[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE]

The Analysis of Homogeneous Ternary Systems: The System Benzene, *n*-Butyl Bromide and Nitrobenzene

BY ROBERT GINELL AND HERBERT SILVERMAN[1]

A graphical method is presented for the analysis of homogeneous ternary systems using data obtained from a measurement of only one physical property on the unknown, followed by the addition of a known amount of a known composition and the determination of the new value of this same property. The isorefractive index graph at 25° of the system benzene, *n*-butyl bromide, nitrobenzene is presented and calculations based on it are given.

Introduction.—The determination of the composition of a homogeneous ternary system is always a troublesome problem. The methods commonly described in the literature depend on the determination of two different properties of the unknown mixture, *e.g.*, refractive index together with specific gravity, followed by reference to previously prepared charts plotting the properties in question as a function of composition. In this paper, a general method for the analysis of homogeneous ternary systems utilizing only one type of measurement will be presented.

Theory.—The method depends on determining the value of a certain property of the unknown mixture; then adding a known weight of either a pure component of the mixture, or of a known mixture of two or three components, to a determined weight of the unknown mixture. The value of the chosen property of the new mixture is then measured. From these data, and graphs of the property as a function of composition, the exact proportions present in the unknown may be readily determined.

In Fig. 1, the line AB is the isorefractive index line (value n_1) somewhere along which lies the composition of the unknown mixture. If now to a known weight W_1 of the unknown mixture, we add an amount W_2 of a mixture of known composition J and redetermine the value of the refractive index, the new composition will lie somewhere between the line AB and the point J, namely, on the isorefractive index line CD. Enough data has now been obtained to enable us to fix points M and N. The determination is based on the fact that as the original unknown of composition M is diluted with J, its composition changes along a straight line connecting M and J (Fig. 1). If the refractive index of the mixture of M and J is n_2, then its composition is N.

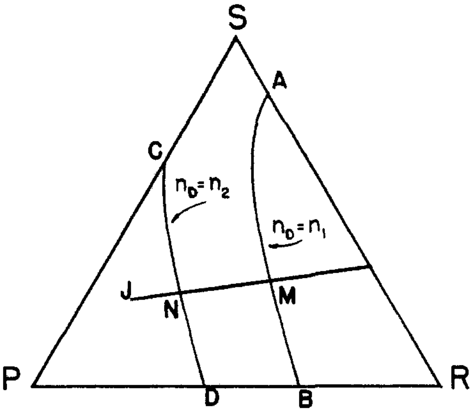

Fig. 1.

To illustrate the actual working of this method, we have chosen the refractive index as the property to be measured, and have determined the refractive indices of mixtures of benzene, nitrobenzene and *n*-butyl bromide. The graph showing the isorefractive index lines is plotted as Fig. 2.

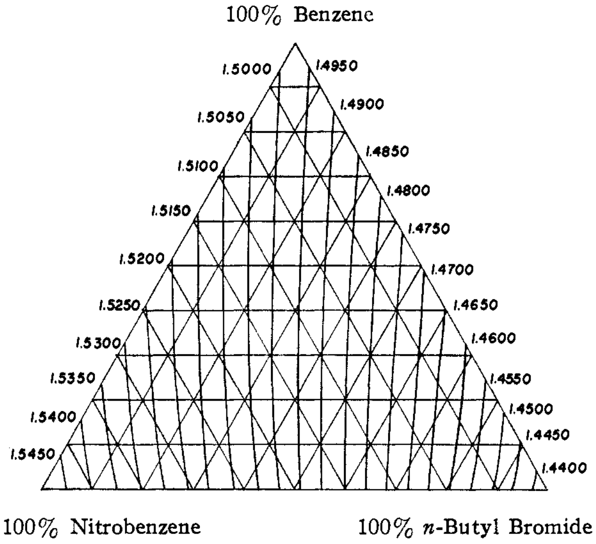

Fig. 2.

Experimental.—The reagents used were normal C.P. materials. The benzene had an $n^{25}\text{D}$ 1.49791, which agrees with the National Bureau of Standards value. The nitrobenzene had an $n^{25}\text{D}$ 1.55023, and the *n*-butyl bromide had an $n^{25}\text{D}$ 1.43617. All measurements were made on a Pulfrich refractometer made by the Zeiss company. The temperature was kept at 25.0 ± 0.1°. Mixtures were made up exactly by weight, and the refractive indices determined immediately.

Method.—(A) The refractive index of the unknown sample M is measured. This index is called n_1. (B) W_2 grams of a mixture of composition J are added to W_1 grams of the unknown, and the refractive index n_2 of this new mixture is determined. (C) The contour lines n_1, n_2 and the point J are plotted on a triangular composition diagram. The lines are constructed from previously prepared graphs for composition *vs.* refractive index. (D) A series of straight lines are drawn on the triangular graph passing through J and crossing the two refractive index contour lines (similar to line JNM in Fig. 1). The percentage of one component, *e.g.*, P is recorded for each composition M as P_M

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and for the corresponding composition N as P_N. There are now two possible methods of procedure.

Method 1.—(a) Plot P_M *vs.* P_N in weight per cent. on rectangular coördinates. This line represents all possible pairs of points having the correct refractive index relationship. (b) From the weight relationships in step (B), another curve can be derived. If the unknown had no component P (*i.e.*, $P_M = 0$), then the amount of P in the new mixture after the known weight W_2 of composition J had been added, can be readily computed as

$$\frac{\text{wt. of P in } W_2 \text{ g. of J}}{W_1 + W_2} \times 100 = P_N$$

This equation provides one point on the second curve. We may also imagine that M had the same composition as J. In this case, the percentage of P in J, P_J, would not have changed. Hence another point on the second curve is provided, the point being $P_M = P_J$ and $P_N = P_J$. Other points on this curve may be computed by assuming percentages of P in M. This step is not necessary since the curve is a straight line, and the first two points described are the simplest to compute. On this curve are contained all possible compositions that can be derived by adding W_2 grams of J to W_1 grams of M. (c) The intersection of these two curves gives us now directly P_N and P_M. The remaining components of the original unknown may be read off on the triangular graph.

Method 2.[2]—Plot P_M *vs.* the ratio of the distances $MN/NP = r$. Since $r = W_2/W_1$, read on the graph, the value of P_M from the value of r calculated from step (B). These distances, which can be obtained with the aid of dividers, are equivalent to plotting $(P_N - P_M)/(P_J - P_M)$ *vs.* P_M.

Discussion.—Occasionally the triangular graph will have more complicated contours than those shown in Fig. 2. In such a case, two intersections may occur if method 1 is used, or equivalently, there may be two values of P_M for which $MN/NP = W_2/W_1$. In this case, the method may be repeated using a further amount of the known mixture J.

TABLE I

Component J was pure nitrobenzene; n_1 1.4724; n_2 1.4985; W_1 11.0898 g.; W_2 5.4079 g.

	Grams per cent. Nitrobenzene	Grams per cent. *n*-Butyl bromide	Grams per cent. Benzene
As prepared	23.42	65.41	11.17
As analyzed (1)	23.8	65.8	10.4
graphically (2)	23.8	65.6	10.6
by method 1 (3)	23.5	65.5	11.0
As analyzed (1)	21.1	63.0	15.9
graphically (2)	21.5	63.5	15.0
by method 2 (3)	22.3	64.1	13.6

Table I shows several determinations of the analysis of a known mixture by both methods 1 and 2. The values obtained from method 2 appear to be not quite as precise as those from method 1, at least in the analyses made thus far. This is due apparently to the extra manipulation or computations necessary in order to eliminate the second curve in method 1.

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[2] This method was suggested by the reviewer, Dr. J. E. Ricci.

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The Ternary Systems $AgBrO_3$–$KBrO_3$–H_2O and $AgClO_3$–$NaClO_3$–H_2O at 25°

BY JOHN E. RICCI AND JACK A. OFFENBACH

For information significant in the preparation of silver salts by aqueous double decomposition, the 25° isotherms of the systems $AgBrO_3$–$KBrO_3$–H_2O and $AgClO_3$–$NaClO_3$–H_2O were studied. While the first is simple the second has two series of solid solutions as in the Roozeboom type V. The distribution between the solid and aqueous phases is such, however, that the preparation of $AgClO_3$ from $AgNO_3$ and $NaClO_3$ easily leads to a pure product.

Since the salts silver bromate and silver chlorate are usually prepared by double decomposition involving an alkali salt, the question of the formation of solid solution between the corresponding bromates or between the corresponding chlorates has to be considered in connection with the purification of the final silver salt. An earlier investigation of the ternary system $AgBrO_3$–$NaBrO_3$–H_2O in the range 5–50°[1] showed the formation of a solid solution extending from pure $AgBrO_3$ to the compound $AgBrO_3 \cdot NaBrO_3$, with a distribution, between liquid and solid phases, such that ordinary recrystallization of $AgBrO_3$ would not lead to purification with respect to any contaminating $NaBrO_3$. The system $AgBrO_3$–$KBrO_3$–H_2O, here reported, shows, on the other hand, no solid solution at all at 25°, so that the reaction of $AgNO_3$ with $KBrO_3$ should give a product easily purified.

Silver chlorate is apparently best prepared[2] by the reaction of $AgNO_3$ and $NaClO_3$ in solution, sodium nitrate being much more soluble than silver chlorate. The final product is obtained pure after a few recrystallizations, despite the formation of solid solution between $AgClO_3$ and $NaClO_3$, which has long been known.[3] The purpose of the present study was to investigate the distribution at room temperature between the solid and the liquid solutions.

As in similar reported investigations, ternary complexes of known composition were made to come to equilibrium at 25°, whereupon the saturated liquid solution was filtered and sampled for analysis. In the bromate system the solution was simply evaporated to dryness for its $KBrO_3$ content, since the solubility of $AgBrO_3$ in presence of $KBrO_3$ was

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[1] J. E. Ricci and J. J. Aleshnick, THIS JOURNAL, **66**, 980 (1944).

[2] D. G. Nicholson and C. E. Holley, "Inorganic Syntheses," Vol. II, W. C. Fernelius, Editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 4.

[3] J. W. Retgers, *Z. physik. Chem.*, **5**, 436 (1890).