

in Fig. 6 whence can be seen that the curve departs from a straight line above 3 *M* concentration.

Summary.

1. On the basis of an empirical equation

$$\log F_a' = \alpha'c - \beta'c^m \quad (2)$$

which relates the activity coefficient of an electrolyte with the molal concentration at a given temperature, and Duhem's equation, equations are derived for calculating the vapor pressures of solutions at this temperature.

2. A rigorous test was made of the validity of Equation 2. It was found to hold for all electrolytes throughout the concentration ranges where available data were examined with the exception of sulfuric and hydrochloric acids. In these cases it holds up to 3 *M* concentration.

3. A very careful and exhaustive study of the activity coefficients of potassium chloride solutions has been made.

4. A careful but less exhaustive study of the activity coefficients of sodium chloride solutions and hydrochloric acid solutions has been made.

5. Values of the parameters of Equation 2 obtained for the above 3 and numerous other electrolytes have been collected and tabulated, from which the vapor pressures and osmotic pressures of their solutions may be calculated.

It is thought that the equation and method here employed, although empirical and an approximation will prove useful in testing the consistency and accuracy of activity data and also will prove of some service in organizing the colligative data of concentrated solutions.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

A SIMPLE THEORY OF THE NEPHELOMETER.¹

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In recent years several instruments have been developed using as a measuring criterion the light diffusely reflected and transmitted by suspensions, and variously called turbidimeters, tyndallmeters and nephelometers. At present there is on the market the Kober nephelometer² (a development of the modification by Richards and Wells of the Dubosq colorimeter) which measures the ratio of the depths of two suspensions of equal brightness either by diffuse reflection or transmission.

These instruments are used to obtain information about the suspension

¹ Published by permission of the Director of the Bureau of Standards.

² Made by Klett Mfg. Co., 202 E. 46th St., New York City.

The readings can be correlated with the concentration, fineness, and other properties of the suspended matter in a purely empirical way, but a theoretical basis for such experimental studies is preferable. Unfortunately the optics of turbid media are extremely complicated, but simple considerations are sufficient to show the general trend of the phenomena.

Diffuse Transmission.

In attempting to derive laws for the tyndallmeter,³ the theory of the late Lord Rayleigh of scattering of light by particles small compared with the wave-length of light, which explains the blue color of the sky and the hues of the sunset, has been applied to dispersoids without much regard to the size of particles; but the particles of suspensions are large compared with the wave-length of light, the Tyndall beam is whitish instead of deep blue so that the law of Rayleigh does not apply. In fact, the appearance of suspensions is due largely to the effects of diffuse reflection. Consider first diffuse transmission. Ignoring the question of directional distribution in the light flux, assume simply that the same fraction $-dI/I$ of the light is lost in each thickness dx of the suspension traversed. That is

$$-dI = \alpha I dx. \quad (1)$$

The coefficient α depends upon the concentration and size, distribution of the particles, the optical properties of the dispersoid, etc., but it is assumed not to vary with the depth x . Integrating, the transmission T of a thickness x , or ratio of transmitted to incident light, is

$$= T \exp.(-\alpha x). \quad (2)$$

The coefficient α can be taken to include the true absorption of the suspending medium, as well as the obstruction of the light by the particles in its path, for neither varies with the depth. But a small fraction of the obstructed light gets back into the original beam after multiple reflections in all directions among the particles, and while this is constant for any given direction, more directions contribute as the light becomes more and more diffused. This secondary reflection coefficient would therefore be expected to increase with the depth, approaching a constant γ when the light becomes perfectly diffused. These conditions are satisfied by the coefficient $\gamma [1 - \exp. (-\frac{\beta x}{\gamma})]$, where β is a constant, so that (1) may be improved by taking

$$\frac{1}{I} \frac{dI}{dx} = \gamma - \alpha - \gamma \exp. \left(-\frac{\beta x}{\gamma} \right). \quad (3)$$

Integrating, as before, the transmission is

$$T = \exp. \left\{ (\gamma - \alpha)x - \frac{\gamma^2}{\beta} \left[1 - \exp. \left(-\frac{\beta x}{\gamma} \right) \right] \right\}. \quad (4)$$

³ W. Mecklenburg, *Kolloid Z.*, **15**, 149 (1914); **16**, 97 (1915).

Since the transmission must vanish for great depths, γ must be less than α , that is, only a small part of the diffusely reflected light ever gets back into the original beam. Equation 4 is too complicated to be useful, but when βx is small compared with γ we have the power series $\exp.(-\frac{\beta x}{\gamma}) = 1 - \frac{\beta}{\gamma} x + \frac{1}{2} (\frac{\beta}{\gamma} x)^2 \dots$, so that (4) gives

$$T = \exp. \left[-\alpha x + \frac{1}{2} \beta x^2 \dots \right], \quad (5)$$

neglecting higher powers. Thus, the effect of multiple reflection drops out completely to a first approximation if it varies slowly with the depth, and the fractional error in Equation 2 is $\frac{1}{2} \beta x^2$ for moderate depths.

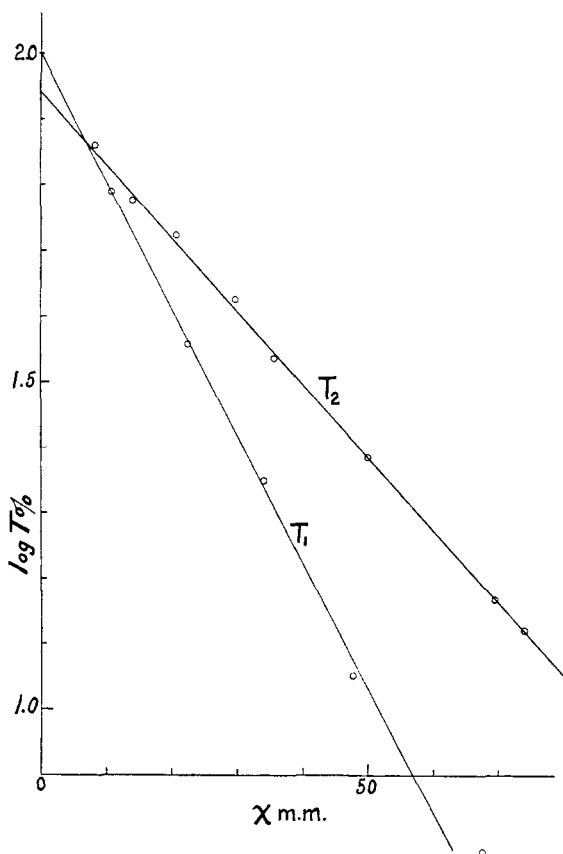


Fig. 1.—Diffuse transmission.

This relation was tested experimentally on a Kober nephelometer in the case of 2 silica suspensions, one containing a concentration of about 5×10^{-5} g. per cc. (50 parts per million) of material which remained in

suspension 20 hours, the other about 12×15^{-5} g./cc. (120 p. p. m.) of larger particles. The latter will be designated by the subscript 1 (T_1 , α_1 , x_1 , etc.), the former by the subscript 2. Two nicol prisms were mounted on one side of the instrument, to measure the transmission of the sample on the other side. In logarithmic form, Equation 5 is

$$2.3 \log T = -\alpha x + \frac{1}{2}\beta x^2 \quad (6)$$

so that if β is small, the logarithm of the transmission should be nearly linear with the depth. This is confirmed by the results in Fig. 1. The initial value of $\log T_2$ (1.942) is probably due to imperfect matching at $x_2 = 0$.

A computation of the value of β after determining α graphically, is given in Table I, neglecting transmissions too near 100%, which are vitiated by lack of precision. Thus over ranges of 50 mm. Equation 5 holds well within the limit of experimental error,⁴ the two samples giving, respectively,

$$\begin{aligned} T_1 &= \exp. [-0.0475x_1 + 0.000096x_1^2] \\ T_2 &= \exp. [-0.0350x_2 + 0.000153x_2^2]. \end{aligned} \quad (7)$$

There is even an indication in the experimental results that the sign of the term in x^3 is again negative, as would be expected from the negative exponential expansion; but the precision is not sufficient to give this much weight.

TABLE I
DIFFUSE TRANSMISSION

Depth	Percentage transmission		$\beta_1 \times 10^5$ ($\alpha_1 = .0475$)
	T_1		
x_1 mm.	Obs.	Calc.	
10.8	60.7	60.5	22
22.4	35.9	36.2	16
34.1	22.3	22.1	21
47.4	12.7	12.8	18
68.1	6.1	6.1	19
			Mean $\beta_1 = .000192$
x_2	Percentage transmission		$\beta_2 \times 10^5$ ($\alpha_2 = .035$)
	T_2		
x_2 mm.	Obs.	Calc.	
20.6	52.6	51.8	37
29.8	42.2	40.3	40
35.7	34.3	34.7	28
50.0	24.2	25.4	27
69.4	16.6	18.4	26
74.0	14.9	17.3	25
			Mean $\beta_2 = .00305$

⁴ Some difficulty was experienced in the photometric work because the nicols did not give a perfectly flat field.

Diffuse Reflection.

Now consider a column of the suspension viewed in the direction of its depth x , but uniformly illuminated from the side by a parallel beam of intensity, I_0 . The portion dI of the reflected intensity coming from the layer dx at the depth x is

$$dI = kI_0 \exp. (-\alpha x) dx, \quad (8)$$

the exponential representing the attenuation in transmission. The coefficient k is probably more nearly constant than α , because of the similarity in the conditions at each layer. Integrating (8), the reflection R of a thickness, x , or ratio of reflected and incident intensities, is thus

$$R = m(1 - T) \quad (9)$$

where $m = k/\alpha$. This is a very simple expression for the diffuse reflection, giving its relation to the diffuse transmission. It is obvious from (9) that the reflection R increases toward the limiting value m with increasing thickness x , because the transmission T decreases exponentially from unity toward zero, as shown in (2), with increasing depth.

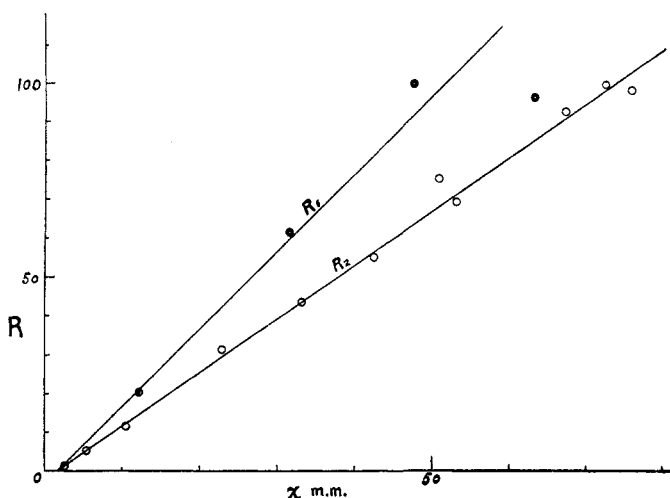


Fig. 2.—Diffuse reflection.

The observed laws of reflection for the 2 silica suspensions before mentioned are shown in Fig. 2. Within the rather large limits of experimental error the reflections are distinctly linear with the depth even to depths of 75 mm. This does not agree with Equation 9; but that equation is deduced on the assumption that the illumination I_0 is uniform. This was tested on the Kober nephelometer. A ground glass diffusion screen, placed upon the cup carriage, increased in brightness approximately linearly with the depth, so that the illumination I_0' is more nearly

$$I_0' = I_0(1 + \omega x) \quad (10)$$

where $\omega = 0.045$.

Introducing this into (8), the reflection becomes, in place of (9), to a second approximation in αx ,

$$R = kx \left[1 - \frac{1}{2}(\alpha - \omega)x \right] \quad (11)$$

so that the effect of the increase in illumination with the depth is to compensate for the attenuation in transmission. The values of the coefficient in the second term for the 2 silica suspensions are, respectively, $+0.001$ and -0.005 . The latter is too large to agree with the results of Fig. 2, but the β -term in (5) has been neglected in deducing (9) and (11).

From these observations it is evident that the law of reflection, as read on the nephelometer, is a fixed function of the depth only so long as the source of light (a concentrated filament lamp) and the collimating lens remain fixed in position, and that this law must be determined empirically. Moreover, there is no simple way of adjusting these parts, when once moved, as there is in the case of transmission. Empirical calibration curves must therefore be frequently redetermined for reliable results.

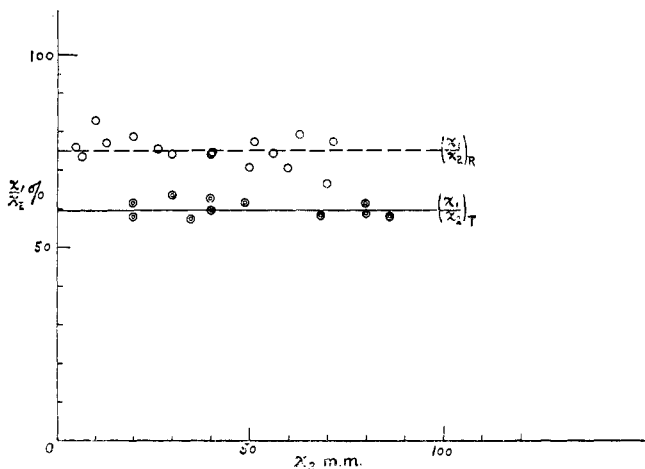


Fig. 3.—Depth ratios.

In the Kober nephelometer 2 suspensions are compared for diffuse transmission, using the opaque cups with transparent bottoms, by varying the depth x_1 of one sample until it matches the other in transmission. It follows from the small values of β in the expression (5) for the transmission, that the ratio of the depths $(x_1/x_2)_T$ of equi-transmitting layers is very nearly constant. The depth ratio $(x_1/x_2)_R$ for equi-reflecting layers is also approximately constant, because the reflections are nearly linear with the depth. This was tested directly on the nephelometer,

with the results shown in Fig. 3. The average deviation of a single determination from the mean of 11 determinations of the transmission depth ratio was 1.9%; while the a. d. of 16 determinations of the reflection depth ratio was 3%. These results show that both ratios are very nearly constant with changes in the depth.

Concentration and Size of Particle.

In order to measure the concentration of the dispersed phase upon the nephelometer, relations between this quantity and the characteristic constants α , k , and m must be known. Confining our attention to *uniform suspensions* (the simplest case), in which all the particles are identical, their size may be specified by a linear dimension, d . For small depths the resultant reflection is due to light reflected from the surfaces of the particles, so that one would expect the constant k to be nearly independent of the wave-length,⁵ and to be proportional to the total surface of the particles per unit volume. This gives

$$k = k' \frac{C}{d} \quad (12)$$

where C is the concentration. The constant k' depends merely upon the arrangement of the particles in space, upon the refractive indices of the two phases, the form of the interfaces, etc.

Assuming Equation 12 it is evident that the diffuse reflection could be used as a measure either of the concentration or of the size of particle of a uniform suspension provided only that one or the other of these properties is known or is kept fixed. This is not difficult in the case of the concentration. But as suspensions are rarely in true equilibrium,⁶ the particles are continually coalescing to form larger aggregates, especially at high concentrations. For stable uniform suspensions with the same constants ($k_1' = k_2'$), (11) and (12) give for the concentration ratio (C_1/C_2) of equi-reflecting layers of small depth

$$\frac{C_1}{C_2} = \frac{d_1}{d_2} \left(\frac{x_2}{x_1} \right)_R. \quad (13)$$

The same relation holds for moderate depths, if the concentration C_2 , size of particle d_2 , and depth x_2 of one suspension be kept fixed. This is what is done in practise. A standard of known concentration, C_2 , is placed in one cup at a fixed depth, x_2 . It is then compared with known dilutions, C_1 giving depths x_1 . Assuming the size of particle to remain constant on dilution, this factor drops out. The resulting calibration curve may be called the *dilution law* (by reflection) of the instrument for this suspension.

⁵ The finer a powder is ground, the less color it shows.

⁶ Tolman has shown that only uniform dispersoids can be in complete thermodynamic equilibrium. THIS JOURNAL, 35, 317 (1913).

Some reflection dilution laws are given by Kober⁷ in his article on nephelometry. He finds his results to be well fitted by the formula

$$\left(\frac{x_1}{x_2}\right)_R = \frac{C_2}{C_1} \left[1 + k \left(1 - \frac{C_2}{C_1} \right) \right] \quad (14)$$

This is a single-constant form of second approximation. Another single-constant formula of a somewhat more flexible type is

$$\frac{C_1}{C_2} = \left(\frac{x_2}{x_1}\right)_R^\xi \quad (15)$$

This gives for Kober's results on ammonia $\xi = 0.9342$, very nearly unity, and agrees to 0.1%. The constant ξ is most simply determined graphically. The logarithms of the depths and concentrations are plotted, and the slope of the resulting straight line is ξ . An approximate form of (15) is very convenient for the slide-rule, and suffices for ratios near unity. When $\delta = 1 - \xi$ is small

$$\frac{C_1}{C_2} = \frac{x_2}{x_1} \left[1 + \delta \left(1 - \frac{x_2}{x_1} \right) \right] \quad (16)$$

This is of the same form as Kober's but with the depth ratio as the independent variable, which is more convenient. For example, in Kober's data ($x_1 = 29.2$, $x_2 = 20$, $C_1/C_2 = 0.7$), Equation 16 gives, since $\delta = 1 - 0.934 = 0.066$, $C_1/C_2 = .685(1 + 0.066 \times 0.315) = 0.700$ which is exact to 0.1%. The error at $C_1/C_2 = 0.5$ is 1.4%. A single determination (10 readings) is seldom precise to 0.5%, and may contain much larger inaccuracies, due to settling, imperfect washing, bubbles, etc.⁸ The constant δ is easily

obtained directly from observed values of $\left(\frac{C_1 x_1 / C_2 x_2 - 1}{1 - x_2 / x_1} \right)$

The departure of (15) from the first approximation (13) is probably due to secondary optical effects, but a slight breaking up of the particles on dilution would explain observed values of the exponent ξ in (15) less than unity. The known difficulty of producing stable suspensions, and the tendency of the particles to coalesce at high concentrations renders this explanation not altogether improbable. Equation 13 also indicates that the ratio of the sizes of particle of two uniform suspensions of the same material and concentration is equal to the depth ratio at equal reflection.

The transmission constant α is the ratio of the reflection constants k

⁷ Kober, *J. Ind. Eng. Chem.*, 10, 562 (1918).

⁸ The mean of 6 determinations at depths between 10 and 30 mm. on the Kober Nephelometer under good conditions gave for the average deviation of a single observation from means of ten, 2.1%. This corresponds to a probable error in the mean of 0.56%; but two consecutive determinations on the same suspension, one with the left cup fixed at 10 mm., the other with the right, gave depth ratios differing by 2%.

and m . Now it seems reasonable to assume that m is independent of the concentration and size of particle. Then (12) gives

$$\alpha = \alpha' \frac{C}{d} \quad (17)$$

where $\alpha' = k'/m$ is a constant, independent of the depth, concentration, and size of particle. If this constant is the same for 2 suspensions, (2) and (17) give at equal transmission

$$\frac{d_1}{d_2} = \frac{C_1}{C_2} \left(\frac{x_1}{x_2} \right)^{\xi}, \quad (18)$$

a first approximation of exactly the same form as (13) for reflections. Hence the depth ratio on dilution should be approximately the same, whether determined by reflection or by transmission. This was verified on the Kober nephelometer, using the silica suspension (No.1), before mentioned. The concentration ratio was measured at six dilutions from 1 to 4, and the exponent ξ in (15) determined for the best straight line by Pearson's method of moments (in this case the same as the method of least squares). By reflection the value of ξ was 0.924, by transmission 0.904, a very close agreement. This indicates that the reflection constant m is practically independent of the concentration, and again favors the supposition that the particles break up on dilution.

The depth ratio, either by reflection or by transmission, can be used to measure the ratio of size of particle (d_1/d_2) in two uniform suspensions with the same constant (k' or α') and of known concentrations. For Equations 13 and 18 state that the particle size is in the same ratio as the depths.⁹ But while finer suspensions transmit less light per unit depth than do coarser ones of the same material and concentration, more light is diffusely reflected by the finer suspensions.

Summary.

The fact that the depth ratios by reflection and by transmission are equal might lead one to think that either method could be used with the same result. But this is so only in an intermediate range of concentrations. For extremely dilute suspensions, say less than 10^{-5} g. per cc., the transmissions are quite insensitive, while the reflection measurement remains sensitive right down to the threshold of vision. By increasing the incident intensity the present Lord Rayleigh has been able to measure the light scattered by gas molecules. On the other hand, for very turbid suspensions the transmission probably follows less complicated laws. Although masses in suspension much too small to be detected by the most delicate balance can be easily measured in a Tyndall beam, the precision of such a

⁹ The depth ratio by transmission has been utilized by Bleining and Pendergast in classifying clay suspensions according to fineness (to be published in the *J. Am. Ceramic Soc.*).

measurement can never exceed that of the best photometry, that is, about 0.2%. For sensitive and rapid work it takes its place with other volumetric methods.

The phenomena of diffuse reflection and transmission are much more complicated than is here represented, many secondary effects occurring that cannot be neglected. The experimental dilution law is an example of the departures which are to be expected. Moreover, the particles are usually distributed in size, and must be studied statistically. But the simple theory represents the general march of the phenomena,¹⁰ and it may serve as a point of departure for experimental investigations.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY. NO. 9.]

THE CRYSTAL STRUCTURES OF POTASSIUM AND AMMONIUM CHLOROSTANNATES.

BY ROSCOE G. DICKINSON.¹

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1. Introduction.

There is a large group of substances of the type R_2MHI_6 where R is potassium, rubidium, cesium, or ammonium; M is one of the platinum metals or tin, antimony, selenium, tellurium or lead; and HI is one of the halogens, chlorine, bromine or iodine. Although few members of this group have been thoroughly studied crystallographically, many of them are apparently isomorphous² and belong to the cubic system. They crystallize chiefly in octahedra, and show a very good octahedral cleavage. There are in addition other salts, such as K_2SiF_6 , which have similar cubic modifications.

Since the crystal structures of these salts presumably differ only in detail, the determination of the structures of one or two of them by means of X-rays should furnish the key to the group as a whole.^{2a} Potassium chlorostannate (K_2SnCl_6) was chosen for the investigation, since definite

¹⁰ See, for example, R. C. Tolman and others, *THIS JOURNAL*, **41**, 575 (1919). Tolman's tyndallmeter measures the diffuse reflection of a single sample at right angles to the incident beam. The (fixed) depth is small, so that Equations 11 and 12 apply. The diameter of particles is found to be fairly linear with the concentration over considerable ranges.

¹ National Research Fellow in Chemistry.

² Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, vol. 1, p. 467.

^{2a} Since the submission of this paper for publication the determination of the structure of another crystal of this series has been published by Wyckoff and Posnjak (*THIS JOURNAL*, **43**, 2292 (1921)). Their results are in entire agreement with those described here, and afford an interesting comparison of interatomic distances.