Potassium Bioxalate and the Standardisation of Alkali Solutions.

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For the standardisation of acid solutions anhydrous sodium car-
bonate is recommended in most text-books of analytical chemistry,
but for that of alkali solutions the matter is not so simple. Oxalic
acid, $H_2C_2O_4.2H_2O$, and potassium tetraoxalate, $KH_3(C_2O_4)_2.2H_2O$, are
often used for that purpose, but they contain water of crystallisation
and it is not always certain that we have them perfectly dry and
with no loss of water of crystallisation. Succinic acid may be obtaineed
in a pure state and has no water of crystallisation and it is generally
used among physico-chemists as recommended by W. Ostwald in his
Physiko-chemische Messungen, but it is not in general use. Thus for
the standardisation of alkali solutions an acid or acid salt in a solid
state, which crystallises without water of crystallisation and can be
obtained pure in every laboratory without much difficulty, is much
to be desired.

Potassium bioxalate crystallises anhydrous at a temperature above
$15°$, and if it could be prepared easily in pure state, it might be used
conveniently for the standardisation of alkali solutions. Its solutions
are, however, incongruently saturated at $25°$ and $30°$ and it can not
be purified at those temperatures by simple crystallisation. But it
forms a congruently saturated solution at $60°$, as may be seen from
the accompanying diagram. For this diagram the data given in the
literature were re-calculated for our purpose.[1] The number of mols of
oxalic acid and of potassium oxalate in 100 mols of water is measured

[1] H. W. Foote snd J. A. Andrew, Amer. Chem. J., **34**, 153 (1905); J. Koppel and
M. Cahn, Zs. anorg. Chem., **60**, 54 (1908).

Mols K₂C₂O₄ in 100 mols H₂O.
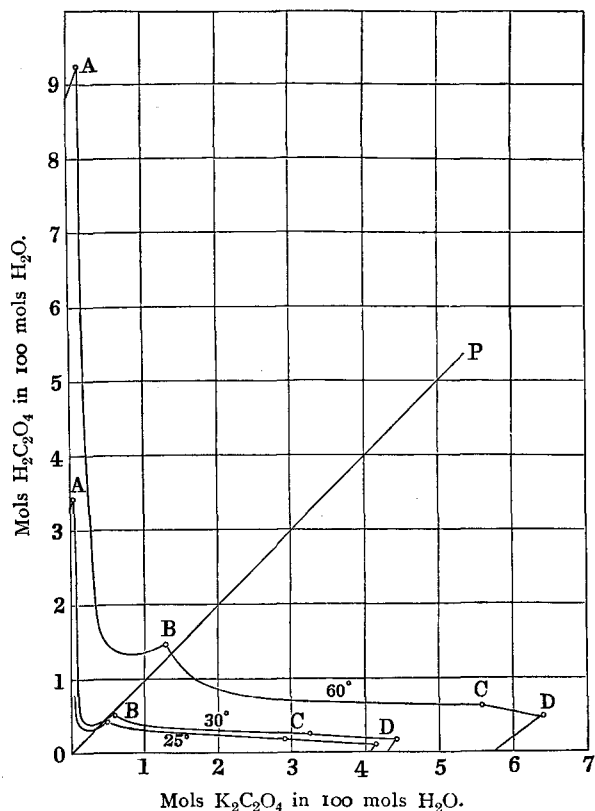
along the axes of the ordinate and abscissa respectively. The curves, AB, BC, and CD, represent respectively the solubilities of the acid salts, $KH_3(C_2O_4)_2.2H_2O$, KHC_2O_4, and $K_4H_2(C_2O_4)_3.2H_2O$, in presence of an excess of either component. The line, OP, bisects the angle between the axes and any pure solution of potassium bioxalate may be represented by a point on the line. From the diagram it may be estimated that at a temperature not very far from 40° the bioxalate begins to form congruently saturated solutions.

In the solutions having the bioxalate as the residue the ratio of oxalic acid and the potassium salt varies between 1 : 1·2 and 1 : 13 at 25° and 1 : 0·9 and 1 : 9 at 60°, so we have in common between these two temperatures the ratio between 1 : 1.2 and 1 : 9. Thus if we take oxalic acid, potassium oxalate, and water in proportions to form a saturated solution of the bioxalate at a certain temperature between 25° and 60° containing the acid and salt in a ratio within the above

stated limits, then any amount of them, added in equivalent quantities and in an anhydrous state to the solution, should separate out as the bioxalate.

Guided by the above principle, the preparation of the bioxalate was tried. As the crystallisation was made to take place at 25°, a solution containing 0·4 mol of oxalic acid and 0·6 mol of the potassium salt in 100 mols of water was chosen as the medium of the crystallisation, and one, two, or five mols of the bioxalate were made to crystallise from it by adding the corresponding quantities of the components in equivalent ratio. The proportions of the materials to be used and the amounts actually taken are given in the following table.

TABLE I.

	Proportions to be used.		Actually taken.
	Mols.	Grams.	Grams.
I.			
H_2O	95·6	1721	500
$K_2C_2O_4.H_2O$	1·6	294·7	80
$H_2C_2O_4.2H_2O$	1·4	176·4	51
II.			
H_2O	92·6	1666	300
$K_2C_2O_4.H_2O$	2·6	478·9	86
$H_2C_2O_4.2H_2O$	2·4	302·4	54·5
III.			
H_2O	83·6	1505	150
$K_2C_2O_4.H_2O$	5·6	1031	103
$H_2C_2O_4.2H_2O$	5·4	680·5	68

The experiments were carried out in the following way:

I. Oxalic acid and potassium oxalate were each thrice recrystallised. The calculated quantities of the materials were taken in an Erlenmeyer flask of about 1000 cc. capacity, stoppered with a cork with a long capillary tube and heated in a water bath to complete dissolution. The stopper was replaced by an ordinary cork and kept in a thermostat at 25° for two days. Then the greater part of the mother liquor was poured off by decantation, the crystals were transferred to filter paper placed on the perforated plate of a porcelain

funnel and the adhering mother liquor was removed by means of a water suction pump. The crystals were washd three times with 50 cc. of water at about 50°, pressed between folded filter paper and finally dried in an air bath at about 110° to a constant weight. The yield was 60 grams against the calculated value of 74, namely 82 per cent.

II, An Erlenmeyer flask of about 600 cc. capacity was used, and as the acid and salt were not completely dissolved the mixture was heated for about one hour. On other points the operation was just the same as in the previous case. The yield was 75 grams against the calculated value of 92, namely 82 per cent.

III. An Erlenmeyer flask of abont 500 cc. capacity was used. As thc greater part of the acid and salt remained undissolved, the mixture was heated for about two hours. For washing of the crystals 200 cc. of water at about 50° were used in three portions. The yield was 107 grams against the calculated value of 128, namely 84 per cent.

The yields in all three cases amounted to about 83 per cent. of the calculated value, and this would be unavoidable as the washing of the crystals requires hot water.

To test for the purity of the bioxalate obtained its decinormal solution as to the acidic hydrogen was prepared and compared with a decinormal solution of succinic acid against a dilute baryta water with phenolphthalein as indicator. The bioxalate solution and the succinic acid solution proved to be exactly in the same equivalent concentration.

The percentage amount of the potassium in the bioxalate obtained was then determined by converting it into the sulphate in the usual way and the following values were obtained against the theoretical value of 30·52 per cent.

I.   30·43,   30·42,   30·42,   and   30·43.

II.   30·43,   30·42,   30·45,   and   30·45.

III.   30·42,   30·45,   30·45,   and   30·43.

As may be seen from the two kinds of testing, there is no difference among the three samples. The values found for the potassium are somewhat low, but as this difference corresponded to a loss of about one milligram in the sulphate and the conversion of the oxalate into

the sulphate is very liable to loss by splitting, the samples may be taken as pure sufficiently at least for the purpose of the standardisation of alkali solutions.

If no thermostat is available, the following procedure may be taken among others. As roughly estimated from the diagram we have a saturated solution of the bioxalate which contain 1·1 mol of the acid and 1·5 mol of the potassium salt in 100 mols of water at 60° and this system is still in equilibrium with the bioxalate as the residue when the temperature is lowered to any degree between 60° and 25°, the excess of the acid and salt separating out as the bioxalate. Thus if we take 80 grams of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$), 160 grams of potassium oxalate ($K_2C_2O_4 \cdot H_2O$), any amount of the mixture in equivalent ratio, and 1000 grams of water diminished by its amount in the equivalent mixture as the water of crystallisation, and after treating the mixture as in the experiments above described, separate the crystals from the mother liquor at any temperature between 60° and 25°, we can obtain the bioxalate in pure state. This lower limit of the temperature can probably be lowered still more, but never lower than 15°.

Summary.

From the standpoint of the phase rule a method of the preparation of pure anhydrous potassium bioxalate was devised and that acid salt is recommended for the standardisation of alkali solutions.