

solutions it will be necessary to delay the report on this dilution until a later date.

Summary

1. A positive potential has been impressed upon the grid instead of the usual negative.
2. The polarization of platinum electrodes by means of a grid current has been used to advantage in the electrometric titrations of some oxidation-reduction reactions.
3. The different variables in this "hook-up" may be varied over a range of 20% without vitiating the results.
4. The equivalence point is indicated by the "kick" of a sensitive galvanometer and possesses the following characteristics: (a) approach is indicated, (b) high sensitivity, (c) over-stepping is immediately apparent, (d) the plotting and recording of readings is unnecessary, (e) tubes of the same type give the same equivalence point, (f) adjustments are unnecessary during titration.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN, CHLORPHENOL RED AND METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS¹

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A great part of the work in the colorimetric determination of hydrogen-ion concentration has been based on the incorrect assumption that equal color in solutions of equal indicator concentration meant equal hydrogen-ion concentration. That this assumption leads to errors of considerable magnitude has been clearly pointed out by Güntelberg and Schiödt.² They show that for the case studied by Szyszkowski³ the error due to the above assumption amounted to several hundred per cent. Consequently, this error is of the greatest importance and a clear understanding of the factors involved is essential.

An indicator is nothing more than a weak acid, or base, where the acid form, or basic form, or both, is colored due to some structural rearrangement. Thus we can have a buffer system just as with any weak electrolyte

¹ Abstracted from the thesis of Elwyn F. Chase presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1931.

² Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

³ Szyszkowski, *ibid.*, **58**, 420 (1907).

and the classical dissociation constant is a good measure of the acid strength. If we consider the acid HI the classical dissociation constant is

$$K_c = \frac{C_{H^+} \cdot C_{I^-}}{C_{HI}} \quad (1)$$

where C_{H^+} really represents $C_{H_3O^+}$. At the half transformation point $C_{HI} = C_{I^-}$ and

$$K_c = C_{H^+} \quad (2)$$

Now it is generally known that K_c changes with change in electrolyte concentration. In the case of monobasic acids these changes depend not only on the electrolyte concentration but also on the particular acid and electrolyte.⁴ The magnitude of these changes will also depend on the ion charge types involved but this will not affect the general equations derived below. If we consider two solutions I and II at the half change point or any other degree of transformation, *i. e.*, C_{I^-}/C_{HI} ratio, from equation (2) it follows that

$$\left(\frac{C_{H^+}}{K_c}\right)_I = \left(\frac{C_{H^+}}{K_c}\right)_{II} \quad (3)$$

If I is the known and II is the unknown, then

$$(C_{H^+})_{II} = (C_{H^+})_I \cdot \frac{(K_c)_{II}}{(K_c)_I} \quad (4)$$

an equal color means equal hydrogen-ion concentration when $(K_c)_{II}/(K_c)_I$ is equal to unity. In other words, $(K_c)_{II}/(K_c)_I$ is the term expressing the so-called "salt error" of indicators. The ratio $(K_c)_{II}/(K_c)_I$ may change several fold⁴ so that the determination of the classical dissociation constants of indicators is essential to the use of the colorimetric method. The present paper deals with the determination of the classical dissociation constants of bromcresol green, chlorphenol red and methyl red in aqueous potassium chloride solutions.

The method of determining the classical dissociation constant depends upon having solutions of suitable known hydrogen-ion concentration and determining experimentally the ratio of the basic and acid forms of the indicator in such solutions. Substitution of these values in equation (1) gives the dissociation constant directly. This method has been used by Friedenthal⁵ and improved upon by Gillespie.⁶ For indicators having half-change points around 0.01 molar hydrogen-ion concentration, it is convenient to use solutions of strong acid as standard but it is not practicable to work in glass with large amounts of salt present at concentrations of strong acid much below 1×10^{-3} . Besides, in unbuffered solutions of this sort one must take into account the buffering action of the

⁴ For examples see Chase and Kilpatrick, *THIS JOURNAL*, **53**, 2589 (1931).

⁵ Friedenthal, *Z. Elektrochem.*, **10**, 114 (1904); Salm, *Z. physik. Chem.*, **57**, 471 (1906).

⁶ Gillespie, *THIS JOURNAL*, **42**, 742 (1920).

indicator system.⁷ In the present study the standards have been the buffer systems of benzoic acid-benzoate, acetic acid-acetate, cacodylic acid-cacodylate and hexahydrobenzoic acid-hexahydrobenzoate. In the first case the hydrogen-ion concentrations were those calculated from the values of the classical dissociation constant of benzoic acid in potassium chloride solutions as given by Chase and Kilpatrick.⁴ In the other cases the hydrogen-ion concentrations were determined by means of the quinhydrone electrode under the same assumptions used in the standardization of the benzoic acid-benzoate system.⁸

Experimental Method

As preliminary experiments showed that different samples of indicator gave different values, we attempted to obtain the purest possible samples of the indicators.⁹ Two samples of bromcresol green (tetrabromo-*m*-cresolsulfonephthalein) were used. The first was crystallized from acetic acid. The second was also crystallized from glacial acetic acid and analysis showed 44% bromine as against a calculated value of 45.8%. The indicator solutions were prepared by shaking a weighed amount of the indicator acid with a dilute solution of sodium hydroxide containing the calculated amount to form the sodium salt. The solution was then centrifuged and diluted to a convenient concentration. Preliminary experiments¹⁰ with another indicator (bromphenol blue) have shown that in the presence of sodium hydroxide of concentration 3×10^{-3} molar and an indicator concentration of 2×10^{-5} molar the blue color disappears completely in about fourteen days. This change seems to be proportional to the hydroxyl-ion concentration and from a study of the increase in the rate of the reaction with increasing potassium chloride concentration (primary kinetic salt effect) appears to be a reaction between two ions. Since the solutions gave tests for the bromide ion, it seems likely that the bromine is replaced by the hydroxyl ion in the compound. For this reason we avoided using the method recommended by Clark¹¹ in which the indicators are ground up with 0.01 molar sodium hydroxide solutions. In fact in later work we have been using the following method to carry out the neutralization more quickly and thus avoid an excess of sodium hydroxide. The indicator is dissolved in alcohol, the calculated amount

⁷ This has been pointed out by Fawcett and Acree, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930), and Kolthoff, *THIS JOURNAL*, **53**, 825 (1931).

⁸ Kilpatrick and Chase, *ibid.*, **53**, 1732 (1931).

⁹ The bromcresol green and chlorphenol red were specially purified and furnished to us through the kindness of Drs. D. Twiss and W. C. Harden of the Chemical Research Laboratory of Hynson, Westcott and Dunning Co., Baltimore, Md.

¹⁰ Experiments carried out with C. E. Gulezian.

¹¹ Clark, "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, Md.

of aqueous sodium hydroxide added, the alcohol evaporated under reduced pressure and the residue taken up in distilled water.

Two samples of chlorphenol red (dichlorophenolsulfonephthalein) were used. The first was purified by repeated solution in sodium carbonate and precipitation by hydrochloric acid. This sample did not dissolve completely in sodium hydroxide. A second sample purified by Harden¹² dissolved completely and immediately in very dilute sodium hydroxide. The second sample gave the following analysis: calcd., sulfur, 7.58; chlorine, 16.76. Found: S, 7.60; Cl, 16.66. A comparison of the dissociation constants of these samples will be given later.

Methyl red (*o*-carboxybenzene-azo-dimethylaniline) was purified by repeated crystallization from toluene. The sample gave a sharp melting point between 176 and 177°.

The stock solutions of the indicators were diluted to a concentration of 5×10^{-4} molar and contained potassium chloride ranging from 0.1 to 3 molar. The colorimeter was of the Gillespie type and is described by Clark.¹³ In all cases the acid form and the basic form were obtained by adding the calculated amount of hydrochloric acid or sodium hydroxide for over 99% conversion.

TABLE I

THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: benzoic acid-benzoate, acetic acid-acetate, hexahydrobenzoic acid-hexahydrobenzoate. Temp., about 25°; indicator, about 5×10^{-5} mole per liter

Electrolyte KCl + NaX moles per liter	Average $K_c \times 10^8$	Number of dets.	a. d., %
0.1000	3.07 (2.33 <i>k</i>)	6	3.5
0.5000	4.03 (3.13 <i>k</i>)	5	2.6
1.000	3.61	9	6.4
1.500	3.46	6	3.6
2.000	2.93	5	5.8
2.500	2.55	6	4.9
3.000	2.38	3	3.8

X, anion of acid used in buffer. *k*, values chosen by Kolthoff.

Table I gives the results with bromcresol green. Column I gives the electrolyte concentration, which is largely potassium chloride. Column II gives the average value of K_c with a value calculated from the values of Kolthoff, given in his recent survey of indicator constants.¹⁴ Kolthoff gives the values in terms of pK_1 and states that the accuracy is supposed to be within 0.05 of a logarithmic unit (12% in K_1). K_1 does not represent the classical dissociation constant but a dissociation constant defined by the equation

¹² Harden, THIS JOURNAL, 52, 4611 (1930).

¹³ Clark, Ref. 11, p. 169.

¹⁴ Kolthoff, J. Phys. Chem., 34, 1466 (1930).

$$pK_1 = P_H - \log \frac{C_B}{C_A} \quad (5)$$

where P_H is the Sørensen P_H . The classical dissociation constant is related to this constant (K_1) by the equation

$$pK_o = pK_1 - pf_H + 0.04 \quad (6)$$

$-\log f_H$ was evaluated, with sufficient accuracy, from the empirical equations of Bjerrum and Unmack¹⁵ and K_o was calculated from the values of Kolthoff for K_1 . Our observed values, which are higher than those given by Kolthoff, were obtained with two different indicator samples and three different buffer systems.

TABLE II
THE CLASSICAL DISSOCIATION CONSTANT OF CHLORPHENOL RED IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: Cacodylic acid-cacodylate. Temp., about 22°. Indicator, about 2.5×10^{-5} moles per liter

Electrolyte, KCl + NaX, moles per liter	Average $K_o \times 10^7$	Number of detns.	a. d., %
0.1000	11.0 (10.7 <i>k</i>)	3	6.7
0.5000	13.4 (13.5 <i>k</i>)	3	5.4
1.000	16.2	2	1.9
1.500	13.1	2	2.1
2.000	13.2	2	2.3
2.500	9.45	2	4.9
3.000	7.90	2	10.0

X, cacodylate. k , values chosen by Kolthoff at 20°.

Table II gives the results for chlorphenol red in cacodylic acid-cacodylate buffers in potassium chloride solutions. The results with the first sample

TABLE III
THE CLASSICAL DISSOCIATION CONSTANT OF METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS

Buffers: Acetic acid-acetate. Temp., about 22°. Indicator, about 1.3×10^{-5} moles per liter

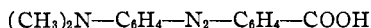
Electrolyte, KCl + NaX, moles per liter	Average $K_o \times 10^8$	Number of detns.	a. d., %
0.1000	10.4 (10.7 <i>k</i>)	5	2.2
0.5000	9.21 (10.7 <i>k</i>)	3	2.9
1.000	7.75	2	5.8
1.500	6.25	2	7.8
2.000	5.33	2	2.6
2.500	3.61	3	3.8
3.000	2.90	2	12.0

X, acetate. k , value chosen by Kolthoff at 20° for electrolyte concentrations from zero to 0.5 mole per liter ($10.7 \times 10^{-8} \pm 12\%$).

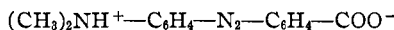
¹⁵ Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, 9, 1 (1929)

of indicator were much lower and are not included. For example, the dissociation constant for the first sample at one molar potassium chloride concentration was 7.7×10^{-7} as compared with 16.2×10^{-7} for the second sample.

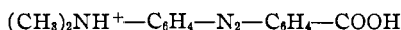
Table III gives the results for methyl red. Methyl red is of particular interest in that it is an indicator of the amphi-ion type. Considering the structure



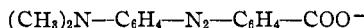
the molecule contains a basic group as well as an acid group. The amino group will tend to pick up protons to form the amphi-ion



In acid solution we have the form



and in basic solution



The dissociation constant is related to the dissociation constant at zero ion concentration by the equation

$$K_c = K_{c_0} \frac{f_{\text{HI}^\pm}}{f_{\text{H}^+} f_{\text{I}^-}}$$

Now Bjerrum¹⁶ has shown that in dilute solution an amphi-ion behaves like a neutral molecule and in more concentrated solution like two ions. Consequently in very dilute solution

$$K_c = K_{c_0} \frac{1}{f_1^2}$$

Thus in dilute solution an exponential salt effect would be expected. In more concentrated solution the activity factor would be such

$$K_c = K_{c_0} \frac{f_1^2}{f_1^2}$$

that a linear salt effect would be expected. The curve for methyl red in Figure 1 shows this effect. The exponential effect below 0.1 molar was not investigated due to the fact that the assumptions involved in the electrometric method for determining the hydrogen-ion concentration are not valid below 0.1 molar. Güntelberg and Schiödt² do indicate the exponential part in the case of methyl orange. In this connection we cannot agree with the statement of Kolthoff¹⁴ that the salt error of methyl orange is extremely small between 0.0 and 0.5μ . If we express the salt error as K_c/K_{c_0} and use the results of Güntelberg and Schiödt, the error is 32% between $\mu = 0.0$ and $\mu = 0.1$.

The curves for bromcresol green and chlorphenol red show that K_c increases with increasing electrolyte concentration, passes through a maximum and then decreases.

¹⁶ Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

The Colorimetric Method.—In using the colorimetric method to determine the hydrogen-ion concentration of an unknown solution, one may simply reverse the method employed here in determining the dissociation constant of the indicator, that is, the ratio of the acid form to the basic form of the indicator is determined and the concentration of the hydrogen ion calculated from the equation

$$C_{H^+} = K_c \frac{C_A}{C_B}$$

where K_c is the correct value of the dissociation constant of the indicator for the particular electrolyte, electrolyte concentration and medium used.

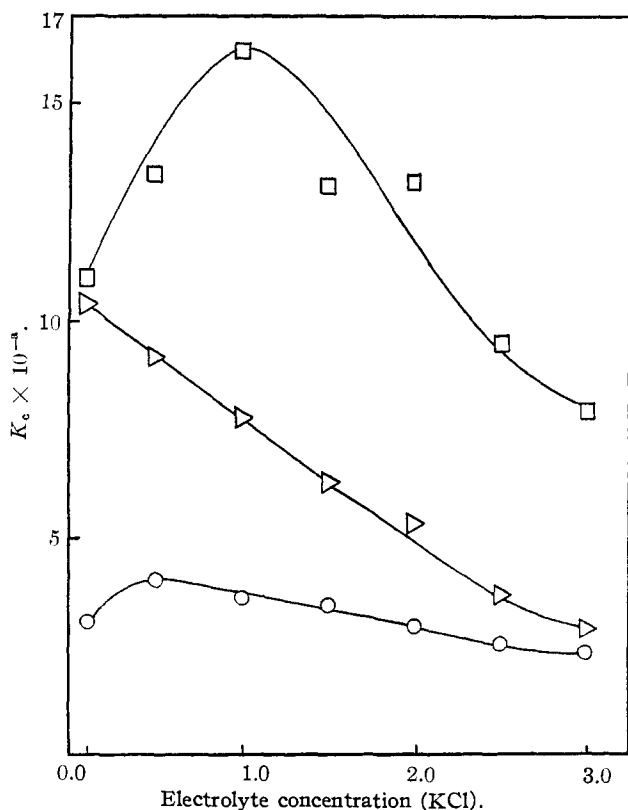


Fig. 1.— K_c for bromcresol green, chlorphenol red and methyl red in potassium chloride solutions: \circ , B.C.G. (scale $\times 10^{-6}$); \square , C.P.R. (scale $\times 10^{-7}$); \triangleright , M.R. (scale $\times 10^{-6}$).

More often the unknown is matched with a standard and the hydrogen-ion concentration calculated by equation (4). In other words the ratio of the values of the dissociation constant of the indicator in the unknown and in the standard must be known. At present these standards are

usually given in Sørensen pH or $p\alpha H$ units, because the electrometric method is considered the standard. The resulting confusion can be avoided in dealing with aqueous solutions by calibrating a suitable set of standard solutions in terms of the hydrogen-ion concentration. A convenient standard is a buffer system: 0.01 molar in a suitable monobasic acid, 0.01 molar in the salt of the same acid and 0.09 molar in potassium chloride. The hydrogen-ion concentration of such buffers can be determined electrometrically, catalytically or colorimetrically, the measurements being referred directly to a solution of strong acid. In order to standardize colorimetrically one would determine the dissociation constants of a less sensitive indicator and then use that indicator to standardize a buffer system of an acid of slightly lower dissociation constant than the indicator. By extending this process to weaker acids the range could be extended.

Table IV gives the values of $K_c/K_{c(0.1)}$ for the three indicators and Fig. 2 presents these ratios graphically. Figure 2 also includes the $K_c/K_{c(0.1)}$ values for the acids used in determining the dissociation constant of the indicators.

TABLE IV
THE $K_c/K_{c(0.1)}$ RATIOS IN POTASSIUM CHLORIDE SOLUTIONS

Electrolyte, KCl + NaX, moles per liter	B. C. G.	C. P. R.	M. R.
0.1	1.00	1.00	1.00
0.5	1.31	1.22	0.89
1.0	1.18	1.48	.75
1.5	1.13	1.20	.61
2.0	0.95	1.20	.51
2.5	.83	0.86	.35
3.0	.78	.72	.28

In order to determine the hydrogen-ion concentration the unknown is matched with the standard at equal indicator concentration and the hydrogen-ion concentration of the standard multiplied by the appropriate value from Table IV. If another concentration of electrolyte is used as standard then we simply multiply the above values by the $K_c/K_{c(\text{standard})}$ ratio. If another electrolyte than potassium chloride is present in the unknown it would be necessary to know the dissociation constant of the indicator in a solution of that electrolyte at the concentration in question. The magnitude of these differences can be seen from a comparison of the dissociation constants of acetic acid in potassium chloride and sodium chloride solutions as taken from Larsson and Adell.¹⁷ The differences up to 0.2 molar are within the experimental error and then increase so that at 3 molar the difference is 12%. Harned and Murphy¹⁸

¹⁷ Larsson and Adell, *Z. physik. Chem.*, [A] **156**, 352 (1931).

¹⁸ Harned and Murphy, *THIS JOURNAL*, **52**, 5079 (1930).

report differences at 0.1 molar concentration. For bromphenol blue Güntelberg and Schiödt give K_c in 3 molar potassium chloride as 11.0×10^{-5} and in 3 molar sodium chloride as 9.4×10^{-5} . For higher valence types the differences would be greater and for accurate work it would be necessary to know the dissociation constant in the medium used. It might be emphasized here that no method of expressing the salt error will avoid these second order effects. The same statement should be made in regard to the effect of non-electrolytes and this part of the solute effect may be more important than is generally realized. In any case it is believed that the above method of expressing salt error in indicator work calls attention to the magnitude of the effect and gives a simple method of correcting for it.

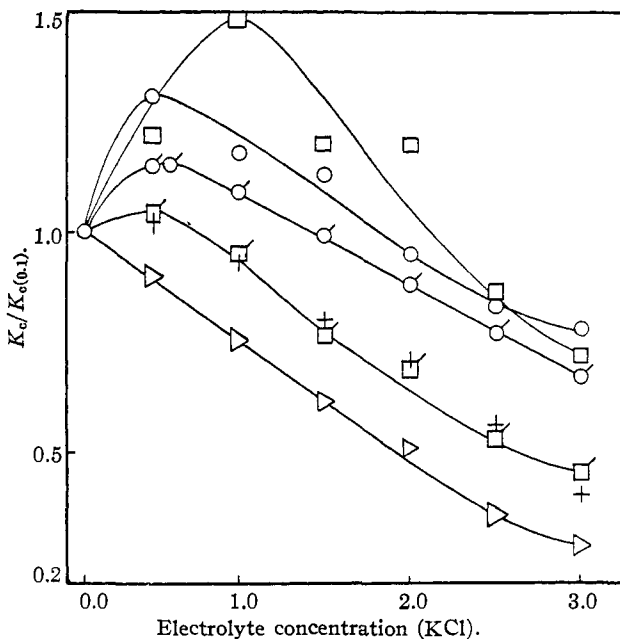


Fig. 2.— $K_c/K_{c(0.1)}$ for B. C. G., C. P. R., M. R., benzoic acid, acetic acid and cacodylic acid in potassium chloride solutions: ○, B. C. G.; □, C. P. R.; ▷, M. R.; ◻, benzoic acid; ◻+, cacodylic acid; +, acetic acid.

Summary

The classical dissociation constants of bromcresol green, chlorphenol red and methyl red in potassium chloride solutions have been determined.

A simple method of expressing salt errors in colorimetric determinations of hydrogen-ion concentration has been given.

PHILADELPHIA, PENNSYLVANIA