Chemistry. — *"On colorimetry and a colorimetric method for determining the dissociation constant of acids."* By Mr. F. H. Eijdman Jr. (Communicated -by Prof. S. Hoogewerff).

On colorimetry.

During the last few years I have been obliged to undertake a large number of colorimetric determinations, which had to be made as accurately as possible.

The impossibility of making really accurate colorimetric determinations without taking a number of precautions, made Knecht [1] utterly reject this method of working. As Knecht's method (titration of the colouring matters by means of titanous chloride) is not applicable in all cases, it was thought that an effort to improve the colorimetric method, would not be undesirable.

PRINCIPLE OF THE COLORIMETRIC METHOD.

Starting from the supposition that *on diluting a solution of a colouring matter, neither the amount, nor the nature of the colouring matter present, undergoes a change*, the principle of the colorimetric method is as a rule indicated as follows:

If we examine in transmitted light two solutions, containing the same colouring matter, the concentrations will be inversely proportional to the heights of the layers of the same colour.

This formulation will be found in Ostwald, Handbuch für Physiko-Chemische Messungen [2] and in Heermann, Coloristische und Textil-chemische Untersuchungen [3].

The first supposition cannot at all be accepted as being generally correct; in fact, in the practice of colorimetry the circumstances, in which it is correct, occur but rarely.

In future those solutions of colouring matters, where these suppositions are permissible and which may, therefore, be determined colimetrically without precautionary measures, will be styled *directly measurable.*

If the colouring matters under examination are not electrolytes, their nature and amount will suffer no change by dilution. Such colouring matters are, therefore, directly measurable.

But with acid, or basic colours, or their salts the case is different, as these can but rarely be determined directly. The cause may be found sometimes in the electrolytic dissociation, in other cases in a

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[1] Journal of the Society of Dyers & Colorists 1904. p. 242.
[2] Ibid. p. 179.
[3] Ibid. p. 63.

hydrolic phenomenon, which plays its part. If we have a solution containing acid colours, whose anions possess a different colour from the undissociated acid, the solution will exhibit a mixed colour composed of the colour of the anions and that of the undivided acid. This phenomenon may be readily demonstrated by means of the acids of the following colouring matters: *Methylorange, metanilyellow* and *benzopurpurin* 4 *B.*

That the change in colour, which these acids undergo when their solution is diluted, must really be explained in this manner, is proved in the second part of this paper, where an application is made of the fact that such dilute solutions may be restored to their original colour by addition of dilute acids [1]).

This explanation disposes of the theory of KUSTER [2]) and of that of GLASER [3]) as to the indicator methylorange and it appears indeed that the methylorange-acid is, for an indicator, a fairly strong acid.

This phenomenon also occurs with salts of acid colours, therefore when testing the so-called acid and directly-dyeing technical colours.

Such a case has been mentioned by C. H. SLUITER [4]), who noticed it when testing solutions of *isonitrosoacetophenonsodium.* He found that these solutions assumed an increasing yellow colour on increased dilution and he rightly attributes this to the more powerful electrolytic dissociation caused by the dilution. In this case the ionisation in $N/10$ solutions had proceeded so far that a further dilution caused no further visible change in colour.

If however we want to measure solutions of *benzo-pure-blue, benzo-azurin* or allied colouring matters, it will be noticed that in solutions containing from 0.1—0.05 gram in a Liter (approximately $N/3000$— $N/6000$)the phenomenon is still of such an interfering nature, owing to the great difference in shade of colour, that a direct measurement is impossible. SLUITER's dissertation only reached me when my researches had already been brought to a close.

In theory, analogous phenomena are possible with basis colours and their salts, but I have not as yet met with any such instances and in fact, have not searched for them.

When salts of very weak acid colours are tested, the hydrolysis proves very troublesome, if the colour of the anions and that of the acids

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[1]) Compare A. A. NOYES and A. A. BLANCHARD Journ. Americ. Chem. Soc. 22 p. 726 and Central Blatt 1901. I. p. 11·n° 15.

[2]) KÜSTER, Zeitschrift für Anorganische Chemie 8 p. 127.

[3]) GLASER, die Indicatoren.

[4]) C. H. SLUITER. Het mechanisme van eenige organische reacties. Academisch Proefschrift. Scheltema en Holkema. 1905.

should be different. As the solutions get more diluted, they exhibit colours approaching the shade of the colour-acid.

A very striking example, which lends itself well for practical demonstration, is furnished by sodium carminate. Sodium alizarate may be also used, only the solutions, on being diluted, soon become turbid, owing to the slight solubility of alizarine.

From these examples it follows that the fundamental principle of colorimetry ought to be expressed as follows:

Solutions of the same colouring matter, when tested colorimetrically, exhibit in layers of the same thickness the same intensity of colour if they possess the same concentration.

THE COLORIMETER.

This apparatus must be so constructed that the liquid under examination may be brought to practically the same concentration as the standard liquid.

The apparatus best suited for this purpose is that of SALLERON [1], modified by KOPPESCHAAR [2]. In this colorimeter the most concentrated of the two solutions is diluted with water until it has the same colour as the weaker solution. From the amount of water added, the desired concentration is calculated. It is a matter of indifference whether the most concentrated or the most diluted solution is used as the standard liquid.

As it is not possible, when using the colorimeter of SALLERON-KOPPESCHAAR, to make rapidly successive readings of a quantity of solution to be measured, the apparatus, which I am now using and which is represented in the annexed drawing, is perhaps to be preferred. It is constructed from a colorimeter of C. H. WOLFF [3]. The tube containing the standard liquid, the *standard tube S* is connected by means of a small horizontal tube E with the glass cylinder A in which a plunger C is suspended. This plunger can be moved up and down by means of a cog-wheel device along the standard B. *In this way the level of the standard solution may be raised or lowered*: by providing B with a scale, the position of the liquid may be read off on the same.

The actual colorimeter stands in the dark chamber D. It consists of the standard tube S and the tube containing the liquid to be measured, the *measuring tube M*.

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[1] Zeitschrift für Anal. Chemie 11 p. 302.

[2] Zeitschrift für Anal. Chemie 38 p. 8.

[3] Dingl. 236. 71.
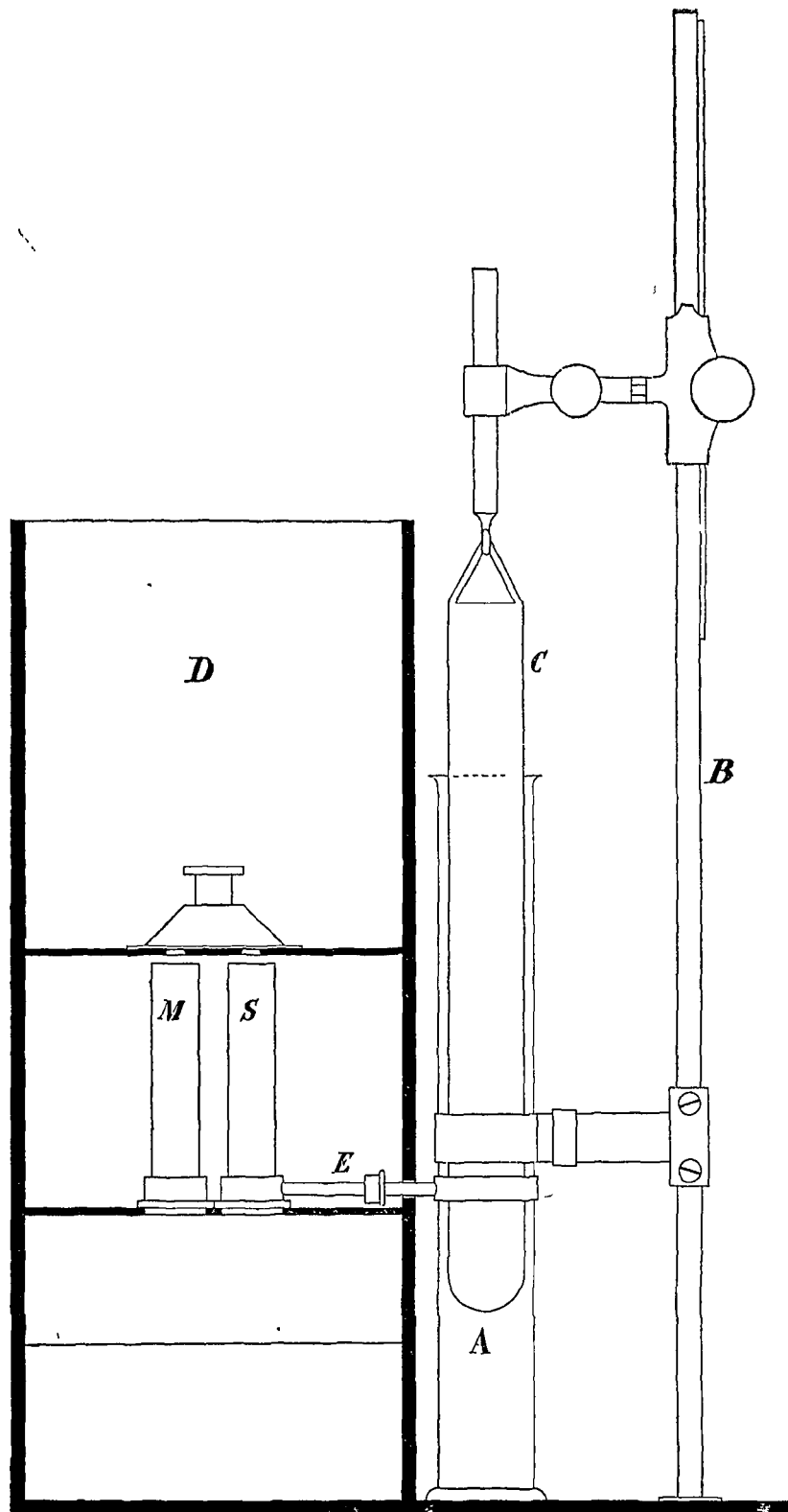
The illumination of such a colorimeter is generally effected by means of a mirror placed below the tubes, which reflects the light from the sky. Owing to the clouds, this illumination may be very irregular, therefore artificial light is preferable. Incandescent light is very satisfactory. With artificial light, however, a mirror cannot be used, as small displacements of the lamp greatly affect the illumination of the two colorimeter tubes; instead of a mirror, a piece of ground milky-glass is then employed.

Above the tubes is placed the optical arrangement, which serves to create a field of vision, which is divided into two parts, one of which is illuminated by the rays, which have traversed the standard tube and the other by those, which have traversed the measuring tube.

In principle, it is preferable to make both halves of the field of vision exactly the same shape, as they are then observed under exactly the same conditions. These conditions are not satisfied by the prism-system of LUMMER and BRODHUN, which has been applied by H. KRÜSS to the WOLFF-colorimeter [1]. The field of vision is here a circle surrounded by a ring. This may, perhaps, partly explain the less favorable report of the Photometer Committee of the Netherland Society of Gasmanufacturers [2].

The prism-system of FRESNEL, generally met with in colorimeters, suffers from the drawback that it is liable to give way, when being cleaned, and cannot then be again properly joined together. This creates in the field a heavy black line of junction, which greatly impedes an accurate observation. A prism made from milky-glass [3] is not advisable on account of the transparency which causes the two halves to illuminate each other in the neighbourhood of the line of junction. An equality of colour is then noticed before it is really a fact.

I use a prism of polished telescope-metal with angles of 45° illuminated by two little mirrors also at angles of 45° placed above the tubes. The line of junction is then hardly visible and the prism is proof against the influences of a laboratory atmosphere.

The apparatus is now used as follows: The standard tube and the vessel *A* are provided with standard liquid, and fixed in such a manner that the height indicated on the rod *B* really corresponds with the position of the liquid in *S*. The standard liquid would have to be more diluted than the solution to be measured. A known

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[1] Zeitschrift für Instrumentenkunde 14. 102.

[2] Report of the said committee 1893.

[3] Ostwald l.c. p. 180.

quantity of the latter is then introduced into the measuring tube M and when the colours are equal, a reading is taken. In many cases it is not possible to take a reading, owing to the difference in shade of colour of the two liquids, but still we are able to see at which heights of the standard liquid this is decidedly darker or lighter than the measuring liquid.

The measuring tube is then filled with water up to the average of those heights and definitive determinations are now made. The difference in concentration between the two liquids is now in most cases so slight, that a difference in shade is no longer perceptible.

In any case it is desirable to dilute the contents of the measuring tube up to the height found and to take a fresh reading, even when determinations may be readily made without dilution.

In the case of acid colours this mode of working can sometimes not be applied. The measuring liquid should then be gradually diluted until, the colours being equal, the height of the measuring liquid is about the same as that of the standard liquid.

In the case of such small differences in the concentration it may be safely assumed that the concentrations are inversely proportional to the height of equally-coloured layers.

The great advantage of this method of working is this, that at the final determination a series of readings can be taken, also that the standard liquid can be alternately changed from darker to equality of colour and from lighter to equality, as is done in polarisation. This renders each determination very certain.

The readings may be rendered much more delicate by placing a coloured piece of glass on the ocular. It is necessary to choose such a colour that the rays of light, transmitted through the measuring liquids are also transmitted through the coloured glass. A trial with a pocket spectroscope or a consultation of FORMÁNEK's work "*Der spectralanalytische Nachweis künstlicher organischer Farbstoffe*", renders the choice easy.

These glasses are readily made by dyeing old photographic plates with basic colours, which is easily done in the cold.

A colorimetric method for determining the dissociation constant of acids.

Acid colours whose anions possess a -colour different from that of the acid itself, and which we will call *indicator-acids*, may be used to determine the dissociation constant of the indicator-acids themselves in the first place, and also of all other colourless acids, if we have

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at our disposal a colourless acid the dissociation constant of which is known with certainty.

PRINCIPLE OF THE METHOD.

If the aqueous solution of an indicator-acid is diluted with water the colour will change in the direction of the colour of the anions. If for the dilution of an indicator-acid solution an isohydric solution of a colourless acid is used, the degree of dissociation will not alter and the colour of the solution will remain the same.

If the solution of the indicator-acid is diluted with water, we may titrate back with an acid of which the concentration of the H-ions is larger than that of the solution of the indicator-acid, until the original-colour is restored. We have then prepared from the water and the acid solution a mixture, which is isohydric with the solution of the indicator acid.

Starting from an acid with a known dissociation constant — *standard acid* — and an arbitrary solution of an indicator-acid we may in the same manner determine the dissociation constant of a second colourless acid, by preparing as directed, from the standard acid as well as from the unknown acid solutions, which are isohydric with the same solution of the indicator-acid. The acid solutions are then mutually isohydric and the calculation of the dissociation constant is readily made from the above data.

THE OPERATION

The above described colorimeter is best suited for this method. The solution of the indicator-acid is introduced both in the standard tube and the measuring tube. The amount of indicator-acid does not matter, provided the quantity of it, in both tubes, is exactly the same. After most carefully adjusting the colours, the contents of the measuring tube are diluted with an accurately known volume of water, say, a cc. If now of a standard acid the dissociation constant is K_A and if from this is prepared a solution of a dilution v_A, we then titrate with this solution the contents of the measuring tube until the colours are again the same. If this should require b cc the dilution at which the solution of the standard acid is isohydric with the given solution of the indicator-acid is :

$$\frac{a + b}{b} \times v_A = V_A.$$

If now the dilution of the indicator-acid is known, or if we have found in the same way the dilution at which an unknown dissociation constant yields an isohydric solution, then, calling both dilutions

V_B, the unknown dissociation constant K_B is found by the following calculation:

If in the solution of the standard acid we call the dissociated part a then

$$\frac{a}{V_A} = C_H,$$

the concentration of the H-ions, therefore,

$$C_H = \frac{K_A}{2}\left[-1 + \sqrt{\left(\frac{4}{K_A V_A} + 1\right)}\right].$$

For the acid with an unknown dissociation constant K_B, we may calculate the same from

$$C_H = \frac{K_B}{2}\left[-1 + \sqrt{\left(\frac{4}{K_B V_B} + \right)}\right],$$

as C_H and V_B are known. It is, however, simpler to make the calculation as follows:

From

$$\frac{a^2}{1 - a} = K V \quad \text{and} \quad \frac{a}{V} = C$$

we find:

$$C^2 = \frac{K}{V} - C K.$$

As both acids are isohydric in dilutions of, respectively, V_A and V_B, C_H will be the same in both, therefore

$$\frac{K_A}{V_A} - C_H K_A = \frac{K_B}{V_B} - C_H K_B$$

from which

$$K_A = K_B \cdot \frac{V_A}{V_B} \cdot \frac{1 - C_H V_B}{1 - C_H V_A}.$$

TEST EXPERIMENTS.

In order so show the accuracy of the process, I have made three determinations. In the first one I have determined the dissociation constant of benzoic acid, taking the constant of salicylic acid as known. In the second experiment 1 have determined the dissociation constant of anthranilic acid, using the figure obtained for benzoic acid. In a third experiment, the dissociation constant of propionic acid has been also determined with the aid of benzoic acid.

Determination of the dissociation constant of benzoic acid.
Given:

$$K_s = 0.00102 \qquad v_s = 150$$
$$v_b = 100$$

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Indicator : metanilyellow-acid. The change in colour of this indicator on dilution was not strong enough. Therefore, the solution was mixed before use, with a few drops of hydrochloric acid, which caused the difference in colour to be more decided and more readily observable. This addition may be made without fear, for the colour is used as the indicator for the concentration of the hydrogen-ions and an equal concentration of the hydrogen-ions always gives the same colour. Only we must take care to use the same indicator solution for the whole series of determinations.

Found:

15 cc of indicator + 50 cc of water. Colour again restored with 9 cc salicylic acid solution, therefore:

$$\frac{50 + 9}{9} \times 150 = 983.5 = V_s$$

15 cc of indicator + 10 cc of water. Colour again restored with average 22.5 cc of benzoic acid solution, therefore

$$\frac{10 + 22.5}{22.5} \times 100 = 144 = V_b$$

from which :

$$C_H = \frac{0.00102}{2}\left[-1 + \sqrt{\left(\frac{4}{0.00102 \times 983.5} + 1\right)}\right] = 0.0006294$$

and :

$$K_b = 0.00102 \cdot \frac{144}{983.5} \cdot \frac{1 - 0.0006294 \times 983.5}{1 - 0006294 \times 144} = \mathbf{0.000063.}$$

By the electrolytic process the value of $K_b = \mathbf{0.00006.}$ [1])

Determination of the dissociation constant of anthranilic acid.

Given: $K_b = 0.00006 \quad v_b = 200$
$$v_a = 100$$

Indicator : methylorange-acid.

Found:

15 cc of the indicator in both cases diluted with 50 cc were titrated back to the original colour.

For this was required

Benzoic acid :   0.87 cc

Anthranilic acid : 1.56 ,,

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[1]) Nernst. Theoretische Chemie, p. 404.

From which :

$$V_b = \frac{50 + 0.87}{0.87} \times 200 = 11690$$

$$V_d = \frac{50 + 1.56}{1.56} \times 100 = 3306$$

$$C_H = \frac{0.00006}{2} \left[-1 + \sqrt{\left(\frac{4}{0.00006 \times 11690} + 1 \right)} \right] = 0.00004749$$

and

$$K_a = 0.00006 \cdot \frac{3306}{11690} \cdot \frac{1 - 11690 \times 0.00004749}{1 - 3306 \times 0.00004749} = \textbf{0.0000089.}$$

The electrolytic process gave **0.0000096.** [1])

Determination of the dissociation constant of propionic acid.

Given : $K_b = 0.00006$ $v_b = 442.5$

$v_p = 1020$

Indicator : methylorange acid.

Found :

15 cc of indicator were diluted with 25 cc of water; the colour was restored on adding 1.5 cc solution of benzoic acid.

$$V_b = \frac{25 + 1.5}{1.5} \times 442.5 = 7816$$

15 cc of indicator were diluted with 10 cc of water; the colour was restored on adding 6 cc solution of propionic acid.

$$V_p = \frac{10 + 6}{6} \times 1020 = 2720$$

$$C_H = \frac{0.00006}{2} \left[-1 + \sqrt{\left(\frac{4}{0.00006 \times 7816} + 1 \right)} \right] = 0.00006261$$

and

$$K_p = 0.00006 \times \frac{2720}{7816} \times \frac{1 - 7816 \times 0\,00006261}{1 - 2720 \times 0\,00006261} = \textbf{0.0000128} [2]).$$

Found by the electrolytic process: **0.0000134.**

This method may, perhaps, prove useful in cases where the electrolytic method meets with difficulties, for instance in the determination of very small concentrations of hydrogen-ions or in the determination of the concentration of hydrogen-ions in presence of other cathions. I intend making further experiments in that direction.

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[1] Ostwald. Zeitschr. für Physik. Chemie 1889, p. 261.

[2] Ostwald. Zeitschr. für Physik. Chemie 1889.