traces of cyclohexene and sulfur dioxide in the exit gases during the reaction and distillation. The finished product also gave positive evidence of traces of these two products. The cyclohexyl sulfite was redistilled a year later and its boiling range and refractive index (n^{25}D 1.4848) were found unchanged. After another two years the material boiled constantly at 165° under 14 mm. with no change in the refractive index. Upon analysis the product contained 13.10% sulfur against 13.02% expected. These results substantiate Voss and Blanke's statements regarding cyclohexyl sulfite.

It was observed that unless the reaction is carried out to completion, as indicated, cyclohexyl sulfite cannot be distilled successfully under vacuum because of the continuous decomposition of the product to sulfur dioxide and cyclohexene. This fact would explain the inability of the French workers to isolate the product. Repeated distillation after long standing has not given evidence of deterioration, excepting for the smell of sulfur dioxide and cyclohexene. It was also observed that cyclohexyl sulfite containing very small amounts of sulfuric acid can be distilled under vacuum without decomposition.

Following the procedure given, no difficulty was experienced in the preparation of other esters such as:

Sulfite	Yield, %	Boiling range, °C.
Dimethyl	84	124–127
Diethyl	Quantitative using slight excess of anhydrous ethanol	154–157
Isopropyl	(Refractionated) 84% on isopropanol	73–74° at 25 mm.
n-Butyl	Yield (refractionated) 92.5% on butanol	124–126° at 29 mm.
Methylhexylcarbinyl	85 (reaction temp. 20–25°)	147–149° at 5–6 mm.

It should be noted that with methanol, ethanol and isopropanol, the reaction should be carried under a lower vacuum because of their low boiling points. It is advantageous to regulate the vacuum so that the alcohol barely refluxes during the addition and later to increase the vacuum.

Summary

Sulfites are obtained in excellent yields from the reaction of primary and secondary alcohols with thionyl chloride using low pressures during the operation.

Cyclohexyl sulfite made by the above procedure is a relatively stable product and can be redistilled repeatedly without change in composition.

ST. LOUIS, MO. RECEIVED JANUARY 31, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON, AND THE DEPARTMENT OF CHEMICAL ENGINEERING, COLUMBIA UNIVERSITY]

On the Thermodynamics of Azeotropic Solutions. I. Shift of Equilibrium in Binary Systems[1]

BY O. REDLICH AND P. W. SCHUTZ

Among the numerous authors who have contributed to the vast amount of experimental data on azeotropic solutions in early and recent times, several have felt the advantages which are to be expected from a thermodynamic discussion.[1a] Obviously thermodynamic predictions are apt to enhance the value of available data and the efficiency of new experimental research, especially in the field of industrial applications.

Apart from the well-known fundamental properties of azeotropic solutions, theoretical discussions either referred to the properties of solutions in general and arrived only at qualitative conclusions regarding the azeotropic properties,[2] or started from special relationships[3] between vapor pressure and composition which are necessarily of restricted validity.

Actually the problem of the shift of azeotropic equilibrium can be easily formulated in a general way and solved by straightforward thermodynamic methods.

The azeotropic equilibrium of a solution of two miscible liquids is characterized by three intensive variables: the composition, which is equal for the liquid and the vapor, the temperature and the pressure. Under the condition, that the azeotropic equilibrium should be maintained, only one of these variables is independent. The shift of equilibrium is therefore exhaustively described by two relations between the variables.

In the development it is assumed only that the vapor is a perfect gas mixture. This restriction can be removed without any essential difficulty but the practical gain would be small and by no means sufficient to justify the complication of the formulas.

In the following, the standard notation of Lewis and Randall is used, the pure components being chosen as reference states. The heats of vaporization of the two components from the solution are denoted by $\Delta H_1 = \Delta H_1^0 - \bar{L}_1$ and $\Delta H_2 = \Delta H_2^0 - \bar{L}_2$, where ΔH_1^0 and ΔH_2^0 are the heats of vaporization of the pure components, and $\bar{L}_1$ and $\bar{L}_2$ the relative partial molal heat contents.

The relationship between azeotropic pressure and temperature is represented by

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{az} = \left(\frac{\partial P}{\partial T}\right)_{N_1} + \left(\frac{\partial P}{\partial N_2}\right)_T \left(\frac{\mathrm{d}N_2}{\mathrm{d}T}\right)_{az} \quad (1)$$

The last term is equal to zero since $(\partial P/\partial N_2)_T = 0$ constitutes one of the fundamental properties of the azeotropic equilibrium.

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[1] Original manuscript received December 23, 1942.

[1a] See for instance R. W. Merriman, *J. Chem. Soc.*, **103**, 628 (1913).

[2] *Cf.* M. S. Wrewsky (Vrevskii), *Z. physik. Chem.*, **83**, 551 (1913), and previous papers.

[3] See H. C. Carlson and A. P. Colburn, *Ind. Eng. Chem.*, **34**, 581 (1942); J. J. van Laar, *Z. physik. Chem.*, **72**, 723 (1900); and refs. 7 and 8.

Thus we obtain

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}\,T}\right)_{az} = \frac{p_1}{P}\left(\frac{\partial\ln p_1}{\partial T}\right)_{N_2} + \frac{p_2}{P}\left(\frac{\partial\ln p_2}{\partial T}\right)_{N_2} \quad (2)$$

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}\,1/T}\right)_{az} = -\frac{N_1\Delta H_1 + N_2\Delta H_2}{R} = -\frac{\Delta H}{R} \quad (3)$$

where ΔH represents the heat of vaporization of one mole of the solution.

The dependence of the azeotropic composition on the temperature is to be derived in a slightly less direct way. With the abbreviation $Q = p_1N_2/p_2N_1$ the maintenance of the azeotropic equilibrium can be represented by

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_{az} = \left(\frac{\partial Q}{\partial T}\right)_{P,N_2} + \left(\frac{\partial Q}{\partial P}\right)_{T,N_2}\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{az} + \left(\frac{\partial Q}{\partial N_2}\right)_{T,P}\left(\frac{\mathrm{d}N_2}{\mathrm{d}T}\right)_{az} = 0 \quad (4)$$

since $Q = 1$ as long as azeotropic equilibrium exists.

The first of the partial differential coefficients is determined by $\Delta H_2 - \Delta H_1$. For the second we derive

$$\left(\frac{\partial\ln Q}{\partial P}\right)_{T,N_2} = \frac{\bar{v}_1' - \bar{v}_1 - \bar{v}_2' + \bar{v}_2}{RT} = \frac{-\bar{v}_1 + \bar{v}_2}{RT} = \frac{v}{P} \quad (5)$$

where the prime indicates the vapor phase and v the ratio of the difference of the partial molal volumes in the liquid to the molal volume of a perfect gas under the given conditions.

In (5) we made use of the relation

$$\bar{v}_1' - \bar{v}_2' = 0 \quad (6)$$

which results from the assumption of a perfect gas phase. The term (5) is in general entirely negligible.

The third partial differential coefficient in (4) is simplified by means of the Duhem–Margules relation

$$N_1\,\mathrm{d}\ln\frac{a_1}{N_1} + N_2\,\mathrm{d}\ln\frac{a_2}{N_2} = 0 \quad (7)$$

which yields

$$\left(\frac{\partial\ln Q}{\partial N_2}\right)_{T,P} = \frac{\partial}{\partial N_2}\left(\ln\frac{a_1}{N_1}\right) - \frac{\partial}{\partial N_2}\left(\ln\frac{a_2}{N_2}\right) = -\frac{1}{N_1}\frac{\partial}{\partial N_2}\left(\ln\frac{a_2}{N_2}\right) \quad (8)$$

Combination of (3), (4), (5) and (8) leads to[3a]

$$\left(\frac{\mathrm{d}\,\frac{1}{T}}{\mathrm{d}N_2}\right)_{az} = \frac{R}{\Delta H_2 - \Delta H_1 - v\Delta H}\;\frac{1}{N_1}\left(\frac{\partial\ln\frac{a_2}{N_2}}{\partial N_2}\right)_{T,P} \quad (9)$$

The third relationship between the three azeotropic variables is immediately derived from (3) and (9)

$$\left(\frac{\mathrm{d}\ln P}{\mathrm{d}N_2}\right)_{az} = -\frac{\Delta H}{\Delta H_2 - \Delta H_1 - v\Delta H}\;\frac{1}{N_1}\left(\frac{\partial\ln\frac{a_2}{N_2}}{\partial N_2}\right)_{T,P} \quad (10)$$

Thermodynamic relations like these need no test in the proper meaning of the word. However, we wish to illustrate the practical application in an example. A complete and accurate set of the data required in equations (9) and (10) is available for hydrochloric acid.[4]

The following procedure was adopted: the data given for $\bar{L}_1$ and $\bar{L}_2$ in the range from 0 to 60° were inter- and extrapolated on $1/T$ graphs. The values (25°) of log (a_2/N_2) were interpolated for $N_2 = 0.05$, 0.1, 0.2. The corresponding values for five temperatures up to 123° were computed and represented as parabolic functions of log N_2. The heats of vaporization ΔH_1 and ΔH_2 were calculated from ΔH_1^0, ΔH_2^0, $\bar{L}_1$ and $\bar{L}_2$. The term $v\Delta H$ was neglected.

The differential coefficients for five points were computed according to (3) and (9). They are listed in Table I. Three of the values of N_2, $1/T$, and log P, as observed by Bonner and his collaborators, were used to calculate two parabolic functions; the values of these functions for the two other points and the differential coefficients derived from them are denoted "par." in Table I.

Considering the various inter- and extrapolations, and differentiations, the agreement between the observed ("parabolic") values and calculated ones, which were derived from entirely independent data, is very satisfactory and indicates the high accuracy of the data.

Discussion.—Equation (3) has the form of the Clausius–Clapeyron equation because the system under condition of azeotropic equilibrium acts just like a one-component system.

All conclusions which will be drawn from equation (9) can be derived in the same way from equation (10), and are therefore immediately applicable also to the pressure–composition relationship.

We discuss equation (9) in order to find the characteristic differences in the azeotropic behavior of certain types of solutions. It is convenient to consider first the factor

$$\frac{1}{N_1}\left(\frac{\partial\ln\frac{a_2}{N_2}}{\partial N_2}\right)_{T,P} = \frac{1}{N_2}\left(\frac{\partial\ln\frac{a_1}{N_1}}{\partial N_1}\right)_{T,P} \quad (11)$$

and later the denominator, $\Delta H_2 - \Delta H_1 - v\,\Delta H$.

Term (11) is zero for a perfect solution, negative if $p_1 > N_1p_1^0$, *i. e.*, especially for the maximum vapor pressure type, positive in the opposite case.

Table I

Azeotropic Functions of Hydrochloric Acid

N_2		0.10603	0.11088	0.11557	0.12157	0.13096
$10^3/T$	obs.	2.5247	2.6103	2.6977	2.8224	3.1073
	par.	...	2.598	...	2.826	...
log P	obs.	3.0864	2.9031	2.6990	2.3979	1.6990
	par.	...	2.897	...	2.407	...
$\mathrm{d}(1/T)/\mathrm{d}N_2$	par.	0.0149	0.0182	0.0214	0.0255	0.0318
	calc.	.0148	.0172	.0192	.0231	.0324
d log $P/\mathrm{d}(1/T)$	par.	2179	2239	2299	2386	2584
	calc.	2231	2277	2298	2334	2397

If the second component dissociates in dilute solution, then

$$\lim_{N_2=0} a_2 = \text{const.}\,N_2^2;\quad \lim_{N_2=0}\frac{\partial}{\partial N_2}\left(\ln\frac{a_2}{N_2}\right) = \infty \quad (12)$$

[3a] N_2 is chosen as the independent variable since (9) and (10) will commonly be used in this form.

[4] W. D. Bonner and B. F. Branting, This Journal, **48**, 3093 (1926); W. D. Bonner and A. C. Titus, *ibid.*, **52**, 633 (1930); W. D. Bonner and R. E. Wallace, *ibid.*, **52**, 1747 (1930); M. Randall and L. E. Young, *ibid.*, **50**, 989 (1928); "International Critical Tables," Vol. V.

Term (11) is therefore positive. This explains why azeotropic electrolytes always belong to the minimum vapor pressure or maximum boiling point type.

The equations (9) and (12) demonstrate that *dissociating* azeotropic *systems* always have an *infinite* azeotropic *temperature range.* In dilute solution, the temperature increases with decreasing concentration of the dissociating substance if its heat of vaporization is larger than that of the solvent. For dilute hydrochloric acid ΔH_2 is greater than ΔH_1 so that $\lim \mathrm{d}T/\mathrm{d}N_2 = -\infty$. In a diagram of the data of Table I one realizes immediately that the T–N_2 curve must have an inflection point at some concentration below the range of the table.

If neither component dissociates, term (11) is always finite.[5] One verifies easily that the left-hand side is finite for $N_2 = 0$, corresponding to a dilute solution of the second component in the first, the right-hand side for $N_2 = 1$.

The integration of (9) from $N_2 = 0$ to $N_2 = 1$ leads, therefore to a finite interval of the azeotropic temperature at least if the denominator $\Delta H_2 - \Delta H_1 - v\Delta H$ is different from zero in the whole interval. This is a matter of some practical interest as distillation at temperatures and pressures outside the azeotropic interval would lead to complete separation. At first, one is inclined to assume that the denominator will vanish or even assume a small value only in rare exceptional cases since heats of vaporization run over a fairly wide range and the denominator contains the difference of two of these quantities. It will be seen later, however, that an assumption of this kind is erroneous and that a small denominator, *i. e.*, a large azeotropic interval, may occur quite frequently and under well defined conditions.

The Isobaric Temperature.—If the vapor pressure–temperature curves of the two pure liquid components cross each other, the temperature at which $p_1^0 = p_2^0$ is of considerable interest.[6] It will be called the "isobaric temperature."

Complete miscibility presupposed, the total vapor pressure–composition curve can assume any of three forms: it may be a straight line, concave or convex. In the first case the system forms a perfect solution, in the latter cases the total vapor pressure has a maximum or minimum as the end-points of the curve are fixed at the same ordinate value. The perfect solution at the isobaric temperature is to be considered as the limiting case of a system azeotropic at any composition.

The result as required in the following discussion can be expressed by either of the statements: "Any system is azeotropic at the isobaric temperature" or: "The azeotropic temperature range always includes the isobaric temperature."

Some information on the shift of azeotropic equilibrium is derived from this fact in connection with Trouton's rule, according to which the ratio of heat of vaporization to absolute temperature is approximately equal for non-associating liquids at those temperatures where their vapor pressures are equal. Trouton's ratio is larger, usually by not more than fifty per cent., for associating substances like alcohols, water, etc.

Trouton's rule defines a family of vapor pressure–temperature curves with the following properties: At a given temperature the heat of vaporization is greater for the less volatile liquid; with increasing temperature the vapor pressures approach one another asymptotically.

Thus a pair of ideal Trouton liquids is always below the isobaric temperature. Actually vapor pressure curves even of non-associating or "normal" liquids frequently cross in the limited interval between the melting points and critical points, the approximate validity of Trouton's rule being indicated by the small angle between the curves.

If the Trouton ratios of the two components do not deviate considerably from each other, the difference between the heats of vaporization and therefore the denominator in equation (9) $\Delta H_2 - \Delta H_1 - v\Delta H = \Delta H_2^0 - \Delta H_1^0 - \bar{L}_2 + \bar{L}_1 - v\Delta H$ is small, inasmuch as the other terms are small in any case. Thus in the neighborhood of the isobaric temperature, a small value of the denominator or a steep slope of the azeotropic temperature–composition curve is to be expected, if Trouton's rule is satisfied by both components or if only both Trouton coefficients are equal.

Small values of the denominator are also to be expected at high temperatures as the heats of vaporization vanish at the critical point. As vapor pressures increase rapidly with increasing temperatures, the formulas derived under the condition of a perfect gas phase cease to be valid at high temperatures, but this fact will hardly impair a qualitative conclusion.

Classification of Non-dissociating Azeotropic Systems.—A convenient classification starts from a "Trouton type" and describes characteristic deviations from this case.

(A) The azeotropic temperature–composition curve of a system of two non-associating liquids starts at $N_2 = 0$ or $N_2 = 1$ at a finite slope. The slope increases with increasing temperature and the curve extends to the critical temperature. The only known case of a system of this "Trouton type," benzene–cyclohexane (Fig. 1), shows a small part of this curve. It may be expected

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[5] This is not a strictly thermodynamic statement. It results from the fact that the behavior of non-dissociating solutes at low concentrations can always be described by $\ln(a_2/N_2) = kN_2^s$ with $s \geqq 1$. Only for ions is $s = 1/2$, due to the long range of interionic forces. Next to these, the forces between zwitterions have the longest range. Already for this case the relation $s = 1$ holds (G. Scatchard and J. Kirkwood, *Physik. Z.*, **33**, 297 (1932)), the more for other types of solutes. However, an appreciably ionized amphoteric electrolyte would constitute an exception inasmuch as, due to the presence of ions, s were equal to 1/2 although no dissociation in the strict sense occurs.

[6] This has been realized already by W. D. Bancroft ("The Phase Rule," Ithaca, New York, 1897), and by S. Young ("Distillation Principles and Processes," London, 1922).

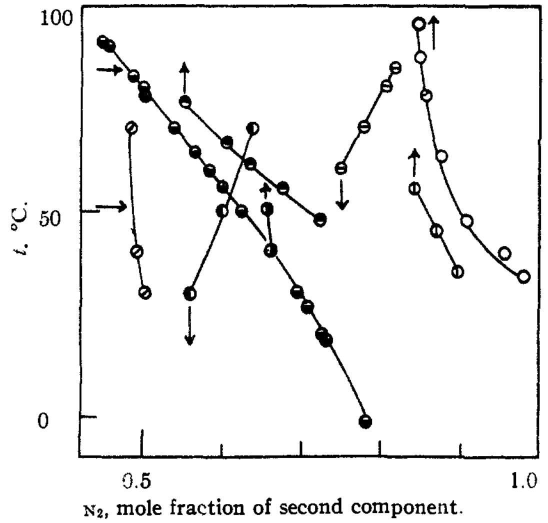

Fig. 1.—Azeotropic temperature as function of the composition. The isobaric temperature is indicated by arrows.

	Components	Isobaric temp.	Ref.
○	Water–ethanol	(high)	*a*
⦶	Ethanol–chloroform	(high)	*b*
◑	Methanol–methyl acetate	(high)	*c*
◓	Ethyl acetate–carbon tetrachloride	84°	*d*
◒	Ethanol–ethyl acetate	84°	*e*
⊘	Benzene–cyclohexane	51.8°	*f*
◐	Heptane–ethanol	−2°	*g*
⊖	Toluene–ethanol	(low)	*h*

[a] J. Wade and R. W. Merriman, *J. Chem. Soc.*, **99**, 997 (1911); R. W. Merriman, *ibid.*, **103**, 628 (1913). [b] G. Scatchard and C. L. Raymond, This Journal, **60**, 1278 (1938). [c] G. Bredig and R. Bayer, *Z. physik. Chem.*, **130**, 15 (1927). [d] P. W. Schutz and R. E. Mallonee, This Journal, **62**, 1491 (1940). [e] R. W. Merriman, *J. Chem. Soc.*, **103**, 1801 (1913); W. Mund and Heim, *Bull. Soc Chim. Belgique*, **41**, 349 (1932), quoted from ref. 8. [f] G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939). [g] C. P. Smyth and E. W. Engel, This Journal, **51**, 2660 (1929). [h] W. A. Wright, *J. Phys. Chem.*, **37**, 233 (1933).

that frequently crystallization will occur before the lower end of the curve is reached.

(B) A similar curve results from two associating liquids if the Trouton coefficients are approximately equal and the isobaric temperature is high (water–ethanol, Fig. 1).

(C) If the Trouton coefficients differ appreciably, *i. e.*, especially in systems composed of an associating and a non-associating component, the slope in general is finite. A steep slope is not strictly excluded as the heats of vaporization still may happen to be equal at some temperature. This temperature, however, must be remote from the isobaric temperature and, therefore, has no particular chance of being included in the azeotropic range. Thus a steep slope will be a rare exception as long as the gas phase is nearly perfect. Considering the previous discussion of term (11), one is justified in extrapolating some of the experimental curves (Fig. 1) of this type to the lower end (ethyl acetate–carbon tetrachloride and ethanol–chloroform) and to the upper end (toluene–ethanol). The extrapolation is less certain in the latter case as approach to critical conditions may result in a considerable change of the slope.

Wrewsky[2] already has stated that in a system with maximum (minimum) vapor pressure the azeotropic concentration of the component with the larger heat of vaporization increases (decreases) with increasing temperature. Considering equation (9) and the previously discussed significance of the isobaric temperature, the direction of the temperature–composition curve is conveniently described also by the following statement: The azeotropic curve of a maximum (minimum) vapor pressure system ends, if at all, on the side of the more (less) volatile component. This is true both of lower and upper ends.

Frequently, though not always, the azeotropic behavior of non-dissociating systems is sufficiently described with the aid of the relationship

$$RT \ln a_2/\mathrm{N}_2 = w\mathrm{N}_1^2 \qquad (13)$$

where w characterizes the interaction between the two components. This has been shown by Herzfeld and Heitler[7] and recently in more detail by Kirejew.[8]

From a practical viewpoint, a thermodynamic examination of ternary systems is perhaps more interesting inasmuch as the experimental investigation requires so much more labor. The thermodynamic discussion, of course, is more complicated, too. Equations for ternary solutions similar to (13), derived by Porter[9] and by Scatchard,[10] greatly simplify the discussion which will be presented in a following paper of this series.

Acknowledgment.—The authors are indebted to Professor George Scatchard, the reviewer of this paper, for important critical advice.

Summary

1. The two thermodynamic relationships connecting the three azeotropic variables (composition, temperature, pressure) of a binary system are expressed in terms of common quantities with the only restriction that the vapor is a perfect gas mixture (equations 3, 9, 10).

2. The azeotropic temperature–composition curves depend in a characteristic way on whether one or both components are normal, dissociating or associating.

3. Dilute azeotropic solutions of a dissociating substance belong necessarily to the minimum vapor pressure type. The slope of the azeotropic

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(7) K. F. Herzfeld and W. Heitler, *Z. Elektrochemie*, **31**, 536 (1925).

(8) V. A. Kirejew, *Acta Phys. Chim., U. R. S. S.*, **13**, 552 (1940); **14**, 371 (1941).

(9) A. W. Porter, *Trans. Faraday Soc.*, **16**, 336 (1921).

(10) G. Scatchard, *ibid.*, **33**, 160 (1937).

temperature–composition curve decreases or increases without limit with decreasing concentration in dilute solutions of a dissociating component, and only of a dissociating component.

4. The term "isobaric temperature" is proposed for the temperature at which the vapor pressures of the pure components are equal. The slope of the azeotropic temperature–composition curve is steep at the isobaric temperature if the deviations from Trouton's rule are small for both components.

5. If the azeotropic temperature–composition curve of a maximum (minimum) vapor pressure system extends to a pure component, this component is the more (less) volatile one. The rule holds both for upper and lower limits of the azeotropic temperature range. In connection with the fact that this range includes the isobaric temperature, the rule conveniently indicates the direction of the curve.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary System Barium Bromate–Barium Chlorate–Water at 25°

BY J. E. RICCI AND S. H. SMILEY

Introduction.—During various attempts to determine bromate in the presence of chlorate by precipitation with excess of barium chloride, it became apparent that the precipitated barium bromate was repeatedly and almost reproducibly contaminated with barium chlorate, despite all precautions for its proper formation in the pure state. The weight of the solid obtained, after the usual drying, was always too high, and its oxidizing equivalent, determined by iodometry, was also too high, indicating the presence of some chlorate. It was consequently suspected that the two salts, barium bromate and barium chlorate, isomorphous and both mono-hydrated, were forming solid solutions from their aqueous solutions. This was verified by a phase rule study of the ternary system involved. Since the resulting solid solution turned out to be a continuous one, the data were therefore used in testing the applicability of a semi-empirical relationship previously reported as describing the distribution of such isomorphous salts in solubility equilibrium between liquid and solid phases.[1]

Experimental Procedure.—The barium bromate used was a C. P. grade of the monohydrate, the purity of which was checked, with the following results: by iodometry, 95.73% $Ba(BrO_3)_2$, and by dehydration to constant weight at 110°, 95.53%. The theoretical value is 95.60%. A C. P. grade of $Ba(ClO_3)_2 \cdot H_2O$ also was used, found to contain 5.69% of water (by drying at 110°) as compared with the theoretical 5.60%. A qualitative test for bromate or other strong oxidizing agents proved negative ($<0.001\%$ as $Ba(BrO_3)_2$).

The experimental procedure for the solubility determinations has been described in similar publications. The temperature of the determinations was 24.95 ± 0.02°. Equilibrium was approached from two directions, in about half of the experiments from undersaturation, *i. e.*, lower temperature, and in the others from higher temperature. In most cases equilibrium was proved by the constancy of the composition of the liquid on repeated analysis. In other cases, although such direct proof was not possible since the solution was all consumed in repeated analyses before actual constancy was established, it is felt that the systems must have been very close to if not at true equilibrium, because care was taken to keep the relative amount of solid phase in the complexes very low, and because of the long period of stirring generally used (one to six, averaging three and one-half, months).

The liquid solution was analyzed after sampling by means of calibrated pipets fitted with filtering tips. The wet residues were either pressed between coarse filter paper or centrifuged briefly, before weighing and analysis.

Water was determined by drying at 110° and bromate was determined iodometrically (in the presence of chlorate) by a procedure already described[2] for a similar investigation on the system sodium bromate–sodium chlorate–water. The correction there reported for the effect of relatively high concentrations of chlorate was verified and applied in the present case. These two determinations allowed the calculation of the percentage of each salt in the various solutions and residues.

A slight complication arose from the fact that final traces of water were not easily driven off at 110°, but required a brief treatment at about 300°. Since this temperature would also cause a slight decomposition of the two salts, especially of the barium bromate, experiments were made to determine the rate of loss of weight of each salt at 300°. The results indicated that after the initial expulsion of traces of water, barium chlorate suffered no measurable loss of weight in one or two hours, while barium bromate lost almost 4 mg. per gram per hour at this temperature, a correction which was then applied in the actual analyses.

Results.—The results are tabulated in Table I, which lists all compositions in weight per cent. The density of the saturated liquid solution was not always measured. Some of the values listed were read from a plot of the density, *d*, against *c*, the total percentage of salt in the saturated solution; the dependence was in fact found to be roughly linear, with an average error of about 0.002, according to the expression

$$d = 0.993 + 0.00935c \qquad (1)$$

The solubility of barium chlorate here found is the same as the accepted value in the literature.[3] The solubility of barium bromate here reported, 0.791%, also agrees well with the important literature values: 0.788%, by Trautz and Anschütz,[3a] and 0.796%, by Harkins.[4]

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[1] Hill, Durham and Ricci, THIS JOURNAL, **62**, 2723 (1940).

[2] Swenson and Ricci, *ibid.*, **61**, 1974 (1939).

[3] (a) Trautz and Anschütz, *Z. physik. Chem.*, **56**, 238 (1906); 27.53%; (b) Foote and Hickey, THIS JOURNAL, **59**, 648 (1937); 27.58%.

[4] Harkins, *ibid.*, **33**, 1807 (1911).