

it depends upon the properties of the membrane as well as of the solution. The Soret effect, or thermal diffusion, in perfect solutions is considered to be entirely the result of irreversible processes and not to represent a thermodynamic equilibrium. In imperfect solutions it consists in part of a reversible effect, equations for which are derived. The compositions of solutions at different temperatures connected with each other through a vapor phase are discussed as examples of heterogeneous non-isothermal equilibria. The equations of the thermocouple are deduced. The precise significance of the quantities in the thermo-electric equations is stated, and the way in which the reversible and irreversible Soret effects may be expected to influence the phenomena is indicated. Non-electric thermocouples furnishing interesting analogies to the electric, are considered. Finally, certain thermocells, consisting of similar electrodes at different temperatures, are discussed.

BERKELEY, CALIFORNIA

---

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF WASHINGTON AND LEE UNIVERSITY]

## FLUOREMETRY. II.<sup>1</sup> THE RELATION BETWEEN FLUORESCENCE AND HYDROGEN-ION CONCENTRATION<sup>2</sup>

BY L. J. DESHA, R. E. SHERRILL AND L. M. HARRISON

RECEIVED JANUARY 7, 1926

PUBLISHED JUNE 5, 1926

While chemical literature abounds with references to the fact that acid or alkali must be added in order to develop maximum fluorescence in solutions of many different substances,<sup>3</sup> little or no attention seems to have been paid to the optimum hydrogen-ion concentration.<sup>4</sup> Having observed that for certain substances there appeared to be a characteristic and rather narrow range of hydrogen-ion concentration within which the change in intensity of fluorescence is most marked, this effect has been investigated with the results here reported.

Comparisons of the relative intensities of fluorescence were made by the method previously described by one of us,<sup>1</sup> which should be consulted for details.<sup>5</sup> Aqueous solutions of colorless substances were uniformly

<sup>1</sup> Desha, *THIS JOURNAL*, **42**, 1350 (1920).

<sup>2</sup> Presented in substance before the Organic Section of the American Chemical Society at the Baltimore Meeting, April 10, 1925.

<sup>3</sup> Among others: (a) Lepine, *Ann. Phys.*, [IX] **4**, 208 (1915). (b) Kauffmann, *Ann.*, **344**, 30 (1906). (c) Winther, *Z. Elektrochem.*, **19**, 389 (1913). (d) Stark and Lipp, *Z. physik. Chem.*, **86**, 36 (1913). (e) Nichols and Merritt, "Studies in Luminescence," Publication No. 152, Carnegie Institution of Washington, 1912.

<sup>4</sup> Aside from the articles of Ley and his co-workers (Ref. 17) the closest approach to a quantitative statement we have been able to find is that of Mecklenburg and Valentiner [*Physik. Z.*, **15**, 267 (1914); *C. A.*, **8**, 1695 (1914)].

<sup>5</sup> In order to avoid a misunderstanding as to the nature of the measurements re-

employed in order to avoid comparisons of emitted light of different colors such as arises from varying the solvent<sup>6</sup> or differences in the depth of layers of colored substances.<sup>3c</sup> Preliminary tests having shown that nothing approaching reproducible results could be expected from un-buffered solutions<sup>7</sup> all of the measurements reported (except for the higher concentrations of acid and alkali) were made upon solutions buffered in the usual way<sup>8</sup> and checked by the hydrogen electrode.

**Specific Action of Chloride Ions.**—It was a matter of some surprise as well as interest to find that the inhibition of fluorescence by chloride ions, already commented upon<sup>1</sup> and previously reported by Stokes<sup>9</sup> and Buckingham<sup>10</sup> in connection with solutions of quinine, applies also to solutions of the sulfonic acids studied. The effect is so marked that it was necessary to omit potassium chloride from the borate-sodium hydroxide buffers used in the region  $P_H$  8–10. This curious effect of halogen ions remains unexplained.

### Fluorescence of Solutions of Naphthol-sulfonic Acids

Among the numerous substances examined in a qualitative way, the naphthol-sulfonic acids were found to be particularly well suited to investigation on account of the brilliancy of the fluorescence and the marked effect of alkali. The following were carefully compared, with the results shown.

ported it should be emphasized that in this method of comparison (a) the only exciting rays concerned are those in the near ultraviolet emitted by the mercury lamp and transmitted by the window used to eliminate visible radiation; (b) the only fluorescent emission taken into consideration is that in the visible region; (c) the intensity measured is that of the entire visible emission and not that of any single portion.

The deviation from the simple inverse proportionality relation, which becomes more marked the farther the concentrations of the solutions compared differ from each other, has been previously discussed. (Ref. 1, pp. 1359–1362.)

<sup>6</sup> Among others, Lepine, Ref. 3 a.

<sup>7</sup> It was desired, if possible, to avoid the use of buffered solutions on account of the opportunity which they afford for "salt errors" such as are shown to exist when the salt content is widely varied; but with the exception of the specific action of halide ions already noted, we encountered no differences from this source which are comparable to the effects of varying hydrogen-ion concentration.

<sup>8</sup> The buffer solutions used were, in general, chosen from those listed by Clark, (a) "The Determination of Hydrogen Ions," 1920, Chap. V. With the sulfonic acids,  $K_2HPO_4$ -NaOH solutions were used from  $P_H$  5.8 to 7.6 and  $H_3BO_3$ -NaOH (without *KCl*) at  $P_H$  8–10. Those designated  $P_H$  12 and 13 were not exactly of these values but were 0.01 and 0.1 *N* as to sodium hydroxide.

For the quinine solutions, Walpole's acetate buffers were used at  $P_H$  5.6–3.6 and phthalate-nitric acid solutions at 3.6–2.2. Higher acidities were obtained by the proper dilutions of sulfuric acid, checked by the hydrogen electrode.

<sup>9</sup> Stokes, *J. Chem. Soc.*, **22**, 174 (1869).

<sup>10</sup> Buckingham, *Z. physik. Chem.*, **14**, 129 (1894).

(A) SODIUM 1-NAPHTHOL-4-SULFONATE <sup>11</sup>								
$P_H$ .....	1.0	5.8	7.0	7.6	8.0	8.6	9.6	13.0
Intensity (% of max.).....	1.0	3.7	12.7	28.0	38.2	74.5	93.1	100.0
(B) 2-NAPHTHOL-3,6-DISULFONIC ACID <sup>12</sup>								
$P_H$ .....	1.0	7.0	8.00	8.6	9.6	10.0	12.0	13.0
Intensity (% of max.).....	0.97	3.15	5.35	13.4	58.6	76.5	100.0	100.0
(C) SODIUM 1-NAPHTHOL-2-SULFONATE <sup>13</sup>								
$P_H$ .....	5.8	7.0	7.6	8.6	9.6	12.0	13.0	
Intensity (% of max.).....	2.55	5.6	9.14	17.6	59.8	95.0	100.0	

**Interpretation.**—The relative intensities were at first calculated in terms of some convenient one of the buffered solutions and the intensity plotted against the Sørensen ( $P_H$ ) values. The general form of the curves thus obtained, with very sharp inclination between 2 units of Sørensen values, was so strikingly similar to the dissociation curves of weak electrolytes that a method for more accurate comparison was sought. To this end the observed relative intensities were recalculated to their fractional parts of the maximum intensity observed in each case. They are here reported in this form and in Figs. 1 and 2 are indicated by the open circles from which the curves are plotted.

If the underlying cause of the change in intensity of fluorescence is ionization, or some intramolecular rearrangement dependent thereon, as in the color change of an indicator, the approximate dissociation constant of the substance should be equal to the hydrogen-ion concentration at which 50% intensity is attained. In Fig. 1, the curve crosses the 50% ordinate at  $P_H$  8.2 and, in Fig. 2, at  $P_H$  9.5 (corresponding to hydrogen-ion concentrations of  $6.3 \times 10^{-9}$  and  $3.2 \times 10^{-10}$ , respectively). Using these values in the formula  $(H^+)[x/(1-x)] = K_a$ , or  $P_H = PK_a + \log [x/(1-x)]$ , the values at which 1 to 99% dissociation should occur were calculated and are plotted as the blackened circles in Figs. 1 and 2.

The agreement between the observed intensities and the calculated dissociation from 20 to 80% appears to be too close to be entirely accidental, and suggests strongly that ionization plays an important, if as yet unde-

<sup>11</sup> The substance used was Eastman preparation No. 232, the solutions compared being  $M \times 10^{-5}$  with respect to it (based on a molecular weight of 246.1).

In preparing solutions for comparison, a typical procedure was to dissolve one millimole of the substance in 100 cc. of water, dilute 10 cc. of this to one liter and add 1.00 of the resulting solution to 9 cc. of buffer solution, previously made up to only  $9/10$  the standard volume. In order to avoid the effects of decomposition in solution (which, for example, in the case of 0.01  $M$  solution of sodium 1-Naphthol-4-sulfonate was found to be about 1% in a day and for other solutions considerably greater) solutions were used for a few hours only after their preparation from the solids.

<sup>12</sup> A preparation, probably of German origin, obtained from the Palo Co. Used in  $M \times 10^{-5}$  concentration (mol. wt., 304.2).

<sup>13</sup> Eastman preparation No. 966, used in  $M \times 10^{-5}$  solutions (mol. wt., 246.1).

finer, part in the fluorescence of these substances. The greater divergence near the extremes of the curves may be due in part at least to the greater inaccuracy in comparisons in the regions of very high and very low intensities.<sup>14</sup> In the absence of independently determined dissociation constants for the substances in question it would be idle to speculate upon the possible nature of the tautomeric change, if any, or as to whether it is the ionization of the sulfonic acid or hydroxyl group which is involved,

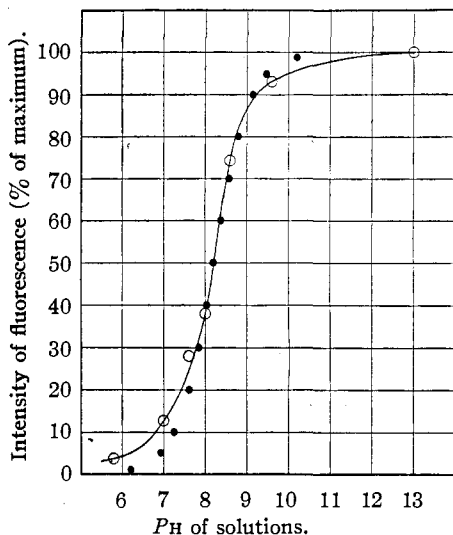


Fig. 1.—Fluorescence of solutions of sodium-1-naphthol-4-sulfonate.

The curve, plotted from the observations indicated by the open circles, shows the relative intensity of fluorescence at various PH values in terms of the maximum observed. The blackened circles indicate the percentage dissociation of an electrolyte of  $K_a = 6.3 \times 10^{-9}$  at the Sørensen values shown.

with sodium hydroxide, the beaker being exposed to ultraviolet radiation. Results were obtained which agreed among themselves as closely as when the same two solutions were titrated in the usual way, using phenolphthalein as indicator. The average value of 1.00 cc. of the acid, in terms of alkali, was 1.028 with phenolphthalein and 1.020 with the fluorescent indicator—a result which might be anticipated from the fact that the half-change of phenolphthalein<sup>15</sup> occurs at PH 9.7 instead of 8.2 as here established for the point of 50% fluorescence. Similar titrations were found possible in the presence of blue coloring matters but are obviously interfered with by yellows and browns which absorb the emitted blue fluorescent light.

<sup>14</sup> Errors of this nature were avoided so far as possible by comparing with each other only those solutions showing similar intensities.

<sup>15</sup> Clark, Ref. 8 a, 1923, p. 133, quoted from Michaelis and Gyemant.

though one would be inclined to suspect the latter. It is hoped, however, to apply the method to some cases where dissociation constants have been or can be independently established.

The difference between isomers is brought out in a comparison of the fluorescence of the 1-naphthol-4-sulfonate and -2-sulfonate. With the former, as shown in Fig. 1, 50% intensity is attained at PH 8.2 while a similar curve drawn for the latter gives 50% intensity at about PH 9.4. In addition it should be mentioned that the maximum intensity of the former is about three times that of an equal concentration of the latter.

The sharpness with which the brilliant fluorescence of these compounds appears when the appropriate Sørensen value is reached may be illustrated by the fact that we have used 1 cc. of a 0.01 M solution of sodium 1-naphthol-4-sulfonate as an indicator in carrying on a dark room titration of sulfuric acid

From the physical standpoint, the immediate cause of the observed increase in fluorescence may be ascribed either (a) to an exaltation of the faint visible fluorescence barely detectable in acid solutions, or (b) to the shifting toward the red, into the visible region, of emission bands which may appear in the ultraviolet even in acid solution. A decision between these two possibilities would be of interest and importance but in the absence of a spectrophotometer the authors are not prepared to make such an investigation.<sup>16</sup> Judging from the results of Ley and Engelhardt<sup>17</sup> either or both may occur in accordance with no rule as yet formulated.

### Fluorescence of Resorcinol and Hydroquinol Disulfonates

These substances were investigated, in the form of their potassium salts, partly because they are examples of compounds containing only the benzene nucleus which exhibit visible fluorescence but chiefly on account of the controversy between Kauffmann<sup>18</sup> and Hantzsch<sup>19</sup> as to whether they fluoresce at all under certain conditions. The potassium salts were prepared according to the directions given by Hantzsch.<sup>20</sup> Both preparations were found to exhibit marked fluorescence in alkaline solutions although the absolute intensity is so much less than that of the naphthol-sulfonic acids (of the order of 1/100 to 1/200 at the maxima) that it was found neces-

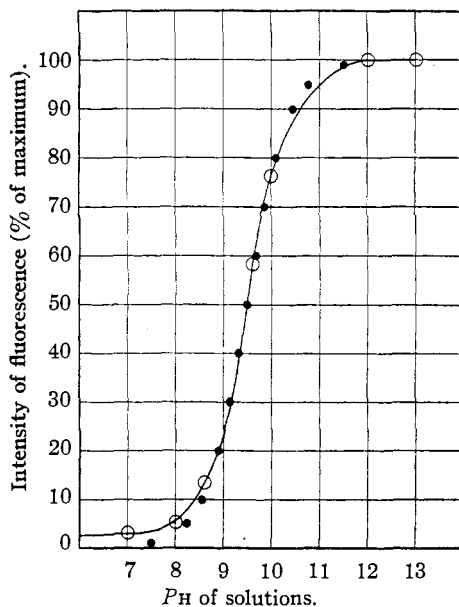


Fig. 2.—Fluorescence of solutions of 2-naphthol 3,6-disulfonic acid.

The curve, plotted from the observations indicated by the open circles, shows the relative intensity of fluorescence at various  $P_H$  values in terms of the maximum observed. The blackened circles indicate the percentage dissociation of an electrolyte of  $K_a = 3.2 \times 10^{-10}$  at the Sørensen values shown.

<sup>16</sup> If anyone, so equipped, is interested in such a study, we would be glad to turn over this phase of the work with certain suggestions as to procedure.

<sup>17</sup> Ley and Engelhardt, *Z. physik. Chem.*, **74**, 1 (1910). See also *Ber.*, **41**, 2509–16 (1908). Ley and Grafe, *Chem. Zentr.*, **1910**, II, 161. Ley, "Die Beziehungen zwischen Farbe und Konstitution bei organischen Verbindungen," Leipzig, 1911.

<sup>18</sup> Kauffmann, (a) *Ber.*, **40**, 838, (b) *Ber.*, 2338, (c) 4547 (1907); (d) **41**, 4422 (1908).

<sup>19</sup> Hantzsch, (a) *Ber.*, **40**, 1572, (b) 3536 (1907); (c) **41**, 1214 (1908).

<sup>20</sup> Ref. 19 b, p. 3537.

sary to use them in  $M \times 10^{-3}$  solutions.<sup>21</sup> The following results were obtained with the hydroquinone compound.

$P_H$ .....	1	7	8.6	9.6	10	12
Intensity.....	1	6	10.3	48.9	123	100
						66

**Rapid Deterioration.**—No difficulty in making comparisons was experienced in solution of  $P_H$  10 or under but in 0.01 *N* sodium hydroxide solution it became at once apparent that a rapid diminution of the fluorescence was taking place between readings, accompanied by a change in the color of the fluorescent light from purplish to blue. Due to this fact (presumably the result of an oxidation of the substance) the Sørensen value of maximum fluorescence could not be determined and no “dissociation” curve is possible.

As the above values indicate, there is a low but appreciable fluorescence on the acid side of neutrality, of an order which might or might not be observed, depending upon the concentration of the substance and the refinement of the method of observation. With a substance as sensitive to alkali as this, experiments in “conductivity water” can have little meaning in view of the almost certain hydrolysis of the salt—even if the absence of free alkali in the product may be assumed. It seems likely that the different results of the two workers referred to may be traced, in part at least, to failure to control the hydrogen-ion concentration and in part to differences in sensitiveness in their methods of observation. The changes in the solutions of the resorcinol salt were of the same character and order of intensity but the fluorescent light is greenish rather than blue.

### Fluorescence of Quinine Solutions

Comparisons were made in buffer solutions containing the alkaloid in a concentration of  $3 M \times 10^{-6}$  (1.134 mg. per liter). The relative intensities of the emitted light, in arbitrary units, are given in the following table and plotted against the corresponding Sørensen values in Fig. 3.

$P_H$ .....	5.6	5.4	5.2	5.0	4.8	4.6	4.4	4.2
Int.....	1.5	2.0	2.5	3.7	4.9	6.2	10.2	16.1
$P_H$ .....	4.0	3.8	3.6	3.4	3.2	3.0	2.8	2.6
Int.....	21.0	32.6	42.5	48.8	54.2	61.1	66.0	72.5
$P_H$ .....	2.4	2.2	1.8	1.22	0.85	0.45		
Int.....	77.5	86.1	97.8	103.2	104.2	107.3		

The slope of the curve at the highest acidity shown indicated that the maximum intensity had not been attained and this was confirmed by the

<sup>21</sup> In comparing the pronounced rise in the intensity of fluorescence of this substance between  $P_H$  8.6 and  $P_H$  10 with the similar values for the naphthol-sulfonic acids it should be recalled that the concentrations of the latter are only  $M \times 10^{-5}$ .

preparation and comparison of solutions, containing quinine in the same concentration as above, in sulfuric acid up to approximately 10 *N*, with results as follows.

H <sub>2</sub> SO <sub>4</sub> , <i>N</i> .....	0.798 ( <i>P<sub>H</sub></i> 0.45)	1.387	4.882	9.963
Intensity.....	107.3	112.5	118.1	126.2

Even at these concentrations of acid it is apparent that no well-defined maximum has been attained and it would appear that we are dealing with some influence other than that of the hydrogen-ion concentration. In the absence of such a maximum it is impossible to plot a curve in the manner used in the other cases but inspection of the experimental curve indicates that it could not conform to that for a simple binary electrolyte.

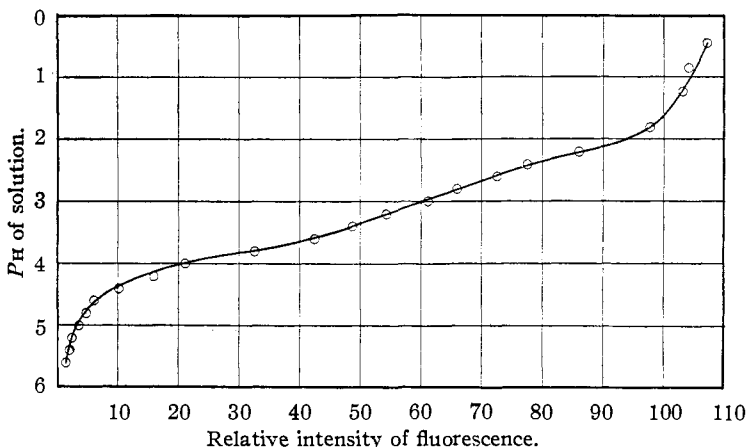


Fig. 3.—Fluorescence of solutions of quinine.

The circles show the experimentally determined relative intensities of fluorescence at the *P<sub>H</sub>* values indicated. The standard for calculation is the intensity at *P<sub>H</sub>* 5.4 taken as 2.

From *P<sub>H</sub>* 5.6 to *P<sub>H</sub>* 3.8 the form is about that which would be expected in such a case, but at higher acidities, the slope is eccentric. As these measurements were made and checked with particular care and agree well among themselves, it seems unlikely that the reported values are seriously affected by experimental errors. The phthalate buffers used in this region can hardly be responsible since the phthalate and acetate buffers of value *P<sub>H</sub>* 3.6 were directly compared and differed in intensity of fluorescence by not more than 0.4%.

It is rather more likely that there is a real reason for the unusual shape of the curve and this reason may be connected with the fact that quinine is a di-acid base. In this connection it should be recalled that Buckingham<sup>10</sup> reached the conclusion that it is the univalent quinine ion which is responsible for the fluorescence of solutions of this substance though, on account

of the totally different experimental conditions, no direct comparisons can be drawn between his work and that now reported.

**Salt Effect.**—Another similarity between change in intensity of fluorescence and the color change of indicators is found in the influence of added neutral salts. In order to determine and demonstrate this effect, solutions of equal quinine content ( $3 M \times 10^{-6}$ ) and equal Sørensen values ( $P_H = 1.31$ , as determined by the hydrogen electrode) containing various proportions of sulfuric acid and sodium sulfate were compared, with the following results: normality in total sulfate, 0.2, 0.4, 1.4; intensity of fluorescence, 100, 94.5, 82.0.

The authors are indebted to a grant from the Warren Fund of the American Academy of Arts and Sciences for the purchase of apparatus for the work here reported and further work along these lines now under way.

### Summary

1. A study has been made of the effect of varying the hydrogen-ion concentration upon the intensity of the fluorescence of certain sulfonic acids and of quinine.

2. For each substance studied there is a characteristic range of 0.2 Sørensen ( $P_H$ ) units within which about 75% of the total change in intensity occurs.

3. The curves obtained show such close agreement with the theoretical dissociation curves of weak electrolytes as to suggest strongly a causal relationship between dissociation and fluorescence.

4. The intensity of fluorescence is affected by the total salt content of the solutions even at equal hydrogen-ion concentrations.

5. Chloride ions inhibit the fluorescence of the sulfonic acids studied as well as that of quinine.

LEXINGTON, VIRGINIA

---

[CONTRIBUTION FROM THE VENABLE HALL OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

## BASIC COPPER SULFATE AT 100°<sup>1</sup>

BY JAMES M. BELL AND GEORGE M. MURPHY<sup>2</sup>

RECEIVED JANUARY 21, 1926

PUBLISHED JUNE 5, 1926

**Introduction.**—Several investigations have been made to determine the formulas of the basic sulfates of copper. It seems probable that in

<sup>1</sup> Since this paper was prepared the December number of the Journal of the Chemical Society has come to our notice. In that JOURNAL, Britton [*J. Chem. Soc.*, **127**, 2796 (1925)] who has made a phase rule study of the basic sulfates of copper at 25°, has also found only one basic sulfate, the formula of which agrees with that obtained by us at 100°.

<sup>2</sup> This paper is constructed from a thesis presented by G. M. Murphy to the Graduate School of the University of North Carolina in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry, June, 1925.