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## Isopiestic Measurements of the Osmotic and Activity Coefficients for the Systems $\text{HClO}_4\text{--LiClO}_4\text{--H}_2\text{O}$ , $\text{HClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$ , and $\text{LiClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$ <sup>1</sup>

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Isopiestic measurements of the osmotic coefficients are presented for the systems  $\text{HClO}_4\text{--LiClO}_4\text{--H}_2\text{O}$ ,  $\text{HClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$ , and  $\text{LiClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$ . Parameters obtained from these results are used to derive the activity coefficients in the mixtures. Estimates of the activity coefficients in the mixtures may be made from information on the limiting two-component systems with an error of 7% or less at concentrations up to 5 *m*. The systems  $\text{HClO}_4\text{--LiClO}_4\text{--H}_2\text{O}$  and  $\text{LiClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$  obey Harned's rule for both components reasonably well over the concentration range studied. For the system  $\text{HClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$  the deviations are greater, especially at the higher concentrations.

The importance of variations of free energies from ideality in chemical equilibria and kinetics is well appreciated. Information concerning these variations is of interest not only for its implications concerning the basic nature of solutions, but also for its fundamental importance in, for example, the study of complexing reactions, estimation of molecular weights by thermodynamic methods, and interpretation of reaction rate data. For aqueous solutions of electrolytes, there is a vast body of data available for two-component systems at 25°. Most cases of practical interest, however, involve mixtures of electrolytes, and it is here that there is a scarcity of data. There is not enough information on many important systems even to allow a check of various plausible procedures for estimation of multicomponent activity coefficients from values of the limiting two-component solutions.

We have been interested for some time in three-component systems, and a few years back, we tested equilibrium ultracentrifugation as a technique for studies in this area.<sup>2</sup> Recently we have started using the isopiestic method. The first system studied was a multicomponent system of solutions having the approximate composition of sea water.<sup>3</sup> Because of their importance as inert media for various studies, we intend to study the behavior of various perchlorate

mixtures. This paper presents the first results of such an investigation: the systems  $\text{HClO}_4\text{--LiClO}_4\text{--H}_2\text{O}$ ,  $\text{HClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$ , and  $\text{LiClO}_4\text{--NaClO}_4\text{--H}_2\text{O}$ .

### Experimental Section

**Materials.** Stock solutions of NaCl were prepared from reagent grade crystals dried overnight at 200°. The concentrations of the solutions were calculated from the weights of dried salt. Analysis of these solutions by measurement of the density to 5 parts/100,000 and comparison with the data of Wirth<sup>4</sup> gave differences in molality of 0.10% or less.

A stock solution of  $\text{H}_2\text{SO}_4$  was prepared from reagent grade concentrated acid. The solution was analyzed by weight titration against  $\text{Na}_2\text{CO}_3$ . Weight titration against a concentrated NaOH solution which had been standardized against potassium acid phthalate gave results about 0.6% higher than the  $\text{Na}_2\text{CO}_3$  titration. Since the direct titration with  $\text{Na}_2\text{CO}_3$  involved fewer

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) R. M. Rush and J. S. Johnson, *J. Phys. Chem.*, **68**, 2321 (1964).

(3) R. M. Rush and J. S. Johnson, *J. Chem. Eng. Data*, **11**, 590 (1966).

(4) H. E. Wirth, R. E. Lindstrom, and J. N. Johnson, *J. Phys. Chem.*, **67**, 2339 (1963).

manipulations and gave more consistent results when the  $\text{H}_2\text{SO}_4$  solutions were compared isopiesticly with the  $\text{NaCl}$  solutions, we used the concentration as determined by this method.

A stock solution of  $\text{HClO}_4$  was prepared from reagent grade concentrated acid. The solution was analyzed by weight titration against  $\text{Na}_2\text{CO}_3$ . Weight titration against a concentrated  $\text{NaOH}$  solution which had been standardized against potassium acid phthalate gave results about 0.6% higher than the  $\text{Na}_2\text{CO}_3$  titration. We used the concentration as determined by the direct titration with  $\text{Na}_2\text{CO}_3$ , for the same reasons as noted above for  $\text{H}_2\text{SO}_4$ . Analysis by dilution, measurement of the density to 5 parts/100,000, and comparison with the data of Wirth<sup>4</sup> gave a molality 0.07% lower than the value obtained from the direct titration with  $\text{Na}_2\text{CO}_3$ .

A stock solution of  $\text{LiClO}_4$  was prepared by neutralizing reagent grade  $\text{HClO}_4$  with solid reagent grade  $\text{LiOH}$  to a pH of 4.5. The solution was analyzed by evaporation of a sample to dryness, heating at 200°, and weighing as  $\text{LiClO}_4$ .

A stock solution of  $\text{NaClO}_4$  was prepared by neutralizing concentrated reagent grade  $\text{HClO}_4$  with solid reagent grade  $\text{NaOH}$  to a pH of 4.5. The solution was analyzed by evaporation of a sample to dryness, heating at 110°, and weighing as  $\text{NaClO}_4$ . Analysis by dilution, measurement of the density to 5 parts/100,000, and comparison with the data of Wirth<sup>4</sup> gave a molality 0.02% lower than that obtained by evaporation to dryness.

Solutions of the various perchlorate mixtures were prepared by weight from the above solutions. Distilled water, passed through a mixed-bed ion-exchange column, was used for the preparation of all solutions.

**Apparatus and Procedure.** The apparatus and procedure have been described previously.<sup>3</sup> The temperature of the bath varied 0.01° or less during the course of an equilibration except for four points where the variation was 0.02°. The temperature of the bath at equilibrium varied from one equilibration run to another within the range of 24.99–25.01°.

Following the weighing of the 12 dishes, the first dish was weighed again; the difference between the two weighings was 0.01% of the weight of the solution, or less. All weights were corrected to their weights *in vacuo*. The dishes were allowed to equilibrate for 2–7 days.

For each set of equilibrations, there were at least two dishes containing the same solution, except as noted in the tables. The maximum difference in concentration among the replicate dishes was 0.1%.

The reference material was  $\text{NaCl}$  up to the limit of its solubility and  $\text{H}_2\text{SO}_4$  for higher concentrations. The osmotic coefficients of these electrolytes were taken from the tables given by Robinson and Stokes.<sup>5</sup>

**Table I:** Isopiestic Concentrations for the Two-Component Systems<sup>a</sup>

|   | $m_{\text{H}_2\text{SO}_4}$ | $m_{\text{HClO}_4}$ | $m_{\text{NaClO}_4}$ |
|---|-----------------------------|---------------------|----------------------|
| A | 8.5700                      | 8.3130              | 17.902 <sup>b</sup>  |
|   | 7.2386                      | 7.2122              | 14.218 <sup>b</sup>  |
|   | 5.7762                      | 5.8971              | 10.473 <sup>b</sup>  |
|   | 4.5470                      | 4.7036              | 7.6032 <sup>b</sup>  |
|   | 3.4117                      | 3.5449              | 5.2181 <sup>b</sup>  |
|   | 2.3218                      | 2.4042              | 3.1973 <sup>b</sup>  |
| D | 8.3244                      | 8.1180              | 17.193               |
|   | 5.3034                      | 5.4478              | 9.3323               |
|   | 3.5829                      | 3.7231              | 5.5585               |
|   | 2.4574                      | 2.5477              | 3.4328               |
| H | 8.4064                      | 8.1892              | 17.426               |
|   | 7.7388                      | 7.6427              | 15.571               |
|   | 7.1752                      | 7.1637              | 14.048               |
|   | 6.2800                      | 6.3680              | 11.722               |
|   | 5.5858                      | 5.7213              | 10.007               |
|   | 4.3945                      | 4.5540              | 7.2651               |
|   | 3.3180                      | 3.4499              | 5.0320               |
|   | 2.4825                      | 2.5748              | 3.4761               |

<sup>a</sup>  $\text{H}_2\text{SO}_4$  as reference material. <sup>b</sup> One dish only.

**Table II:** Isopiestic Concentrations for the Two-Component Systems<sup>a</sup>

|   | $m_{\text{NaCl}}$ | $m_{\text{HClO}_4}$ | $m_{\text{LiClO}_4}$ | $m_{\text{NaClO}_4}$ |
|---|-------------------|---------------------|----------------------|----------------------|
| B | 5.3454            | 4.0087              |                      | 6.1283               |
|   | 4.2536            | 3.2931              |                      | 4.7440               |
|   | 2.9916            | 2.4240              |                      | 3.2280               |
|   | 2.2088            | 1.8563              |                      | 2.3362               |
|   | 1.5771            | 1.3747              |                      | 1.6389 <sup>b</sup>  |
| C | 1.6304            | 1.4150              |                      | 1.6964               |
|   | 1.1303            | 1.0150              |                      | 1.1603               |
|   | 0.8191            | 0.7538              |                      | 0.8340               |
|   | 0.5915            | 0.5552              |                      | 0.5988               |
| E | 5.9796            |                     | 4.4666               |                      |
|   | 5.1742            |                     | 3.9166               |                      |
|   | 3.8196            |                     | 2.9714               |                      |
|   | 2.8004            |                     | 2.2462               |                      |
|   | 1.9970            |                     | 1.6569 <sup>b</sup>  |                      |
| F | 5.7563            |                     | 4.3176               |                      |
|   | 4.9916            |                     | 3.7924               |                      |
|   | 4.1008            |                     | 3.1710               |                      |
|   | 3.2162            |                     | 2.5448               |                      |
|   | 2.3548            |                     | 1.9224               |                      |
|   | 1.7073            |                     | 1.4394               |                      |
| G | 2.6685            |                     | 2.1516               |                      |
|   | 2.1380            |                     | 1.7631               |                      |
|   | 1.5503            |                     | 1.3202               |                      |
|   | 1.1544            |                     | 1.0103               |                      |
|   | 0.8378            |                     | 0.7528               |                      |

<sup>a</sup>  $\text{NaCl}$  as reference material. <sup>b</sup> One dish only.

(5) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, revised, Butterworth and Co. Ltd., London, 1965.

## Results

The isopiestic molalities for the limiting two-component systems,  $\text{HClO}_4\text{-H}_2\text{O}$ ,  $\text{LiClO}_4\text{-H}_2\text{O}$ , and  $\text{NaClO}_4\text{-H}_2\text{O}$ , are given in Tables I and II. The isopiestic molalities and the osmotic coefficients for the three-component systems,  $\text{HClO}_4\text{-LiClO}_4\text{-H}_2\text{O}$ ,  $\text{HClO}_4\text{-NaClO}_4\text{-H}_2\text{O}$ , and  $\text{LiClO}_4\text{-NaClO}_4\text{-H}_2\text{O}$ , are given in Tables III-VI.

**Table III:** Isopiestic Concentrations and Osmotic Coefficients for the System  $\text{HClO}_4(\text{A})\text{-LiClO}_4(\text{B})\text{-H}_2\text{O}$

|   | $m_{\text{NaCl}}$ | $m$    | $y_B$  | $\phi$ (obsd) |
|---|-------------------|--------|--------|---------------|
| E | 5.9796            | 4.4224 | 0.2509 | 1.7145        |
|   |                   | 4.4366 | 0.4997 | 1.7090        |
|   |                   | 4.4513 | 0.7474 | 1.7033        |
|   | 5.1742            | 3.9010 | 0.2509 | 1.5991        |
|   |                   | 3.9043 | 0.4997 | 1.5977        |
|   |                   | 3.9100 | 0.7474 | 1.5954        |
|   | 3.8196            | 2.9880 | 0.2509 | 1.4093        |
|   |                   | 2.9802 | 0.4997 | 1.4130        |
|   |                   | 2.9746 | 0.7474 | 1.4157        |
|   | 2.8004            | 2.2725 | 0.2509 | 1.2711        |
|   |                   | 2.2609 | 0.4997 | 1.2776        |
|   |                   | 2.2518 | 0.7474 | 1.2828        |
|   | 1.9970            | 1.6834 | 0.2509 | 1.1657        |
|   |                   | 1.6728 | 0.4997 | 1.1731        |
|   |                   | 1.6637 | 0.7474 | 1.1795        |

## Treatment of Results

In the interpretation of the above data, we follow the procedure of Scatchard,<sup>6</sup> who starts with the excess free energy,  $G^e$ . The excess free energy is the total free energy of the solution less that of the components in their standard state, and less the ideal free energy represented by the concentration terms. Scatchard uses the dimensionless form,  $G^e/RT$ , where  $R$  is the gas constant and  $T$  is the absolute temperature. He expresses it as a sum of contributions calculated from the limiting two-component solutions ( $A$  terms, solute indicated by single subscript), contributions involving concentrations of two solute components (a series of  $B$  terms, the solutes indicated by a double subscript),

(6) G. Scatchard, *J. Amer. Chem. Soc.*, **83**, 2636 (1961). For the convenience of readers who may wish to follow the development in detail, we list several misprints in the equations. Equation 1 should read:  $G^e/RT = (G - G^*)/RT + \sum_i n_i(1 - \ln n_i/n_0w_0) = \sum_i n_i A_i \sqrt{I} + \sum_{ij} n_i n_j (B_{ij} + C_{ij} \sqrt{I})/n_0w_0 + \sum_{ijk} n_i n_j n_k (D_{ijk} + E_{ijk} \sqrt{I})/(n_0w_0)^2 + \dots$ . The first line of eq 8 should read:  $-\partial(G^e/RT \sum_i n_i^*)/\partial(\ln n_0w_0) = (\sum_i i m_i / \sum_i m_i^*)(\phi - 1) = \dots$ . The final factor in eq 15 should be  $y_B^3$ . The equations on p 2639 should read:  $B_{AB}^{(0,2)} - \beta_{AB}^{(0,2)} + 3(B_{AB}^{(1,2)} - \beta_{AB}^{(1,2)}) = -1/2(\beta_{AB}^{(0,2)} + 3\beta_{AB}^{(1,2)})(\nu_B m_B/I_B) \ln y_B = A_B + \alpha_B + [- (\alpha_B - \alpha_A) + \beta_{AB}^{(0,1)} + 4\beta_{AB}^{(0,2)}/3] y_A - \beta_{AB}^{(0,2)} y_A^2$  (17). The correlation of Harned's symbols with Scatchard's, on p 2640, should be:  $\alpha_{12} - j[(\alpha_B - \alpha_A) + \beta_{AB}^{(0,1)} + 2\beta_{AB}^{(0,2)}/3]/2.303 \nu_A I, \alpha_{21}^{(0)} - k[(\alpha_A - \alpha_B) + \beta_{AB}^{(0,1)} + 4\beta_{AB}^{(0,2)}/3]/2.303 \nu_B I, \beta_{21} + k\beta_{AB}^{(0,2)}/2.303 \nu_B I^2$ . In the section concerning the Debye-Hückel treatment, it should be noted that  $\mathcal{D} = 2(-1.17)$  for aqueous solution at 25°.

**Table IV:** Isopiestic Concentrations and Osmotic Coefficients for the System  $\text{HClO}_4(\text{A})\text{-NaClO}_4(\text{B})\text{-H}_2\text{O}^a$

|   | $m_{\text{H}_2\text{SO}_4}$ | $m$     | $y_B$  | $\phi$ (obsd) |
|---|-----------------------------|---------|--------|---------------|
| A | 8.5700                      | 9.5588  | 0.2486 | 2.3548        |
|   |                             | 11.3156 | 0.5005 | 1.9892        |
|   |                             | 13.8616 | 0.7493 | 1.6238        |
|   | 7.2386                      | 8.1744  | 0.2486 | 2.1319        |
|   |                             | 9.5044  | 0.5005 | 1.8336        |
|   |                             | 11.3730 | 0.7493 | 1.5323        |
|   | 5.7762                      | 6.5680  | 0.2486 | 1.8666        |
|   |                             | 7.4696  | 0.5005 | 1.6413        |
|   |                             | 8.6928  | 0.7493 | 1.4104        |
|   | 4.5470                      | 5.1536  | 0.2486 | 1.6331        |
|   |                             | 5.7437  | 0.5005 | 1.4653        |
|   |                             | 6.5180  | 0.7493 | 1.2913        |
|   | 3.4117                      | 3.8176  | 0.2486 | 1.4169        |
|   |                             | 4.1682  | 0.5005 | 1.2978        |
|   |                             | 4.6144  | 0.7493 | 1.1723        |
|   | 2.3218                      | 2.5398  | 0.2486 | 1.2218        |
|   |                             | 2.7113  | 0.5005 | 1.1445        |
|   |                             | 2.9222  | 0.7493 | 1.0619        |
| H | 8.4064                      | 9.3976  | 0.2486 | 2.3267        |
|   |                             | 11.0989 | 0.5007 | 1.9700        |
|   |                             | 13.5577 | 0.7496 | 1.6127        |
|   | 7.7388                      | 8.7077  | 0.2486 | 2.2169        |
|   |                             | 10.1928 | 0.5007 | 1.8939        |
|   |                             | 12.3084 | 0.7496 | 1.5684        |
|   | 7.1752                      | 8.1110  | 0.2486 | 2.1191        |
|   |                             | 9.4192  | 0.5007 | 1.8248        |
|   |                             | 11.2588 | 0.7496 | 1.5266        |
|   | 6.2800                      | 7.1348  | 0.2486 | 1.9580        |
|   |                             | 8.1760  | 0.5007 | 1.7086        |
|   |                             | 9.6088  | 0.7496 | 1.4539        |
|   | 5.5858                      | 6.3551  | 0.2486 | 1.8300        |
|   |                             | 7.2034  | 0.5007 | 1.6145        |
|   |                             | 8.3514  | 0.7496 | 1.3925        |
|   | 4.3945                      | 4.9770  | 0.2486 | 1.6026        |
|   |                             | 5.5206  | 0.5007 | 1.4448        |
|   |                             | 6.2561  | 0.7496 | 1.2749        |
|   | 3.3180                      | 3.7080  | 0.2486 | 1.3989        |
|   |                             | 4.0402  | 0.5007 | 1.2836        |
|   |                             | 4.4633  | 0.7496 | 1.1619        |
|   | 2.4825                      | 2.7272  | 0.2486 | 1.2480        |
|   |                             | 2.9206  | 0.5007 | 1.1653        |
|   |                             | 3.1616  | 0.7496 | 1.0765        |

<sup>a</sup>  $\text{H}_2\text{SO}_4$  as reference material.

and higher terms for systems with more than three components. Concentrations are expressed in ionic strength units. The  $A$ 's and  $B$ 's are functions of temperature and pressure, and ionic strength. For convenience in computation, we have expanded these parameters a little differently than Scatchard. Our  $A$  for each electrolyte consists of a Debye-Hückel term

**Table V:** Isopiestic Concentrations and Osmotic Coefficients for the System  $\text{HClO}_4(\text{A})\text{--NaClO}_4(\text{B})\text{--H}_2\text{O}^a$ 

|   | $m_{\text{NaCl}}$ | $m$    | $y_{\text{B}}$ | $\phi$ (obsd) |
|---|-------------------|--------|----------------|---------------|
| B | 5.3454            | 4.3479 | 0.2486         | 1.4985        |
|   |                   | 4.7850 | 0.5005         | 1.3617        |
|   |                   | 5.3502 | 0.7493         | 1.2178        |
|   | 4.2536            | 3.5320 | 0.2486         | 1.3666        |
|   |                   | 3.8369 | 0.5005         | 1.2580        |
|   |                   | 4.2236 | 0.7493         | 1.1429        |
|   | 2.9916            | 2.5611 | 0.2486         | 1.2196        |
|   |                   | 2.7338 | 0.5005         | 1.1426        |
|   |                   | 2.9480 | 0.7493         | 1.0596        |
|   | 2.2088            | 1.9398 | 0.2486         | 1.1327        |
|   |                   | 2.0444 | 0.5005         | 1.0747        |
|   |                   | 2.1716 | 0.7493         | 1.0118        |
|   | 1.5771            | 1.4218 | 0.2486         | 1.0655        |
|   |                   | 1.4807 | 0.5005         | 1.0231        |
|   |                   | 1.5509 | 0.7493         | 0.9768        |
| C | 1.6304            | 1.4656 | 0.2486         | 1.0716        |
|   |                   | 1.5282 | 0.5005         | 1.0277        |
|   |                   | 1.6026 | 0.7493         | 0.9800        |
|   | 1.1303            | 1.0416 | 0.2486         | 1.0206        |
|   |                   | 1.0748 | 0.5005         | 0.9891        |
|   |                   | 1.1132 | 0.7493         | 0.9550        |
|   | 0.8191            | 0.7688 | 0.2486         | 0.9902        |
|   |                   | 0.7875 | 0.5005         | 0.9667        |
|   |                   | 0.8084 | 0.7493         | 0.9417        |
|   | 0.5915            | 0.5635 | 0.2486         | 0.9695        |
|   |                   | 0.5739 | 0.5005         | 0.9519        |
|   |                   | 0.5852 | 0.7493         | 0.9335        |

<sup>a</sup> NaCl as a reference material.

and a power series in  $I$ . As many  $B$  terms are used as are necessary to represent the three-component data; each of our  $B$  terms is an integral power series in  $I$  (see eq 8 and 9).

By differentiation of appropriate excess-energy functions with respect to amount of solvent, an expression involving the osmotic coefficient,  $\phi$ , of the solutions is obtained; by differentiating with respect to number of moles of component  $J$ , an expression for the activity coefficient,  $\gamma_{\pm J}$ , is obtained. (Guggenheim<sup>7</sup> has used a similar procedure in a discussion of mixtures of 1:1 electrolytes, although his discussion was limited to concentrations at which power-series terms linear in concentration are adequate.) These equations involve the  $A$  and  $B$  coefficients and their partial derivatives,  $\alpha$  and  $\beta$ , with respect to  $\ln I$ . The coefficients in the equations for  $\phi$  necessary to fit experimental data are also the coefficients in the  $\ln \gamma_{\pm}$  equations, and activity coefficients can be evaluated from  $\phi$  for two- and three-component solutions without going through the cumbersome conventional integration procedure, with the difficulties it involves near the limit of zero concentration. This treatment, instead,

**Table VI:** Isopiestic Concentrations and Osmotic Coefficients for the System  $\text{LiClO}_4(\text{A})\text{--NaClO}_4(\text{B})\text{--H}_2\text{O}$ 

|   | $m_{\text{NaCl}}$ | $m$    | $y_{\text{B}}$ | $\phi$ (obsd) |
|---|-------------------|--------|----------------|---------------|
| F | 5.7563            | 4.6958 | 0.2509         | 1.5332        |
|   |                   | 5.1715 | 0.4982         | 1.3922        |
|   |                   | 5.8212 | 0.7562         | 1.2368        |
|   | 4.9916            | 4.1018 | 0.2509         | 1.4499        |
|   |                   | 4.4881 | 0.4982         | 1.3251        |
|   |                   | 5.0087 | 0.7562         | 1.1874        |
|   | 4.1008            | 3.4056 | 0.2509         | 1.3527        |
|   |                   | 3.6946 | 0.4982         | 1.2468        |
|   |                   | 4.0782 | 0.7562         | 1.1296        |
|   | 3.2162            | 2.7105 | 0.2509         | 1.2571        |
|   |                   | 2.9122 | 0.4982         | 1.1700        |
|   |                   | 3.1734 | 0.7562         | 1.0737        |
|   | 2.3548            | 2.0279 | 0.2509         | 1.1652        |
|   |                   | 2.1534 | 0.4982         | 1.0973        |
|   |                   | 2.3122 | 0.7562         | 1.0219        |
| G | 1.7073            | 1.5046 | 0.2509         | 1.0974        |
|   |                   | 1.5804 | 0.4982         | 1.0448        |
|   |                   | 1.6739 | 0.7562         | 0.9864        |
|   | 2.6685            | 2.2780 | 0.2509         | 1.1983        |
|   |                   | 2.4294 | 0.4982         | 1.1237        |
|   |                   | 2.6244 | 0.7562         | 1.0402        |
|   | 2.1380            | 1.8541 | 0.2509         | 1.1423        |
|   |                   | 1.9620 | 0.4982         | 1.0795        |
|   |                   | 2.0980 | 0.7562         | 1.0095        |
|   | 1.5503            | 1.3760 | 0.2509         | 1.0808        |
|   |                   | 1.4408 | 0.4982         | 1.0322        |
|   |                   | 1.5206 | 0.7562         | 0.9780        |
|   | 1.1544            | 1.0453 | 0.2509         | 1.0398        |
|   |                   | 1.0858 | 0.4982         | 1.0010        |
|   |                   | 1.1338 | 0.7562         | 0.9586        |
|   | 0.8378            | 0.7736 | 0.2509         | 1.0072        |
|   |                   | 0.7974 | 0.4982         | 0.9772        |
|   |                   | 0.8246 | 0.7562         | 0.9449        |

implicitly makes use of the known Debye-Hückel expressions for  $\phi$  and  $\ln \gamma_{\pm}$  in dilute solutions.

The equation for  $\phi$  of a three-component mixture is (ref 6, eq 14)

$$\phi = 1 + \frac{I}{\nu_A m_A + \nu_B m_B} \{ \alpha_A + (\alpha_B - \alpha_A) y_B + \beta_{AB}^{(0)} y_B (1 - y_B) + \beta_{AB}^{(1)} y_B (1 - y_B) (1 - 2y_B) \} \quad (1)$$

where

$$\alpha_J = \frac{2S}{a_J^3 I} \left[ 1 + a_J I^{1/2} - \frac{1}{1 + a_J I^{1/2}} - 2 \ln (1 + a_J I^{1/2}) \right] + a_J^{(1)} I + a_J^{(2)} I^2 + a_J^{(3)} I^3 + a_J^{(4)} I^4 \quad (2)$$

(7) E. A. Guggenheim, "Applications of Statistical Mechanics," Clarendon Press, Oxford, 1966.

Table VII:  $a$  Parameters for the Two-Component Systems (Eq 2)

|  | $a^{(1)}$ | $a^{(2)}$ | $a^{(3)}$ | $a^{(4)}$      | $\sigma$ |
|--|-----------|-----------|-----------|----------------|----------|
| 1a $\text{HClO}_4$ , all data                    | 0.23770   | 0.03666   | -0.00204  | 0.000046       | 0.0022   |
| 1b $\text{HClO}_4$ , NaCl as reference material  | 0.2588    | 0.01164   | 0.00600   | -0.000740      | 0.0005   |
| 2 $\text{LiClO}_4$                               | 0.3434    | -0.01570  | 0.00678   | -0.000666      | 0.0007   |
| 3a $\text{NaClO}_4$ , all data                   | 0.00894   | 0.01102   | -0.000950 | 0.0000236      | 0.0030   |
| 3b $\text{NaClO}_4$ , NaCl as reference material | 0.00172   | 0.01276   | -0.000890 | 0 <sup>a</sup> | 0.0005   |

<sup>a</sup> Not varied; fixed at zero.

$$\beta_{AB}^{(0)} = b_{AB}^{(0,1)}I + b_{AB}^{(0,2)}I^2 + b_{AB}^{(0,3)}I^3 \quad (3)$$

$$\beta_{AB}^{(1)} = b_{AB}^{(1,2)}I^2 + b_{AB}^{(1,3)}I^3 \quad (4)$$

and where  $y_J$  is the ionic strength fraction  $I_J/I$  for any component  $J$ ,  $a_J$  is the distance of closest approach parameter for any component  $J$ ,  $\nu_J$  is the number of ions per molecule of component  $J$ ,  $I$  is the ionic strength on the molality scale, and  $S = -1.17082$  (aqueous solutions at 25°). For a mixture of two 1:1 electrolytes,  $I/(\nu_A m_A + \nu_B m_B) = 0.5$  and  $I = m = m_A + m_B$ , the total molality. It should be noted that our  $b_{AB}^{(j,k)}$  are Scatchard's  $\beta_{AB}^{(j,k)}/I^k$ .

The equations for the activity coefficients of components A and B are (ref 6, eq 15)

$$\ln \gamma_{\pm A} = \frac{I_A}{\nu_A m_A} [A_A + \alpha_A + (\alpha_B - \alpha_A) y_B + \beta_{AB}^{(0)} y_B + (B_{AB}^{(0)} - \beta_{AB}^{(0)}) y_B^2 + \beta_{AB}^{(1)} y_B + 3(B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^2 - 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^3] \quad (5)$$

$$\ln \gamma_{\pm B} = \frac{I_B}{\nu_B m_B} [A_B + \alpha_B + (\alpha_A - \alpha_B) y_A + \beta_{AB}^{(0)} y_A + (B_{AB}^{(0)} - \beta_{AB}^{(0)}) y_A^2 - \beta_{AB}^{(1)} y_A - 3(B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^2 + 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^3] \quad (6)$$

where

$$(A_J + \alpha_J) = \frac{2SI^{1/2}}{1 + a_J I^{1/2}} + 2a_J^{(1)}I + \frac{3}{2}a_J^{(2)}I^2 + \frac{4}{3}a_J^{(3)}I^3 + \frac{5}{4}a_J^{(4)}I^4 \quad (7)$$

$$B_{AB}^{(0)} = b_{AB}^{(0,1)}I + \frac{1}{2}b_{AB}^{(0,2)}I^2 + \frac{1}{3}b_{AB}^{(0,3)}I^3 \quad (8)$$

$$B_{AB}^{(1)} = \frac{1}{2}b_{AB}^{(1,2)}I^2 + \frac{1}{3}b_{AB}^{(1,3)}I^3 \quad (9)$$

For a mixture of 1:1 electrolytes  $I_A/\nu_A m_A = I_B/\nu_B m_B = 0.5$ .

The values of the power-series coefficients,  $a_J^{(n)}$ , and the distance of closest approach parameter,  $a_J$ , in eq 2 are obtained from the osmotic coefficients of the individual components, in this study by the method of least squares. These coefficients can then be used in eq 7 to calculate the contribution of the individual

components to the activity coefficients. The osmotic coefficients for the mixture are then used to obtain the  $b$  coefficients of eq 3 and 4, again by the method of least squares. These in turn define the  $B$  coefficients of eq 8 and 9.

It should be noted that, since the Debye-Hückel contributions of the two-component systems appear only in the  $A$  and  $\alpha$  terms, the distance of closest approach parameter need not be the same for the two components of the mixture.

## Discussion

**Two-Component Systems.** The values of the  $a$  coefficients for the two-component systems are given in Table VII. The deviations from the fitted equations are shown in Figure 1. In all cases, a satisfactory fit could be obtained with  $a$  fixed at the value 1.5. The standard deviation,  $\sigma = [\sum d^2/(n - k)]^{1/2}$ , where  $d$  is the deviation,  $n$  is the number of observations,  $k$  is the number of variable parameters, and the summation is over all observations, is also given in this table.

1.  $\text{HClO}_4$ . Two sets of parameters are given in Table VII for  $\text{HClO}_4$ . The solubility of  $\text{LiClO}_4$  limits

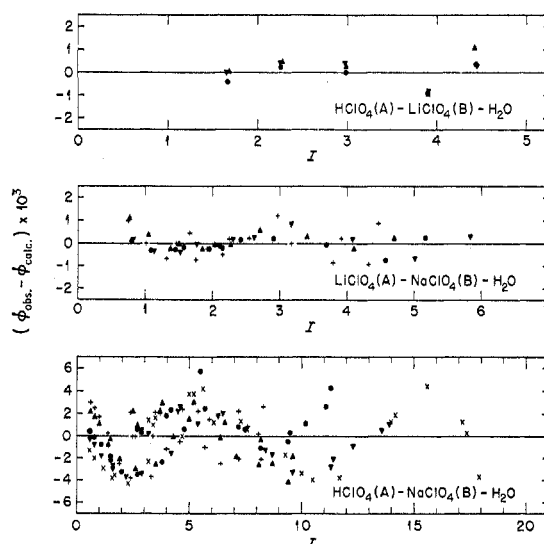


Figure 1. Deviations of osmotic coefficients for two- and three-component data from fitted equations (symbol,  $y_B$ : +, 0.0;  $\Delta$ , 0.25;  $\circ$ , 0.5;  $\nabla$ , 0.75;  $\times$ , 1.0).

the concentration range of mixtures containing this salt to approximately the range covered by NaCl as the reference salt. Parameters for  $\text{HClO}_4$  were derived for the entire range of concentrations and for the concentration range covered by NaCl as reference salt. In both cases, the osmotic coefficients calculated with these parameters agree with those tabulated by Robinson and Stokes<sup>5</sup> with an average deviation without regard to sign of 0.003 and a maximum deviation of 0.009 in  $\phi$ .

2.  $\text{LiClO}_4$ . The osmotic coefficients derived from the parameters given in Table VII agree with those tabulated by Robinson and Stokes,<sup>5</sup> with an average deviation of 0.003 and a maximum deviation of 0.013 in  $\phi$ .

3.  $\text{NaClO}_4$ . As with  $\text{HClO}_4$ , a separate set of parameters was derived for the data with NaCl as the reference material. Literature values for the osmotic coefficients of  $\text{NaClO}_4$  go up to only 6  $m$ .<sup>5</sup> Within this range, our values agree with those tabulated by Robinson and Stokes<sup>5</sup> with an average deviation of 0.003 and a maximum deviation of 0.005 in  $\phi$ . Table VIII gives values of the osmotic coefficients and activity coefficients of  $\text{NaClO}_4$  at even molalities from 6 to 18  $m$  as a supplement to the tables in the literature.<sup>5</sup> The data in this table were calculated using parameter set 3a of Table VII.

**Table VIII:** Osmotic and Activity Coefficients for  $\text{NaClO}_4$  at High Concentrations

| $m$ | $\phi$ | $\gamma_{\pm}$ | $m$ | $\phi$ | $\gamma_{\pm}$ |
|-----|--------|----------------|-----|--------|----------------|
| 6   | 1.0579 | 0.684          | 13  | 1.2118 | 0.887          |
| 7   | 1.0888 | 0.713          | 14  | 1.2218 | 0.910          |
| 8   | 1.1174 | 0.744          | 15  | 1.2306 | 0.933          |
| 9   | 1.1430 | 0.775          | 16  | 1.2392 | 0.955          |
| 10  | 1.1653 | 0.805          | 17  | 1.2493 | 0.979          |
| 11  | 1.1841 | 0.834          | 18  | 1.2626 | 1.007          |
| 12  | 1.1994 | 0.862          |     |        |                |

From the above discussion, it is clear that our measurements on the two-component systems are in satisfactory agreement with values in the literature, thus lending confidence to the accuracy of our three-component values.

**Three-Component Systems.** The values of the  $b$  parameters for the three-component systems are given in Table IX. The deviations from the fitted equations are also shown in Figure 1. For each system, fits were obtained using combinations of parameters other than those shown in the table. The sets of parameters given in Table IX are those with the least number of parameters which do not represent a significant increase in the standard deviation ( $\sigma$ ).

In considering the activity coefficients in the mix-

**Table IX:**  $b$  Parameters for the Three-Component Systems (Eq 3 and 4)

|                                       | $\text{HClO}_4(\text{A})\text{--}\text{LiClO}_4(\text{B})$ | $\text{HClO}_4(\text{A})\text{--}\text{NaClO}_4(\text{B})$ | $\text{LiClO}_4(\text{A})\text{--}\text{NaClO}_4(\text{B})$ |
|---------------------------------------|--|--|---|
| Two-component parameters <sup>a</sup> | 1b, 2  | 1a, 3a   | 2, 3b   |
| $b_{AB}^{(0,1)}$                      | 0.0308   | 0.0609   | 0.0158  |
| $b_{AB}^{(0,2)}$                      | -0.00637   | -0.03213   | -0.0202   |
| $b_{AB}^{(0,3)}$                      | 0 <sup>b</sup>   | 0.000319   | 0.00105   |
| $b_{AB}^{(1,2)}$                      | 0 <sup>b</sup>   | 0 <sup>b</sup>   | 0.00420   |
| $b_{AB}^{(1,3)}$                      | 0 <sup>b</sup>   | -0.000513  | -0.00097  |
| $\sigma$                              | 0.0006   | 0.0022   | 0.0004  |

<sup>a</sup> See Table VII. <sup>b</sup> Not varied; fixed at zero.

tures, it is convenient to define a deviation function  $\delta$  such that

$$\delta_J = \log \gamma_{\pm J} - (\log \gamma_{\pm J})_\alpha \quad (10)$$

where  $(\log \gamma_{\pm J})_\alpha$  is obtained from eq 5 or 6 using only the parameters for the limiting two-component systems, i.e., with the  $b$  coefficients all equal to zero. Thus

$$\delta_A = \frac{I_A}{\nu_A m_A} [\beta_{AB}^{(0)} y_B + (B_{AB}^{(0)} - \beta_{AB}^{(0)}) y_B^2 + \beta_{AB}^{(1)} y_B + 3(B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^2 - 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^3] \times 0.4343 \quad (11)$$

$$\delta_B = \frac{I_B}{\nu_B m_B} [\beta_{AB}^{(0)} y_A + (B_{AB}^{(0)} - \beta_{AB}^{(0)}) y_A^2 - \beta_{AB}^{(1)} y_A - 3(B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^2 + 2(2B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^3] \times 0.4343 \quad (12)$$

This deviation function indicates how well the activity coefficients in the mixture can be estimated from the limiting two-component osmotic coefficient data. By the Brønsted rule (as extended by Scatchard) for obtaining activity coefficients of electrolytes in mixed solutions,  $\delta = 0$ , and the value of  $\delta$  can be taken as a measure of the success of this rule. In addition, it is possible to observe how well a given component obeys Harned's rule.<sup>8</sup> A plot of  $\delta$  as a function of ionic strength fraction at a given ionic strength should be linear if Harned's rule is obeyed for the component in question.

1.  $\text{HClO}_4\text{--LiClO}_4\text{--H}_2\text{O}$ . This system was investigated over a shorter range of concentrations, partly because of the limited solubility of  $\text{LiClO}_4$  and partly because of the proximity of the osmotic coefficients of  $\text{HClO}_4$  and  $\text{LiClO}_4$ . The osmotic coefficients of this system can be fitted quite well with only the two cross parameters  $b_{AB}^{(0,1)}$  and  $b_{AB}^{(0,2)}$  (see Table IX). The behavior of the deviation function  $\delta$  at ionic strengths

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 14.

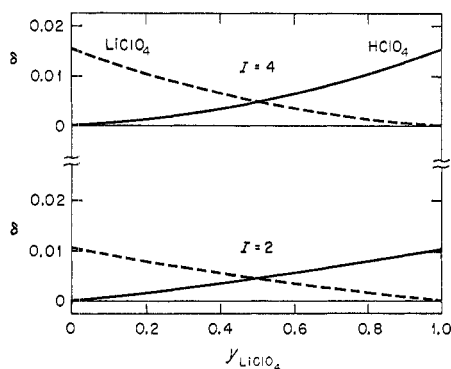


Figure 2. Deviation function,  $\delta$ , for the system  $\text{HClO}_4\text{-LiClO}_4\text{-H}_2\text{O}$ .

2 and 4 is shown in Figure 2. As can be seen in this figure, the maximum error in approximating the activity coefficients from the limiting two-component data is 2% in  $\gamma_{\pm}$  at  $I = 2$  and 4% at  $I = 4$ . The maximum deviation from linearity (Harned's rule) is 0.1% in  $\gamma_{\pm}$  at  $I = 4$  and even less at  $I = 2$ . It is apparent from Figure 2 and from eq 11 and 12 that, if  $\beta_{AB}^{(1)}$  is zero, the  $\delta$  functions for the two components of the mixture are mirror images.

2.  $\text{HClO}_4\text{-NaClO}_4\text{-H}_2\text{O}$ . Because of the high solubility of  $\text{HClO}_4$  and  $\text{NaClO}_4$ , this system was investigated over the greatest range of concentrations (0.6–14 *m*). This system can be represented adequately with four cross parameters,  $b_{AB}^{(0,1)}$ ,  $b_{AB}^{(0,2)}$ ,  $b_{AB}^{(0,3)}$ , and  $b_{AB}^{(1,3)}$  (see Table IX). Inclusion of the parameter  $b_{AB}^{(1,2)}$  did not improve the standard deviation ( $\sigma$ ). Fixing  $b_{AB}^{(0,3)}$  at zero produced almost as good a fit ( $\sigma = 0.0028$ ) as that given in Table IX. The behavior of the deviation function,  $\delta$ , at three ionic strengths is shown in Figure 3. The maximum error in approximating the activity coefficients from the limiting two-component data is 2, 7, and 50% in  $\gamma_{\pm}$  at  $I = 1, 5$ , and 9, respectively. The maximum deviation from linearity at these same ionic strengths is 0.3, 6, and 20% in  $\gamma_{\pm}$ , respectively. It is clear from Figure 3 that the deviation from linearity (Harned's rule) is greater for the activity coefficient of  $\text{HClO}_4$  than for that of  $\text{NaClO}_4$ .

3.  $\text{LiClO}_4\text{-NaClO}_4\text{-H}_2\text{O}$ . Investigation of this system was also limited by the solubility of  $\text{LiClO}_4$ . Since the osmotic coefficients of  $\text{LiClO}_4$  and  $\text{NaClO}_4$  are quite different, the investigation was extended to lower concentrations than with the  $\text{HClO}_4\text{-LiClO}_4\text{-H}_2\text{O}$  system. This system requires all five cross parameters (see Table IX) for the best fit to the data, although the fit is almost as good ( $\sigma = 0.0009$ ) using only the two parameters  $b_{AB}^{(0,1)}$  and  $b_{AB}^{(0,2)}$ . The behavior of the deviation function,  $\delta$ , at three ionic strengths is shown in Figure 4. The maximum error in approximating the activity coefficients from the limiting two-component data is 0.4, 2, and 7% in  $\gamma_{\pm}$  at  $I = 1, 3$ , and 5, respectively. The maximum deviation from linearity at

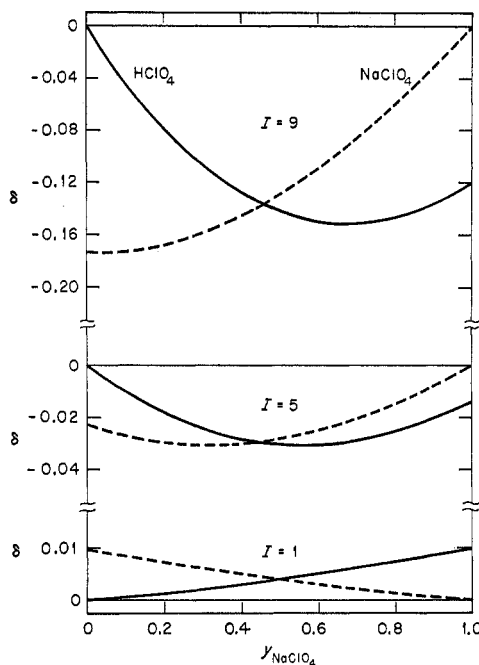


Figure 3. Deviation function,  $\delta$ , for the system  $\text{HClO}_4\text{-NaClO}_4\text{-H}_2\text{O}$ .

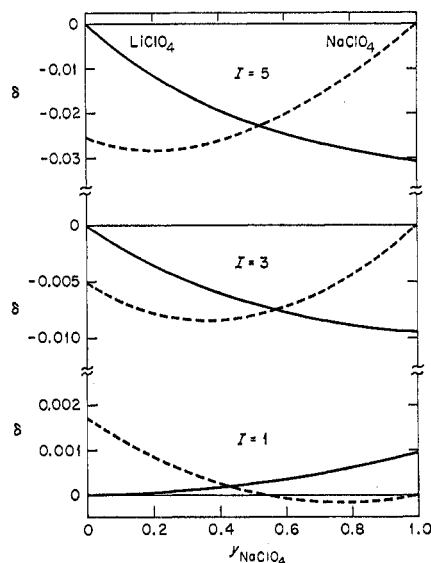


Figure 4. Deviation function,  $\delta$ , for the system  $\text{LiClO}_4\text{-NaClO}_4\text{-H}_2\text{O}$ .

these same ionic strengths is 0.2, 1, and 2% in  $\gamma_{\pm}$ , respectively.

From the above discussion, it is apparent that the equations given by Scatchard provide an adequate and convenient means of representing the osmotic coefficients of three-component mixtures. In addition, these equations provide a simple method for the calculation of the activity coefficients that is not dependent on an integration to zero concentration, as is the case with the McKay-Perring method.<sup>9</sup> We have re-

(9) H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.*, **49**, 163 (1953).

cently shown that the Scatchard approach, as outlined above, agrees well with the McKay-Perring method for the system NaCl-KCl-H<sub>2</sub>O.<sup>10</sup>

The Scatchard equations also provide a convenient way of approximating the osmotic or activity coefficients in the three-component mixture from the data on the limiting two-component systems alone. Guggenheim<sup>7</sup> also has found for many dilute solutions of 1:1 electrolytes that activity coefficients for mixtures can be estimated to a good approximation from two-component data. In the examples given here, the error in  $\gamma_{\pm}$  introduced by this approximation is, at most, 7% at ionic strengths up to five. For the one system studied at higher concentrations, HClO<sub>4</sub>-

NaClO<sub>4</sub>-H<sub>2</sub>O, this approximation produces a much greater error. For the systems HClO<sub>4</sub>-LiClO<sub>4</sub>-H<sub>2</sub>O and LiClO<sub>4</sub>-NaClO<sub>4</sub>-H<sub>2</sub>O, Harned's rule is followed for both components within a few per cent up to  $I = 5$ . For the system HClO<sub>4</sub>-NaClO<sub>4</sub>-H<sub>2</sub>O, the deviation from Harned's rule is quite noticeable even at  $I = 5$ . The activity coefficients of HClO<sub>4</sub> show a greater deviation than those of NaClO<sub>4</sub>.

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(10) R. M. Rush and R. A. Robinson, *J. Tenn. Acad. Sci.*, in press

## Photodecomposition of Aqueous Solutions of Barium Azide

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The kinetics of gas evolution and the formation of ammonia, hydrazine, and hydroxylamine when aqueous solutions of barium azide are photolyzed with light from a low-pressure mercury lamp are investigated as a function of intensity, time of irradiation, and the concentration of the solution. Earlier work on the change in pH of such solutions as a function of time of irradiation by Bonnemay has been repeated. Results indicate that the pH rises steeply and finally attains a constant value. In extremely dilute solutions, if the reaction is followed to completion, the pH eventually begins to decrease. A possible explanation as to why Bonnemay found that the reaction is heterogeneous in certain concentration ranges is included. This is discussed in the light of the possible interference of CO<sub>2</sub> and of the photodecomposition of secondary products.

### Introduction

Studies on the photodecomposition of aqueous solutions of azides have been undertaken by Gleu,<sup>2</sup> Bonnemay,<sup>3</sup> and Shinohara, *et al.*<sup>4</sup> The latter workers added mercuric salt to the azide solution before photolyzing. During photolysis the hydrogen atoms formed ( $\text{N}_3^- + \text{H}_2\text{O} \xrightarrow{h\nu} \text{H} + \text{OH}^- + \text{N}_3$ ) reduce the mercuric salt and give mercurous azide; the pH of the solution remains unchanged. The experimental conditions, such as degassing of the solution, description of light source, *etc.*, which we find to be of great importance in these studies, are explicitly described by Shinohara, *et al.*<sup>4</sup> The other workers, Gleu<sup>2</sup> and Bonnemay,<sup>3</sup> do not describe their conditions in detail, although they both studied the photolysis of aqueous solutions of NaN<sub>3</sub> without any intentional use of a scavenger. Gleu<sup>2</sup> used as a light source a Hg lamp which was immersed in the experimental solution, the solution being contained in a closed vessel at a constant temperature.

He analyzed only the final products of decomposition. The products of decomposition are N<sub>2</sub>H<sub>4</sub>, NH<sub>4</sub>OH, NH<sub>2</sub>OH, N<sub>2</sub>, and a trace of H<sub>2</sub>, and are independent of the pH of the solution. Bonnemay did not immerse the Hg lamp in the solution but used a quartz vessel as a container and a low-pressure mercury lamp as an external source ( $\lambda \sim 2537 \text{ \AA}$ ). He followed the reaction by observing the destruction of azide ions (colorimetrically, using FeCl<sub>3</sub>) and the increase in the pH using a pH meter. He found that in the concentration range 2.3 *N* to saturation the reaction is homogeneous and does not depend on the vessel used. The reaction has the following characteristics. There is an induction period (pH  $\sim 9$ ), a rapid rise in the pH, a

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(2) K. Gleu, *Ber. Bunsenges. Phys. Chem.*, **61**, 702 (1928).

(3) M. Bonnemay, *J. Chem. Phys.*, **41**, 18 (1944).

(4) K. Shinohara, T. Shida, and N. Saito, *ibid.*, **38**, 1985 (1963).