

versal of the current provides an important check on the experiment that was not made by Janssen. As was shown in the work on concentration boundaries<sup>5</sup> it should also be noted that electroosmotic streaming is not negligible, even in the Tiselius cell, at the lower salt concentrations studied by Janssen. The existence of the new electrokinetic effect postulated by him still remains, therefore, to be demonstrated.

**Acknowledgments.**—The author is indebted to Dr. D. A. MacInnes of these Laboratories for his sustaining interest in this research and for valuable criticism of the manuscript.

### Conclusion

A moving boundary method is described for the determination of non-electrolyte transport in solutions of electrolytes through which current is passing. Although measuring the same property of the solution as the gravimetric procedures previously available it has several advantages. No analyses are required and, since the non-electro-

lyte is not present at the electrodes, it does not have to be stable against electrochemical decomposition. Consequently a variety of non-electrolytes may be studied. As sensitive criteria for the validity of a result are the requirements that the boundary displacement per faraday be independent of the direction and magnitude of the current and that the spreading of a boundary with time does not differ appreciably from that due to diffusion alone. The time and effort involved in an experiment is but a fraction of that required by the gravimetric procedure.

Since the boundary displacement per faraday varies with the nature of the added non-electrolyte it is now clear that the early interpretation is incorrect. It is to be hoped, however, that with the aid of a more elaborate theory the results may yield information as to the composition of the mixed solvent in the immediate neighborhood of an ion in terms of the bulk composition and the electrical properties of the components.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

## The Measurement of Vapor Pressures of Aqueous Solutions by Bi-thermal Equilibration Through the Vapor Phase

BY R. H. STOKES<sup>1</sup>

### Introduction

The isopiestic method<sup>1a</sup> of determining the vapor pressures of aqueous solutions, though it has proved easily the most practical of the various techniques available, has been hampered from the first by uncertainties about the vapor pressures of the reference solution. Most of the isopiestic measurements have been made against potassium chloride or sodium chloride, so that they are limited to the region of water activities greater than 0.75. Robinson<sup>2</sup> has recently surveyed the existing measurements for these two salts at 25°, and correlated them with many others by means of isopiestic measurements. As a result a reasonably reliable set of standard data is now available. For more concentrated solutions, however, the position has been far from satisfactory. Hitherto we have generally used sulfuric acid as the reference substance, as it is obtainable in good purity and can be readily analyzed. Unfortunately however it is not easy to select a "best" set of vapor pressure data for its concentrated solutions at 25°. The most recent measurements are those of Shankman and Gordon<sup>3</sup> by the static method.

They pointed out serious discrepancies between their results and those derived from e.m.f. measurements by Harned and Hamer.<sup>4</sup> Recent calculations<sup>5</sup> show that these e.m.f. measurements, made on two different types of cell, with different cell reactions, show a remarkable degree of internal self-consistency in regard to both the water activities and the partial molal heat contents of the water. This makes the choice between them and the direct vapor pressure measurements more difficult. Attempts to check the vapor pressure of sulfuric acid by isopiestic measurements against other solutions have not been helpful; thus the isopiestic ratios of sulfuric acid to sodium hydroxide<sup>6</sup> show that the water activities calculated by Åkerlöf and Kegeles<sup>7</sup> from their e.m.f. measurements on sodium hydroxide are not consistent with either of the above sets of data for sulfuric acid. Gibson and Adams<sup>8</sup> using the same design of apparatus as was later used by Shankman and Gordon, measured the vapor pressures of lithium chloride solutions at 20.28°. Robinson<sup>9</sup> has measured the isopiestic ratios of sulfuric acid to lithium chloride at this temperature, from which he obtains values for sulfuric acid by taking the

(1) Present address: Chemistry Department, University of Western Australia, Nedlands, W. A.

(1a) R. A. Robinson and D. A. Sinclair, *THIS JOURNAL*, **56**, 1830 (1934).

(2) R. A. Robinson, *Trans. Roy. Soc. N. Z.*, **75** (II), 203 (1945).

(3) S. Shankman and A. R. Gordon, *THIS JOURNAL*, **61**, 2370 (1939).

(4) H. S. Harned and W. J. Hamer, *ibid.*, **57**, 27 (1935).

(5) R. H. Stokes, *ibid.*, **67**, 1686 (1945).

(6) R. H. Stokes, *ibid.*, **67**, 1689 (1945).

(7) G. Åkerlöf and G. Kegeles, *ibid.*, **62**, 620 (1940).

(8) R. E. Gibson and L. H. Adams, *ibid.*, **55**, 2679 (1933).

(9) R. A. Robinson, private communication, 1945.

data of Gibson and Adams as standard; upon correcting to 25° he finds that the results do not agree satisfactorily with those of either Shankman and Gordon or Harned and Hamer.

The need for new measurements on concentrated solutions is evident: the present work was undertaken in the hope of reducing the confusion and making possible a definite choice of one or other set of data. The vapor pressures of a number of concentrated solutions have been measured by a new independent method, and the results compared with existing data.

### Experimental

The method consists in principle of establishing a steady state by distillation between the solution at 25° and pure water at a known lower temperature  $t_1$ . When the steady state is attained, the pressures on the two sides must be equal. Let  $p_1$  be the known vapor pressure of pure water at  $t_1$ . Then the vapor pressure of the solution at 25° is also  $p_1$ . Let the vapor pressure of pure water at 25° be  $p_2$  (23.756 mm.). Then the water activity of the solution at 25° is  $a_w = p_1/p_2$ . The dew-point method, which is little used outside hygrometry, involves the same measurements, but the fact that the vapor surrounding the polished thimble is not in thermal equilibrium with the condensed moisture makes this method unsuited to exact work. The possibilities of the present method were recognized by Weir,<sup>10</sup> whose results however are not of the accuracy required here.

To obtain results significant in the fourth decimal place of the water activity requires that the temperatures of the solution and the water be closely controlled and accurately measured. The measurement of the temperature difference is more important than that of the absolute temperatures, as may readily be shown from tables of the vapor pressure of water; an accuracy of 0.002° in the temperature difference is a reasonable aim while for the absolute temperatures 0.03° would be sufficient.

The equilibration vessel is shown in Fig. 1.

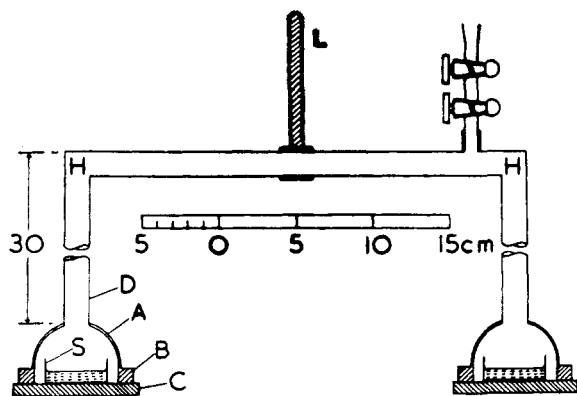


Fig. 1. The equilibration vessel.

The rims of the copper domes A were soldered to brass rings B, the lower faces of which were turned and lapped to fit the flat copper plates C. The resulting "bells" were connected by the thin-walled copper tube D, so that each leg could be placed in a separate thermostat. The horizontal portion H-H of the tube carried a side-tube for evacuation and a lever L by means of which the apparatus could be rocked about H-H as axis, in bearings attached to the walls of the thermostats. The whole interior of the equilibration vessel, and the copper plates, were heavily silver-plated.

The thermostats were 60 cm. long, 60 cm. deep and 30 cm. wide; they were lagged with insulating board and extremely vigorously stirred. The thermoregulators have been described elsewhere<sup>11</sup>; they were capable of controlling the temperature to  $\pm 0.001^\circ$  provided that the mercury surfaces were regularly cleaned. In order to prevent condensation in the tube H-H it was necessary to keep the colder thermostat (containing the water side of the equilibration vessel) below the room temperature. The necessary cooling was obtained by admitting near the stirrer a flow of water from a refrigerated storage tank, the surplus being pumped back to the tank. For temperatures down to 15° it was possible to substitute tap-water for the refrigerated supply. The rate of admission of cold water was adjusted so as to hold the temperature just above that required; the regulator then operated an electromagnetic valve which slightly increased the flow. It was not found practical to work at temperatures below 6° owing to the large volume of cold water which had to be circulated.

The temperatures were measured by means of solid-stem thermometers divided in hundredths of a degree, having ranges of 0-6, 9-21, 14-25, 15-21 and 20-26°. Shortly after the completion of the work these were calibrated at each degree by the National Standards Laboratory of Australia, under the conditions of total immersion in which they were used, with an accuracy of at least  $\pm 0.004^\circ$ . As an aid to interpolation between the points at which the calibration was made, and also to provide a quick means for routine checking of the temperature difference, a 100-junction copper-constantan thermo-element was built into the thermostats, with the "hot" junctions in the 25° bath and the "cold" ones in the other. Shielded cables carried its e.m.f. to a Leeds and Northrup K-2 potentiometer. Since the e.m.f. was more than 4 mv. per degree, readings to 0.01 mv. were as accurate as the thermometer calibration justified, though readings to 0.005 mv. could be obtained. The thermo-element was made in 10 sections, each comprising 10 junctions mounted in a glass tube passing through rubber stoppers in the thermostat walls. Free circulation of water among the tubes thus en-

(10) A. R. Weir, *Coll. Czech. Chem. Comm.*, **8**, 149 (1936).

(11) R. H. Stokes, *New Zealand J. Sci. Tech.*, **27B**, 75 (1945).

sured a rapid transfer of heat to all the couples. The instrument was calibrated *in situ* against the thermometers, one bath being held at 25° while the other was set close to each round degree and held till the e.m.f. was constant. The absence of stray e.m.f.'s was checked by the fact that zero e.m.f. was observed when both baths were at the same temperature; electrical earthing of the tanks and cable sheaths was necessary to ensure this.

The temperature difference,  $\Delta T$ , was found to be related to the thermocouple e.m.f.,  $E$ , by the quadratic

$$\Delta T = 0.2350E + 0.0000690E^2$$

with deviations of the order of the precision of the thermometer calibrations, averaging  $\pm 0.0035^\circ$ . This equation was used in calculating the water activities, taking the values for the vapor pressure of water given in the "International Critical Tables."<sup>12</sup> These are based on work done at the Physikalisch Technische Reichsanstalt about 1909; in 1934 Osborne and Meyers<sup>13</sup> made a critical survey of existing data and published a table giving values for  $p_t/p_{25}$  which do not differ by more than 0.0001 from the I.C.T. values, in the range 0–25°. Examination of their graphs suggests that the vapor pressures should be reliable to at least 0.005 mm., or say 0.0002 in the water activity for present purposes.

The method for setting up for a run was as follows: On one of the plates C was placed a flat-bottomed silver dish containing the solution; on the other, a similar dish of pure water. The bells were then sealed on with stopcock grease, and the system roughly evacuated for about an hour. No water-trap was used at this stage as it caused too great a loss of water. Then a final evacuation was given for about ten minutes with a Hyvac pump guarded by a phosphorus pentoxide tube; this stage required careful judgment, as if it was carried too far the system might be pumped dry. When the pressure gage had indicated 4 to 5 mm. (the vapor pressure of ice) for a few minutes, the taps were closed and the equilibration vessel was removed to the thermostats. Though twenty-four hours' rocking was found to be just sufficient, thirty-six to forty-eight hours was usually given. The rate of rocking was about 10 swings per minute, through an arc of 45°. The temperatures and e.m.f. readings were checked regularly during the run, particularly during the last eight hours. A thermometer was also placed near the exposed horizontal portion H–H of the connecting tube, and the room temperature adjusted to keep its readings well above that of the colder thermostat. At the end of the run some air was admitted to suppress distillation; the apparatus was removed and quickly opened, and the solution

poured off into a tared weighing bottle. This was done within thirty seconds of removal from the thermostat, and the loss or gain of water during this time was found not to exceed 1 mg.; as the weight of solution was about 5 g. this could be neglected. The concentration of the equilibrium solution was then determined by analysis of the weighed portion.

Some of the objections which may be raised to the method described above are: (1) The temperatures of the contents of the bells might not be exactly those of the thermostats, owing to heat conduction through the vapor and the connecting tube. In order to check this, the depth of immersion of the bells was doubled by lengthening the vertical portions of the tube. The equilibrium concentration for a given temperature difference was unchanged, within the limits of reproducibility. (2) If any gas besides water vapor were present, there might be a thermal diffusion effect which would enable the partial pressure of water on the two sides to remain different at equilibrium. Ibbs<sup>14</sup> found that for a mixture of 88.6% nitrogen with 11.4% carbon dioxide, the thermal diffusion effect gave rise to approximately 0.5% separation for the case  $\log T_1/T_2 = 0.3$ . In the present case the maximum value of  $\log T_1/T_2$  is about 0.03; and furthermore the separation factor would almost certainly be much smaller for the case of water vapor containing only traces of air, so that this effect is scarcely likely to cause an error exceeding one or two units in the fourth decimal place of the water activity. (3) The system as a whole is not in thermal equilibrium. There is, however, thermal equilibrium in each side considered separately, and the temperature gradient through the vapor occurs in a region remote from the liquid phases and cannot therefore interfere. (4) There is some difficulty in knowing (how long) the length of time which should be allowed for the establishment of equilibrium. This seems to depend on the degree of freedom from foreign gases attained during the evacuation. Clearly if water vapor only were present, the rate of distillation would depend only on the rate of heat transfer to and from the liquids, as a bodily movement of vapor would occur. In the presence of other gases, however, such a bodily movement of vapor would set up a higher concentration of these gases on the condensation side of the system and distillation would stop until the slower process of diffusion re-established a uniform composition in the vapor phase. Owing to the greater length of the vapor path, this defect is more marked than in the isopiestic method and caused a number of failures, of which a fairly reliable symptom was the absence, on opening the apparatus, of droplets of condensed water on the *outside* of the water dish.

Measurements were made on several substances, the results being given in Table I.

(12) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 211.

(13) N. S. Osborne and C. H. Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

(14) T. L. Ibbs, *Proc. Roy. Soc. (London)*, **107A**, 470 (1925).

TABLE I  
 EXPERIMENTAL RESULTS

<i>m</i>	<i>E</i> (mv.)	<i>a<sub>w</sub></i>	<i>m</i>	<i>E</i> (mv.)	<i>a<sub>w</sub></i>
		NaCl			NaOH
4.041	11.48	0.8496	8.595	37.93	0.5734
4.037	11.48	.8496	8.600	37.93	.5734
4.031	11.48	.8496	8.610	37.94	.5734
4.905	14.77	.8102	9.157	41.92	.5393
4.906	14.75	.8105	9.150	41.92	.5393
4.914	14.75	.8105	9.140	41.89	.5395
5.862	18.62	.7660	9.764	46.58	.5015
5.859	18.59	.7663	9.767	46.55	.5017
5.866	18.62	.7660	9.758	46.485	.5022
		NaOH	10.818	54.83	.4401
5.085	16.935	0.7851	10.827	54.84	.4400
5.161	17.35	.7804	10.831	54.99	.4390
5.167	17.37	.7797	10.860	55.19	.4375
5.920	21.16	.7380	11.470	60.18	.4037
5.934	21.23	.7372	11.470	60.18	.4037
5.931	21.24	.7371	12.018	64.69	.3751
6.639	25.12	.6959	12.025	64.61	.3756
6.632	25.145	.6957	12.020	64.64	.3754
6.630	25.08	.6963	13.802	79.38	.2934
7.365	29.60	.6508	13.811	79.37	.2934
7.374	29.64	.6504	13.834	79.69	.2919
7.359	29.53	.6515		CaCl <sub>2</sub>	
8.029	33.90	.6099	3.024	20.31	0.7473
8.019	33.83	.6105	3.021	20.31	.7473
8.011	33.78	.6110	3.019	20.31	.7473
			3.036	20.45	.7457

$$\Delta T = 0.2350E + 0.0000690E^2$$

I. Sodium Chloride.—A few test runs were made on this substance, the equilibrium concentrations being determined by gravimetric analysis as silver chloride.

II. Sodium Hydroxide.—This substance was selected for the main work, owing to its inertness toward silver, the ease with which it can be analyzed, and the fact that the isopiestic ratios of sodium hydroxide to sulfuric acid have been accurately measured.<sup>6</sup> (It has also been shown that the small amount of carbonate left after settling saturated sodium hydroxide is without appreciable effect on the vapor pressure, if the total alkali is calculated as sodium hydroxide.) The solution was stored, manipulated and analyzed as described in reference (6). As a check on the purity of the dried sodium carbonate which was the primary standard for the acid used in the weight-titrations, the carbonate was weight-titrated against hydrochloric acid standardized gravimetrically as silver chloride; the results indicated 99.98% purity.

III. Calcium Chloride.—Four runs were made near 3 *M* for checking against the dynamic measurements of Bechtold and Newton.<sup>15</sup> The solutions were analyzed for chloride as silver chloride.

(15) M. F. Bechtold and R. F. Newton, THIS JOURNAL, 62, 1390 (1940).

As will be seen from Table I, measurements were usually made in triplicate at each temperature, but owing to the cleaning and resetting of the thermoregulators between runs, the temperature difference was not quite the same each time. Small corrections, determined by plotting suitable functions of molality and activity, were then applied so as to make each of the triplicate sets refer to one molality; this correction was usually only in the fourth place of *a<sub>w</sub>*, and could not introduce an error greater than 0.0001. The mean water activities and mean deviations from each group of results are summarized in Table II. The reproducibility is seen to be about equal to that obtained by the static method by Shankman and Gordon, who quote results ranging over 0.0004 in *a<sub>w</sub>*.

 TABLE II  
 AVERAGED VALUES OF THE EXPERIMENTAL DATA

Solute	<i>m</i>	<i>a<sub>w</sub></i>	Mean devia.	<i>m</i> <sub>H<sub>2</sub>SO<sub>4</sub></sub>	Devi- ation function. <i>x</i> <sub>1</sub>
NaCl	4.040	0.8495	0.0001	3.026	1.0777
	4.910	.8103	.0002	3.587	1.0808
	5.860	.7662	.0001	4.180	1.0814
NaOH	5.160	.7805	.0003	3.993	1.0816
	5.930	.7374	.0002	4.560	1.0812
	6.630	.6962	.0003	5.092	1.0801
	7.360	.6513	.0001	5.668	1.0787
	8.020	.6104	.0000	6.206	1.0783
	8.600	.5735	.0003	6.692	1.0781
	9.150	.5393	.0003	7.164	0.8585
	9.760	.5020	.0002	7.694	0.8592
10.830	.4393	.0003	8.653	0.8600	
11.470	.4037	.0000	9.238	0.8600	
12.020	.3750	.0004	9.746	0.8604	
13.800	.2935	.0002	11.403	0.8608	
CaCl <sub>2</sub>	3.033	.7464	.0003	4.455	1.0823

$$x_1 = a_w + 0.0754m \quad 3 < m < 7$$

$$x_2 = a_w + 0.05m - 0.0035(m - 10.5)^2 \quad 6 < m < 12$$

where *m* is the sulfuric acid molality. The molalities recorded in the fifth column are those of sulfuric acid solutions isopiestic with the different solutions whose molalities are given in the second column.

## Discussion

The results for sodium hydroxide agree closely with those given in an earlier paper, up to 7 *M*. At higher concentrations the new values of the water activity are slightly higher. The result for 3.033 *M* calcium chloride, *a<sub>w</sub>* = 0.7464 compares very well with 0.7458 obtained by Bechtold and Newton<sup>15</sup> at the same concentration. The three results for sodium chloride agree well with the "best" values which Robinson<sup>2</sup> recently computed by combining data from various sources.

The twelve values for sodium hydroxide, the three for sodium chloride, and the one for calcium

chloride can all be used to calculate vapor pressures of sulfuric acid, since the isopiestic ratios of each of these substances to sulfuric acid are accurately known. Table II includes the sulfuric acid molality isopiestic with each of the solutions. For graphical comparison with other results it is necessary to plot deviation functions, as the range of  $a_w$  values between 3 and 12  $M$  sulfuric acid is too great for accurate direct plotting. In Fig. 2 are shown the two deviation functions  $x_1 = a_w + 0.0754 m$  (between 3 and 7  $M$ ) and  $x_2 = a_w + 0.05 m - 0.0035 (m - 10.5)^2$  (between 6 and 12  $M$ ) where  $m$  is the sulfuric acid molality. The direct vapor pressure measurements of Shankman and Gordon on sulfuric acid are also shown, as solid circles. The measurements of Olynyk and Gordon<sup>16</sup> on sodium chloride, combined with the sodium chloride-sulfuric acid isopiestic ratios, yield the points shown as crosses.

It is seen that in the region where comparison is possible, the present work gives a curve lying between those of Shankman and Gordon, and Olynyk and Gordon, differing from them only in the fourth decimal place of the water activity. At higher concentrations the present work continues to give water activities slightly and consistently higher than those of Shankman and Gordon, the average difference read from Fig. 2 being 0.0008. While this difference is only about twice the reproducibility of either set of results, there is perhaps some justification for preferring the present curve: first, the scattering of points from the curve is rather less than in Shankman and Gordon's results; secondly in the range 3 to 4.5  $M$  it lies between two curves based on measurements from the same laboratory. Against this must be set the fact that Shankman and Gordon measured the vapor pressure of sulfuric acid itself, while the present curve and that derived from the data of Olynyk and Gordon are indirect to the extent that they also involve isopiestic comparisons between sulfuric acid and the substances whose vapor pressure was actually determined. These comparisons, however, can scarcely introduce uncertainties of more than 0.0003 in the water activity, even at the highest concentrations.

The electromotive force measurements of Harned and Hamer<sup>4</sup> lead to the crossed circles of Fig. 2. There can now be little doubt that these results are wrong, though it is extremely difficult to see where errors of this magnitude could enter. Since the two cells used by Harned and Hamer had only the hydrogen electrode and the sulfuric

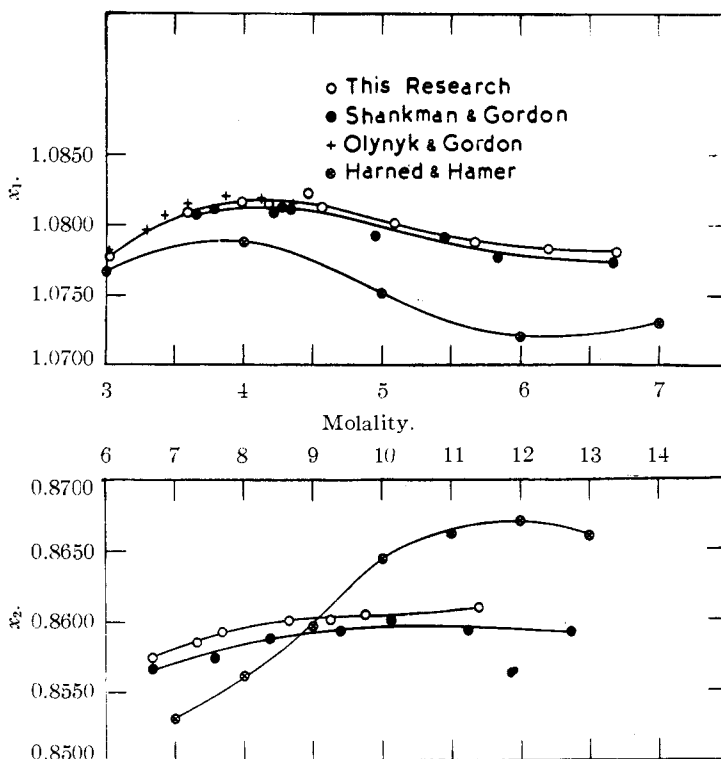


Fig. 2.—Deviation functions for water activities of sulfuric acid at 25°:  $x_1 = a_w + 0.0754 m$ ;  $x_2 = a_w + 0.05 m - 0.0035 (m - 10.5)^2$ .

acid solution in common (the other electrodes being mercury-mercurous sulfate in one case and lead sulfate-lead oxide in the other, with different cell reactions in consequence) it is not possible to blame factors such as the solubility of lead or mercurous sulfates in the electrolyte; and if the trouble is due to a slight irreversibility of the hydrogen electrode in concentrated sulfuric acid solutions, it is astonishing that the two cells should agree as closely as was the case.

It is desirable to establish a set of standard values for sulfuric acid, arising out of this new work and the comparisons in Fig. 2. Below 3  $M$  the best course is probably to derive values from the sodium chloride-sulfuric acid isopiestic ratios and the sodium chloride standard values. This gives a curve joining up smoothly with the values of Table III, which are derived from the present work. The choice between these values and the smoothed data given by Shankman and Gordon is difficult; Table III however gives a rather

TABLE III  
WATER ACTIVITIES IN SULFURIC ACID SOLUTIONS AT 25°

$m$	$a_w$	$m$	$a_w$	$m$	$a_w$
3.0	0.8515	6.0	0.6260	9.0	0.4180
3.5	.8166	6.5	.5880	9.5	.3887
4.0	.7800	7.0	.5509	10.0	.3612
4.5	.7422	7.5	.5153	10.5	.3355
5.0	.7033	8.0	.4813	11.0	.3112
5.5	.6644	8.5	.4488	11.5	.2889

(16) P. Olynyk and A. R. Gordon, *ibid.*, **65**, 204 (1943).

smoother set of first and second differences. Above 11.5 *M* the work of Shankman and Gordon is the only source of information of the necessary accuracy, and therefore the final values of Table III are arranged so as to join smoothly on to their values for more concentrated solutions.

**Acknowledgments.**—The writer wishes to thank Dr. R. A. Robinson for valuable help and encouragement in carrying out this work; also Messrs. Imperial Chemical Industries, Limited, for a substantial grant toward the cost of the apparatus, the Chemical Society (London) for a grant from their Research Fund and the the Dominion Laboratory of New Zealand for the loan of thermometers.

### Summary

Measurements of the vapor pressures of sodium hydroxide solutions have been made by a method depending on vapor-phase equilibration of the solution at 25° with pure water at a lower temperature. The results are in fair agreement with those obtained by combining the isopiestic ratios of sodium hydroxide to sulfuric acid with the static vapor pressure measurements of Shankman and Gordon on sulfuric acid, and support the latter against electromotive force results. A set of standard values for the water activity in sulfuric acid solutions at 25°, for use in isopiestic measurements on concentrated solutions, is proposed.

NEDLANDS, WEST AUSTRALIA RECEIVED OCTOBER 25, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE SCHOOL OF MEDICINE, THE JOHNS HOPKINS UNIVERSITY]

## The Luminosity and Chromaticity of Indicators as a Function of *pH*

BY JUDSON J. VAN WYK AND W. MANSFIELD CLARK

In the visual method of using an indicator for the determination of *pH* there is obtained, ideally, a "match" between the tested solution and a standard, and to this end there must be fulfilled certain specifications which are so well known that they need not be reviewed here. In practice the precision attained depends upon the ability of the eye to discriminate between standard and tested solution when there is not a match. The requirements for discrimination may be resolved arbitrarily into the capabilities of individual eyes and those factors of chromaticity that have been developed for the standard observer. We shall confine attention to the properties of three indicators that can be described in terms of luminosity and the chromaticity diagram as developed for the standard observer. The indicators are phenol red, brom thymol blue and *p*-nitrophenol.

The treatment, as adopted by the International Commission on Illumination, provides a convenient method for specifying the three major characteristics of color: namely, luminosity, dominant wave length, and purity. The latter two are specified by chromaticity coordinates on the standard chromaticity diagram (Fig. 1). The method of obtaining these specifications may be briefly summarized.

The color of a solution when illuminated by a standard source is specified first in terms of the quantity of each of three standard primary colors, or basic stimuli, which would be required to synthesize an equivalent stimulus. To arrive at this specification the only experimental data required, in addition to those incorporated in tables,<sup>1</sup> are the spectral transmittances, *T*, of the particular solution at each 10 *mμ* interval throughout the visible spectrum. For the computations it is necessary to obtain from published tables<sup>1,2</sup> the spectral distribution of radiant power

in a standard source at each of the selected intervals and trichromatic coefficients at the same intervals. These data are used in a simple, but lengthy, calculation to determine the total amounts of the primaries, *X*, *Y* and *Z*, which would be required to synthesize a stimulus matching that of the solution.

Because of the choice of basic stimuli the computed value of *Y* is a measure of the luminosity or "brightness"<sup>1</sup> of the solution.

For obtaining chromaticity coordinates, the relative amounts of the required primary stimuli rather than the absolute amounts are used. These values are obtained from the relations

$$x = \frac{X}{X + Y + Z} \quad y = \frac{Y}{X + Y + Z} \quad z = \frac{Z}{X + Y + Z}$$

and because  $x + y + z$  equals 1, *x* and *y* are sufficient as coordinates on the chromaticity diagram (see Fig. 1). From enlarged diagrams published by Hardy,<sup>1</sup> the dominant wave length and purity are obtained.

On the chromaticity diagram (Fig. 1) the pure spectral colors fall on the peripheral curve and illuminant C at point C. The dominant wave length is the wave length at the intersection of the peripheral curve with a line drawn through the locus of the illuminant and that of the particular color. In the case of the non-spectral purples, the dominant wave length is that of the complementary color. The purity of a color is represented by the ratio of the distance between the locus of the particular color and the illuminant, to the distance between the locus of the illuminant and the periphery.

### Determination of Transmittancy

In order to compute the luminosity values and chromaticity coordinates for the three indicators at a number of different *pH* values it was necessary to know accurately the transmittancies of each solution at 10 *mμ* intervals through the visible spectrum. The absorption coefficients of the un-ionized form of the indicator, and of the ionized form, were experimentally determined, and the transmittancies at intermediate values of  $\alpha$  were calculated from these data on the assumption that at constant ionic strength the following relations hold

(1) A. C. Hardy, "Handbook of Colorimetry," Technology Press, Cambridge, Mass., 1936.

(2) Report of the Committee on Colorimetry, *J. Optical Soc. Am.*, **34**, 245, 633 (1944).