finitely dilute solutions. For concentrated solutions certain complications can be expected in the experimental determination of osmotic pressures using mixed solvents, especially if a dynamic approach is employed.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# The Concentration Distribution in Two-Salt Moving Boundaries

BY L. G. LONGSWORTH

**Introduction.**—The development of the schlieren scanning technique[1] for studying the electrophoresis of proteins has, somewhat unexpectedly, provided a tool with which to investigate in detail the moving boundaries that have been used for the measurement of the transference numbers of strong electrolytes. Such boundaries, it will be recalled, are formed between two solutions of binary salts having a common ion, the salt present in the region into which the boundary moves on passage of the electric current being called the "leading" electrolyte whereas that behind the boundary is termed the "indicator" electrolyte. Boundaries of this type will be called "two-salt" boundaries in order to distinguish them from other types of moving boundaries such as protein boundaries[2] and concentration boundaries.[3]

According to the theory developed by Weber[4] the mixing effect of inter-diffusion at a two-salt boundary is balanced by a separating effect due to ion migration[5] if the mobility, $u_i$, of the indicator ion constituent is less than the mobility, $u_l$, of the leading ion constituent and if the current is passed in the appropriate direction. Under these conditions the concentration distribution in the boundary for a given current density $I$ is independent of the time and the boundary velocity is given by the relation

$$v = IT_l/FC_l \qquad (1)$$

in which $F$ is the faraday, $T_l$ the transference number of the leading ion constituent and $C_l$ is the concentration, in equivalents per milliliter, in the body of the leading solution. Whereas the concentrations of the salt solutions forming the boundary initially may be selected independently of each other, the concentration, $C_i$, of the column of indicator electrolyte that is formed by the advancing boundary is not independent of $C_l$ but is given by the relation

$$C_i = C_lT_i/T_l \qquad (2)$$

in which $T_i$ is the transference number of the indicator ion at the concentration $C_i$. If the boundary is formed initially between the leading solution and the indicator solution at a concentration $C_i'$ which is different from that, $C_i$, required by equation (2), then, as will be demonstrated later in this paper, a concentration boundary between the indicator salt at the two concentrations $C_i$ and $C_i'$ remains near the initial boundary position as the two-salt boundary advances.

In addition to the requirement that $u_i < u_l$ there is the restriction that the boundary system be stable gravitationally. This means that if the indicator solution is less dense than the leading solution the latter must be underneath and the boundary must descend. If the indicator solution is more dense than the leading solution the latter must be on top and the boundary must rise. Moreover, since the densities of most salt solutions increase with increasing concentration, gravitational stability also requires that the initial indicator concentration, $C_i'$, be equal to or greater than that, $C_i$, of the adjusted indicator solution for a rising boundary whereas for a descending boundary $C_i' \leq C_i$.

Under the conditions prevailing in previous work with two-salt boundaries the transition from one solution to the other occurs within less than a millimeter. Such a sharp boundary can be located accurately with the aid of relatively simple optical arrangements, advantage being taken of the difference of refractive index at the boundary, and this is sufficient for a determination of the boundary displacement and hence the transference number $T_l$. The optical devices previously employed have not, however, given information concerning the magnitude and distribution of the gradients in the boundary and the manner in which these vary with the current. This information can now be obtained with the aid of the schlieren scanning camera. It is the purpose of this paper to report measurements of the gradients in typical boundaries and to show that they are in agreement with Weber's theory.[4]

**Experimental Results.**—The patterns of Fig. 1, recorded during the electrolysis at 0.5°, of 0.1 $N$ potassium iodate:0.1 $N$ potassium chloride at a current density of 0.00655 amp./sq. cm., are typical of the results obtained in this research. The time interval between all of the patterns after the second was one hour. In order to avoid overlapping of the concentration boundary peak, each successive pattern has been displaced a fixed distance vertically. The line $h_0$ in each pattern

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[1] Longsworth, THIS JOURNAL, **61**, 529 (1939).

[2] Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

[3] Longsworth, THIS JOURNAL, **65**, 1755 (1943).

[4] H. Weber, "Die partiellen Differential-Gleichungen der mathematischen Physik," Braunschweig, 1910, 5th edition, chapter 24.

[5] MacInnes and Cowperthwaite, *Proc. Natl. Acad. Sci.*, **15**, 18 (1929).

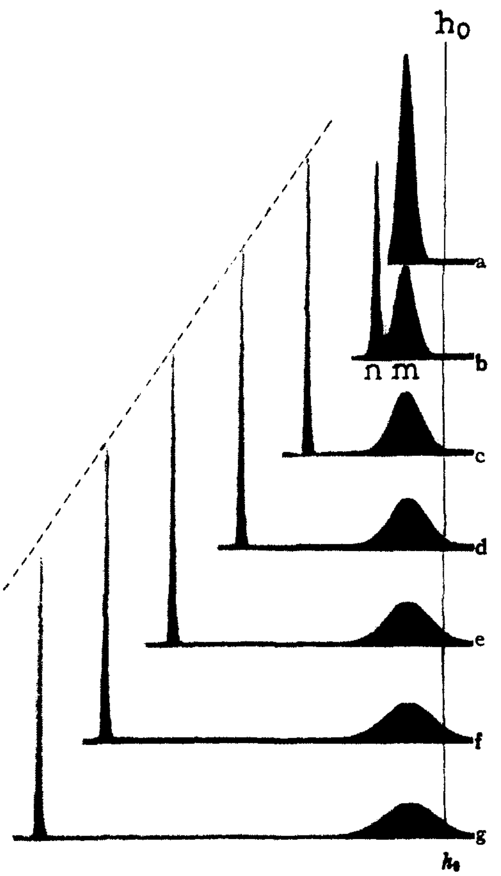

Fig. 1.—Schlieren scanning patterns obtained during the electrolysis of a boundary formed initially between 0.1 *N* $KIO_3$ and 0.1 *N* KCl.

is due to a graduation on the cell that serves as a reference mark from which all boundary displacements are measured. Except for the necessity of automatic regulation of the current[6] in work with two-salt boundaries, the apparatus and experimental procedures employed have been adequately described in recent papers by the author.[3,7]

Several features of the direct moving boundary method, previously inferred but unconfirmed experimentally, are at once apparent in Fig. 1. The first pattern, a, was obtained after the boundary had been formed and shifted from behind the opaque horizontal plates of the cell, but before the electric field was applied. On passage of the current this boundary separated, as shown in Fig. 1b, into the concentration boundary, *m*, between potassium iodate at the concentrations $C_i$ and 0.1 *N* and the two-salt boundary, *n*, between potassium iodate at the concentration $C_i$ and 0.1 *N* potassium chloride. On continued electrolysis, Figs. 1b–g, the concentration boundary spread progressively due to diffusion whereas the two-salt boundary acquired, by the time the pattern of Fig. 1c was recorded, a salt distribution that remained unchanged.

With the patterns arranged as in Fig. 1, the constancy of the maximum gradient in the two-salt boundary is indicated by the fact that these maxima fall on a straight line. The slight decrease in the height of the peak as the boundary approaches the upper end of the channel, Fig. 1g, is probably due to a small convergence error inherent in the optical system[8] and not to a change in the salt distribution through the boundary. In one experiment in which the boundary displacement was balanced by addition of solution, thereby holding it at the same level and consequently maintaining the convergence error at a constant value, the salt distribution in the boundary did not vary during continuous electrolysis for two weeks.

As recently shown experimentally,[3] the displacement of the concentration boundary, *m*, of Fig. 1, is proportional to the difference of transference number between the two solutions of potassium iodate forming this boundary. The quantity of electricity passed in this experiment, although sufficient to cause the two-salt boundary, *n*, to move the length of the channel, was not large enough to permit a reliable determination of the concentration boundary displacement. The area of the peak corresponding to the boundary at *m* does, however, afford a measure of the concentration adjustment of the indicator electrolyte. Since the refractive index increment[9] for 0.1 *N* potassium iodate, using the mercury yellow line, is 0.00282 and the area of the concentration boundary corresponds to $\Delta n = 0.00102$, the adjusted concentration $C_i$ is 0.0640 *N*. The displacement of the two-salt boundary in Fig. 1 gives a value of 0.504 for the anion transference number, $T_l$, of 0.1 *N* potassium chloride at 0.5°, in agreement with that, 0.505, obtained by extrapolation of the data of Allgood, Le Roy and Gordon.[10] Substitution of these figures in equation (2) gives 0.323 as the anion transference number, $T_i$, of 0.064 *N* potassium iodate. Since the precision of the refraction increments from measurements of pattern areas is about $\pm 1 \times 10^{-5}$, the error in $T_i$ is probably not more than 1%. Although this error is greater than that characteristic of the direct de-

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(6) Longsworth and MacInnes, THIS JOURNAL, **60**, 3070 (1938).

(7) Longsworth, *Chem. Rev.*, **30**, 323 (1942).

(8) Svensson, *Kolloid-Z.*, **90**, 141 (1940).

(9) The refraction increments reported here have been determined at 0.5° with the aid of the schlieren scanning camera and a 60° hollow prism cell. The prism, filled with water, was placed in the thermostat in the focus of the camera, set for minimum deviation, and a scanning photograph was obtained. The prism was then rinsed and filled with a salt solution of known concentration and again photographed. The deflection D due to the salt solution is connected with the refractive index difference $\Delta n$ and the prism angle $\alpha$ by the relation (R. W. Wood, "Physical Optics," The Macmillan Co., New York, N. Y., 1924) $\Delta n = \sin {}^1/_2(\alpha + D)/\sin {}^1/_2\alpha$. The reproducibility of this differential method, $\Delta n \pm 5 \times 10^{-6}$, compares favorably with that attainable with the Zeiss-Pulfrich refractometer. I have not been able to find data in the literature for comparison with my values at 0°. I have, therefore, also made measurements at 10°, 18 and 30° for several salts and these are in agreement with the best available data. Contrary to the general impression, the temperature coefficient of the refraction increment is not negligible for many salts at temperatures in the neighborhood of 0°.

(10) Allgood, Le Roy and Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

termination of $T_l$ for the leading solution from the displacement of the two-salt boundary, the method just outlined will be useful when other methods are not available.

Another feature of the direct moving boundary method is illustrated in Fig. 2. In this figure the patterns of a 0.064 *N* potassium iodate: 0.1 *N* potassium chloride boundary, obtained during electrolysis at three different current densities, have been placed at the corresponding positions on the current axis. When mounted in this manner the maximum gradient of each pattern falls on a straight line passing through the origin, *i. e.*, this gradient is directly proportional to the current. With currents heavier than that corresponding to Fig. 2 c the light deflected by the steepest gradients in the boundary fails to enter the camera objective. Some idea of the sharpness of the boundaries used for routine transference number determinations may be obtained from the fact that the current densities employed range from five to ten times the maximum value used in the present research.

With lithium chloride as the indicator electrolyte for the potassium chloride, the boundary descends since the leading solution is heavier and must remain below. Moreover, the initial indicator salt concentration, $C_i'$, should, therefore, be equal to, or less than, the adjusted concentration, $C_i$. Thus when a 0.05 *N* lithium chloride: 0.1 *N* potassium chloride boundary was studied in the same manner as the potassium iodate: potassium chloride boundary a stable concentration boundary was left behind near the initial position as the two-salt boundary descended. Since the refraction increment for 0.05 *N* lithium chloride is $0.00047_5$ and the area of the concentration boundary corresponded to an increment of $0.00008_7$, the adjusted concentration, $C_i$, may be computed to be 0.0592 *N* and $T_i$, by equation (1), is 0.294. When a 0.1 *N* lithium chloride solution was used to form the boundary, this solution, being heavier than the underlying 0.059 *N* solution produced by the migration of the two-salt boundary, mixed with the latter and the resulting schliere were clearly visible in the focus of the camera. This convective circulation partially penetrated the boundary, distorting it and causing it to move too rapidly. Similar disturbances were also apparent when the lithium chloride concentration was 0.065 *N*.

**The Theory of Two-Salt Boundaries.**—As has been shown conclusively in previous experimental work,[11] a two-salt boundary moves with a constant velocity under the influence of a constant current density. The present research demonstrates that under these conditions the concentration distribution through the boundary also does not change with the time. The concentrations are, therefore, functions of the time *t* and the coordinate *h*, *i. e.*, the vertical height in the channel, of the form

$$c = f(h - vt) \tag{3}$$

in which *v* is the boundary velocity. This relation is the basis of Weber's theory for the concentration distribution in a two-salt boundary. The following is a brief statement of his theory.

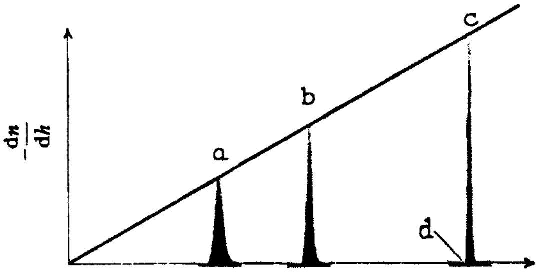

Fig. 2.—Patterns of a 0.064 *N* $KIO_3$: 0.1 *N* KCl boundary at three different current densities.

As has been shown in an earlier paper[11] the equation of continuity for an ion of the *j*-th kind is

$$\frac{\partial c_j}{\partial t} = \frac{\partial}{\partial h}\left[\frac{c_j u_j}{|z_j|}\left(\frac{\partial \mu_j}{\partial h} + z_j\frac{\partial E}{\partial h}\right)\right] \tag{4}$$

and the expression for the current density is

$$I = -F\sum_{j=1}^{j=s}\frac{c_j u_j}{z_i}\left(\frac{\partial \mu_j}{\partial h} + z_j\frac{\partial E}{\partial h}\right) \tag{5}$$

In these equations *E* and $\mu$ are the electrical and chemical potentials, respectively, both expressed in volts. The valence of an ion, account being taken of its sign, is denoted by *z* whereas $|z|$ indicates the magnitude only.

Since $\partial c/\partial t = -vf'(h - vt) = -v\partial c/\partial h$ from equation (3), equation (4) becomes, after integration

$$vc_j + \frac{c_j u_j}{|z_j|}\left(\frac{d\mu_j}{dh} + z_j\frac{dE}{dh}\right) = A_j \tag{6}$$

in which $A_j$ is a constant of integration. Since the present treatment will be restricted to a system in which the leading ion, l, and indicator ion, i, are monovalent cations, c denoting the common monovalent anion, equation (6) becomes

$$vc_i + c_i u_i(d\mu_i/dh + dE/dh) = A_i \tag{7}$$

$$vc_l + c_l u_l(d\mu_l/dh + dE/dh) = A_l \tag{8}$$

$$vc_c + c_c u_c(d\mu_c/dh - dE/dh) = A_c \tag{9}$$

At $h = +\infty$, $c_i = 0$ and $A_i = 0$ while at $h = -\infty$, $c_l = 0$ and $A_l = 0$. Moreover, if equation (9) be subtracted from the sum of equations (7) and (8), it will be noted, on comparison with equation (5), that $A_c = I/F$ since electrical neutrality requires that $c_i + c_l - c_c = 0$.

Elimination of $dE/dh$ between equations (7) and (8), followed by integration, assuming the mobilities to be constant, gives

$$\mu_i - \mu_l = (1/u_l - 1/u_i)vh + B' \tag{10}$$

If, now, the approximation is made that

$$\mu = \mu_0 + k \ln c \tag{11}$$

in which $k = RT/F$, *R* being the gas constant in

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[11] MacInnes and Longsworth, *Chem. Rev.*, 11, 171 (1932).

joules per degree and $T$ the absolute temperature, equation (10) may be written

$$\ln(c_i/c_l) = (1/u_l - 1/u_i)vh/k + B \qquad (12)$$

If the origin is taken at that level in the boundary for which $c_i = c_l$, the constant of integration, $B$, is zero. Equation (12) can then be written

$$\ln c_i + vh/ku_i = \ln c_l + vh/ku_l = \ln \psi \qquad (13)$$

thereby defining a function, $\psi$ ($h$), that remains to be determined. Elimination of $\mu_i$ and $c_i$ between equations (11), (13) and (7) yields

$$\mathrm{d}E/\mathrm{d}h = -k\mathrm{d}\ln\psi/\mathrm{d}h \qquad (14)$$

If $\sigma$ is defined as $(e^{-vh/ku_i} + e^{-vh/ku_l})$, then

$$c_c = c_i + c_l = \psi\sigma \qquad (15)$$

Substitution of equations (11), (14) and (15) in equation (9) gives

$$\mathrm{d}\psi + \left(\frac{v}{2ku_c} + \frac{\mathrm{d}\ln\sqrt{\sigma}}{\mathrm{d}h}\right)\psi\mathrm{d}h = \frac{I}{2kFu_c\sigma}\,\mathrm{d}h$$

Since $\sigma$ is a known function of $h$, this is an equation of the Bernouilli type[12] whose integrating factor is $\sqrt{\sigma}\,e^{vh/2ku_c}$ and whose solution is, therefore

$$\psi = \frac{I\,e^{-vh/2ku_c}}{2kFu_c\sqrt{\sigma}}\int_{-\infty}^{h}\frac{e^{vh/2ku_c}}{\sqrt{\sigma}}\,\mathrm{d}h$$

the lower limit of integration being determined from the condition that $\psi$ must vanish for $h = -\infty$. This is the result obtained by Weber. The same result is also obtained if i and l are monovalent anions.

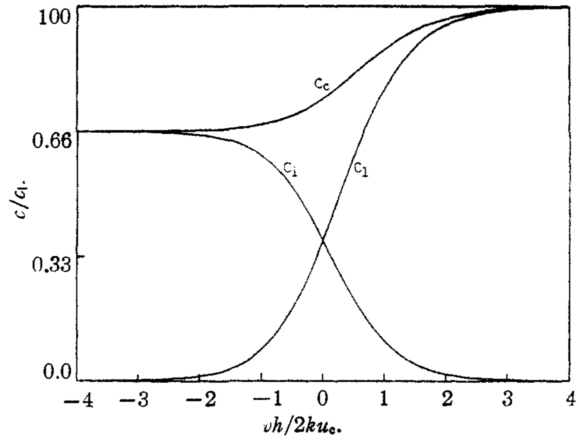

Fig. 3.—The theoretical concentration distributions of the indicator ion, i, the leading ion, l, and the common ion, c, in a typical two-salt moving boundary.

Computations with the foregoing relations are greatly facilitated if the mobilities $u_c$ and $u_l$ are simple multiples of $u_i$, which is very nearly the case for the boundaries studied in this research. Thus, by combining the transference numbers reported earlier in this paper with conductance data, one obtains, at 0° and for 0.1 $N$ solutions, $Fu_K = 35.4 \simeq Fu_{Cl} = 35.9$ whereas $Fu_{Li} = 15.0 \simeq Fu_{IO_3} = 16.2 \simeq {}^1/_2\,Fu_{Cl}$. Consequently a close approximation is made by taking

$$2u_i = u_l = u_c = 35.6/F \qquad (16)$$

Equation (13) then becomes, on reference to equation (1)

$$c_l/C_l = 1 - \sinh^{-1} y/y\sqrt{1 + y^2} \qquad (17)$$

and

$$c_i = c_l/y^2 \qquad (18)$$

in which $vh/2ku_c = \ln y$.

These functions are plotted in Fig. 3 and indicate the distribution of concentrations in a typical two-salt boundary.

Differentiation of equations (17) and (18) yields

$$\frac{2ku_c}{vC_l}\frac{\mathrm{d}c_l}{\mathrm{d}h} = \frac{1}{1 + y^2}\left(\frac{1 + 2y^2}{y\sqrt{1 + y^2}}\sinh^{-1} y - 1\right) \qquad (19)$$

$$\frac{2ku_c}{vC_l}\frac{\mathrm{d}c_i}{\mathrm{d}h} = \frac{1}{y^2}\left(\frac{2ku_c}{vC_l}\frac{\mathrm{d}c_l}{\mathrm{d}h} - 2\frac{c_l}{C_l}\right) \qquad (20)$$

The lower curve of Fig. 4 is a plot, in the reduced coördinates $vh/2ku_c$ and $(2ku_c/vC_l)\mathrm{d}c/\mathrm{d}h$, of equation (19) after multiplication of the left hand term by 10.8, the equivalent refractive increment for potassium chloride, while the upper curve corresponds to equation (20) after multiplication by 28.2, the increment for potassium iodate. The intermediate curve of Fig. 4 is the sum of the upper and lower curves and represents, therefore, the theoretical gradient curve, $\mathrm{d}n/\mathrm{d}h$, of the total refractive index. In so far as the theory is valid, this curve should correspond to those recorded experimentally. The scale of ordinates in Fig. 4 has been inverted to conform to the current practice in the publication of electrophoretic patterns.

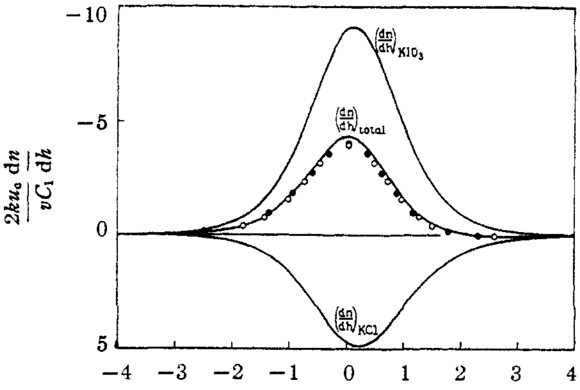

Fig. 4.—Distribution of the gradients $\mathrm{d}n/\mathrm{d}h$, of refractive index in a 0.064 $N$ $KIO_3$:0.1 $N$ KCl boundary.

With the aid of a two-coördinate comparator points were taken from the first two patterns illustrated in Fig. 2 and plotted as the circles and dots, respectively, in Fig. 4.[13] The agreement between

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[12] E. B. Wilson, "Advanced Calculus," Ginn and Co., Boston, 1911, p. 210.

[13] Points taken from the pattern of Fig. 2c, corresponding to the highest current density, have not been plotted in Fig. 4 since this sharp boundary appears to be subject to a slight curvature error[8]. A comparison between theory and experiment similar to that of Fig. 4 was also made for the descending lithium chloride: potassium chloride boundary and substantial agreement was found, the somewhat greater deviations being due to divergence of the lithium ion mobility from the relation assumed in equation (16).

the theory and experiment shown in this figure is surprisingly close, particularly in view of the simplifying assumptions that were found necessary. This agreement would appear to confirm completely the postulated mechanism, *i. e.*, that the boundary is the result of the interaction of diffusion and of ionic migration, and gives us still further confidence in the moving boundary method.

Since the maximum in the total gradient curve does not occur at $h = 0$, it is essential to locate this maximum accurately in order to have a reference point on the abscissa scale from which to plot the experimental data. For this purpose the expression for $d^2n/dh^2$ was obtained, set equal to zero, and the roots determined from a plot of the function. The position of the maximum depends, of course, on the relative values of the equivalent refraction increments and occurs at $\ln y = 0.419$ for the lithium chloride:potassium chloride boundary and at $\ln y = 0.037$ for the potassium iodate:potassium chloride boundary. In the latter case the theory also predicts a slight minimum in the gradient curve at $\ln y = 2.8$. It is of considerable interest that close inspection of the patterns reveals this minimum (see d of Fig. 2, for example) and that both its position and magnitude are in agreement with the theory. Owing to the relatively great density of potassium iodate solutions the minimum in the refractive index gradient curve is not accompanied by a corresponding minimum in the density gradient and the boundary remains, therefore, gravitationally stable.

The author is indebted to Dr. D. A. MacInnes of these Laboratories for his continued interest and helpful discussion.

### Summary

Salt boundaries of the type used for the direct determination of transference numbers have been studied with the aid of the schlieren scanning camera. Several features of the direct moving boundary method that were assumed in previous work have now been confirmed experimentally. Under the influence of a constant current the concentration distribution through a moving boundary does not change with the time and is given accurately by Weber's theory. Moreover, the adjusted concentration of the indicator solution, and hence its transference number, may be determined from the electrophoretic patterns.

NEW YORK, N. Y. RECEIVED NOVEMBER 19, 1943

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY]

# The System Ammonium Nitrate–Sodium Nitrate

BY EDWARD O. HOLMES, JR., AND DAVID REVINSON

In connection with the volunteer research program conducted by the Committee on Eutectics of the National Research Council, the senior author found that he was unable to confirm the accepted data on the system ammonium nitrate–sodium nitrate that he used to standardize his technique. The discrepancies in the determination of the points on the solubility curves were so large as to suggest that the work of Early and Lowry[1] on this system might be in error.

As a result, this investigation was begun to redetermine all parts of the system and to study the various factors that might lead to error such as (1) the method of purification of materials, (2) the length of drying of the purified materials and (3) the technique of determining points on the curve.

**Purification of Materials.**—The pure ammonium nitrate was supplied by the Committee on Eutectics.[2] It was of highest purity and the dry material was found by analysis to contain 100.01% ammonium nitrate. It was ground frequently and kept in a desiccator over Anhydrone for the entire period of the research. This material was used in all determinations.

The sodium nitrate (Merck Reagent) was further purified by two methods: (A) thrice recrystallized from water, ground frequently and kept over Anhydrone; (B) precipitated by concentrated nitric acid, washed with water, twice recrystallized, ground and kept over Anhydrone.

**Thermometers.**—Two thermometers used were of the twenty-four inch 0.1° type. Both were calibrated against the melting points of pure organic compounds and one by the Bureau of Standards, in addition.

### The Melting Point Measurements

(a) **Standard Microtechnique.**—This technique consisted in weighing out a sample of a tenth of a gram into a three-inch test-tube, fusing the mixture and stirring until clear, cooling and removing the solid melt, grinding it to a powder, introducing a portion of the ground material into a 2-mm. capillary tube and then determining the point at which the last crystals disappeared on very slow heating.

It was found that the Thiele–Dennis melting point apparatus did not give satisfactory results, so a melting point apparatus had to be devised that would permit better heat control and give more uniform results. This was accomplished by building a special gas control valve for the conventional apparatus which consists of a beaker full of oil over a microburner, and surrounding the bulb of the thermometer by a glass basket into which the capillary melting point tube was placed. A description of this apparatus can be found in the *Journal of Chemical Education.*[3]

This method worked quite satisfactorily for the left-hand side of the system, the solubility curve of ammonium nitrate, but difficulty was experienced on the right-hand side, the solubility curve of sodium nitrate. The trouble was caused by a rapid settling out of solid sodium nitrate

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(1) R. G. Early and T. M. Lowry, *J. Chem. Soc.*, **121**, 963 (1922).

(2) Courtesy of Professor Edward Mack, Jr., Chairman.

(3) Edward O. Holmes, Jr., *J. Chem. Ed.*, **20**, 239–240 (1943).