$$\log_{10} K = \frac{525.8}{T} - 1.1470.$$

The corresponding expression for the free-energy decrease $-\Delta F$ in calories attending the reaction $Ag_2S + H_2 = 2Ag + H_2S$ at any temperature T between 750° and 890° A. is

$$-\Delta F = RT \log_e K = 2408 - 5.253\ T.$$

With respect to the concordance of these equations with the observations it may be stated that the first equation, which is derived from the average values of the equilibrium constant at 749.15° and 889.63°, gives for that constant at the intermediate temperature 811.25° the value 0.317, while the average value derived from the observations in that temperature region is 0.325. It may also be mentioned that the results of the 3 experiments (20 to 22 in Table I) in which the equilibrium was approached in the direction opposite to that in which the values on which the equation is based were obtained are in fair agreement with the results computed by the equation; namely, these three experiments gave for the equilibrium constant the values 0.376 at 727.6° A., 0.318 at 783.0° A., and 0.303 at 830.9° A., while those computed from the equation for these temperatures are 0.376, 0.335, and 0.306.

CAMBRIDGE, MASS.

THE DETERMINATION OF CHLORINE WITH THE NEPHELOMETER.

BY ARTHUR B. LAMB, PAUL W. CARLETON AND W. B. MELDRUM.

Received December 1, 1919.

In the study of the concentration of the vapor of "mustard gas" and similar non-volatile toxic liquids over areas sprayed with them, large samples of the contaminated air were collected, the toxic gas absorbed therefrom in alcohol, and after special treatment the chlorine was liberated as chloride and determined as such. These "war gases" are so very toxic that extremely minute quantities are significant, and in spite of the large samples of air which were collected (13 liters) it was necessary not only to detect but to measure amounts of chlorine as small as a few thousandths of a milligram.

For the rapid and approximate estimation of these amounts the copper flame test[2] gave useful results, as did also the selenious acid method of Yablick, Perrott and Furman,[3] but before these methods had been developed, and indeed afterwards when a more quantitative determina-

[1] Published by permission of Maj.-Gen. W. L. Sibert, Director, Chemical Warfare Service, U. S. A.

[2] Lamb, Carleton, Hughes and Nichols, THIS JOURNAL, 42, 78 (1920).

[3] *Ibid.*, 42, 266 (*seq.*) (1920).

tion was desired, resort was had to the nephelometric method perfected by Richards and Wells.[1]

These authors have, however, applied the method only to aqueous solutions, while we were obliged to use an alcoholic solution for the absorption of the toxic gases, and it was desirable if possible to apply the method directly to this solution. Moreover, Wells[2] in particular, has shown that the development of a maximum opalescence varies greatly with the conditions and that different concentrations require different treatment. Finally, in spite of the great delicacy of this method, the quantities of chloride with which we had to deal were so minute that the method had to be pushed to its utmost refinement.

For these reasons and also to adapt the method to the routine analysis of our many hundreds of samples, a study of it was undertaken, particularly with reference to the development of opalescence, with the result that a number of facts were disclosed which we believe will be of interest to any who may be confronted with analytical problems of this kind.

We first carefully determined the reproducibility of our nephelometric readings. Next, using permanent standards, we studied the development of opalescence and perfected a method for obtaining rapidly a maximum and constant opalescence. We finally studied the effect of diffuse daylight on the opalescence, and very briefly the relative intensities of opalescence of silver chloride suspensions in water, 50% alcohol and 50% acetic acid.

Reproducibility of Nephelometer Readings.

The nephelometers used were of the Kober type.[3] The only alteration was to coat the cement on the plungers with a thin layer of paraffin, in order to avoid any contamination of the solution.

Directions for the use of the instruments are given in full by Kober. Our procedure was briefly as follows: At the beginning of a series of analyses both cups of the instrument and both plungers were rinsed first with distilled water and then with the standard suspension (silica or silver chloride) to be used. They were nearly filled with this solution and placed in position in the instrument. The position of the left-hand cup was adjusted until the scale reading was exactly "20.0;" the position of the right-hand cup was then adjusted until the illuminations on both sides were equal, this being determined as the average of several independent settings. This setting was retained for the whole series of comparisons with the standard.

[1] Richards, *Proc. Amer. Acad. Arts Sci.*, **29**, 74 (1893); Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904); Richards and Wells, THIS JOURNAL, **27**, 485 (1905); Wells, *Am. Chem. J.*, **35**, 99 (1906); Richards, *Ibid.*, **35**, 510 (1906).

[2] *Am. Chem. J.*, **35**, 99 (1905).

J. Ind. Eng. Chem., **7**, 843 (1915); *J. Biol. Chem.*, **13**, 485 (1912); **29**, 155 (1917).

The solution in the left-hand cup was then discarded, the cup and plunger rinsed with the solution next to be used, and the cup nearly filled with the solution as before. It was placed in position in the instrument and the height adjusted until illuminations on both sides were again equal. The scale reading was recorded and the results computed using the formula given by Kober.

$$Y = (20/F) - (1 - F) \times 20 \times (0.052/F^2).$$

Where Y signifies the scale reading, F the concentration, and 0.052 is the nephelometric constant.

There are several precautions either not mentioned by Kober, or not sufficiently emphasized, which must be observed if the utmost accuracy in the use of this nephelometer is to be obtained. In the first place, a very serious error may be introduced if the eyepiece of the instrument is not kept in exactly the same position throughout a series of comparisons. Not only does alteration of the position of the eyepiece vary the distribution of light over the field but it changes very considerably the relative positions of the cups for equal illuminations. Thus, in one case, the turning of the eyepiece through 180° caused a change in setting of the left-hand cup from 21.4 to 14.7, the right-hand cup remaining in the same position.[1]

Second, a very appreciable error may result from a variation in the light conditions in successive comparisons, unless the position of the cup in its holder is always exactly the same. We found it advizable to mark the cup for this purpose.

Third, the precise matching of two faintly opalescent solutions is difficult. The only practical method of attaining readings of satisfactory accuracy is to raise the left-hand cup until there is a shadow just distinctly visible on the right-hand side of the divided field, then to lower it until a shadow of the same distinctness is visible on the left, and to take the mean of the extreme readings. Moreover, with these faint opalescences satisfactory results can be obtained only when the eyes have acquired their maximum sensitiveness by remaining in the dark for 5 or 10 minutes. Similarly, too long continued observation tires the eyes sufficiently to produce a marked decrease in the accuracy of the settings.

Adopting all the precautions above-mentioned, a series of comparisons of silver chloride suspensions at different concentrations was carried out. The solutions were prepared by adding enough alcohol to appropriate quantities of very dilute standard sodium chloride solutions to bring the volume up to 20 cc., adding 10 cc. of 0.1 M nitric acid to this, followed by a large excess (10 cc.) of 0.005 M silver nitrate solution, making a total volume of 40 cc. The resulting solutions all, therefore, contained ap-

[1] This defect has been remedied in recent models of the instrument.

proximately 50% alcohol. For preparing the dilute solutions the following standard solutions of sodium chloride were employed:

Final solutions. Molar Conc. NaCl $\times 10^{+5}$.	Initial solutions. Molar conc. NaCl.
0.37– 1.00	0.000100
2.00– 4.5	0.000200
9.0	0.000400
18.0 –75	0.00200

The reagents had to be purified with care in order to secure reproducible results. Chlorine-free alcohol was secured by the distillation of commercial, 92% alcohol from sodium or potassium hydroxide, using about 2 g. of potassium hydroxide for 700 cc. of alcohol. The water and the nitric acid were also specially redistilled. To eliminate individual differences, the observations were made by 3 different observers. The results obtained are collected in Table I.

TABLE I.—REPRODUCIBILITY OF SETTINGS.

Molar conc. $\times 10^{+5}$.	Total[a] wt. Cl. mg.	Observer.	Successive settings, means of R't and L't.			Average.	Deviation from average. Max.	Av. ±
0.37	0.0053	A	10.3	11.6	11.6	11.2	0.9	0.6
0.37	0.0053	B	13.5	12.3	11.4	12.4	1.1	0.7
0.37	0.0053	C	13.1	12.0	12.1	12.4	0.7	0.5
0.50	0.0071	C	14.8	14.6	14.0	14.5	0.5	0.3
1.00	0.0142	C	14.5	14.9	14.4	14.6	0.5	0.2
2.00	0.0284	A	9.7	9.9	10.3	10.0	0.3	0.2
2.00	0.0284	B	9.7	9.7	10.6	10.0	0.6	0.4
4.5	0.064	B	15.1	15.1	15.1	15.1	0.0	0.0
9.0	0.128	A	15.6	15.8	15.8	15.7	0.1	0.1
9.0	0.128	B	15.6	15.3	15.9	15.6	0.3	0.2
18.0	0.256	B	15.8	16.1	16.4	16.2	0.4	0.2
45.0	0.64	B	17.2	17.3	16.9	17.1	0.2	0.2
75.0	1.06	B	18.3	17.6	17.8	17.9	0.4	0.3

[a] This refers to the total weight of chlorine in the 40 cc. sample used in the nephelometer.

It is evident from this table that over the range of concentration studied ($0.37 - 75 \times 10^{-5} M$) the average deviation is not more than about 2 or 3%. It is also interesting to note that this deviation is least for intermediate opalescences ($5 \times 10^{-5} M$). At these concentrations the settings can be made more rapidly and easily than at higher or lower concentrations. At low concentrations the fields are too faint, and at high concentrations too brilliant for accurate matching. This is confirmed by the average differences between the maximum and minimum settings, as shown, for instance, by the typical results collected in the following table:

TABLE II.—DIFFERENCES BETWEEN MAXIMUM AND MINIMUM SETTINGS.

Total wt. Cl. mg.....	0.0053	0.0071	0.0142	0.0284	0.064	0.128	0.256	0.64	1.06
Diff.....	5.4	4.0	2.8	3.8	2.7	1.9	2.1	2.4	3.1

The average differences are least in the region of intermediate concentrations.

The Development of Opalescence.

Richards and Wells[1] point out that the rate of development of opalescence is decidedly variable in pure water, but by adding a considerable quantity of nitric acid to the solution under comparison, the maximum opalescence is quickly attained by each suspension, and persists unchanged in relative intensity for hours. In all of our solutions we have, therefore, used a very large excess of dil. nitric acid, (10 cc. of 0.1 M).

The existence of progressive changes in the state of the precipitate was fully recognized by Richards early in the development of nephelometry, although he did not measure them quantitatively. His method of overcoming uncertainties from this cause was as follows: "The unknown solutions to be estimated must be treated in exactly the same way as the known standard solutions, which serve as the basis of comparison."[2]

Evidently this method is entirely legitimate and must give accurate results when any reasonable time of standing is allowed.

Wells[3] studied the rate of development of opalescence of these solutions in more detail and used fixed standards of ground glass, which showed that the above constancy, while real, was only relative, and that the opalescence after reaching a maximum decreases very slowly in the dilute solutions and very rapidly in the concentrated ones. He recommends that the opalescences of the dilute solutions (0.000,005 M) be read within 30 minutes, and of concentrated solutions (0.000,05 M) within 4 minutes after precipitation.

It is evident that there are at least 2 effects operative in this phenomenon —one, the progressive increase in the size and number of particles, due to the precipitation of the dissolved silver chloride, another the coalescence of particles so that their net opalescent effect diminishes. In the concentrated solutions, at least, this coalescence progresses so far that visible coagulation occurs. Since precipitation has a steadily decreasing velocity while the coalescence continues indefinitely, there results a period of growth in the intensity of opalescence followed by a usually longer period of decay.

In order to study these questions further, and in particular as applied to our alcoholic solutions, we first prepared a standard of constant opalescence. This was a suspension of kieselguhr made by shaking the finely ground material with distilled water, allowing it to stand for 72 hours and then siphoning off the supernatant liquid. The faintly opalescent

[1] THIS JOURNAL, 27, 485 (1905).

[2] Theodore W. Richards, "Note Concerning the Use of the Nephelometer," *Am. Chem. J.*, 35, 511 (1906).

[3] *Am. Chem. J.*, 35, 99 (1906).

solution thus obtained was approximately equivalent in the nephelometer to the 4.5×10^{-5} M silver chloride standard. The permanence of this suspension was tested by filling the two cups of the nephelometer with the same suspension, and comparing with each other after various time intervals. The left cup and its contents remained undisturbed throughout the series, while the right was emptied, refilled with freshly shaken solution and replaced in the same position before each reading. Typical results were as follows:

TABLE III.—PERMANENCE OF KIESELGUHR STANDARD.

Time, min...	0	5	10	15	20	25	30	40	50	60	70
Reading.....	15.9	16.0	15.5	15.6	15.5	15.5	15.6	15.6	15.5	15.0	14.6

From these results it is evident that the kieselguhr remained suspended for at least an hour before there was any decided indication of settling, and that if suitable care be taken in replacing the cup in the holder the readings can be closely reproduced. Using this suspension as a standard, measurements of the change of opalescence of the silver chloride suspension with time were made. The silver chloride suspension was prepared as before and was 2.00×10^{-5} M. It was allowed to stand at 20° for the time intervals indicated in the table, and was then compared with the kieselguhr standard. The opalescences are represented in percentages of that attained after one hour's standing.

TABLE IV.—CHANGE OF OPALESCENCE WITH TIME AT 20°.
Conc. = 2.00×10^{-5} M.

Time of standing, min.....	7	15	30	45	60	90	120	180
Opalescence, per cent.....	81	93	98	102	(100)	102	101	102

A similar suspension of silver chloride was then prepared and heated to 60° for the times indicated, cooled to room temperature and compared with the kieselguhr standard as before. The results are expressed in percentages of the opalescence of the above standard.

TABLE V.—CHANGE OF OPALESCENCE WITH TIME AT 60°.
Conc. = 2.00×10^{-5} M.

Time of heating, min.....	3	10	25	40	60
Opalescence, per cent.....	85	112	120	120[a]	109[a]

[a] Visibly coagulated.

These experiments show that the opalescence at 20° increases slowly to an almost constant value in an hour. Heating to 60° not only hastens the attainment, but results in a still greater opalescence, which, however, falls off on continued heating. There is, moreover, marked evidence of coagulation after 30 minutes.

Similar measurements made at 40° indicated that the rapid coagulation observed at 60° did not then occur. A series of experiments covering a considerable range of concentrations were, therefore, carried out at this temperature. Samples were prepared as before using appropriate quanti-

ties of sodium chloride solutions. They were heated for various times at 40° and then cooled and read. For comparison, observations were made on similar solutions kept for 60 minutes at 20° and not heated, and these together with the others are included in Table VI.

TABLE VI.—CHANGE OF OPALESCENCE WITH TIME AT 40°.

Conc. $\times 10^5$ M.	Total weight Cl. mg.	Time, min. Temp.	60. 20°. %		30. 40°. %	60. 40°. %	
0.37	0.0053		69		(100)	99	
2.00	0.0284		71		(100)	98	
9.0	0.128		87		(100)	98	
9.0	0.128		88			99	
9.0	0.128		91	87		104	99
9.0	0.128		84			96	
30.0	0.426		95		(100)	100	
30.0	0.426		91	93		99[a]	100
30.0	0.426		94			100[a]	

[a] Visibly coagulated.

These results confirm our previous conclusion that at room temperature the maximum opalescence is not by any means attained within an hour, particularly at the lower concentrations. They further show that over a wide range of concentrations a substantially constant opalescence is attained after 30 minutes' heating at 40°, and that further heating at this temperature is without noticeable effect.

It is important, however, to know how long this maximum opalescence developed by heating will persist unchanged at room temperature. To determine this a similar series of suspensions of different concentrations was prepared, heated as usual at 40° for 30 minutes, cooled and allowed to stand. At intervals samples were pipetted out and compared with freshly prepared suspensions. The results are given in Table VII.

TABLE VII.—EFFECT OF STANDING AT ROOM TEMPERATURE AFTER HEATING.
Samples Heated 30 Min. at 40°.

		Percentage Opalescence. Time of standing after heating.				
Conc. $\times 10^5$ M.	Total weight Cl. Mg.	Min. 0.	30.	90.	180.	300.
2.00	0.0284	99	...	...	97	101
2.00	0.0284	100	102	102	96	...
9.0	0.128	99	...	100	85	74
9.0	0.128	100	...	...	89	...
30.0	0.426	101	99	84	71	50

These results show that faintly opalescent suspensions are stable for several hours, but that the strongly opalescent suspensions produced by high concentrations show a perceptible decrease after an hour. These latter should then be read within a half hour after cooling.

As a result of the above observations the procedure adopted in all of our routine analyses was to place the sample immediately after precipita-

tion in a water bath kept at 40° for at least 30 minutes. It was then cooled rapidly to room temperature and within 30 minutes compared in a nephelometer with suitable standards similarly prepared.

This technique appears superior to that of Wells in two respects—it not only develops a maximum and more constant opalescence, particularly in the case of the more concentrated solutions, but it also is simpler in that the same procedure is applicable over a wide range of concentrations. The results in Tables VI and VII, where the suspensions were treated by this standard technique, show that a maximum deviation of 4% for any single analysis, and a still greater accuracy for the average of several analyses can be counted upon. This estimate is confirmed by the results in Table VIII, and by a large number of other analyses not cited here.

The Effect of Light on Opalescence.

Exposure to direct sunlight produces so great a change in the color and the nature of the silver chloride suspensions that nephelometric readings on such samples are quite out of the question. Wells states that he could detect no effect of a 2-hour exposure to the light of the nephelometer on the opalescence of his suspensions. We find that with suspensions prepared and "developed" as above, exposure to diffuse daylight has a perceptible effect, especially in the more concentrated solutions. This is shown by experiments collected in Table VIII.

TABLE VIII.—EFFECT OF DIFFUSE DAYLIGHT ON OPALESCENCE.
Temperature, 20°.

Molar conc. $\times 10^5$.	Total wt. Cl. Mg.			Time, min. 0.	60.	120.	180.
2.00	0.0284	% Opalescence	in dark	(100)	102	98	96
			in light	102	99	94	88
9.0	0.128	% Opalescence	in dark	(100)	99	97	89
			in light	102	98	91	81
30.0	0.426	% Opalescence	in dark	(100)	100	92	74
			in light	96	92	82	55

It is evident that the opalescence decreases more rapidly with the time when the suspensions are exposed to light than when they are kept in the dark, particularly in the more concentrated solutions.

Opalescence in Other Solvents.

The solvent so far employed was always an approximate 50% ethyl-alcohol-water mixture. It appeared of interest to compare the opalescence developed by the same amount of silver chloride in other solvents. Suspensions were, therefore, prepared as before, except that in place of the alcohol, in one case water and in another glacial acetic acid was substituted. This gave, on the one hand, a suspension in water and, on the other hand, in approximately 50% acetic acid solution. The suspensions were all heated for 35 minutes to 40°, cooled rapidly and compared with

a suspension in a 50% alcoholic solution, treated in a similar way. The results expressed in percentages of the opalescence of the 50% alcoholic solution are given in Table IX.

TABLE IX.—OPALESCENCE IN VARIOUS SOLVENTS.

Solvent.	Molar conc. × 10^5. 6.2.	23.
50% alcohol	(100)	(100)
Water	115	115
50% acetic acid	101	102

The opalescence in 50% acetic acid is substantially the same as in 50% alcohol; that in water is somewhat greater, but no effect of concentration is evident.

Summary.

It has been shown that:

(1) In a 50% alcohol-water solution, heating silver chloride suspensions of widely differing concentrations to 40° for 30 minutes after precipitation, produces a more intense and constant opalescence than can be attained at room temperature; further heating for 30 minutes at 40°, or standing at room temperature for an hour produces no perceptible change in this opalescence.

(2) Using this technique, chlorides in such solutions can be estimated with an average deviation of about 3 to 4% over concentrations ranging between 4 and 300 × 10^{-6} M.

(3) Opalescence in such solutions decays more rapidly in diffuse daylight than in the dark.

(4) The opalescence of the same quantity of silver chloride in water is about 15% greater than in 50% alcohol or 50% acetic acid.

Certain phases of this problem are being studied further by Meldrum.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE AND FUNGICIDE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE ARSENATES OF CALCIUM. I. EQUILIBRIUM IN THE SYSTEM ARSENIC PENTOXIDE, CALCIUM OXIDE, WATER AT 35° (ACID SECTION).

By C. M. SMITH.

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Owing to the commercial importance which calcium arsenate has recently assumed as an agricultural spray material more detailed knowledge of its chemical and physical properties has become essential. One of the most important questions in relation to a spray for use on vegetation is its behavior with water, which may and often does result in the liberation of so called "soluble" arsenic—including in that term not only the arsenic which may be present as a soluble impurity but also that which