ammonia has been studied at the critical temperature of ammonia, but no indication of decomposition has been obtained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE IONIZATION PRODUCTS FROM THE SALTS OF PHENOLPHTHALEIN.

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1. Introduction.

Investigations of the properties of dissolved electrolytes, of mixed valence type, are complicated by the probable presence of intermediate ions. Determinations of the concentrations of such ions have been based upon measurements of properties which are modified by all the substances present. Neither measurements of conductivity, of density, of refractive index, of dispersive power, nor of freezing-point lowering and boiling-point raising, uniquely determin the concentration of any one of the substances present; but when one of these substances is colored, its color does uniquely measure its concentration. It, therefore, seems desirable to carry on an investigation of the concentration of intermediate ions by colorimetric measurements.

Most colored substances which might give intermediate ions in solution are unsuited to such measurements in a simple colorimeter, because two or more of the substances present in solution are colored. Cupric chloride, for example, may give three substances—the unionized cupric chloride, cupric ion, and intermediate ion—each of which has a color of its own. It has been found[1] that phenolphthalein is a dibasic acid whose solutions are colored only when the doubly charged ion is formed. As several methods exist for the determination of the concentration of un-ionized substances in the solution, phenolphthalein is entirely suited to an investigation of the concentration of its intermediate ion.

2. Substances Present in Colored Phenolphthalein Solutions.

In phenolphthalein solution, which has been partially converted to the colored form by the addition of alkali, the un-ionized acid and also its mono- and dibasic ions have been assumed to be present. These may each exist in an equilibrium of tautomeric forms, but as a change in hydrogen ion concentration does not affect these equilibria, all tautomeric modifications may be considered together. The un-ionized acid ($H_2C_{20}H_{12}O_4$) will then be designated by H_2In; the intermediate ion ($HC_{20}H_{12}O_4^-$) by HIn^-, and the divalent ion ($C_{20}H_{12}O_4^{--}$) by In^{--}. Only

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[1] R. Wegscheider, *Z. Electrochem.*, **14**, 510 (1908); L. Rosenstein, THIS JOURNAL, **34**, 1117 (1912).

the last is colored. The concentrations of these substances are related to one another, and to that of hydrogen ion, as follows:

$$H_2In \rightleftarrows H^+ + HIn^-$$

$$K_1 = \frac{(H^+) \times (HIn^-)}{(H_2In)} \qquad (1)$$

$$HIn^- \leftrightarrows H^+ + In^{--}$$

$$K_2 = \frac{(H^+) \times (In^{--})}{(HIn^-)} \qquad (2)$$

And finally,

$$(H_2In) + (HIN^-) + (In^{--}) = C \qquad (3)$$

where C is the total concentration of phenolphthalein.

By combining equations (1), (2) and (3) the following relation between the concentrations of HIn^- and hydrogen ion is obtained:

$$(HIn^-)\left(\frac{(H^+)}{K_1} + 1 + \frac{K_2}{(H^+)}\right) = C. \qquad (4)$$

In order that the concentration of intermediate ion shall be a maximum $((H^+)/K_1 + 1 + K_2/(H^+))$ must be a minimum; and calling this coefficient A,

$$\frac{dA}{d(H^+)} = 0 = \frac{1}{K_1} - \frac{K_2}{(H^+)^2}$$

or

$$(H^+)_m = \sqrt{K_1K_2} \qquad (5)$$

where $(H^+)_m$ is the concentration of hydrogen ion at which the concentration of HIn^- is a maximum.

From equations (4) and (5),

$$(HIn^-)_{\max} = \frac{C}{1 + 2\sqrt{K_2/K_1}} \qquad (6)$$

and by combining equations (1), (2) and (5),

$$(In^{--})_m = (H_2In)_m \qquad (7)$$

where the subscript has the same meaning as in equation (5). This equation states that the concentrations of divalent ion and of un-ionized substance are equal when the concentration of the intermediate ion reaches its maximum value.

The two constants, K_1 and K_2 in these equations have previously been calculated from a single set of experimental data on the *assumption* that they are truly constant; and from these constants the concentration of intermediate ion present in solutions of phenolphthalein of various concentrations of hydrogen ion may be calculated. The value of K_1 has been found[1] to be 11.5×10^{-10}; and of the product[2] K_1K_2, 32.5×10^{-20}. Then, from equation (5)

$$(H^+)_m = \sqrt{32.5 \times 10^{-20}} = 5.71 \times 10^{-10}.$$

And from equation (6),

$$\frac{(HIn^-)_{max}}{C} = \frac{1}{1 + (2 \times 0.497)} = 0.502$$

From equations (7) and (3)

$$\frac{(In^{--})_m}{C} = \frac{(H_2In)_m}{C} = 0.249$$

If the assumptions regarding the constancy of K_1 and K_2 are justified, the concentration of intermediate ion will reach a maximum value of 50.2 per cent. of the total phenolphthalein present when the hydrogen ion concentration is 5.71×10^{-10} mols per liter. The concentration of un-ionized acid and of the colored ion will then be equal, and each 24.9 per cent. of the total phenolphthalein. Independent and more direct determination of the variation of HIn^- concentration with that of hydrogen ion would verify these conclusions only if the original assumptions are correct.

3. Experimental Methods and Results.

A method for the determination of unionized phenolphthalein, in any solution, consists in the measurement of the concentration of phenolphthalein in a benzene phase which is in equilibrium with the solution. Preliminary experiments showed that the distribution ratio of un-ionized phenolphthalein between benzene and water is of such a magnitude as to make its experimental determination practicable; and furthermore, that the products of ionization do not enter the benzene phase. The color of the solution is a measure of the concentration of the doubly-charged ion; the color after complete conversion by the addition of a small excess of alkali is a measure of the total phenolphthalein. The intermediate ion concentration is then obtained by difference (equation 3).

The distribution ratio of phenolphthalein, between Kahlbaum's thiophene free benzene and conductivity water, was determined by shaking mixtures, in various proportions, of benzene and saturated phenolphthalein solution. The phases were separated and the phenolphthalein contained in an aliquot part of the benzene was extracted by shaking with dilute alkali; the extract was diluted to known volume and then compared, in a Stammer colorimeter, with the aqueous phase which had been completely transformed by the addition of dilute alkali. From the instrument readings and the dilution above referred to, the distribution ratio was calculated. The results are given in Table I.

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[1] L. Rosenstein, *loc. cit.*

[2] See note at the end of this article.

TABLE I.—DISTRIBUTION RATIO OF PHENOLPHTHALEIN BETWEEN BENZENE AND WATER.

1. Expt.	2. Cc. aqueous solution.	3. Cc. benzene.	4. Dil. of extract.	5. Instrument readings.	6.	7. Distribution ratio.
				Aqueous.	Extract.	
1	220	33	10 : 150	151.9	133.3	13.14
2	240	8	10 : 150	151.4	132.1	13.09
3	180	72	10 : 150	151.3	131.3	13.02
					Mean	13.08

Columns two and three give the volume of saturated aqueous phenolphthalein solution and of benzene taken; column four gives the ratio of the volume of benzene solution to the volume to which its extract was diluted; columns five and six give the number of millimeters of a standard phenolphthalein solution equivalent in color respectively to 150 millimeters of the aqueous solution and of the diluted extract[1]; column seven gives the ratio of the phenolphthalein concentration in benzene to that in water.

To determin the relative concentrations of the three forms of phenolphthalein (H_2In, HIn^-, and In^{--}), partially transformed solutions were shaken with benzene, the phases were separated, and the relative concentrations of phenolphthalein in them determined as described above. In addition, the fraction of transformed phenolphthalein in the aqueous layer was similarly determined. The results are given in Table II.

TABLE II.—EXPERIMENTAL DATA ON PARTIALLY TRANSFORMED PHENOLPHTHALEIN SOLUTIONS.

Expt.	Cc. sat. aqueous sol.	Cc. water.	Cc. benzene.	Dil. of extract.	Instrument readings.		
					Aqueous solutions.		
					Partially transformed.	Completely transformed.	Extract.
0	225	0	20	10: 100	10.6	148.6	139.2
1	225	0	25	10: 100	27.1	148.6	60.2
2	191	34	25	10: 50	42.4	148.6	82.5
3	158	67	25	10: 50	60.3	148.6	57.2
4	135	90	25	10: 50	83.0	148.6	27.1

Columns two, three and four give the proportions of phenolphthalein solution, water, and benzene taken. In each experiment approximately 1 cc. of sodium carbonate solution (saturated at 20°) was added, and the desired degree of transformation was attained by the addition of normal hydrochloric acid. In this way the concentration of neutral salt in all the solutions was made the same. The significance of column five is the same as that of column four, Table I. Columns six and eight give the number of millimeters of the completely converted aqueous solution, equivalent to 150 mm. of the partially transformed aqueous solution,

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[1] The figures in columns five and six and all other instrument readings to follow are each a mean of eight settings.

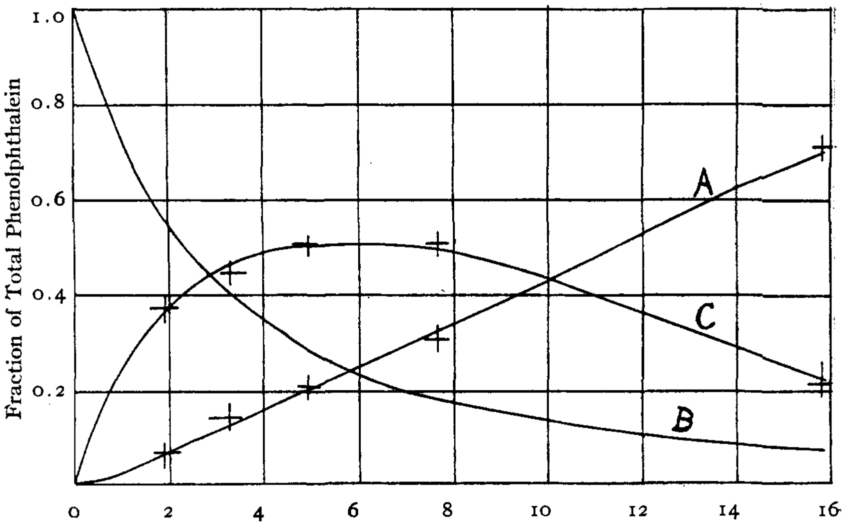
and of the diluted extract, respectively. Column seven is the mean of forty settings of the colorimeter with identical solutions in both tubes, the length of the fixed column being 150 mm.

From the data in Table II were calculated the fractions of the phenolphthalein present in the solutions as H_2In, HIn^-, and In^{--}. These results are given in Table III.

TABLE III.—RELATIVE CONCENTRATIONS OF H_2In, HIn^-, AND In^{--} IN PARTIALLY TRANSFORMED PHENOLPHTHALEIN SOLUTION.

1. Experiment.	2. Fraction H_2In.	3. Fraction HIn^-.	4. Fraction. In^{--}.	5. $(H^+) \times 10^{10}$.
0[1]	0.716	0.213	0.071	15.7
1	0.309	0.509	0.182	7.63
2	0.212	0.503	0.285	4.95
3	0.147	0.448	0.405	3.25
4	0.070	0.372	0.558	1.93

The figures in column two are the fraction of phenolphthalein present as undissociated acid; they were obtained from those in columns five, seven and eight, in Table II, and the mean value of the distribution ratio from Table I. Column four gives the ratio of the figures in columns six and seven of Table II, *i. e.*, the fraction of phenolphthalein present as doubly charged ion. Column three gives the fraction of phenolphthalein present as intermediate ion, and was obtained by difference (see equation



Concentration of Hydrogen Ion × 10^{10}.

Fig. 1.

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[1] A determination was made in a solution of 10.6 × 10^{-10} molal hydrogen ion. The values found were, $(H_2In) = 0.546$; $(HIn^-) = 0.337$; $(In^=) = 0.118$. Some large error was made in this determination, so the results were discarded.

3). Column five gives the concentration of hydrogen ion, calculated from the figures in column four by means of the formula given by Rosenstein[1].

The results of these experiments are shown graphically in Fig. 1. The curves A and B show the variation, with the hydrogen ion concentration, of the un-ionized phenolphthalein and of the colored ion, respectively. The concentration of the doubly charged ion becomes the same as that of the un-ionized substance when the concentration of hydrogen ion is 5.8×10^{-10} mols per l.; and at about this concentration the curve C, which represents the fraction of phenolphthalein present as intermediate ion, reaches a maximum. These facts are in complete accord with the statements contained in equations five and six, and therefore corroborate the assumptions from which these equations are derived.

Summary.

1. The distribution ratio of phenolphthalein between benzene and water has been found colorimetrically to be 13.1, the concentration in benzene being the greater.

2. The fraction of un-ionized phenolphthalein in solutions of different hydrogen ion concentrations was determined by shaking out with benzene; the fraction of doubly charged ion in the same solutions was found from their colors.

3. The sum of the two fractions above mentioned was always much less than unity; the maximum observed difference from unity being 0.509 at a hydrogen ion concentration of 7.63×10^{-10} m. per l. This difference represents the fraction of phenolphthalein present as intermediate ion.

4. By means of the two constants for phenolphthalein previously determined, and by assuming that the divalent ion from phenolphthalein alone is colored, it was shown that in a solution containing a concentration of hydrogen ion of 5.71×10^{-10} mols per l. the concentration of intermediate ion should be a maximum and equal to 50.2 per cent. of the phenolphthalein present, 24.9 per cent. of the phenolphthalein should be present as divalent ion, and 24.9 per cent. as un-ionized phenolphthalein. It has been found graphically that at a concentration of hydrogen ion of 5.8×10^{-10} mols per l. the concentration of intermediate ion is a maximum and equal to 50.5 per cent. of the phenolphthalein present.

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NOTES.

A Simple Form of Absorption Bulb.—The many forms of bulbs that have been devised for the absorption of certain constituents from gaseous mixtures are so constructed as to leave considerable air space above the surface of the absorbent. To displace thoroughly all of the sample of

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[1] *Loc. cit.*