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COPPER AND ZINC XANTHATES

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For a number of years after the introduction of flotation there was very little theory to account for the separations that could be made by the process. Satisfactory results were obtained only after prolonged experimentation, in which the operator made many changes in physical and chemical conditions without being able to predict just what the effects would be. Our knowledge of the underlying principle of flotation is still in a somewhat chaotic condition; in fact none of our experienced operators yet acknowledges the existence of a working theory. We are however, beginning to understand why some minerals float and why others do not, and are able to prescribe with some degree of certainty the physical and chemical treatment that should be applied to a given ore.

Modern selective flotation, as applied to sulphide minerals, may be said to date from our first use of the xanthates and similar compounds. That the effects of these reagents are mainly chemical in nature is the general belief of practical operators and this view seems to be sustained by observation and experiment.[1]

With the above thoughts in mind the author has endeavored to, in this thesis, obtain some exact figures upon the reactions and solubilities of copper and zinc

xanthates. The desire to know the solubilities of metal xanthates in water and in potassium cyanide was brought about by S. P. Warren in his thesis on "Soluble Metal Xanthates and Their Effect on Differential Flotation".[2]

The determination of the composition of these xanthates was performed in an attempt to agree or disagree with the work of Maryan P. Matuszak of the U.S. Bureau of Mines.[3] Matuszak's work deals entirely with the ethyl xanthate. In this work the method used for the determination of copper does not follow the method used by Matuszak.

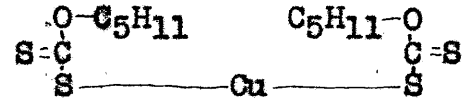
The material presented in this thesis deals entirely with the purified xanthates of copper and zinc, and purposely avoids anything to do with the mechanics of flotation.

The author would like to acknowledge the earnest cooperation and guidance of W. W. Howe, Associate Professor of Physical Chemistry, and S. P. Warren, Associate Professor of Metallurgy, both of the Colorado School of Mines.

In view of the capricious behavior exhibited in all of this work on reactions and solubilities the author has decided to abstain from the presentation of any exact experimential results and to be content with formulating the only conclusions that may with certainty be drawn from the whole body of experimental data. These conclusions may be summarized -

Part 1

Cupric Iso Amyl Xanthate has the formula



The theoretical and the determined percentages of sulphur and copper are given below.

Theoretical		Determined	
Copper (in cupric)	16.30	Copper	15.50
Copper (in cuprous)	28.04		
Sulphur (in cupric)	32.88	Sulphur	21.88
Sulphur (in cuprous)	28.47		

The xanthate of copper was determined to be cupric in form. This is directly opposite to the results obtained by Matuszak of the Bureau of Mines.[3] Mr. Matuszak in his own article names five recent workers who have determined

the salt to be cupric. Keffer[4] in his book on xanthate analysis gives the determination of a cupric salt. All the results obtained in this experimentation tend toward the cupric state.

Zinc Iso Amyl Xanthate has the same structural form as the copper salt except that it forms a hydrate. The theoretical and the determined percentages of sulphur and zinc are given below.

Theoretical		Determined	
Zinc	15.98	Zinc	15.40
Sulphur	31.29	Sulphur	29.75

Determination of the hydrate of zinc

weight before drying	2.3285	
weight after drying	2.2262	
loss	0.1023	
$\frac{0.1023}{2.3284} = 0.044$	$0.044 \times 409.9 = 18.02$	

This shows one molecule of water in combination corresponding to the formula $Zn(S_2COC_5H_{11})_2 \cdot HOH$. All samples were run on the hydrated salt as heating decomposes the salt.

The compounds which were used to form the xanthates were: Potassium Hydroxide (saturated), Carbon Bisulphide, and Iso Amyl Alcohol. The composition and properties of these three are known. When these three compounds are put together in equal proportions (by volume) they form a potassium iso amyl xanthate as follows:

$$CS_2 + C_5H_{11}OH + KOH \rightarrow S=\overset{O-C_5H_{11}}{\underset{S-K}{C}}$$

Many experiments were run in an attempt to form amyl xanthates from secondary and tertiary compounds but no results were obtained. It is believed that when mixtures of these alcohols are used to form xanthates that over 90 percent of the resulting xanthate is of the iso form.

The xanthates of copper and zinc were formed in the following manner:

$$Cu(NO_3)_2 + 2\ S=\overset{O-C_5H_{11}}{\underset{S-K}{C}} \longrightarrow Cu(S_2COC_5H_{11})_2 + 2KNO_3$$

Part 2

The reaction between sodium cyanide and the xanthates shows how it is possible to suppress copper and zinc in a flotation cell. The zinc salt is much more soluble than the copper salt.

$$4NaCN + CuX_2 \rightarrow Na_2Cu(CN)_4 + 2NaX$$

$$4NaCN + ZnX_2 \rightarrow Na_2Zn(CN)_4 + 2NaX$$

Cupric ion and cyanide give cuprous cyanide ion and cyanogen (or cyanate in ammonia solutions). [5]

$$2Cu^{++} + 4CN^{-} \rightarrow 2Cu(CN) + C_2N_2$$

Copper will form a complex cyanide with an excess of the reagent. [6]

$$2Cu^{++} + 8CN^{-} \rightarrow 2Cu(CN)_3 + C_2N_2$$

Data showing the relative solubility of copper and zinc xanthates in Potassium Cyanide.

cc of 10% KCN	0.4g ZnX_2	0.4g CuX_2
4	93%	--
6	96	--
8	100	60%
20	--	66
40	--	67

Cupric xanthates as cupric sulphides will not form complex ions with ammonia.

$$NH_4OH + CuX_2 \rightarrow \text{No reaction}$$

$$NH_4OH + ZnX_2 \rightarrow Zn(NH_3)_4(OH)_2 + 2NH_4X + 4H_2O$$

The great insolubility of CuX_2 is shown here because there is no blue color produced due to the complex Cu ammonia salts which would be present if CuX_2 dissolved.

Both salts are partially soluble in sodium pyro phosphate.

$$Na_4P_2O_7 + 2CuX_2 \rightarrow Cu_2P_2O_7 + 4NaX$$

$$Na_4P_2O_7 + 2XnX_2 \rightarrow Zn_2P_2O_7 + 4NaX$$

It can easily be seen by the graph No. 1 that while both salts dissolve slightly, the zinc is still much more soluble than the copper.

By adding copper ammonia acetate it is found that the zinc is forced into solution while the copper is brought out as the insoluble xanthate.

$$Cu(NH_3)_4(Ac)_2 + CuX_2 \rightarrow \text{No reaction}$$

$$Cu(NH_3)_4(Ac)_2 + ZnX_2 \rightarrow Zn(NH_3)_4(Ac)_2 + CuX_2$$

This reaction can easily be seen by adding ZnX_2 to copper ammonium acetate and noting the precipitate of copper xanthate, as the yellow precipitate.

Both copper and zinc xanthate remain insoluble in zinc ammonia acetate. This reagent may be added as a separator between copper, zinc - iron, nickle.

The addition of copper sulphate to a solution tends to diminish the solubility of these xanthates.

Part 3

The solubilities in water at 25° C were found to be:

Cupric Xanthate 3.77×10^{-5} mols per liter

Zinc Xanthate 5.81×10^{-5} mols per liter

The solubility in water of copper and zinc xanthates was determined by first getting the equivalent conductance of potassium xanthate at infinite dilution and then the equivalent conductance of the xanthate ion. A possibility of error may arise in the fact that xanthate solutions if allowed to remain in contact with the platinized electrodes may poison them.

The data on this experiment shows how these salts tend to hold the soluble portion. A side experiment was run to determine if any of the salt went into solution on standing over night. The following results will show that this is true; but upon boiling out again the first results were obtained again.

	Zinc Xanthate	Copper Xanthate
First boiling out	1700 ohms	2200 ohms
Standing over night	1300	2000
Reboiling	1700	2200

In all the results given on conductance, the third figure (in the resistance) is doubtful.

I THE COMPOSITION OF COPPER AND ZINC XANTHATES

Method

Potassium Iso Amyl Xanthate was used through all the experimentation. This was made by shaking together equal volumes of carbon disulphide, iso amyl alcohol and potassium hydroxide (saturated). It is necessary to keep this cool during the formation. The precipitate was dissolved in acetone. This allows a separation of the unconsumed reactants in a separatory funnel. The acetone is evaporated and the xanthate recovered.[7] The xanthates of copper and zinc were formed by adding to a water solution of the purified potassium iso amyl xanthate the nitrate of the salt. The resulting precipitate was filtered and washed with distilled water three times. An attempt at further purification by crystallization from an acetone solution proved to be by analysis unsuccessful. The percentage sulphur was determined by the Allen and Bishop Method.[8] The percentage copper was determined by the Cyanide Method[9] and the zinc was determined by the Ferrocyanide Method.[10]

Experimental Results

Percent Sulphur Determined

In Cupric Iso Amyl Xanthate - - - -	20.25%
	20.94
	21.88
In Zinc Iso Amyl Xanthate - - - -	29.37
	29.95
	29.57
	30.30
	29.55

Percent Copper Determined

In cupric Iso Amyl Xanthate - - - -	13.08
	14.37
	15.55
	15.55

Percent Zinc Determined

In Zinc Iso Amyl Xanthate (hydrate) -	17.14
	15.20
	15.43
	15.35

II THE REACTIONS OF COPPER AND ZINC XANTHATES WITH POTASSIUM CYANIDE, AMMONIUM HYDROXIDE, SODIUM PYRO PHOSPHATE, CUPRIA AMMONIUM ACETATE, ZINC AMMONIUM ACETATE, AND COPPER SULPHATE

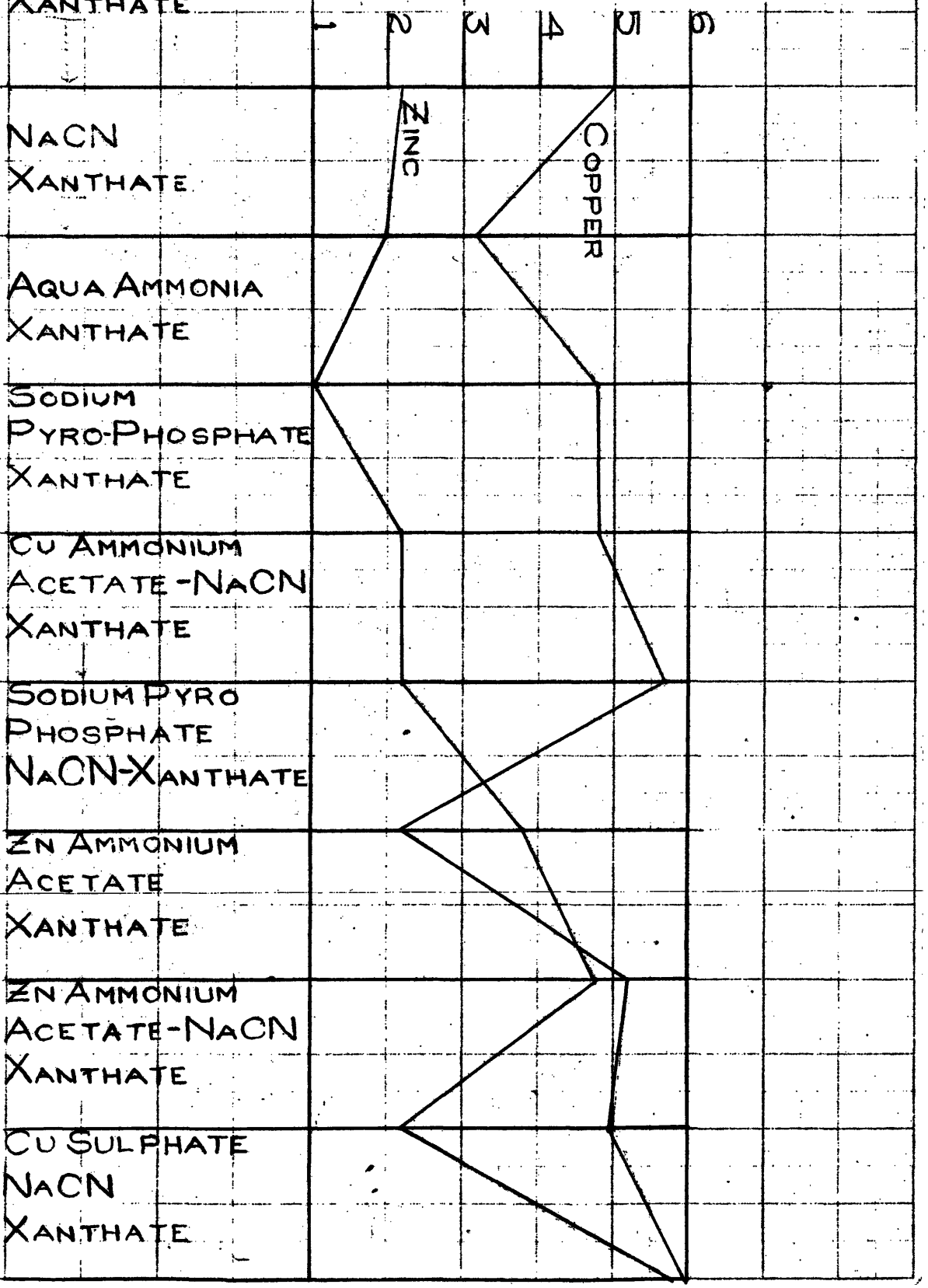
Method

The reactions of copper and zinc were determined by experiment and consulation of references. Results were also obtained from the class work in ore dressing at the Colorado School of Mines under the direction of S.P. Warren. Illustration Number One shows the results of this experimentation.

CHART No. 1

RELATIVE SOLUBILITIES IN FLOATION REAGENTS

No. 1 GREATEST SOLUBILITY No. 6 LEAST SOLUBILITY



III THE SOLUBILITIES OF COPPER AND ZINC XANTHATES IN CONDUCTANCE WATER

The solubility of these xanthates in water was determined by the conductance method and checked by the EMF method.

Conductance Method

Theory -- The equivalent conductance of a dilute salt solution is almost as large as the equivalent conductance of that salt at infinite dilution, calculated from the ionic conductance by Kohlrausch's Law. As the salt solution becomes more dilute its equivalent conductance approaches this limiting value, in other words, that it is completely dissociated. If the specific conductance of the water is determined, the specific conductance of the ions of the salt may be calculated by simple subtraction.

$$L_{solution} - L_{water} = L_{ions}$$

By assumption and definition

$$\Lambda_v = \Lambda_\infty = L_{ions} \times V = \frac{1000 \times L_{ions}}{C}$$

where the symbols have the significance assigned to them in Ex. 42 Daniels Williams and Mathews, and C is the concentration of the salt in gram equivalents per liter. Solving for C

$$C = \frac{1000 \times L_{ions}}{\Lambda_\infty}$$

Procedure

The specific conductance of the water to be used was first tested. The material to be tested was then washed several times with this water to remove any soluble impurities. After the impurities had been removed, the material was boiled with conductance water and filtered, using a well washed filter, into an Erlenmeyer flask of Pyrex glass which had been thoroughly cleaned. The conductance cell was washed with the solution to be tested and then filled. The cell was placed in a constant temperature bath, which was kept at 25° C, and the resistance determined. The resistance across the cell was determined by the use of a Wheatstone Box Bridge and checked with a Post Office Bridge. A capacity of .0005 MFD was placed across the resistance box. The sound was furnished by a Vreeland Oscillator.

Experimental Results

The resistance of the water used varied between 5400 and 7000 ohms. The water was tested before each run and this figure used in determining the result.

The cell constant for the cell used was found to be 0.0153.

Resistance of Potassium Xanthate solutions

1/50N	1/100 N	1/1000 N	1/10000 N
7.0	14.5	120	726
	15.9	129	731
	15.2	135	850
	15.2	138	900
		140	920
		141	1075
		141	1080
			1080

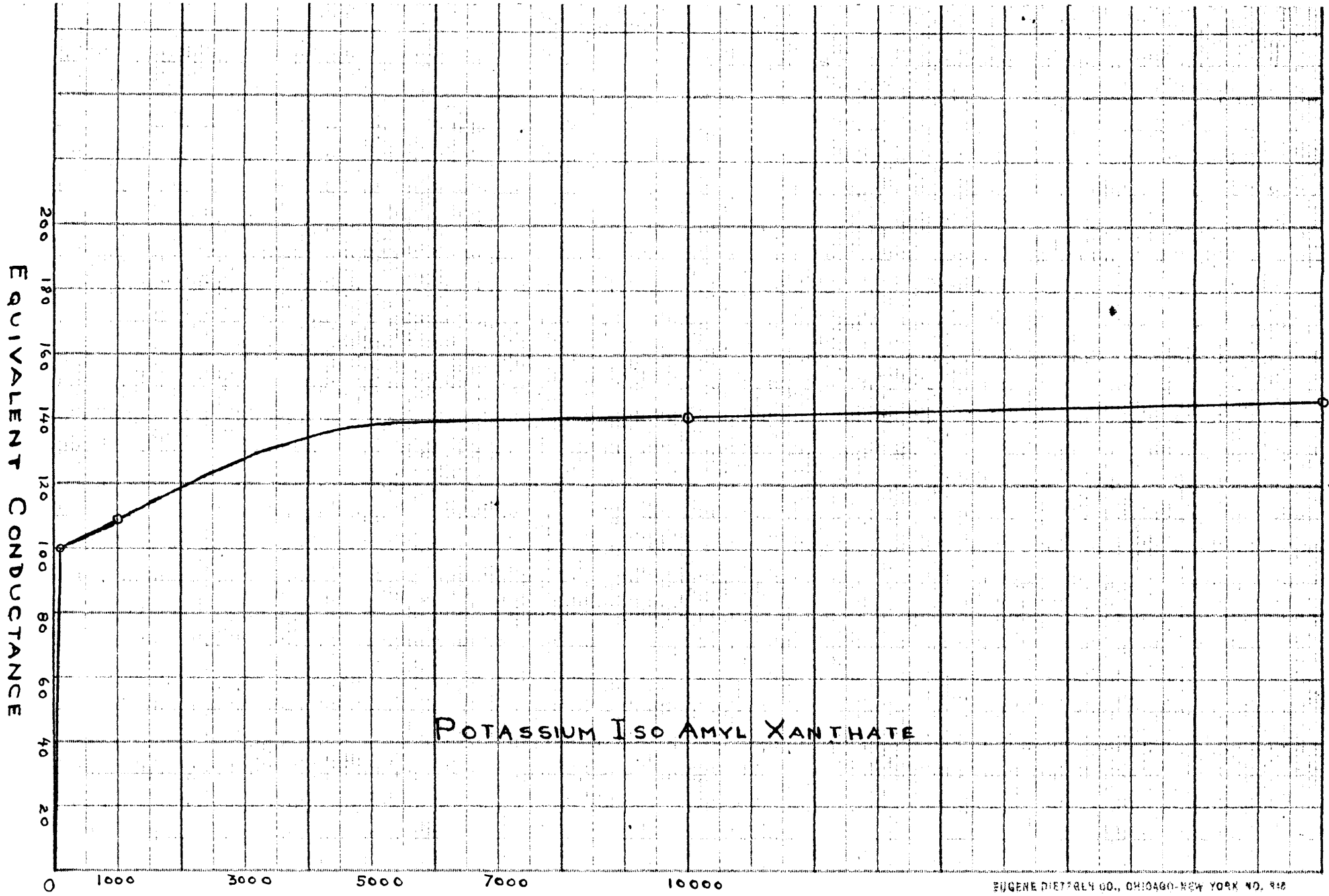
Equivalent Conductance of Potassium Xanthate solutions

$$N/100 = \frac{.0153}{\frac{1000 \times 15.2}{1/100}} = 100.06$$

$$N/1000 = \frac{.0153}{\frac{1000 \times 141}{1/1000}} = 108.51$$

$$N/10000 = \frac{.0153}{\frac{1000 \times 1080}{1/10000}} = 141.13$$

By constructing a graph with the results the equivalent conductance of Potassium Xanthate at infinite dilution can be interpolated to be $\Lambda_\circ = 146$.


EQUIVALENT CONDUCTANCE
200
180
160
140
120
100
80
60
40
20
0
1000
3000
5000
7000
10000
POTASSIUM ISO AMYL XANTHATE
EUGENE DIETZGEN CO., CHICAGO-NEW YORK NO. 848
VOLUME IN LITERS CONTAINING
ONE EQUIVALENT WEIGHT

Resistance of Conductance Water Saturated With -

Zinc Xanthate	Copper Xanthate
454	1230
497	1390
511	1500
525	1590
621	1900
650	1990
965	2150
1270	2260
1740	2200
1700	2200
1700	2200
1700	2200

Method of Calculating the Concentration of Copper and Zinc Xanthates in Conductance Water.

The equivalent conductance of the copper and zinc xanthates at infinite dilution was obtained by adding together the ionic conductance of the metal and the xanthate. The concentration of these salts in water was calculated as shown later.

The ionic conductance of potassium was obtained from the International Critical Tables[11] by converting the value given for 18°C to 25°C, the temperature used in the experiment.

If we plot the conductance values for copper and zinc sulphates[11] we can obtain values for these sulphates at infinite dilution. Then by subtracting the sulphate ion and converting to 25°C the ionic conductance of copper and zinc may be obtained.

	Λ_o potassium xanthate	146
minus	Λ_o potassium ion	74.95
equals	Λ_o xanthate ion	71.05
plus ½	Λ_o zinc ion	53.0
equals	Λ_o zinc xanthate	124.05

$$L_{solution} - L_{water} = .000007227$$

$$C = \frac{1000 \times L}{\Lambda_o}$$

$$C = \frac{1000 \times .000007227}{124.05} = 5.81 \times 10^{-5}$$

	Λ_o xanthate ion	71.05
plus ½	Λ_o copper ion	54.1
equals	Λ_o copper xanthate	125.15

$$C = \frac{1000 \times .000004724}{125.15} = 3.77 \times 10^{-5}$$

EMF Method

The second method was suggested by T. P. Campbell, Associate Professor of Metallurgy at the Colorado School of Mines. The EMF method was run by setting of duplicate cells in the following manner. - On one side a zinc electrode was placed in contact with 0.1m zinc sulphate and in the other side the zinc electrode was placed in contact with 0.01m potassium xanthate solution (saturated with zinc xanthate). These half cells were connected by a saturated potassium chloride salt bridge. The zinc cell when first set up gave a reversed potential, but upon standing one week gave the correct polarity.

The copper cells were made up by placing a copper electrode in contact with 0.1m copper sulphate on one side and a copper electrode in contact with 0.01m potassium xanthate (saturated with copper xanthate) on the other side. These half cells were connected together by a saturated potassium chloride salt bridge. The copper cells showed the correct polarity when first made up.

The cells were always run in duplicate and kept at 25°C by the use of a constant temperature bath. The EMF was measured by the use of a Queen Type Potentiometer.

Experimential Results

The EMF Method was run to check the conductance Method. Uncertain voltages were obtained from both cells. The average EMF at 25°C was 0.24 volts for zinc and 0.26 volts for copper. Using these figures, and calculating as shown in Getman (12) the following results were obtained.

Zinc	Copper
$E = \frac{.0595}{n} \log \frac{m_2 \alpha_2}{m_1 \alpha_1}$	$E = \frac{.0595}{n} \log \frac{m_2 \alpha_2}{m_1 \alpha_1}$
$\log \frac{m_2 \alpha_2}{m_1 \alpha_1} = \frac{E\ n}{.0595}$	$\log \frac{m_2 \alpha_2}{m_1 \alpha_1} = \frac{E\ n}{.0595}$
$\log \frac{.1 \times .383}{c} = \frac{.24 \times 2}{.0595} = 8.067$	$\log \frac{.1 \times .362}{c} = \frac{.26 \times 2}{.0595} = 8.739$
$\frac{.0383}{c} = 1.166 \times 10^{8}$	$\frac{.0362}{c} = 5.49 \times 10^{8}$
$c = 3.285 \times 10^{-10}$	$c = 6.594 \times 10^{-11}$
$s = 3.285 \times 10^{-10} \times (.00685)^2$	$s = 6.594 \times 10^{-11} \times (.00685)^2$
$s = 1.543 \times 10^{-14}$	$s = 3.097 \times 10^{-15}$
$\sqrt[3]{\frac{s}{4}} = 1.568 \times 10^{-5}$ mols / liter	$\sqrt[3]{\frac{s}{4}} = 0.9182 \times 10^{-5}$ mols/liter

Discussion of Cell Calculations

There is some question as to the justification of applying activity coefficients, and activities to the voltage equation ordinarily used for concentration cells of this type. After a review of the data it was decided to make the calculations in terms of conductance ratios.

If we plot the conductance values for copper and zinc sulphates (11) we can obtain values for these sulphates

at infinite dilution. The conductance ratios are obtained by dividing the conductance of the salt (at 25° C and the desired molality) by the conductance at infinite dilution.

Salt	Molality	Λ	Λ_∞	α
Copper Sulphate	0.1	43.5[a]	120[d]	0.362
Zinc Sulphate	0.1	44.8[b]	117[d]	0.383
Potassium Xanthate	0.01	100.06[c]	146[c]	0.685

[a] International Critical Tables Vol. 6, page 236

[b] International Critical Tables Vol. 6, page 235

[c] By experiment - see page 14

[d] These figures were interpolated by the intersection of zero concentration with a straight line drawn through the three lowest points in a plot of conductance against the square root of the concentration.

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