as to whether this extra ion could have any detrimental effect on the equal-opalescence end-point was raised and investigated by Johnson.[5] From an elaborate series of tests involving extra ions of diverse valence and charge, he concluded that "when the tests are made with the necessary precautions, the accuracy claimed for the nephelometric method...may be attained in so far as any effects due to the presence of extra compounds come into consideration." However, in some more recent experiments with silver chloride solutions containing 0.6 mole of potassium nitrate per liter, Johnson and Low[6] found that the ratio of the opalescences of the "excess Ag" and "excess Cl" suspensions ranged from 1.35 to 1.65, indicating that the presence of this extra compound caused the concentration of the chloride ion to be apparently greater than the silver. Even though a concentration of potassium nitrate as great as 0.6 molar would hardly be present in an analytical solution, it seemed advisable to repeat these experiments, especially since this compound was not included among those used by Johnson in his earlier experiments referred to above.

To test the possible effect of potassium nitrate on the equal opalescence end-point, four solutions were prepared, each containing the same amounts of silver chloride and nitric acid, 5.2 $\times 10^{-6}$ and 0.3 mole per liter, respectively, and varying amounts of potassium nitrate, which was freed from chloride impurities by recrystallization. The comparison of the "excess Cl" and the "excess Ag" suspensions prepared from the four solutions by the "uniform" method yielded the following results.

Molar concn. of KNO_3	0.0	0.2	0.4	0.6
Ratio, concn. Cl/concn. Ag	1.03	1.06	1.03	1.05

Since the original saturated solution of silver chloride which was diluted in the preparation of these solutions had a ratio of 0.98, the present results show a very slight increase in the chloride content. This is conceivably due to traces of chlorine present in the reagents involved in the preparation of the solutions, although great pains were taken to test for and avoid such contamination. It would appear, therefore, that under proper conditions, equal opalescence tests are not vitiated by the presence of potassium nitrate in solution, even in concentrations as large as 0.6 molar.

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[3] Richards and Staehler, THIS JOURNAL, **29**, 635 (1907).

[4] Johnson, *J. Phys. Chem.*, **35**, 830 (1931).

[5] Johnson, *ibid.*, **35**, 2237 (1931).

[6] Johnson and Low, *J. Phys. Chem.*, **36**, 2393 (1932). After the completion of the present report, we were informed that this published figure should have been 0.06 *M*.