[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Formation and Some Derived Thermodynamic Properties of NaCl–NaBr Solid Solutions[1,2]

BY M. A. FINEMAN AND W. E. WALLACE

The ability of certain pairs of the alkali halides to form solid solutions over wide ranges of composition has long been recognized.[3] Although these solutions have been studied extensively, only in a few instances have there been careful determinations of their thermal properties.[4,5] Much of the available thermochemical information pertaining to the alkali halide solid solutions is based upon experiments performed prior to 1920. These studies,[6] dealing mostly with determinations of their heats of formation, yielded results which by present standards are somewhat lacking in precision. The desirability of improving on the older work is readily apparent.

Several years ago Fontell,[5] employing modern calorimetric techniques, determined the heats of formation of a series of potassium chloride–potassium bromide solid solutions and demonstrated[7] the utility of the results obtained in establishing the limits of mutual solid solubility of the two salts. This paper describes a similar study for the sodium chloride–sodium bromide system. The experimental heats of formation are of additional interest in that they may be used in testing the results of a calculation of these quantities made by Tobolsky[8] with the aid of the Born theory of ionic solids.

Experimental

Method.—The heats of formation were obtained by determining the difference in the heats of solution of a solid solution and a mechanical mixture of the same total mass and composition. The difference equals the negative of the heat of formation of the solid solution.[9] In this study a twin differential calorimeter was used so that the mixture and solid solution could be dissolved simultaneously, one in each side of the calorimeter, and the difference could be measured directly. Since the same quantity of solvent (water) was used in both halves, no heat of dilution correction was necessary.

Apparatus.—The calorimeter was essentially a modification of the Lange-type[10] heat of dilution calorimeter currently in use in this Laboratory. Instead of the single divided Dewar used by Lange, two Dewar flasks of about 1200-ml. capacity served as the calorimeter vessels. These were provided with the usual accessories (heater, stirrer, device for introducing the sample, etc.) and were immersed in a thermostat kept at 25 ± 0.003°. The temperature differences between the two calorimeters were measured using a 25-junction copper–constantan thermel in conjunction with a Leeds and Northrup type HS galvanometer. The sensitivity of the temperature-measuring equipment was such that 0.02 cal. produced about 1 mm. galvanometer deflection. In actual operation the galvanometer was used essentially as a null instrument in that, during the experiment, electrical energy was supplied to the side containing the mixture to compensate for the differences in heats of solution of the mixture and solid solution.

The samples to be dissolved were sealed into thin glass bulbs, brought to thermal equilibrium with the solvent and then crushed. Blank determinations indicated that the heat of crushing was negligible. The quantity of sample used varied from 0.025 to 0.043 mole, and the measured heat effects ranged from 3.75 to 14.20 calories.

To test the over-all effectiveness of the calorimeter, several determinations of the heats of solution of potassium chloride and sodium chloride were made. The results, when extrapolated to infinite dilution, were for sodium chloride 925 ± 1 cal./mole and for potassium chloride 4113 ± 3 cal./mole. These values agree with the literature[11,12] values to within 0.2% or less.

Materials Used and the Preparation of the Solid Solutions.—The sodium chloride was a Mallinckrodt Analytical Reagent, twice recrystallized from doubly distilled water by evaporation to one-half the original volume. The salt was then dried by fusing in a muffle furnace. Gravimetric analysis showed that the halogen content was 99.98%.

Two batches of sodium bromide were prepared. The first batch (batch A) was a Mallinckrodt Analytical Reagent which had been recrystallized three times from distilled water and dried by fusion. It has been shown that sodium bromide cannot be freed of sodium chloride by this procedure because of the formation of solid solutions.[13] By precipitating as the silver halides, the composition was determined to be 99.53 and 0.47% by weight of sodium bromide and sodium chloride, respectively. The second batch (batch B) was prepared from distilled bromine and Sorenson Primary Standard sodium oxalate by a procedure similar to that described by Baxter and Grover.[14] The bromine and sodium oxalate were Eimer and Amend Tested Purity Reagents. Gravimetric bromide analysis gave a value that was 99.93% of the theoretical value.

Preliminary experiments showed that there was no observable difference in the heats of formation of solid solutions of the same concentrations prepared from batch A and batch B. Therefore, the solid solutions were prepared entirely from batch A sodium bromide. Batch B was used to prepare the mechanical mixtures of the two pure salts.

The solid solutions were prepared from appropriate

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(1) From a thesis submitted by Mr. M. A. Fineman in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pittsburgh, 1948.

(2) This research was supported in part by the Office of Naval Research.

(3) W. C. Blasdale, "Equilibria in Saturated Salt Solutions," The Chemical Catalog Co., Inc., New York, N. Y., 1927, p. 88.

(4) M. M. Popov, *Z. physik. Chem.*, **A147,** 302 (1930); **A167,** 180 (1933).

(5) N. Fontell, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **X6,** 1 (1939).

(6) G. Bruni, *Chem. Rev.*, **1,** 345 (1925).

(7) N. Fontell, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **X12,** 1 (1929).

(8) A. V. Tobolsky, *J. Chem. Phys.*, **10,** 187 (1942).

(9) The term "heats of formation of the solid solution" refers throughout this paper to the reaction NaCl(s) + NaBr(s) → (NaCl + NaBr) solid solution. In other words the reference state has been chosen to be that of the pure *compounds*. The same convention is employed in later sections where entropies and free energies of formation of the solid solution are mentioned.

(10) E. Lange and A. L. Robinson, *Chem. Rev.*, **9,** 89 (1931).

(11) S. G. Lipsett, F. M. G. Johnson and O. Maass, THIS JOURNAL, **49,** 925 (1927).

(12) E. Lange and J. Monheim, *Z. physik. Chem.*, **A150,** 349 (1930).

(13) T. Batuecas and J. I. Fernandez-Alonso, *Z. physik. Chem.*, **A190,** 272 (1942).

(14) G. P. Baxter and F. L. Grover, THIS JOURNAL, **37,** 1027 (1915).

amounts of sodium chloride and sodium bromide by fusing them together in a platinum dish and crystallizing by pouring into a cold platinum dish. The solid solution was then annealed at 650° for at least forty-eight hours. The exact concentrations were obtained gravimetrically by precipitation of the silver halides.

Physical State of the Solid Solutions.—It is well known that when a melt composed of two substances exhibiting extensive solid solubility is allowed to solidify, a non-homogeneous solid phase results due to the preferential crystallizing out of the higher melting component. Upon annealing the solid at a temperature sufficiently high for rapid diffusion in the lattice, usually near its melting point, the material is rendered homogeneous. It was with the intention of obtaining homogeneous solid solutions, as well as to eliminate possible defects in the crystals, that the annealing procedure was employed.

The studies of Matsen and Beach[15] on the rates of formation of homogeneous sodium chloride–sodium bromide solid solutions were of considerable value in deciding upon the proper annealing conditions. They observed that an intimate mixture of pure sodium chloride and sodium bromide formed a completely homogeneous solid solution in one to two hours at 700°, in fourteen hours at 600°, and in seventy-two hours at 500°. The X-ray diffraction patterns of the "mixture" were used to follow the course of the reaction. Interpolating the results of Matsen and Beach for 650°, a homogeneous solid solution in four and one-half to five hours was anticipated, had the starting material been a mixture of the two pure salts. Since the starting materials were non-homogeneous solid solutions, annealing times of four and one-half to five hours or less should have been adequate. Actually all samples were annealed for forty-eight hours or more.

The annealed samples were divided into two portions, one of which was used in the calorimetric work and the other subjected to X-ray diffraction analysis. Diffraction patterns of all nine solid solutions and both pure salts were obtained. The diffraction lines were uniformly sharp for all eleven samples and the derived lattice spacings when plotted against composition lay on a smooth curve with an average deviation of less than 0.01%.[16] There was complete absence of any evidence in the diffraction patterns suggesting non-homogeneity, crystal imperfections, or coexistence of two or more phases in any of the solid solutions.

As an additional test of the effectiveness of the annealing procedure a large batch of non-homogeneous solution (mole fraction 0.4927 of sodium bromide) was prepared and divided into three portions. One portion was annealed for twenty hours, the second for forty-eight hours, and the third for ninety-six hours. The measured differences in heat contents were −3.3 ± 3.2 cal./mole for the forty-eight-hour sample and −2.3 ± 3.1 cal./mole for the ninety-six-hour sample relative to the twenty-hour sample. In view of the insignificant change in heat content accompanying the final forty-eight hours of annealing and since the total annealing time exceeded by a factor of twenty that expected from the work of Matsen and Beach,[14] there appeared to be reasonable assurance that forty-eight hours of annealing was adequate for obtaining homogeneous solid solutions.

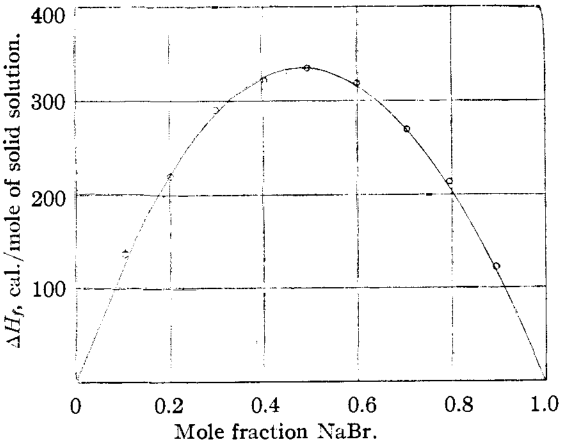

Fig. 1.—The heats of formation of sodium chloride–sodium bromide solid solutions as a function of composition. The curve is calculated from equation 1.

It should perhaps be pointed out that some of the solid solutions whose heats of formation are reported in this paper exist as a single-phase solid at 25° only in the metastable state, if the phase diagram derived in a later section is valid. Some of the X-ray diffraction patterns were taken about five weeks after the calorimetric determinations had been made. No indication of a transformation into the stable, two-phase system was apparent in that period of time.

Heats of Formation of the Solid Solutions.—The mean experimental values for the heats of formation of the sodium chloride–sodium bromide solutions in calories per mole of solid solution are listed in Table I.

TABLE I

EXPERIMENTAL HEATS OF FORMATION OF NaCl–NaBr SOLID SOLUTIONS AT 25°

N_2, (mole fraction of NaBr)	Experiments	Heats of formation (cal./mole of solid solution)
0.1018	4	136.7 ± 0.6
.2019	4	220.5 ± 0.6
.2982	4	291.9 ± 1.4
.4029	4	323.5 ± 1.5
.4927	6	335.5 ± 2.1
.5977	4	319.9 ± 0.6
.7007	4	271.0 ± 0.3
.7922	4	213.7 ± 0.5
.8947	4	122.6 ± 0.9

The tabular suitability test[17] indicated that a cubic equation was satisfactory for representing the data contained in Table I. Employing the method of least squares the following relationship

$$\Delta H_f = 1433N_2 - 1616N_2^2 + 182.8N_2^3 \qquad (1)$$

was obtained where N_2 is the mole fraction of sodium bromide.[18]

The experimental values and the curve drawn from equation 1 are shown in Fig. 1.

Relative Partial Molal Heat Contents.—The relative partial molal heat contents with respect to the pure solids can be derived from the heats of formation using the equations

$$\overline{H}_1 - H_1^s = \Delta H_f - N_2 \frac{d(\Delta H_f)}{dN_2} \qquad (2)$$

$$\overline{H}_2 - H_2^s = \Delta H_f + (1 - N_2) \frac{d(\Delta H_f)}{dN_2} \qquad (3)$$

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[15] F. A. Matsen and J. Y. Beach, THIS JOURNAL, **63**, 3470 (1941).

[16] Unpublished measurements by Dr. J. E. Nickels and the authors.

[17] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 60.

[18] In the remaining part of this article subscripts 1 and 2 will apply to sodium chloride and sodium bromide, respectively. Furthermore, unless there is a statement to the contrary, any thermodynamic property of formation will refer to one mole of the solid solution.

Substituting equation 1 into the above relations

$$\bar{H}_1 - H_1^s = 1616N_2^2 - 365.6N_2^3 \qquad (4)$$

$$\bar{H}_2 - H_2^s = 1068N_1^2 + 265.6N_1^3 \qquad (5)$$

The Free Energies of Formation and the Limits of Solid Solubility.—It is usually assumed that the entropy of a crystalline solution exceeds that of its components by an amount

$$\Delta S = -R\,[N_2 \ln N_2 + (1 - N_2) \ln (1 - N_2)] \qquad (6)$$

if the components are sufficiently alike for there to be a random distribution of the particles over the lattice sites.[7,8,19] This identifies the entropy of formation with the entropy of random mixing and neglects possible contributions due to changes in the vibrational entropy. It appears that equation 6 should give[20] a fairly satisfactory estimate of the entropy of formation of a solid solution exhibiting only small departures from ideality unless some unusual behavior is in evidence, as, for example, order–disorder phenomena.[21] Since the alkali halide solid solutions give no evidence of forming ordered structures[22] and in view of the small departures from ideality revealed by the heats of formation for the sodium chloride–sodium bromide system (ΔH_f less than 0.2% of the lattice energies), equation 6 together with equation 1 has been used to determine the free energies of formation.

$$\Delta F = 1433N_2 - 1616N_2^2 + 182.8N_2^3 + RT[N_2 \ln N_2 + (1 - N_2) \ln (1 - N_2)] \qquad (7)$$

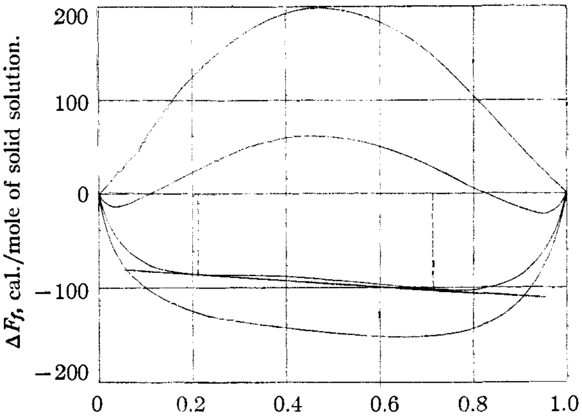

Fig. 2.—The free energies of formation of sodium chloride–sodium bromide solid solutions at various temperatures. From top to bottom the curves refer to 100, 200, 310 and 350°K. The 310°K. curve shows a common tangent, and the dashed lines represent the solubility limits.

The variation of ΔF with composition at several temperatures is shown in Fig. 2.

Employing equation 7, the limits of solid solubility can be determined at various temperatures by the method of common tangents.[23] By setting the second and third derivatives of ΔF with concentrations equal to zero[24] the critical solution temperature and composition were found to be 341° K. and 0.45 mole fraction of sodium bromide, respectively. The computed solubility diagram is shown in Fig. 3.

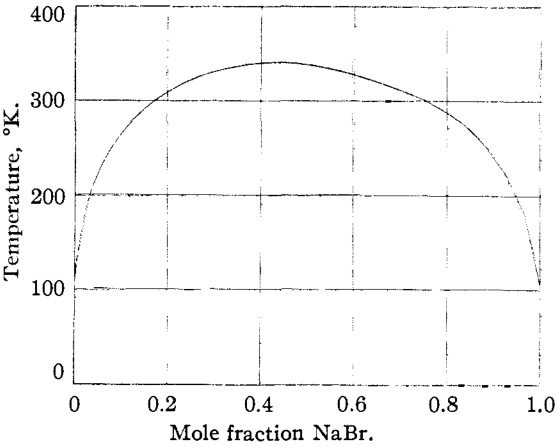

Fig. 3.—The mutual solid solubilities of sodium chloride and sodium bromide at various temperatures calculated from equation 7.

It should be understood that the reliability of the computed phase diagram depends upon the correctness with which equation 6 accounts for the entropy changes accompanying solid solution formation. In this paper equation 6 has been assumed to be valid for all temperatures between 0 and 350° K. for reasons stated earlier. If this is true, ΔC_p must vanish and ΔH_f must be independent of temperature over that temperature range.[19] The authors were unable to find in the published literature any experimental data for ΔS, ΔH_f or ΔC_p for sodium chloride–sodium bromide solid solutions nor, for that matter, any experimental solid solubility data pertaining to this system. Since it would be difficult to assess the effect on the calculated solubility curve of even small deviations of the entropy from that of random mixing without knowing how these deviations vary with temperature and composition, the curve given in Fig. 3 should perhaps be regarded as provisional in nature, pending experimental validation of equation 6. As a provisional phase diagram it is of interest only because of the lack of experimental solid solubility data for this system and because it suggests that the stable system below 300° K. would consist of

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(19) J. C. Slater, "Introduction to Chemical Physics," McGraw-Hill Book Co., New York, N. Y., 1939, p. 277.

(20) E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1**, 444 (1933). The validity of equation 6 was established at 25° for a silver chloride-silver bromide solid solution. In addition ΔC_p for the solution process was stated to be insignificantly different from zero from 15 to 298°K. ΔC_p must vanish over the temperature range for which equation 6 is valid.

(21) F. C. Nix and W. Shockley, *Rev. Mod. Phys.*, **10**, 1 (1938).

(22) M. V. Laue, *Ann. Physik*, **78**, 167–176 (1925).

(23) F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940, p. 499.

(24) J. H. Hildebrand, "Solubility of Non-electrolytes," Reinhold Publishing Corp., New York, N. Y., 1936, p. 144.

two phases over a major portion of the composition range.

Comparison and Evaluation of Calculated and Observed Heats of Formation.—Tobolsky[8] has developed an expression, based upon the Born theory of ionic salts and Vegard's law, which can be used to approximate values for the heats of formation of sodium chloride–sodium bromide solid solutions. A comparison of the calculated and observed quantities is made in Table II and it is readily apparent that the two are not in satisfactory agreement. In view of the precision of the measured heats it seems that the calculated values must be considerably in error. This is not too surprising for it appears that Tobolsky was not principally concerned with developing an exact theoretical expression.

TABLE II

CALCULATED AND OBSERVED HEATS OF FORMATION

N_2	Heats of formation, cal./mole of solid solution Experimental	Calculated
0.0	0	0
0.1	127	56
0.2	224	99
0.3	290	129
0.4	327	146
0.5	336	151[a]
0.6	318	145
0.7	274	126
0.8	206	95
0.9	114	53
1.0	0	0

[a] This differs from the result (118 cal./mole) given in Tobolsky's paper.[8] Evidently he used an approximate expression for his computations whereas the above results were computed using his complete expression.

For the purpose of interpreting the heat measurements presented in this paper insofar as is possible in terms of Tobolsky's development, the authors have examined his formulation in some detail. It appears that there are several factors which could account for the deviations in Table II, some or all of which may actually be involved. It is to be noted that Tobolsky expresses the heat of formation as the difference in lattice energies of the solid solution and a mechanical mixture. Since the lattice energies are large (about 180,000 cal.) compared to the difference, it is evident that the calculated heats will be quite sensitive to small errors in the lattice energies. For example, uncertainties of 0.05% in the lattice energies would introduce an error of about 80% in the difference. To calculate the heat of formation with a precision of 10%, the lattice energies would have to be known to about 0.005%. Obviously, there are many factors to be considered in computing lattice energies with this degree of precision.

It is appropriate to inquire as to the possibility of explaining the deviations in terms of uncertainties in the lattice spacings. On the surface one might think that, to compute the heat of formation precise to 10%, values for the lattice spacing precise to 0.005% or better would be required. Actually, this is not the case since the form of Tobolsky's equation, when Vegard's law is assumed, is such as to render the calculated results less sensitive to errors in the lattice parameters. In fact, uncertainties of 0.1% in the lattice spacings introduce only about 5 cal. in the ΔH_f value.[25] The lattice constants of many pure materials, including the alkali halides, have been established with precision considerably better than 0.1%, so that the failure of the calculated and observed heats to agree cannot be ascribed to uncertainties in the lattice spacings.

Focussing attention on the assumption that Vegard's law holds for this system, it is observed that if the actual lattice parameter (anion–cation distance) of the solid solution exceeds the spacing computed from Vegard's law by only 0.003 Å. the value listed in Table II would be increased by 180 calories, just the amount necessary for agreement with the observed value. Accordingly, it would be possible to explain the differences noted by assuming small positive deviations from Vegard's law. The determination of the lattice spacings for this system is currently under way in this Laboratory and preliminary results indicate that there are positive deviations from Vegard's law amounting to approximately 0.004 Å. The close agreement of this quantity and the deviation required to bring the observed and computed heats into agreement might be regarded as confirming the essential validity of Tobolsky's approximation. However, the authors are inclined to regard the agreement as fortuitous.

In comparing the calculated and observed heats it has been tacitly assumed that the theory of ionic crystals used in evaluating the lattice energies is sufficiently refined to make the comparison meaningful. This assumption is certainly open to some question. May[26] has made a thorough study of the relative stability of the cesium chloride and sodium chloride-type lattices for cesium chloride and ammonium chloride. To account for the stability of the cesium chloride-type lattice he found it necessary to introduce additional parameters into the repulsion part of the Born–Mayer expression for the lattice energies. No attempt has been made to apply May's type of reasoning to the present problem. However, it has been observed that the calculated heats are quite sensitive to the form of the repulsion potential. In Tobolsky's expression, based on the old Born theory where the repulsion was assumed to vary inversely as some high power (8–10) of the distance of separation, the contribution arising from the repulsion term accounts for $^1/_8$ of the total value. Some calculations by the authors using the newer exponential expression for the repulsion term give a value for the repulsion energy

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(25) This statement and the remainder of this section refer to a 50 mole % solid solution.

(26) A. May, *Phys. Rev.*, **52**, 339 (1937).

alone approximately equalling the entire computed result listed in Table II. In view of the sensitivity of the calculations to the type of repulsion potential chosen it would seem that an adequate accounting for the observed results cannot be made until a more detailed picture of the repulsive forces is provided.

Summary

The heats of formation at 25° of sodium chloride–sodium bromide solid solutions have been measured at intervals of 10 mole per cent. A cubic equation has been fitted to these data by the method of least squares. Equations are given from which the partial molal heat contents relative to the pure solids can be calculated.

By assuming the entropy of formation is that of random mixing, the free energies of formation were obtained.

The limits of solubility have been determined graphically by the method of common tangents from 0 to 350°K. The critical solution temperature and concentration have also been calculated. With these data the solid solubility diagram has been constructed.

A comparison of the heats of solution as obtained in this research with those calculated by Tobolsky has been made. The differences noted have been discussed in terms of possible inadequacies in Tobolsky's development.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

An Investigation of the Streaming Birefringence of Amylose Solutions[1]

BY JOSEPH F. FOSTER AND IRWIN H. LEPOW[2]

Starch is now considered to consist of two components, the amylose fraction being essentially a linear polymer while the amylopectin fraction is highly ramified. The problem of distinguishing between such polymeric types by the usual physical-chemical studies of their solutions is difficult since both have high frictional coefficients. On the other hand it seems possible that the two types of polymers might behave quite differently with regard to their orientability in a streaming gradient since this property depends primarily on length rather than just asymmetry or frictional coefficient. For this reason an extensive study of the streaming birefringence of these starch fractions has been undertaken.

Peterlin and Samec[3] attempted to orient both amylose and amylopectin from several types of starch without success and concluded both fractions to be very nearly spherical. The present paper shows on the contrary that the amylose component is readily orientable.

Experimental

Apparatus.—The concentric cylinder apparatus was patterned after that described in detail by Edsall, *et al.*[4] It consists of two concentric stainless steel cylinders of mean radius 3.22 cm. separated by a gap of 1.0 mm. The inner cylinder is driven through a flexible shaft by a 0.22-h.p. 15-volt direct current motor. The armature and field circuits of this motor are separately excited by two direct current generators. This enables control of the motor by means of the standard Ward–Leonard circuit and enables the attainment of constant speeds with adequate torque over a wide range, from approximately 100 to 3000 r.p.m. The outer cylinder is jacketed for circulation of water.

The filter-isolated green line of a type AH-4 General Electric mercury arc is used as the light source. This is condensed on a slit placed at the focal point of a collimating lens. The essentially parallel light then passes in succession the polarizing Nicol prism, the lower window of the apparatus, the gap between the cylinders, upper window, analyzing Nicol, 90° prism and observing telescope. For making measurements of magnitude of double refraction a $\lambda/4$ plate (and sometimes a quartz half-shadow wedge) are placed in the path just ahead of the analyzer.

It will be noted that the gap width in this apparatus is four times as great as that in the apparatus of Edsall.[4] This reduces the maximum gradient attainable, but greatly simplifies the optical problem.

Solvent.—One of the best molecular solvents for starch and its fractions is ethylenediamine. Glycerol, while not in itself a good solvent for amylose, can be added in almost unlimited quantity to solutions of amylose in ethylenediamine without impairing the clarity or reducing the stability. In this way solutions of high viscosity can be prepared, greatly enhancing the ease of orientability in the streaming gradient. All runs reported in this paper have been made in such mixed solvents. Furthermore, no effort was made to dehydrate the reagents,[5] since it would be almost impossible to keep the solutions anhydrous. The exact composition of the solvents is not important so long as the viscosity is known. Viscosities were measured (in Ostwald type viscometers) on several mixtures of ethylenediamine and glycerol at 19, 25 and 40°. Plots of log η *vs.* temperature for the various compositions were very nearly linear and parallel. Viscosities at other temperatures and compositions were obtained by interpolation from this graph.

Materials Studied.—All amylose samples studied were prepared by fractionation after the method of Schoch[6] which involves crystallization of the complex formed with one of the higher (4–6 carbon) alcohols. All were recrystallized from one to five times.

Methods.—The solutions were made up entirely by weight. The amylose was first dissolved in the ethylenediamine, contained in a glass-stoppered flask, with the aid of mechanical agitation. The glycerol was then added,

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[1] Journal Paper No. J-1552 of the Iowa Agricultural Experiment Station, Ames, Iowa; Project No. 817. Supported in part by a grant from the Corn Industries Research Foundation.

[2] Present address, Lederle Laboratories Division, American Cyanamid Company, Pearl River, New York.

[3] Peterlin and Samec, *Kolloid Z.*, **109**, 96 (1944).

[4] J. T. Edsall, C. G. Gordon, J. W. Mehl, H. Scheinberg and D. W. Mann, *Rev. Sci. Instruments*, **15**, 243 (1944).

[5] Eastman Kodak Co. 95–100% ethylenediamine and General Chemical Co. C. P. glycerol were used without further purification.

[6] T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942).