THE QUANTITATIVE OPTICAL DETERMINATION OF SODIUM AND POTASSIUM CHLORIDES.

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In the analysis of the average igneous rock the alkalis generally represent less than ten per cent of the total constituents that are present. The standard methods for their determination all call for the separation and weighing of the alkalis in the form of the combined chlorides. Potassium is then generally separated and determined gravimetrically while sodium is obtained by difference. In a great many cases the total aklalis are present in such small amounts that it is impossible to accurately separate them so they are often reported as Na_2O+K_2O. The following method for the determination of sodium and potassium is based upon the the microscopic determination of the index of refraction of a fusion of the combined chlorides and is, therefore, equally well adapted to either large or small precipitates. The maximum error should be less than 2 per cent and in many cases should be well under one per cent. In an analysis in which the total alkalis represent 10 per cent of the total constituents this would give an error of 0.2 per cent on the whole sample, and in cases where the alkalis represent 3 per cent or less the error would be under 0.06 per cent on the whole sample.

The index of refraction of potassium chloride for the *D* line is 1.490 and of sodium 1.544. If a mixture of these chlorides be fused and cooled so as to give a solid solution the index of refraction of the material would lie somewhere between these values. The percentage of sodium chloride would be $n-1.490/1.544-1.490$. In this case the accuracy of the determination would depend upon the accuracy of the determination of the index of refraction. If the index of refraction be determined to the third decimal place the accuracy of the determination of potassium and sodium chlorides would be 2 per cent. This condition cannot exist, however, because of the formation of a series of double salts with the general formula $x\mathrm{KCl}\cdot y\mathrm{NaCl}$.

It was also found impossible to produce a glass because the melts could not be quenched quickly enough even when they were taken directly from the blast lamp and poured into amyl alcohol.

Kurnakow and Zemezuznyj[1] have studied the fusion curves of of the alkali halogens and published the curve reproduced in Fig.1. They found that molten KCl and molten NaCl were miscible in all proportions. The freezing point of these mixtures is represented by the curve ABC. In studying the rate of cooling of the solidified melts, from the freezing point to room temperature, they found that those mixtures lying in the range of 25.0–75.0 per cent NaCl show a sharp break in the cooling curve near 400°C. The curve PQR shows the temperature at which this break takes place for the various mixtures. At this point the temperature remains constant for a considerable period of time and this was interpreted as being due to the breaking down of the mixed crystals of chlorides with the evolution of heat. E. Janecke[2] has extended this curve by the use of dilatometric methods to cover the complete

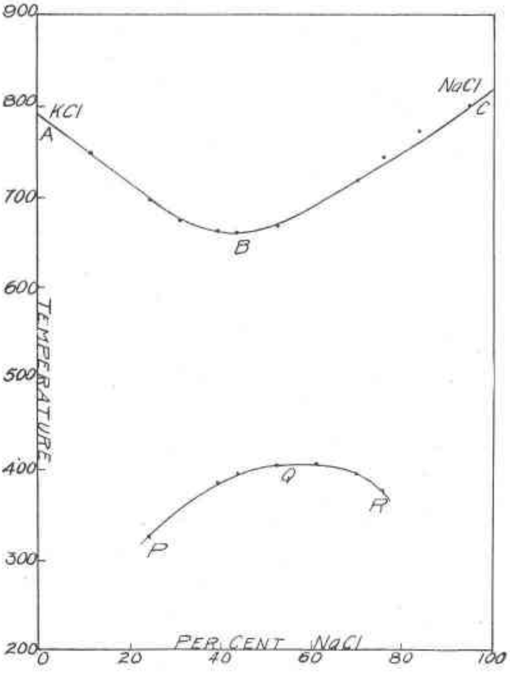

Fig. 1.

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[1] *Z. anorg. Chem.*, **52,** 186 (1907).

[2] *Z. physik. Chem.*, **90,** 296 (1915).

range of possible mixtures. G. Tammann[3] also states that a continuous series of mixed crystals exists above 500°C and that the phenomena observed when the mixed crystals are cooled must be attributed to the separation of the components. According to the authorities cited above no evidence of the existence of definite double salts was found. The terms solid solution, isomorphous mixture, and mixed crystals were used interchangeably to describe a condition similiar to that existing in the plagioclase feldspars.

The microscopic examination of a series of melts in this laboratory showed that KCl and NaCl do not form a continuous series similar to the plagioclase feldspars but that double salts with the general formula $x\mathrm{KCl}\cdot y\mathrm{NaCl}$ were formed. With the exception of those cases in which KCl and NaCl are present in definite molecular proportions corresponding to a possible double salt, two distinct components separate from a fusion. The following double salts with the corresponding indices of refraction were determined. Above and below this series, double salts of the two chlorides[4] exist but the resulting compounds approach each other so closely in their composition that it is impossible to determine them definitely. The indices of refraction of these compounds would vary by less then 0.001 and the accuracy of the optical method employed is not greater than this variation. There is also some evidence of solid solution near the end members of the series but this could not be definitely established.

	N	% KCl	% NaCl
$7\mathrm{KCl}\cdot 2\mathrm{NaCl}$	1.500	81.70	18.30
$5\mathrm{KCl}\cdot 2\mathrm{NaCl}$	1.503	76.13	23.87
$3\mathrm{KCl}\cdot 2\mathrm{NaCl}$	1.5085	65.68	34.32
$\mathrm{KCl}\cdot \mathrm{NaCl}$	1.514	56.04	43.96
$3\mathrm{KCl}\cdot 4\mathrm{NaCl}$	1.518	48.89	51.11
$2\mathrm{KCl}\cdot 3\mathrm{NaCl}$	1.519	45.95	54.05
$\mathrm{KCl}\cdot 2\mathrm{NaCl}$	1.523	38.94	61.06
$\mathrm{KCl}\cdot 3\mathrm{NaCl}$	1.528	29.83	70.17
$\mathrm{KCl}\cdot 5\mathrm{NaCl}$	1.533	20.33	79.67
$\mathrm{KCl}\cdot 7\mathrm{NaCl}$	1.536	15.42	84.58

These double salts were determined by mixing index liquids upon the microscopic slide until they matched the salt (using the Becke method and Na light) and then immediately determining

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[3] *Nachr. Ges. Wiss., Göttingen,* 422 (1919).

[4] Nearly conclusive evidence of the existence of $\mathrm{KCl}\cdot 9\mathrm{NaCl}$ was found.

the index of refraction of the liquid by inverting the slide on the Abbe refractometer. This reduces the error due to temperature variations to a minimum. Because of the isotropic nature of the melts and the perfect cubical cleavage which gives vertical contacts between the liquid and the substance it is possible to determine the index of refraction to 0.0007.

An X-ray diffraction pattern taken by Dr. Ramsdell of this laboratory confirmed the work of Kurnakow and others[5] and established the fact that the double salts break down into their components upon cooling. Therefore the index of refraction of a double salt as recorded was not determined upon the actual compound but was the additive index[6] of intimate mixtures of KCl and NaCl. This break down in the structure is submicroscopic and no evidence of it is observed under the microscope.

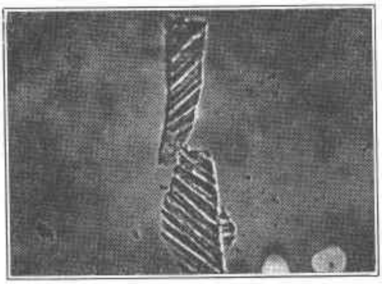

Fig. 2. (x115)

The light lines in the photograph are the Becke lines at the contact of the two components. The position of the Becke line does not mark the exact contact but lies to one side.

The use of the double salts in the determination of the amounts of KCl and NaCl may best be shown by an example. Fig. 2 is a photomicrograph of a solidified melt which contains 65 per cent NaCl. It is evident from the photograph that two components are present, one of which has a slightly higher index of refraction than the other. From Fig. 3 it may seen that in a melt of this composition two compounds, $KCl \cdot 2NaCl$ and $KCl \cdot 3NaCl$, should develop and their respective indices of refraction should be 1.523 and 1.528. Theoretically there should be 57 per cent of $KCl \cdot 2NaCl$ present. In Fig. 2 it is evident that the material

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[5] *Op. cit.*

[6] Posnjak, E and Merwin, H. E., *Am. J. Sc.*, 47, 321 (1919).

with the lower index of refraction is present in slightly greater amounts then the other. If we were to estimate from Fig. 2 that the two components, KCl·2NaCl and KCl·3NaCl, were present in equal proportions, the calculated percentage of NaCl in the melt would be 65.6 %. If the estimate of the proportions was 2:1 the calculated percentage of NaCl would be 64.1 %. This shows that a relatively large error in the estimation of the proportions of the double salts yields however a small error in the calculated value of the amount of NaCl present. In certain ranges, such as 51.1–54.1 % of NaCl the degree of accuracy is much greater. In practice it is not necessary to determine very accurately the index of refraction because any value lying between the indices of refraction of two adjacent salts (Fig. 3) determines what double salts are present.

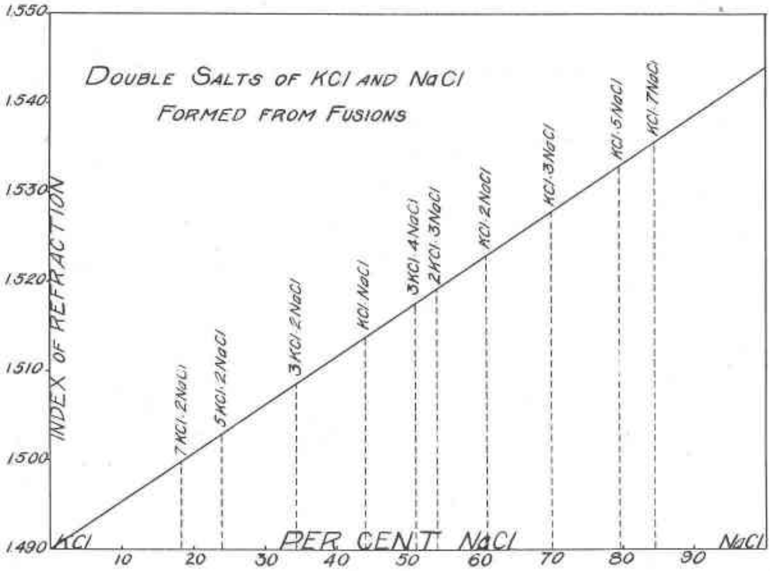

FIG. 3.

Near the end members of the series the situation is somewhat more difficult because it is necessary to accurately determine the index of refraction. Two components may be present but their compositions, and therefore their indices, are so close together that the above method cannot be applied. In this range the accuracy of the determination of KCl and NaCl depends upon the accuracy of the determination of the index of refraction. If an index intermediate between the two components is determined and taken as the average value of the index of the melt the error in all cases will be less than 2 per cent.

In working with very small precipitates the errors of technique are greater than those of the microscopic determination. One of the chief sources of error is the tendency of the salt to decrepitate while drying the precipitate before fusing. This is due to the occluded solvent and is common to all methods for the determination of potassium and sodium as chlorides. The small precipitates are best fused in a small platinum cone similar to the platinum filter cones. The shrinkage of the melt upon cooling loosens it from the side of the cone and it readily drops out. It is well to crush and grind this globule and refuse it in order to insure complete mixing. The precipitate should not be heated above the fusion point because of the tendency of the chlorides to volatilize.

While this method leaves much to be desired it is a beginning in the application of petrographic methods to chemical quantitative microscopic determinations. It has been used satisfactorily as a laboratory exercise in one of our classes. In this class work only intermediate mixtures were used because of the difficulty in working near the end members of the series.

In the determination of potassium and sodium the petrographic method must compete with well established and accurate chemical methods so its practicability is confined to small precipitates. It should be possible, however, to apply similar optical methods to some of the more difficult quantitative separations such as the separation of strontium from calcium.